Materials Horizons: From Nature to Nanomaterials

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Kapil Parihar *Editors*

Friction Ridge Analysis

Applications of Nanoparticles for Latent Fingerprint Development

Springer

Materials Horizons: From Nature to Nanomaterials

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Chapter 1
Role of Nanotechnology in Latent Fingerprint Development

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Introduction

In order to analyze and manipulate objects with length scales between 1 and 100 nm, nanotechnology involves research and technological development at the atomic, molecular, and macromolecular sizes. The features and functions of objects at this scale, i.e., "nanoparticles," are unique and very different from those of objects at a larger scale. Nanoparticles' small size, surface tailorability, increased solubility, and multifunctionality provide scientists with a wealth of new study opportunities. The name "Nano" is derived from the Greek word for dwarf and refers to one billionth (10–9) of a nanometre (nm). It deals with new materials or devices that are 100 nm in size or less. Nanomaterials have applications in a variety of fields, including electronics, engineering, physical sciences, materials sciences, and medical science [40].

Nanotechnology plays a major role in forensic science in addition to being essential in many other sectors. The most recent advancement in forensic science is a branch known as "Nano-Forensics" or "Forensic Nanotechnology" [2]. One of the innovative applications of the development of nanosensors and nanodevices is the identification of anonymous evidence that is difficult to detect using the present approaches [3].

The creation of nanofingerprints, the next generation of fingerprint development methods, has lately demonstrated a significant potential. Fingerprints are one of the

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most significant pieces of evidence discovered at the crime scene since they are accepted as universal indicators of human identity [56].

Fingerprints are known to be the primary evidence at the crime scene even in this era of DNA fingerprinting as they are abundant and have durability that persists for long period of time than DNA does. Fingerprints are the impression of the friction ridge skin found on the tips of the finger. When a finger contacts to any surface it leaves a fingerprint impression. But most of the fingerprints are not visible to human eye though they are present on the surface, these types of fingerprints are referred to as latent fingerprints. Since, latent fingerprints are invisible thus its development and identification become a quite challenging task for the forensic expert. There are ample number of conventional techniques used for developing latent fingerprints. Chemical techniques like, iodine fuming, ninhydrin, silver nitrate, and cyanoacrylate. Whereas physical techniques include fingerprint powers, i.e., magnetic, white, black, and fluorescent [15]. Each technique of fingerprint examination depends on the surface where the fingerprint has been deposited. Therefore, the surface nature is considered as the main factor for choosing a particular physical or chemical technique. Thus, most of the chemical techniques are applicable on porous surface while, physical techniques namely fingerprint powder are found more competent toward nonporous surfaces. But with the change of time, the technology as well as the crime are also upgraded. Thus, conventional techniques are found less effective when it comes to detecting old fingerprint, their stability, and contrast which fades over period of time [3]. Therefore, over the past few years forensic nanoscientists have been applying different properties of nanomaterials in order to enhance the fingerprint visibility and tried to upgrade the conventional method that has been used since nineteenth century. The use of nanomaterials in the forensic domain of fingerprint analysis has changed the perspective of identifying fingerprint [24]. It emerges as a new domain of forensic science which is named as nanofingerprinting. A good example of this domain can be seen in latent fingerprint identification [48].

Traditional methods for developing latent fingerprints include powder dusting, ninhydrin spraying, iodine fuming, and silver nitrate soaking. Under many typical conditions, these traditional procedures are highly efficient in recovering latent prints. However, latent prints can be left behind on items or surfaces that have uncommon qualities, such as wet surfaces, backgrounds with multiple colors, surfaces that have been contaminated with blood or other bodily fluids, or objects with peculiar curves or patterns.

Nanotechnology in Forensic Science

Nanotechnology is also known as a universal purpose technology due to its significant and major impact on almost all industries and all areas of civilization. Therefore, the utility of this technology in forensic investigation is abundant and the major role of this technology in various fields of forensic science is briefly given below [45].

- **Forensic Toxicology**: Forensic toxicology uses nanotechnology to identify and measure various harmful compounds in a variety of samples, including blood, saliva, hair, vitreous humor, skeletal remains, and even fingerprint samples. The spectroscopic characteristics of nanoparticles and their potential use in the identification or detection of illegal narcotics like cocaine from fingerprint samples led researchers to this conclusion. This utilizes nanoparticles like gold nanoparticles, silver nanoparticles, and titanium oxide nanoparticles and they have been proven to enhance the limit of detection of such illegal drugs from fingerprint samples. A nanosensor for the identification of drugs like date rape drug (clonazepam) via modified gold nanoparticles from blood and skeletal remains has also been developed [48].
- **Forensic DNA Fingerprinting**: The quantification of post-PCR (polymerase chain reaction) is the most recent and exclusive application of forensic nanotechnology utilizing the microfluidic systems. With the help of these, DNA samples can be quantified in a very quick span, within 30 min. They can be quantified even when present in nanolitre scale by using the Agilent 2100 bioanalyzer which is commercially available in the market. They are at present, employed for quantification of mitochondrial DNA in various investigating agencies for forensic purposes. Owing to their minute size, the potential of such devices for being applicable at crime scene is widely significant [48].
- **Explosives**: Terrorist activities have been largely increased in the recent years, and due to this the detection of hidden explosive materials has become a difficult task for investigators and hence situations like these call for specialized and sensitive techniques for detection of such explosive materials in order to protect the citizens. The ability of nanostructures to serve as sensors for different chemical and biological components, including explosives, has been established through contemporary research and development studies in nanomaterials. For these uses, extremely compact devices with strong sensing capabilities are being developed. The nanosensor approaches with the highest potential to develop workable technological platforms for trace explosive detection include electronic noses, nanocurcumin-based probes, lasing plasmo-nanocavities, nanowire/nanotube, and nanomechanical devices [48].
- **Fingerprint development**: Fingerprints are the impressions left by the friction ridges of the distal phalanges of the fingers. Due to the presence of sweat pores on the surface of skin, it leaves an impression on the surface that it comes in contact with. These fingerprints are mostly present in the latent (invisible) form unless the fingers are stained using any kind of materials [48].

The fingerprints are unique impressions, i.e., it varies from one individual to the other and this feature of fingerprint makes it a great aid in criminal identification or even for identification of human beings in general. The three class categories of fingerprint impression types are Loops, Whorls, and Arches but the features that make fingerprints unique are the minute ridge details like bifurcation, trifurcation, dot, bridge, short ridge, island, etc., which are also termed as "minutiae." The presence, location, and angle of these minutiae are what makes a person's fingerprint different from another [32]. For the development of fingerprints, a variety of methods have been devised and being adapted by investigating officers or forensic scientists. These methods include physical and chemical methods for development of the fingerprints. In physical methods, powder-like substances are spread over the potential areas where the fingerprints are suspected in a crime scene using special light brushes [53]. These materials get adhered on the surface of the raised ridge patterns and make the impressions visible. And in the chemical methods, some sort of chemicals are sprayed or made in contact with the fingerprint, that develops the impression [9, 34].

Nanomaterials are now being adapted for the visualization of fingerprints [59]. Owing to their very minute structures, the adherence of nanoparticles on the finger impressions is a lot more to that of the ones developed by normal powders. And the quantity of powder being used for development is also too less [40]. The decipherment of fingerprints becomes really easy and effective by using the nanomaterials and this in turn makes the nanoparticles an excellent tool for fingerprint development [46]. There are a number of nanomaterials that have been used till now for the development of fingerprints like nanoparticles of gold, silver, silica, titanium dioxide, zinc oxide, aluminum oxide, carbon nanoparticles, rare earth metals, quantum dots, and a lot more [44]. They are found effective on surfaces of different nature and of varying contrast. They have also been found useful on wet surfaces where the conventional powder either do not work or produce effective results [28, 33].

Conventional Techniques Versus Nanomaterials for Fingerprint Development

The fingerprints are majorly found in the invisible or latent form on the scene of crime. This calls for the need of making them visible by means of some method or tool. There are numerous kinds of methods that are being used for this purpose. The most widely accepted technique is the powder technique as it is easy to use and gives better results. The emergence of nanotechnology in fingerprints has made a significant impact in the fingerprint visualization and they are of course over powering the traditional methods that are being used till date. Having being particles of very tiny size, the result produced by them is very detailed and clear. This in turn is clearly making

the nanoparticles more advantageous over the conventional fingerprint development techniques.

The conventional methods of fingerprint development include (a) Physical method and (b) Chemical method. The physical methods involve usage of powder particles like black powder, white powder, magnetic powder, grey powder, fluorescent powder, aluminum powder, red bronze powder, dragon's blood powder, etc. Apart from these, many powders derived from natural sources have also been found to be used for development of fingerprint like powdered spices, powdered seeds and flowers, etc. It basically can include any kind of powdery material that can stick to the surface of fingerprint and make it visible. The chemical techniques include iodine fuming method, silver nitrate method, ninhydrin method, osmium tetroxide method, chem print method, silver physical developer, hydrofluoric acid method, tannic acid method, osmic acid method, mercuric iodide method, bromine method, Fleming's reagent method, etc. These conventional methods have been practiced since a very long time and also have several demerits. Nanoparticles overcome such demerits and have improved the fingerprint development field to a very great extent by providing efficient results [25, 56]. Nanoparticles in fingerprint development are still a less explored field and are currently being studied by many scientists in order to make it even more advantageous than it is at present. The difference between the conventional fingerprint development techniques and nanomaterials have been given in Table 1.1.

Commonly Used Nanoparticles in Latent Fingerprint Development

Nanoparticles have lately shown considerable promise in the production of nanofingerprints, the next generation of fingerprint development procedures. Different nanopowders are used for LFPs development as shown in Figure 1.1. The procedure used to produce a latent fingerprint is determined by both the content of the latent fingerprint and the characteristics of the material [11]. Currently, a variety of procedures are being utilized to produce latent fingerprints, including iodine fuming, ninhydrin, silver nitrate, and cyanoacrylate. In the case of older prints, however, the environment may have polluted them. In such cases, the fingerprints' responsiveness to detection by the above-mentioned approaches may be diminished [11]. As a result, nanotechnologies have mostly been utilized to generate latent fingerprints in order to better identify them over the last few generations [14, 71]. Furthermore, the technology allows for new fingerprints to be created better selectivity, greater background contrast, and higher sensitivity are all examples of approaches with superior attributes. Nanoparticles of various forms and their uses In the next sections, we'll look at how to recognize latent fingerprints.

Table 1.1 Difference between conventional methods of fingerprint development and nanotechnology for fingerprint development

S. No	Factors	Conventional methods	Nanotechnology
1.	Adherence	Although, they produce good result, the adherence capability of these is comparatively lesser due to the large particle size	The adherence of nanoparticles on finger impressions is excellent as particles are quite strongly and quickly adhered [25]
2.	Ridge details	Due to lesser adherence, the ridge details might not be as clear as it is in the case with nanoparticles	The ridge details are very clearly identifiable owing to the ultra-small size of particles [47]
3.	Smudge	They are heavier and hence this increases the chance of smudging	Since they are very light weight, the chances of smudging are very less [52]
4.	Detection of old prints	They have not been found very useful in the detection of old prints and hence not very effective	They have been found to have detected very old prints as they get stuck to them quickly [49]
5.	Stability	The developed prints have not been found stable for a longer period of time	The prints developed via nanoparticles have been found stable for a very long duration [50]
6.	Contrast	The contrast with respect to the background is not always very good	It gives better contrast results when compared to those of conventional techniques [50]
7.	Cost	Most of the materials being used are expensive	There are many emerging nanoparticles that have been worked upon that have proved to be very cost-effective [50]
8.	Effectiveness	They are less effective when compared to nanoparticles	They have given extremely effective results [50]

Silver Nanoparticles

According to the literature, metallic silver has an affinity for the organic components of fingerprint. Based on this idea, silver nanoparticles have been used since 1970 as a reagent in the silver physical developer (Ag-PD) method for the visibility of latent fingerprints on porous paper surfaces. In the Ag-PD method, an oxidation-reduction pair is used to convert an aqueous solution of silver nitrate to metallic silver. The fingerprint remnant can be visible on the paper surface as a dark grey or black silver picture because the silver nanoparticles (1–200 nm) produced during the reaction interact with the organic components of the fingerprint remnant. Positively charged fingerprint remnants and negatively charged silver colloids are attracted to one another by an electric force and this leads to the formation of fingerprint [11, 60]. Other studies have shown that the Ag-PD approach is effective for detecting latent fingerprints on porous objects, particularly when viewed on products that have been wet intentionally or inadvertently [60]. Nonetheless, the procedure has one flaw:

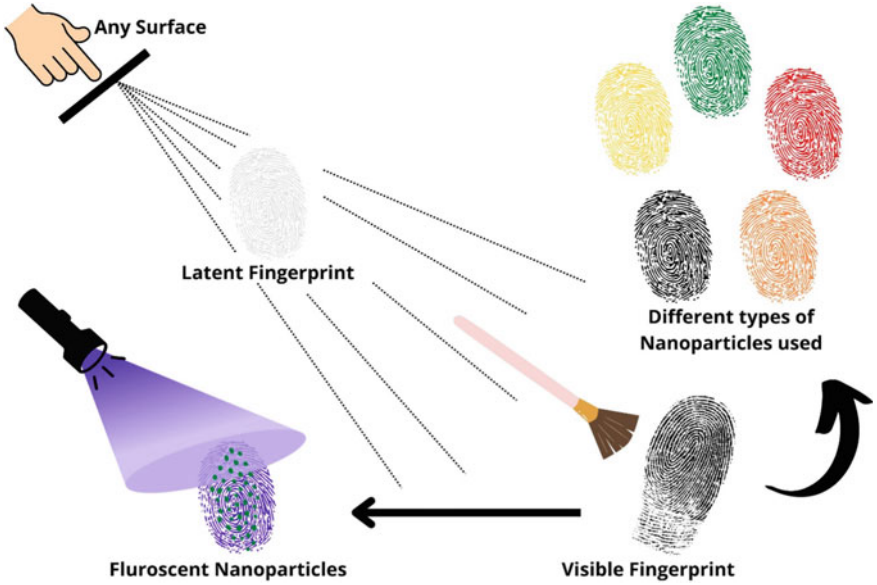

Fig. 1.1 Nanoparticles used in development of latent fingerprints on different surfaces for friction ridge analysis

the fingerprints are difficult to see when using only the AgPD solution. To solve this difficulty, gold nanoparticles stabilized with a citrate ion were applied to the fingerprint before the Ag-PD solution was applied [12, 60].

Zinc Oxide Nanoparticles (ZnO-NPs)

A review of the literature indicates that zinc oxide exhibits exceptional characteristics, including a wide bandgap (3.37 eV), a high excitation binding energy (60 MeV), which allows its transition to occur even at room temperature, and an extra adhesive property that makes contact with the lipids and proteins in the fingerprint residue possible at ambient temperatures. In order to develop old fingerprints on nonporous surfaces, ZnO nanoparticles in the form of a nanopowder were used [20, 50, 71]. The produced fingerprint included distinct ridge features that fluoresced under UV light. Sydney University researchers recently found that ZnO nanopowders (20 nm) not only make clear prints but also glow in UV light when wet [48]. When exposed to long-wave UV light, nanostructured zinc oxide creates a good fluorescence image of the latent fingerprints, as shown by many researchers [5, 15]. A unique nanopowder combination including $ZnOSiO_2$ has been discovered to be successful in producing latent fingerprints on various nonporous surfaces [20].

Gold Nanoparticles (AuNPs)

Gold nanoparticles (AuNPs) are crucial in the production of latent fingerprints due to their inert nature, high selectivity and sensitivity, and characteristics that allow the produced fingerprints to be kept for a lengthy period of time. Due to these characteristics, gold nanoparticles were used in a two-step sol-gel method called multimetal deposition (MMD) to increase the visibility of latent fingerprints. Before being subjected to a solution of silver physical developer, the fingerprint-bearing surface was submerged in a solution of gold nanoparticles (stabilized in citrate ion medium) (Ag-PD) [21]. Gold nanoparticles bond to the fingerprint residue, catalyzing the precipitation of silver ions to metallic silver. As a result of the ionic interactions between both the negative charges Au NPs and the positively charged fingerprint remnant, a silver picture of the latent fingerprint is generated. However, the MMD approach is limited in its use since it needs the object holding the fingerprints to be immersed in an aqueous solution of gold nanoparticles. As a result, the procedure is ineffective for producing prints on surfaces such as walls and floors at crime scenes, or for any object too large to soak in a desktop bath.

Aluminum Oxide Nanoparticles (Al_2O_3–NPs)

For the recognition of latent fingerprints, a harmless, eco-friendly nanopowder was produced. Al_2O_3 nanoparticles coated with a naturally colored dye (eosin yellow) and hydrophobic seed extract were used to create the nanopowder. The Cyamopsis tetragonoloba (guar bean) seed extract behaved as a hydrophobic material, repelling water molecules and allowing the small powder particles to attach to the oily elements of the latent fingerprints. The use of nanopowder in the development of latent fingermarks not only enables clear visibility on diverse porous and nonporous surfaces but also recognizes fading latent fingerprints.

Titanium Oxide Nanoparticles (TiO_2-NPs)

Because of its intriguing optical, electrical, and photocatalytic capabilities, nanocrystalline (TiO_2) has been intensively studied. Several publications on the use of TiO_2 nanoparticles in the creation of latent fingerprints have been reported. Saunders detected fingerprints on porous and nonporous surfaces using a TiO_2 particle dispersion [10]. Wade [65] discovered that micron-sized TiO_2 particles performed well in producing latent fingerprints on dark and nonporous surfaces, allowing them to be employed as a white fingerprint powder or a white tiny particle reagent. TiO_2 nanoparticles were employed in a solution or paste form. If used as a substitution for slippery powder on both sides of the tape, it produced great results. Bergeron [8]

demonstrated that TiO_2 particles suspended in methanol might improve the visibility of bloody prints on nonporous and some semi-porous surfaces. TiO_2 was first used in a methanol carrier as part of the application method, and then the surface was washed with pure methanol. Nonporous surfaces produced amazing ridge features with tertiary-level detail. Bloody prints that were recent and those that were older (more than a month old) did not differ noticeably. The results for porous surfaces were unsatisfactory, showing either a flimsy finger outline or no result at all. Methanol can be replaced with water, although doing so has some disadvantages, including decreased contrast and substantially longer processing times. When compared to current magnetically fluorescent powders, the novel powder produced substantially less background development while being somewhat weaker in fluorescence intensity. The nanoparticles produced latent markings with great depth and vibrancy than standard-sized powders.

Silica Nanoparticles (SiO_2-NPs)

Because of their simplicity of synthesis and ability to coat dyes, which inhibits photo-decomposition, silica nanoparticles (SiO_2-NPs) serve as a unique approach to increasing the identification of latent fingerprints [72]. Because of their coating ability, the nanoparticles were functionalized with dye particles to recognize the fingerprint residues, and the outer shell of SiO_2-NPs was functionalized to create interaction with organic compounds of latent fingerprints such as amino acids and proteins to enhance the latent fingerprint image on a variety of object surfaces. According to one research, the electrostatic process between the silica nanoparticles and the fingerprint residue is comparable to the contact that occurs during the identification of latent fingerprints by gold nanoparticles using the multimetal deposition approach [5].

Carbon Nanoparticles

Because of their unusual optical features, fluorescent carbon nanoparticles (CNPs), also referred to as carbon dots (CDs), have attracted a lot of attention in recent years [62, 77], this makes them potential chemical and biological options for optoelectronic devices, sensors, biological probes, photovoltaics, and solar cells [1, 21, 26, 27, 76]. CNPs offer a number of benefits, including nontoxicity, biocompatibility, water solubility, and environmental friendliness, but they also have drawbacks, such as poor luminous intensity. It has been observed that CNPs with N/S co-doped photoluminescence can be improved, implying that the production of nontoxic doped carbon nanoparticles from the suitable raw material could be promising [75]. Carbogenic nanoparticles (also known as C-dots) are a new type of high-performance photoluminescent (PL) nanoemitter that has a lot of potential in multicolor printing, bioimaging,

selective sensing, and catalysis [4, 25, 30, 36, 37, 58]. C-dots are biocompatible and nontoxic to humans and the environment, unlike traditional polyaromatic dyes and heavy metals-based quantum dots [77].

Li [35] showed carbon nanoparticles (CNPs) combined with starch to produce a nanocomposite were used to demonstrate a new method of LFP detection. Using pyrolysis techniques, CNPs were made from malic acid and ammonium oxalate as source materials. To give these CNPs color, starch powder is used. These CNPs, which are incorporated in the starch nanocomposite, have unique qualities such as improved luminescence and strong chemical properties, and thus may be used as novel luminescent compounds for LFP detection on porous and nonporous surfaces. The use of this nanocomposite has resulted in a sharper recognition of fingerprint ridges and improved comparison of fingerprint pictures. On aluminum foil substrates with solution state CDs submerged in 5 s, the LFP detection was examined. Due to the large sweat pores on the aluminum foil substrates, these CDs produced good pictures. The CDs solution was also used with spray techniques to identify new and aged fingerprint pictures on fingerprint residue substrates such as glass slides, metal, plastic, and leather.

A few QDs stained on fingerprints demonstrated high visible fluorescence when activated by ultraviolet (UV) light to improve contrast. However, because QDs have a heavy metal core, the intrinsic toxicity of QDs is becoming a growing problem, limiting their long-term usage. As a result, fluorescent CNPs, rather than QDs, are the ideal choice for detecting latent fingerprints since they are biocompatible and nontoxic to people and the environment. CNPs, on the other hand, readily lose their luminous capabilities in the solid form, making fluorescent powder production challenging. CNP photoluminescence research has been concentrated on the solution state; however, solid-state physics and photoluminescence performance of anhydrous CNPs have received far less attention. On the surface of biological materials like cotton, fur, and silk, CNPs' solid-state photoluminescence can be visible, but not on the surfaces of nonliving and artificial materials like glass, stone, chemical fiber, and plastic. Because of their characteristics, CNPs should be utilized in fluorescent ink and anti-counterfeiting auxiliary assessment [66].

Rare Earth Metal Nanoparticle

Because of their superior chemical and physical features, such as wide surface area and high fluorescence intensity, fluorescent nanoparticles for latent fingerprints have gained substantial study attention in forensic science during the last 10 years [7, 39, 41, 63]. Due to the intense fluorescence emission, employing nanomaterials for fingerprint formation can result in improved contrast and reduced background interference. Furthermore, the nanomaterials' surface modification technique is modern and adaptable, resulting in great selectivity in fingerprint creation [22, 28, 31, 73].

Due to their small particle size, large surface area, high quantum yields, high fluorescent intensity, narrow emission peak, and good optical stability, rare earth

fluorescent nanomaterials were recently demonstrated to be effective fluorescent labels for the development of latent fingerprints [57–59]. YVO_4:Eu and $LaPO_4$:Ce,Tb rare earth fluorescent nanoparticles were reported as efficient fluorescent labels for the improved formation of latent fingerprints by Ref. [28], who were inspired by the aforementioned notions. Furthermore, the rare earth YVO4:Eu nanocrystals and LaPO4:Ce,Tb nanobelts have been effectively used to photograph latent fingerprints on a variety of smooth substrates. The fluorescent nanoparticles' high contrast, sensitivity, and background interference in latent fingerprint generation are also thoroughly examined. As a consequence, the findings show that the two types of rare earth fluorescent nanomaterials have a lot of potential for forensic latent fingerprint imaging.

A recent work [25] depicted revolutionary new fluorescent substances such as NaYF4:Yb and Er, which address all of the problems of fingerprint identification at real crime scenes on extremely various substrates, such as low sensitivity, low assessment, background noise, and autofluorescence interference. The fluorescence intensity of NaYF4:Yb, Er substances has improved, which is dependent on oleic acid volume, temperature, duration of response, and phase composition. These fluorescent materials successfully detected LFPs on a variety of substrates, including glass, ceramics, black and multicolored marbles, notice sheets, Chinese paper money, and plastic plates. Compared to commonly used powders like bronze powders, magnetic powders, and inexpensive emission powders, this luminescence powder can also produce good-quality fingerprint images on specific substrates when NaYF4:Yb and Er powders are added. This is because it has better sensitivity, good assessment, less background interference, and low autofluorescence interference.

A research work [55] revealed that acceptable quality LFP pictures may be generated when a radical purple luminescence powder is decorated with silica nanoparticles to form hybrid substances. Europium (Eu3) ion is an uncommon rare earth element that emits red and has nonpoisonous effects on consumers when used in LFP detection.

Quantum Dots

Semiconductor nanocrystals, also referred to as quantum dots (QDs), have drawn a lot of interest in comparison to conventional organic fluorophores because of their distinctive optical and electrical characteristics, including size-tunable light emission, photobleaching resistance, and simultaneous excitation of multiple fluorescence colors [19, 23, 29]. Because of their exceptional fluorescence qualities, quantum dots have piqued the interest of forensic science professionals in the identification of latent fingerprints in recent years. CdS QDs have been utilized to produce latent fingerprints from the first generation [42, 43]. Several QDs systems had examined successively, like CdSe and CdTe [6, 38, 69, 70]. In aqueous solution, II-VI semiconductor QDs such as CdS, CdSe, and ZnSe QDs were produced, but their quantum yield (QY) was low and they were unstable, which limited their applicability [64]. In

comparison to these QDs, CdTe QDs have a higher luminous quantum efficiency. The emission wavelength of CdTe QDs varies depending on the size of the nanocrystals, ranging from green to near infrared. As a result, "Multi-color QDs" may be created from CdTe QDs. In addition, glutathione, L-cysteine, thioglycolic acid (TGA), and mercaptopropionic acid can be used to cap CdTe QDs in an aqueous phase (MPA) [23, 54, 74].

Future Aspects

As discussed earlier, different types of nanoparticles had shown great effect in the development of latent fingerprint. In future, the researchers should look for ecofriendly material which will be utilized in developing latent fingerprints as some of the existing powders are very harmful in nature and show hazardous effects on human. And the investigating officers are continuously in contact with those powders. Also look for waste material which can be utilized to make nanopowder. Study should be done on fluorescent nanoparticles which are made from waste material as well as ecofriendly and easily available which will be very useful in developing latent fingerprints on any surface.

Conclusion

Nowadays, the value for nanomaterials in every field is increasing widely due to the fact that it has a lot of applications in every field. Previous researches have shown that nanoparticles have a vital role in the forensic science field as well. They can be used to develop latent fingerprints. Owing to its very small size, i.e., nano size, these particles provide excellent results in the development of fingerprints. These nano-sized powders have been found efficient on surfaces of all natures ranging from very porous surfaces to nonporous ones. The ridge characteristics, that is minutiae from the developed fingerprints can be visualized very clearly and can easily be extracted or located. The above-mentioned NPs have been shown to be a viable, effective, and environment-friendly method for detecting latent fingerprints on porous, nonporous, and semi-porous surfaces. The findings show that the NP has a specific interaction with fingerprint residue, resulting in clear and crisp pictures of the ridges. The nano-material developed in the aforementioned study has advanced qualities that make it acceptable for use in forensic dermatoglyphics, which creates latent fingerprints in any circumstance, regardless of substrate type or color. The nanoparticles have the capacity to create latent fingerprints, according to experiments conducted by many scientists, and may be utilized for investigation, crime scene search, and research and development.

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Chapter 2
Functionalization of Nanomaterials for Fingerprinting

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Introduction

Nanotechnology is a fast-expanding science in the realm of "forensics" that uses diverse nanomaterials to detect evidence on many sources of crimes such as weapons, biological samples, and residues to identify offenders [1–4]. Nanotechnology is a rapidly growing discipline of research that has its fingers in practically every field. Because of the advancement of nanotechnology, nanomaterials are now extensively employed in criminological studies for examination and assessment. The growth of emergent nanoparticle techniques is being combined with latent fingerprinting in nanotechnology, which is a developing topic in forensic research. Particulate features ranging in size from 1 to 100 nm are referred to as nanoparticles [5]. Nanomaterials are one-of-a-kind because of their small size and ability to change mechanical, electrical, and optical properties [6]. Prior to a court verdict, forensic evidence is critical in identifying perpetrators through investigations done at crime sites [7, 8]. Psychiatry, pathology, toxicology, entomology, anthropology, and odontology are some of the branches of science that have been used in criminal investigations [9, 10]. Botany and ballistics are often utilized to supplement technical advances in these fields of study. Forensic technologies in use include fingerprints, sound profiles, earprints, and handwriting analysis [11]. In order to solve crimes, forensic evidence is primarily obtained as fingerprints and blood stains employing spectrophotometry [12–14]. With the passage of time, however, both technology and criminality have advanced. As a result, traditional techniques have been proven to be less successful in detecting old fingerprints, their stability, and contrast that diminishes over time. As a result,

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forensic nanoscientists have been experimenting with different features of nanomaterials in order to improve fingerprint visibility and try to improve a procedure that has been employed since the nineteenth century. The introduction of nanomaterials in forensic fingerprint analysis has altered the perception of fingerprint identification. Nano-fingerprinting is a new field of forensic science that has emerged. Latent fingerprint identification is a good example of this domain [15]. Diverse types of nanoparticles with various morphologies have been created and exploited in forensic applications throughout the last two decades. To identify fingerprints, metal nanoparticles such as silver and gold, oxide-based nanoparticles (oxides of iron, titanium, europium, and zinc oxide), nanoparticles of silica-based metal oxide, quantum dots of cadmium sulfide, cadmium selenide, cadmium telluride, polymers dots, carbon dots are well used to identify latent fingerprints [16–27].

Chemistry of Surface Functionalization Concentrating Covalent as Well as Non-Covalent Bonds

Surface functionalization of nanoparticles (NPs) is a procedure to facilitate improved features of NPs that will be useful in various applications. Different functional groups present on the surface of different types of nanomaterials and their chemical properties are exploited in the earliest steps of functionalization. In most cases, the primary stage of surface modification engrosses using homo/hetero bifunctional-cross-linkers to adjoin an organic functional group (R-COOH, R-NH_2, etc.) that can be used to bind biological molecules. Aminosilanes, which are generally involved in the introduction of an amino group on the surface of nanoparticles following bio-conjugation, are the most commonly used linkers for nanoparticles of silica [28, 29]. To functionalize noble metals like gold, crosslinkers capable of interacting with the metal containing –NH_2 or –SH groups and successively generating a covalent bond can be exploited. Functional groups at the opposite end of bifunctional linkers (for instance thiocarboxylic acids), can be employed to bind ligands [30]. The ligand exchange process, which involves replacing the novel surfaces having different functional groups for example amine, diol, carboxylic acid, and thiol can easily alter metal oxides [31]. A significant fraction of sp_2 hybridized carbon atoms in carbon-based nanostructures can be used to form functional groups. On the surface of NPs, oxidation can result in the formation of −COOH, −OH, and −C = O [32]; it is possible to create halogenated carbon through halogenation, which can then be further changed, for example, by reacting with the amine group [33]. Different types of functional groups can be inserted by cycloaddition [34]. Figure 2.1 lists the many types of nanomaterials, their chemical groups and/or compositions, as well as the appropriate chemicals or techniques for surface modification with crosslinkers. Surface modification of NPs can be accomplished in two ways: (i) non-covalent and (ii) covalent conjugation. The non-covalent method relies on a large number of weak interactions viz. Van der Waals forces, electrostatic bond, hydrophobic contacts, ionic forces, absorption, and

hydrogen bonding, and is particularly effective with metallic and silica NPs [35–37]. Non-covalent bonds generally have the gain of being simple and usually do not affect the structure of the molecules utilized or their interactions with biological targets. Non-covalent changes, on the other hand, are easily altered by factors such as pH and ionic strength [38]. Depending on the NP composition, many different ways can be used to obtain the covalent bond strategy [39–41]. Furthermore, employing successive functionalization, this technique allows for changes at multiple levels [42, 43]. This approach can be used to create structures that serve numerous purposes [44, 45], like diagnosis followed by therapy for implementing the theranostic approach [46, 47]. Various linker molecules are typically used to covalently attach ligands to the surface of NPs. PEG is an example of a homo-bifunctional or hetero-bifunctional linker that may be synthesized with certain functional groups at the end and utilized to execute a variety of functionalization activities. Pagels et al. demonstrated how the manufacture of specialized hetero-bifunctional PEG molecules is still an lively research subject and how this molecule can be tremendously valuable in the development of effective nanoplatforms for medical applications [48]. PEG can also be used as a spacer for molecules having higher molecular weight to space them transversely on the surface of the nanoparticles and as a result steric hindrance of bound ligands can be reduced, in turn allowing the high-density bio-conjugation [49]. Non-covalent interactions are typically used to load nanoparticles with compounds that must be released into target cells, such as medicine or RNAi, whereas covalent bonds are used to bind ligands that are effective for targeting and/or reducing NP toxicity. The use of sensitive bonding, such as pH or heat sensitivity, to construct nanoplatforms for controlled drug release has recently received considerable attention [50–52]. When compared to the normal milieu, the tumor microenvironment is extremely acidic. pH-sensitive nano-platforms can be created for precise drug release induced by the acidity of the tumor environment. In a recent study, a pH-sensitive cationic polymer called PBAE was utilized to coat doxorubicin-loaded liposome NPs. In addition, the surface of the NPs was changed with hyaluronic acid (HA) to allow active targeting via CD44. In vivo tests confirmed the in vitro findings, demonstrating that DOX-loaded NPs prevented tumor growth more effectively than free DOX while also reducing negative effects [53]. Taleb et al. provide another example of pH-sensitive NPs [54]. In this study, mesoporous silicon nanoparticles were functionalized with amine-conjugated phenylboronic acid that was pH-sensitive and covalently bonded to dopamine. The nanoparticles release dopamine in a mildly acidic environment, similar to that of a tumor, due to the hydrolysis of the boronic-ester connection between the two molecules. The suppression of vascular endothelial cell migration and tubule formation was achieved as a result of this intelligent release [55].

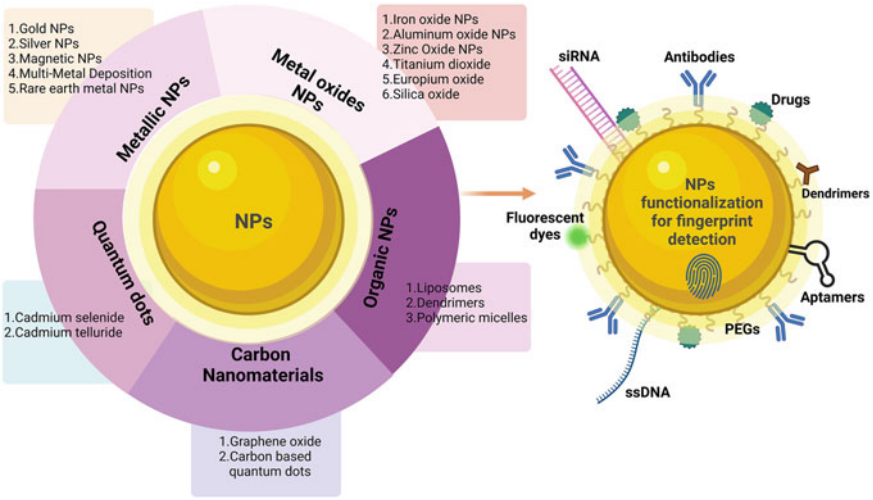

Fig. 2.1 Scheme showing functionalization of nanoparticles for latent fingerprint detection

Nanoparticles and Fingerprinting

The frictional ridge skin at the tips of our fingers creates a unique pattern of ridges and valleys that is unique to each individual. Their pattern, which is unique to each individual and does not alter during a person's life, has achieved ultimate importance in forensics; even identical twins have different fingerprints [56]. The use of nanotechnology to create latent fingerprints has several advantages, including increased selectivity, improved background contrast, and increased sensitivity. The following sections cover the various types of nanoparticles and their uses in the recognition of latent fingerprints:

Since 1970, metallic silver nanoparticles have been utilized as a reagent in the Ag-PD method for the viewing of latent fingerprints on porous paper surfaces. Due to the electrostatic force of attraction, the silver nanoparticles (1–200 nm) formed during the oxidation–reduction couple reaction interact with the organic constituents of the fingerprint residue, allowing the impression to be visualized as a dark grey or black silver image on the paper surface. If there is any $CaCO_3$ filler on the print-bearing surface, it should be acid pre-treated. The fingerprint was treated with gold nanoparticles stabilized with citrate ion before being treated with Ag-PD solution to improve visibility. Because of their inert nature, great selectivity, and sensitivity, gold nanoparticles (AuNPs) play an important role in the formation of latent fingerprints. At a low pH, colloidal gold (Au) with particle sizes of 14 nm or 30 nm performs the same purpose [56–60].

In both porous and non-porous surfaces, functionalized colloidal gold with a long-chain hydrophobic molecule (octadecanethiol) in a petroleum ether carrier is used to produce fingerprints [57–61].

The carboxylic acid functions of fingermark constituents are targeted using amine-functionalized europium oxide nanoparticles. It is used in conjunction with the SPR technique, which involves an incubation period followed by photoluminescent detection [62]. Because of its high luminosity, Al_2O_3:Eu^{3+} is the greatest option for fingerprint creation when compared to regular luminescent powders [60]. Cds nanocrystals capped with dioctyl sulfosuccinate in heptanes/mixture of hexanes leave a fingerprint on soft drink cans and aluminum foil that had been fumed with cyanoacrylate ester [62–64]. CdSe ZnS-capped nanocrystals can be covalently bound to amino acid components of fingermark residue on non-porous surfaces and the developed prints are stabilized by octadecaneamine [57, 58, 62].

For latent fingerprint development, CdS luminous quantum dots are used to facilitate the formation of four starburst dendrimers. Metal sulfide nanopowders, such as TiO_2 ZnO, FeO black powder, ZnO–SiO_2 nanopowders, and metal oxide nanopowders, can be utilized to produce latent fingerprints [59, 62, 64]. For the identification of aged latent fingerprints on model surfaces, nanoscale IR luminous Egyptian blue pigment particles coated with cetrimonium bromide provide lipophilic surfaces [65]. Worley and coworkers at Los Alamos National Laboratory used the non-destructive Micro-X ray Fluorescence (MXRF) technology to create latent fingerprint images. For imaging purposes, the inorganic components contained in the fingerprint residue are identified [63, 64]. In addition to the widely utilized physical and chemical methods for developing latent fingerprints, the advanced techniques such as ToF–SIMS (Time-of-Flight Secondary Ion Mass Spectrometry), DESIMS (Desorption Electrospray Ionization Mass Spectrometry), powdering method, ink-jet-printed array, chromatography, SALDI (Surface Assisted Laser Desorption/Ionization coupled with mass spectroscopy), MALDI (Matrix Assisted Laser Desorption/Ionization mass spectroscopy), Infrared spectroscopy, Raman spectroscopy, including acid dyes, CA (cyanoacrylate fuming) and gold, zinc, and silver evaporation could be used for visualization fingerprints [56].

Nanomaterials Intended for Fingerprint Detection

Nanomaterials have alluring properties such as a large surface area, compactness, optical properties, and the ability to easily change the surface using several capping agents. On fingerprint residues, these properties interact well with a variety of non-porous and porous materials. Nanomaterials offered better-quality fingerprint images, clearer ridge patterns, and less background interference due to hydrophilic attractions on fingerprint components of substrates [66]. Nanomaterials offer wide range of applications for detecting both new as well as aged fingerprints on a variety of substrates.

Core–Shell Nanoparticle Featuring Aptamer Functionalization

The aptamer is a short oligonucleotide and primarily single-stranded. With these properties, in the presence of a target, this oligosaccharide could be molded into a three-dimensional structure allowing for exact recognition. Aptamer's unrivaled qualities, like ease of structure change, strong affinity, and selectivity, flexible design, biochemical stability, and slightly synthetic nature, make it an ideal choice for developing latent fingerprints. These carbohydrate molecules could easily be linked to lysozymes, which are a common component of human sweat [67].

Zhao et al. produced Au nanoparticles following Fren's approach [68, 69]. They used TEM (transmission electron microscope) to characterize Au NPs and Au/PNTP/SiO_2 lysozyme binding aptamer nanoparticles. For detection of latent fingerprints on the glass surface, they employed modified sandwiched SERS probes. They were able to place nanoprobes conveniently on the ridges of fingermarks and all three levels of fingerprint were recognized, including pattern, individual characteristics, and pores [70].

Upconversion nanoparticles for fingerprint development

As fingerprints are an important piece of proof at crime scenes and latent prints are frequently discovered, the most frequent method for generating these prints is by dusting powder on the latent fingerprints [71]. But, certain limitations such as poor contrast, very low sensitivity in addition to inference in the background are major problems associated. The need for alternative methods has led to the development of a spate of novel processes. UCNPs (Upconversion nanoparticles) and QDs (quantum dots) like fluorescent nanoparticles assist in the development of latent fingerprints with improved bond and sensitivity [58, 72–74]. UCNPs are far better than other forms of nanoparticles especially in terms of converting long wavelength light into shorter wavelength emission following the multiphoton process [74–78]. UCNPs get excited by near-infrared light, making them to generate intense visible fluorescence. Consequently, they could improve contrast as well as sensitivity during latent fingerprint detection procedure and reduction of background interference.

Conversely, QDs utilize UV radiation for fluorescence of substrate and significant autofluorescence disturbances [75, 79–81]. In contrast, UCNPs use near-infrared radiation to emit visible light, which prevents the substratum from interfering with autofluorescence. Fingerprints include DNA, which is secure under the NIR rays and does not damage the eyes or skin of the grip as does UV light. The flexible luminous particles NaYF4: Yb, Er39 and YVO4:Yb, Er40 can be used to produce invisible fingerprints in various areas that allow for semi-permeable and non-invasive, and the solution is commercially accessible. Due to the uneven size and shape, small scattering and distance of 0.2 to 2 m, the correlation between fingerprint residues is

reduced, leading to a decrease in sensitivity. Wang et al. did research on NaYF4:Yb, Er nanoparticles to see how effective it was with the aptamer binding lysozyme to detect lysozyme detection in remnants of fingerprints to detect hidden fingerprints. Because it required the chemical modification of upconversion nanoparticles (260 nm) through complex processes, this technology closed the complex phases and it was impossible to employ in the crime scene. Fingerprints were applied to the UCNPs solution for 30 min.

Wang et al. established a method for fusing NaYF4:Yb, Er fluorescent upconversion nanoparticles (UCNPs) with the maximum probable fluorescence strength under near-infrared (NIR) treatment utilizing an oleic acid-based solvothermal process [82]. For the composition phase, size, and intensity of the UC fluorescence of the upconversion nanoparticles, factors such as volume, duration, optimization, and reaction temperature of oleic acid have been examined [77]. Therefore, fingerprints were fluorescently labeled using UCNPs as there was a likelihood that UCNPs would release visible light if exited at NIR to 980 nm. On a range of substrates the dormant fingerprints were tested including black marbles, white clay tiles, and transparent glass, as well as different foundation colors and solid foundation autofluorescence. These findings were compared to typical powder dusting methods, and it was found that UCNPs are much more sensitive, have superior contrast quality, a smaller amount of interference by autofluorescence as well as having lower inference of the background. As a result of this study, it was discovered that upconversion nanoparticles added under improved environment are a all-round fluorescent marker for the rapid progress of finger impressions and could be used in criminological science [82, 83].

Nanoparticles of Iron Oxide

Iron oxide NPs adhere to the fingerprint ridges, allowing unseen finger impressions to be seen [84]. It has the ability to change its size to a different hue, which fluctuates depending on whether it is unannealed or annealed. Owing to its physical affinity with deposits of fingermark such as sebum, perspiration, and other impurities, the powderd nanoparticles were employed, which aided in the generation and detection of imperceptible impressions of finger. A green method was used to synthesize both annealed as well as unannealed iron oxide NPs and their characterization was done with the help of XRD. With the aid of EDAX purity of the NPs was validated [85]. On both impermeable as well as permeable surfaces, latent finger impressions were generated [85, 86]. When comparing the absorbent and non-absorbent surfaces, the absorbent surface had more developed fingerprints [64, 87].

Nanopowders Made of Carbon Dots

C-dot nanoparticles, a rapidly growing class of carbon nanoparticles, perform as high-performance nano emitters with applications in bio-imaging, multi-color printing, catalysts, and bio-sensors. They are biologically compatible and have no toxic effects on humans in addition to the environment. C-dots increase the fluorescence intensity while improving colloidal stability. Because of extensive clustering and metallurgical merits, the pure type of carbon dots tends to gather in the form of powder, and as per the reports, the C-dot powder is not photoactive. The nanopowder makes the ridge patterns apparent. The color tuneability of the fingerprints formed is in response to the incident beam wavelength. The fingerprints appeared blue, green, or red according to the range of incident light [88].

In an experiment, however no signal was detected when c-dots were absent. Fingerprints were created on beverage bottle using C-dot nanopowder, which showed deficient contrast under field radiance were high and only fading ridge patterns under green light were observed. The improved characteristics were assessed under blue and violet rays at the same time [89].

$MgAl_2O_4$ Nanoparticles Engrafted with Cu^{2+}

The combustion process was used to make Cu^{2+} engrafted $MgAl_20_4$ nanoparticles utilizing the chelating ligand triethanolamine. The optical property was tested using the UV-DRS method, and the characterization was done using the TEM and XRD methods. Magnesium has photocatalytic activity, which aids in the brush method of amplifying latent fingerprints under UV light. The powder was applied on even surfaces such as metallic and lead crystal to develop and enhance the latent fingerprints, which were then visualized by falling ultraviolet light (254 nm). The improved prints were having poor quality, with individual traits and pores not evident [90].

Nanophosphors of Calcium Molybdate

From host lattice, metal-molybdates have the unique ability to transfer energy to the small ions, making it the only oxide compound with spectacular luminous properties. Calcium molybdate is a metal-molybdate having 141/a space group and a translucent property that allows different light ranges to pass through without affecting the luminescence effect. In comparison to other oxide materials, this material has adequate chemical and physical properties. The $CaMoO_4$ synthesis process takes 12 h and produces particles that are 1–2 micron in size. This work created a method for producing nanostructures shaped as spherical and molded with nanoparticle building blocks that are relatively faster [91]. Nanopowders have been studied for their optical

and structural properties, which enable them to detect the invisible finger impression on a variety of surfaces [27, 91]. XRD, SEM, EDX, and FTIR were used to depict the results. The $CaMoO_4$ was inhibited with Eu^{3+} and Tb^{3+} ions, and the qualities of luminescence were detected in it enabling the detection of invisible fingerprints. It was capable of detecting ridge details in fingerprints. Under visible light, the latent prints may be seen with improved contrast and reduced background interference. Latent fingerprints were developed on a variety of non-porous surfaces, including a CD (compact disc), a slide of glass, and a cup made up of stainless steel. As a result, hidden finger impressions were generated and recognized over a diverse surface utilizing phosphor materials. The finger impressions were created by means of a brush applying nanopowder to the surface. The nano-sized powder was bound on ridges, not the grooves of fingerprints. As a result, it revealed minuscule ridges and pores of sweat with superb contrast and minimal background interference. Affinity of powder for the latent fingerprints was boosted via moisture and greasy components. The calcium molybdate is strongly bound with the small amount of aminoacids found in the finger marks which could not be seen by naked eyes. As a result, after nine days of exposure to the ambient environment, the fingerprints were evident [27].

Core–Shell Functional Nanomaterials Composed of SiO_2@LaOF: Eu^{3+}

Silica is a substance that can modify its size on its own and is used in core–shell-built components. The nanoparticles act as shells that are encrusted with silica, resulting in the creation of phosphors with a spherical core–shell configuration. A sphere shaped non-agglomerated, element can be primed with only a few alterations or fabrications to the experiment's parameters. The nanoparticles that have been manufactured aid in the enhancement of brightness, high-quality resolution, and the diminution of light scattering. The nanoparticles in question can be employed for a variety of purposes, including anti-counterfeiting, biological imaging, and other types of display systems [58, 92]. The core–shell nanoparticles, which are rare-earth doped nano phosphors, exhibited several distinct characteristics, including sharp absorption and line emission in an UV–visible spectrophotometer having a high quantum yield, incomparable biocompatibility, less toxicity, good chemical as well as thermal stability, extended life, and superior photostability. The trivalent-lanthanide-ions may be unified and assembled as crystal with fluoride as a host, and it demonstrates excellent luminescence even at ambient temperature. Eu^{3+} ions can be employed as the supreme dopant in a variety of hosts to produce a red color discharge, which is referred to as long photoluminescence [92]. These specific nanomaterials have a higher refractive index. Modification of surface is one of the most proficient techniques which could be utilized to adjust or minimize the space between quenching and luminous centers of nanomaterials, diminish surface imperfections, and reduce non-radiative

channels. The luminous quality of a core–shell nanostructure improves as a result of these alterations.

Rare-earth doped nanoparticles having a diameter of less than 100 nm have received increased attention as surface-based research, particularly for recognizing invisible finger impressions. XRD, SEM, TEM, and EPR were used to characterize the samples. The latent fingerprints were created on an impermeable surface made of metal, tin foil, and a stapling mechanism using SiO_2@LaOF:Eu^{3+} nanoparticles. It was found that level 2 ridge formations which were not visible under white light could be easily seen under 254 nm UV rays. At 254 nm UV light, some sort of background interference was observed but the ridge characteristics were visible. The nanopowder was castoff on several absorbent materials like deck cards and covers of journal notes with background interference observed at 254 nm under UV light, and the ridge characteristics were visible. For the confirmation of the efficacy of fluorescent powders, certain covered composite invisible finger impressions were taken on a tin-foil surface and dyed using SiO_2@LaOF:Eu^{3+} nanoparticles and viewed under white light as well as 254 nm ultraviolet light. Under both illuminations, every bit of three layers was observable, signifying the efficacy of fluorescent tagging agents for imaging of fingerprints. From day one and following a whole month, the imperceptible finger impressions stained on tin foil were retained. The prints were not visible on the surface only after a week [92, 93].

Nanoparticles of Aluminum Oxide

Formation of aluminum oxide nanoparticles following a green method includes a coating of eosin yellow (dye) and seed extract. This approach was non-toxic and eco-friendly, which aid the formation of the invisible finger impression. The hydrophobic component *Cyamopsis tetragonoloba* seed extract repelled water particles and helped the powder particles attach to the oily material of the invisible finger impressions. This improved the visibility of prints on a variety of non-porous and porous surfaces. This was also useful in identifying faded latent fingerprints [64].

Nd^{3+} Sensitized Upconversion Nanostructure-Based Dual-Channel Emitting Optical Probe

The nano phosphors made with lanthanide upconversion are useful in a variety of sectors because they reduce fluorescence interference in the background and have a good signal to noise ratio. The Nd^{3+} sensitized $NaYbF_4$:Tm@$NaYF_4$:Yb@$NaNdF_4$:Yb graded designed nanoparticles produce near-infrared photons, with luminescence and excitation occurring at 808 nm, 696 and 980 nm [39]. The $NaYbF_4$ core supports successful Tm^{3+} zeal transmission. The $NaYF_4$:Yb interlayer efficiently prevents the

Tm^{3+} to Nd^{3+} cross-relaxation process. As a result, it aided in the enhancement of luminous property manufacturing. The Nd^{3+} aided in the shift of excitation wavelength from 980 to 808 nm. The heat effect caused by laser has been weakly repelled, leading to a new technique for the secretion of near-infrared rays at 980 nm. The produced nanoparticles were utilized to generate image development for invisible fingerprints and bloody fingerprints, which revealed details well under 808 nm excitation and had a high signal to noise ratio with no thermal damage to the fingerprint sample. These nanoparticles could be employed in forensic applications to improve print quality [94].

Imaging of Finger Impressions via N-doped Carbon Dots

When excited at 350 nm, polyvinylpyrrolidone (PVP) polymers were employed to synthesize N-doped carbon dots using the hydrothermal technique, resulting in beaming fluorescent waves. These carbon dots were used to recognize finger impressions, and they displayed the unique qualities of the fingerprint as a distinct, vivid figure. The surface functional group of N-doped carbon dots is CeNHe, which provides as a reason for the biomolecule's contact with them, resulting in the production of exact fluorescent designs. The fluorescence emission, which was triggered by the different fluorophores' designs, revealed three key components on the surface of the N-carbon dots nanoparticles. If the concentration is less than 0.01 mg/mL, they are non-hazardous in nature. Carbon dots were employed as fluorescent tags to image finger impressions on two substances in this study: tweezers and the plastic surface. When lit at 360 nm, the result exhibited good finger impression images, with visible ridges in the emission of orange color obtained with the use of filters that helped in transmitting the long wavelength to reduce background fluorescence and permitted detailed imaging. For simple comparison and recognition of finger impression minutiae, the second copy must be snapped with the use of a filter that illuminates the same wavelengths as the one castoff for viewing [95, 96].

Nanoparticles of Silver

Qin devised a simple and effective technology for seeing latent fingerprints processed by eccrine and sebaceous glands using silver and gold nanoparticles created by an electrochemical process in 2013 [97]. The electrodeposition method [98, 99] was chosen because it only happens between the ridges of fingerprints and the free conductive surface in valleys. This procedure improved the contrast and showed greater benefit because it is a simple, high-resolution, non-hazardous, and quick procedure for enhancing invisible fingerprints on rough, smooth, clean, and dirty conductive exteriors performed in aqueous solution, making it suitable for a damp piece of evidence [100]. Between the elevations of fingerprints, different metal surfaces such

as stainless steel and platinum were taken, and silver and gold were electrodeposited on the metallic substrate. In comparison to the unclean surface, the findings revealed distinct images of invisible finger marks on pristine metal surfaces.

Nanoparticles of Zinc Oxide (ZnO-NPs)

Zinc oxide has a high excitation binding energy (60 meV) and a wide bandgap (3.37 eV), which aids in the transition of zinc oxide at room temperature. It also contains an epoxy resin asset, allowing collaboration between proteins and lipids present as fingerprint residues at ambient temperature. To enhance the ancient concealed finer impressions on impermeable exteriors, zinc oxide was employed in the form of nanopowders. It aided in the development of distinctive fingerprint ridge details that fluoresced under UV light. Zinc oxide nanopowders produce clear prints and illuminate naturally under UV light in moist settings, according to research conducted by Sydney University. It also produces a better fluorescence image when irradiated with long-wave UV light, according to other studies [64].

Arshad et al. used the traditional heating method to make ZnO-SiO_2 nanopowder from $Zn(CH_3COO_2 \cdot 2H_2O$, $Na_2SiO_3 \cdot 5H_2O$, and NaOH. FTIR, XRD, energy dispersive X-ray (EDX) analysis, scanning electron microscope, and TEM were used to characterize the material. The particles of ZnO-SiO_2 nanopowder measured by TEM were 32.9 nm in size. With the use of small particle reagents and powder dusting procedures, latent finger impressions were enhanced on a variety of semi-permeable and non-porous substrates such as calculators, board markers, and laptops. On damp impermeable substrates, the SPR technique has also been applied. When compared to commercial powders, they produced clear quality prints with 2^{nd}- and 3^{rd} level minutiae of ridges, and they gave superior visibility and only clung to the ridges, unlike white powder, which adhered to the entire surface [101].

Luthra et al. contributed to the development of latent fingerprints by synthesizing new metal oxide nanoparticles (tin oxide and zinc oxide) using a chemical precipitation method in the form of dry powder. Zinc acetate and NaOH were used for zinc oxide nanoparticles, and tin chloride and NaOH were used for tin oxide nanoparticles, followed by ethanol. X-ray diffraction, UV–visible spectroscopy, and FTIR were used to characterize the material. The ZnO crystals maintained 14.75 nm in size, while tin oxide measured 90 nm. These powders were applied to impermeable substrates such as lead crystal, plastic, and glossy cardboard to develop latent finger impressions. In comparison to tin oxide nanoparticles, zinc oxide nanoparticles produced clearer and more enhanced fingerprints on all three surfaces, according to the study [102].

Using Au and Zn particles, the vacuum metal deposition technique has been used to generate a latent finger impression on plastic surfaces [103]. In this experiment, a simplified vacuum deposition procedure was used to generate a distinctive mark. Zinc oxide could collect on the surface of polyethylene terephthalate (PET) after it has thermally disappeared in a vacuum framework. While zinc was utilized to generate a

unique dormant mark in gold/zinc vacuum metal deposition, the following zinc store mostly reacted to zinc oxide(x) when exposed to air or when zinc was deposited in the presence of oxygen [104]. In the meantime, consistent zinc oxide films were legally covered onto non-metallic substances on various objects using vacuum dissipation techniques [105–107]. As a result, using the vacuum statement of ZnO to generate a unique imprint on plastic surfaces is advantageous. Without using gold groups as the seed layer, the warm disappearing of ZnO was used to create a unique idle mark on polyethylene terephthalate in this study. Zinc oxide affidavit and gold/zinc vacuum metal deposition were considered for improving the unique mark on polyethylene terephthalate. Without the use of gold kernels, there is no advancement of a unique mark over polyethylene terephthalate after unadulterated Zn assertion. The results were consistent with what had been reported [103], revealing Zn's weak testifying capacity on the plastic surface. The unique finger impression made by the gold/zinc vacuum metal deposition method using gold and zinc materials shows a distinct contrast between the margins and valleys of the unique finger impression. The gold/zinc vacuum metal deposition process demonstrated an usual enhancement in metallic shine. Zinc oxide evidence also creates a typical improvement with a clear differentiation between distinctive finger impression edges and valleys. Zinc oxide affidavit is used to make a dark distinctive mark. It was discovered that zinc oxide could be easily applied to the valley between different finger impression edges and the free surface of polyethylene terephthalate. Along these lines, in addition to single metallic vacuum metal deposition [103], vacuum vanishing of Zinc oxide can also be used to generate inert finger impressions on polyethylene terephthalate substrates, without the need for first spreading of a tiny coating of gold or cyanoacrylate material. In comparison to ancient samples, zinc oxide acquired a distinct pattern. On the finger impression, however, zinc oxide deposition can produce a distinct preferable mark over gold/zinc vacuum metal deposition after 1 month and 15 days [108]. Furthermore, comparison with older samples revealed that ZnO deposition resulted in distinct patterns on fingerprints, with ZnO marks showing preferable characteristics over gold/zinc vacuum metal deposition after 1 month and 15 days [109].

Nanoparticles of Gold (AuNPs)

Gold nanoparticles (AuNPs) performed an important role in the advancement of the dormant finger impressions process because of their dormant behavior, improved discernment, affectability, and features that enable the capacity of the generated finger impressions for a long timeframe [109, 110]. The gold nanoparticles were used in the multi-metal deposition because of their substantial qualities, which improve the permeability of the latent fingerprints using the two-advance sol–gel approach. The gold nanoparticles solution (balanced out in the medium of citrate ion) was used to absorb the substrate with a distinct finger impression, followed by the expansion of silver physical developer (Ag-PD solution) [62, 110]. The resulting latent fingerprints were characterized using a UV–Vis spectrophotometer. Gold nanoparticles bind to

finger imprint residues and mobilize Ag particle precipitation into metallic Ag [72, 101, 111]. A silver image of the latent unique finger impression is obtained due to the electrostatic interaction between the cationic-charged finger impression remnant and anionic-charged Au nanoparticles. The usage of the multi-metal deposition process is limited, as it necessitates washing the item with fingerprints in a fluid arrangement of gold nanoparticles. As a result, the technique isn't suitable for creating prints on surfaces such as walls and floors, or for any item too large to be absorbed by a work area shower and this procedure is costly [64].

Nanomaterials were employed to produce latent fingerprints because they enhance latent prints better. It improves the disparity and finger impressions by increasing the surface interaction with the endogenic material present on the elevations. This research focuses on the exploration of molecular-level information encoded in latent fingerprints, as most scientists focused on visualizing fingerprints at a physical level. The dominating presentation of nanomaterials in improving the affectability and particularity in estimating sciences [111, 112] is a major hallmark. Because of surface plasmon resonance (SPR), when gold metal is nanosized, it exhibits distinct visual characteristics. A variety of blue to red colors can be generated by changing the size and shape of gold nanoparticles. The fascinating property was used in colorimetric detection, surface-upgraded Raman scattering, and bioimaging [112–114]. The light of gold nanoparticles combined with ultraviolet light can cause rapid heat in a small number of nanoparticles. The unique property may aid in the efficient desorption/ionization of particles accumulated on gold nanoparticle surfaces. Gold nanoparticles have two qualities that have been combined. The imaging of inactive finger impressions was done using gold sputtering, and TEM was used to characterize AuNPs. For the representation and atomic imaging of latent finger impressions, imaging mass spectrometry was used to coordinate specific features of gold nanoparticles. The visual representations of inactive finger impressions are shown by two distinct colors (blue and pink), which emerge from various surface plasmon resonance (SPR) groups of gold nanoparticles. The gold nanoparticles' laser desorption/ionization properties allow for quick investigation of endogenic and exogenic mixes implanted in latent finger impressions and imaging their appropriations without disrupting the distinctive mark designs. The simultaneous perception of latent finger impressions and the account for atomic photographs provide proof of a unique way of life, as well as identify unsafe chemicals and settle concealing fingerprints. The technique was used to portray the progression of a visual image of latent finger impressions in a parched state. It can save compound data implanted in the unique mark for later mass spectrometry analysis. Examining latent finger impressions with unaided eyes is possible thanks to the numerous types of gold nanoparticles with different surface plasmon resonance features. Gold nanoparticles' laser desorption/ionization property makes it a successful process for examining small particles inside invisible fingermarks and determining the age of atomic images. The reciprocal idea of the twofold photographs of invisible fingermarks, i.e., ocular and atomic pictures, provides a physical example of fingerprints for single ID and reveals substance data within fingerprints for scientific tests. The electrical conductivity of gold nanoparticles was recently discovered

by examining them under a scanning electron microscope (SEM) for the examination of fingerprints at a minuscule scale, revealing that the AuNPs could serve as a viable mechanism for crossing over various imaging methods from clearly visible to infinitesimal (scanning electron microscopy assessment) stages and uniform to atomic examination (mass spectrometric imaging) [115].

Nanoparticles Based on Oligomer/Silica Hybrid

The red-emissive silica nanoparticles were made by doping it with conjugated Oligomer Fluorescence Dioxaborolane Benzothiadiazole (OFDBT), which performed well in imaging invisible finger impressions. In comparison to hydroxyl or amino group modification, the epoxy groups played a substantial role in the preparation technique due to their morphological and optical qualities. Epoxy, amino, and hydroxyl groups were used to create three different types of nanoparticles. The reverse micelle approach was used to arrange the Oligomer Fluorescence Dioxaborolane Benzothiadiazole/Silica Oxide-Epoxy nanoparticles, and the final product was achieved by freeze-drying in the form of pink color powder. The Oligomer Fluorescence Dioxaborolane Benzothiadiazole/Silicon dioxide-OH nanoparticles were also made utilizing the reverse micelle process with silane as a component and collected as a red powder by freeze-drying. The synthesis of Oligomer Fluorescence Dioxaborolane Benzothiadiazole/Silicon Dioxide-NH_2 nanoparticles was similar to that of Oligomer Fluorescence Dioxaborolane Benzothiadiazole/Silicon Dioxide-Epoxy nanoparticles, except that 3-aminopropyl trimethoxy silane was used instead of 3-glycidyloxypropyl trimeth DLS, scanning electron microscope, NMR, MALDI, and ultraviolet visible spectrophotometer were used to characterize nanoparticles [67, 116–118]. The Oligomer Fluorescence Dioxaborolane Benzothiadiazole/Silicon Dioxide-Epoxy nanoparticles had a sphere-shaped 20 nm size, which was useful for mixing with finger impression elevations during the mechanical method. Because of the molecular dispersion property of silica nanoparticles, the quantum yield and photostability of Oligomer Fluorescence Dioxaborolane Benzothiadiazole were significantly changed. The obtained Oligomer Fluorescence Dioxaborolane Benzothiadiazole/Silicon Dioxide-Epoxy nanopowder displayed kinfolk to the fingerprint's material emissions, forming pictures with fluorescence characters with higher firmness and detailing in it.

The higher sensitivity of the nanoparticles allowed for improved visualization of latent finger marks in images. Due to weak association with solvents like water, the OFDBT/SiO_2-OH nanoparticles displayed spherical particles with a size of 42 nm, but without obvious aggregation. The increased number of amino groups led to uneven geometries in these nanoparticles, as observed by dynamic light scattering in water. The OFDBT/Silicon Dioxide-Epoxy nanoparticles had an average size of 25 nm, while the other group of nanoparticles exhibited a wide size range with a maximum size of approximately 280 nm. The OFDBT/Silicon Dioxide-OH nanoparticles and OFDBT/Silicon Dioxide-NH_2 nanoparticles had hydrodynamic

diameters of 50 nm and 120 nm, respectively. Scanning electron microscopy results were comparable, and light microscopy and fluorescence microscopy showed the ability of OFDBT/Silicon Dioxide-Epoxy nanoparticles to accumulate under dry conditions. OFDBT/Silicon Dioxide-OH nanoparticles, on the other hand, exhibited single dispersion, while a significant amount of powder was observed in OFDBT/Silicon Dioxide-NH_2 nanoparticles [67, 116–118].

Summary and Future Prospects

In this chapter, we emphasized the employment of a range of nanoparticles that could be used as an agent to develop fingerprints on different surfaces. A number of approaches are being developed which are discussed in detail in the preceding sections describing how different forms of nanoparticles made up of different materials could be employed for the development of latent fingerprints. The chapter focused the advantages of nanoparticles over traditional materials for the better visualization of diminished fingerprints which are difficult to develop using traditional methods. In recent times, different shaped and sized nanoparticles made of different materials, viz. silica, gold, silver and zinc have shown makeable potential for developing finger marks, which are conversed in detail. Employment of these nanoparticles exhibited tremendous potential in fingerprint development at a minuscule scale. Furthermore, employment nanoparticles require minimal usage of reagents and are less lingering. Keeping the above discussion in mind, it can be concluded that nanoparticles bear the potential to change the current scenario for the development of fingerprints as they are quick, use minimal chemicals and exhibit amazing optical properties depending on the size of the prepared materials.

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Chapter 3
Latent Fingerprint Development from Magnetic Nanoparticles

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Introduction

With the advancement in various fields of forensic science, many new research articles are published making latent fingerprints visible. Fingerprints being unique has the potential in many a case and their development has become a top priority task in forensic science. Developing fingerprints with powders for their detection, imaging, and identification has become the most common technique in crime investigation [1, 2]. Dusting methods are majorly used by policemen in screening the crime scene for developing the latent fingerprint. Some trouble can also occur like the physical and chemical nature of the surface, fingerprint donor, contaminants present, environmental conditions, and age of latent fingerprint [3–5]. Various literatures are published discussing chemical and physical techniques to overcome these troubles in visualizing the latent fingerprints on various surfaces. There are conventional methods which get adhere to the sticky secretion by the pores present on ridges of fingerprints on the various surface. While the chemical substances interact with the organic or inorganic residue present on the surface due to the impression left by fingerprint [6–12].

Due to various challenges, be that stickiness on surface or lifting from the surfaces it has been quite a challenging task, some methods are discussed in different literature [3, 13–19]. Here in the situation, MNPs have the advantage of lifting latent fingerprints (LFPs) easily by use of ordinary or permanent magnets and also have

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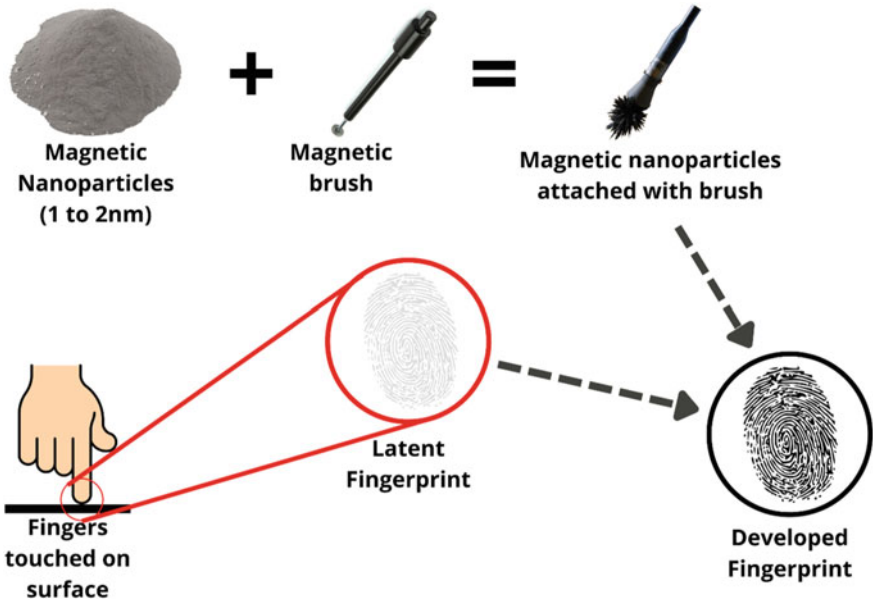

Fig. 3.1 An image showing development of latent fingerprint with the help magnetic nanoparticle

high visualizing power. In the technology of developing LFPs by means of magnetic nanoparticle powder, here the powder in dry form adheres to organic or inorganic substances present in the fingerprint present on the surface. It is very vital to select an MNP with respect to the surface, particle, and the type of remaining fingerprints. Figure 3.1 shows the development of LFPs on the surface using a magnetic brush and MNPs.

The finer magnetic powder has the ability to adhere more to organic or inorganic substances than the coarse one [1]. Fingerprints on the surface will have a complex mixture of natural organic and inorganic particles, so lipophilicity and size of the particle are very crucial parameters to get a high visualization of latent fingerprints on the surface. MNPs such as Fe_3O_4 and also $Fe_3O_4@SiO_2$ have polar nature because of their negative charge and the presence of –OH formulates hydrogen bonds with polar compounds such as moisture as well as Vander Waals dispersion forces and attraction due to dipole–dipole [9, 20–22]. In order to achieve better results during the development of fingerprints, there is a need to create lipophilic interaction between the residue and dusting agent [3]. For creating MNPs more attention should be given to their lipophilicity which can solve the above-mentioned problem of lipophilic interaction and efficiency of the powder. Lipophilic interactions with respect to MNPs are referred to as the ability of the MNPs to attract the residue present in the fingerprint such as fats, oil, lipid, and non-polar substances.

With respect to other used methods or techniques for the development of LFPs, MNPs have few advantages over them. MNPs have strong magnetism, with the help

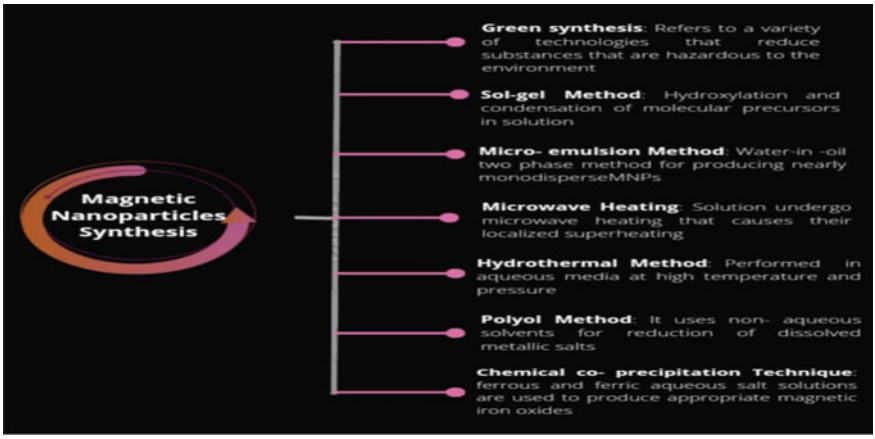

Fig. 3.2 The figure shows the different synthesis methods of the magnetic nanoparticle

of this property we can recover and recycle the used powder. With the help of a magnetic brush and an external magnetic field, the excess powder can be recycled and utilized and aerosol formation due to dispersion in the air of these MNPs can be prevented as it can damage the health of a person who is developing the LFPs. MNPs has also the property of high sensitivity, as the size of MNPs is small, they can reflect very fine ridge details by adhering to the moisture resent on the fingerprint due to sweat pores. A very small amount of MNPs used can give the development of LFPs. With advantage MNPs also has some disadvantages as for producing a high cost is required and there is a limitation for scale-up production and the mobility depends on the environment compatibilities [23]. Figure 3.2 discusses the different methods which can be used for the synthesis of MNPs.

Magnetic Nanoparticles Synthesis

Diacetylene (DA) Powder

For the synthesis of Diacetylene, a mixture of $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ was added to deionized water. The mixture was heated at the temperature of 78 °C and to maintain the pH of the mixture addition of dilute aqueous ammonia hydroxide was done. For 24 h the sample solution was heated at the same temperature and once the heating is done, filtration was done for the Fe_3O_4 particle. Fe_3O_4 particles were collected and then again washed with deionized water and then dried in the vacuum condition so that 53% of the desired magnetite nanoparticles is afforded. Then for the preparation of Diacetylene—Magnetite Composites, a crucible was taken, and in that mixture of 10,12-pentacosadiynoic acid (1.0 g) and magnetic nanoparticles (500 mg)

in tetrahydrofuran (10 mL) was gently ground till the evaporation of solvents is completed.

The fingerprint was successfully developed using the DA powder over the solid substrate. The immobilization of DA powder was achieved by moving the magnet under the solid substrate. The excess powder was removed using an air blower. To irradiate the Diacetylene-immobilized image a UV light is used and heat treatment was provided at last to convert the blue phase to the red phase image. The most perceptible image was formed when the weight ratio of Pentacosadiynoic acid (PCDA) to MNP was 20:1 because the red color shows more fluorescent, and a well-developed ridge was clearly visible under a fluorescence microscope. It was observed that the sebaceous lipid-like DA molecules facilitate the immobilization of the DA on fingerprint ridge structures [24].

Fe_3O_4 GSH-Pt NCs

The co-precipitation method for the synthesis of Fe_3O_4 was used. The mixture of NaOH and KNO_3 was added to H_2O. This solution was added to Fe_3O_4 solution and heated at 25 °C for half an Hour. After that centrifuge at 10,000 rpm for 15 min was done then washing with deionized water was done thrice. Polyethyleneimine (PEI) solution was ultrasound for 15 min and then the Fe_3O_4 was added to that and heated at 80 °C. Then microwave-irradiated in the microwave and then ultracentrifuged. With centrifugation, the precipitate is washed with deionized water to obtain PEI- Fe_3O_4 solution. To fabricate glutathione (GSH)-Pt NCs, GSH was added to H_2PtCl_4 with continuous and fast stirring. When the mixture was mixed evenly then it was ultrasound and then heated in the microwave oven, this step was repeated to get GSH-Pt NCs. For fabrication of Fe_3O_4 on GSH-Pt NCs powder, the solution created above was mixed evenly at room temperature, the + ve and -ve charged solution experienced electrostatic adsorption and Fe_3O_4 GSH-Pt NCs core–shell microspheres were obtained.

Fingerprints were developed on a dark wood desktop. The Fe_3O_4 GSH-Pt NCs powder was applied with the help of a brush in a clockwise direction alongside ridges. A successful fluorescent image was obtained by a self-assembled development observation system [25].

Lipophilic Fe_3O_4@SiO_2@MeMFNPs

For synthesis of Fe_3O_4 magnetic nanoparticles, a mixture in deionized water under the nitrogen atmosphere and mechanical stirring of ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) and ferric chloride hexahydrate $FeCl_3{\cdot}6H_20$. And for adjusting the pH to 9–11, an aqueous solution of NH3 was added and stirring was provided. After that filtrate was washed with distilled water and black precipitate of Fe_3O_4

was collected with the help of external magnet. Then for preparation of silica-coated Fe_3O_4 MNPs, an ultrasonic premixing of black precipitate of Fe_3O_4 in ethanol. After that aqueous NH_3 and TEOS were added, then mechanical stirring was provided and with the help of external magnet, a silica-coated Fe_3O_4 precipitate was collected and dried under the vacuum at room temperature. Then a lipophilic nature was provided to silica-coated Fe_3O_4 with methyl moieties based grafting of precursor trimethoxymethylsilane (TMMS). In a dry toluene which had silica-coated magnetic nanoparticle, TMMS was added. The mixture formed was stirred for 24 h and the solution was washed many times with toluene and ethanol, and in vacuum condition powder was dried and lipophilic magnetic nanoparticles were formed.

The fingerprints were developed and the magnetic property of the powder was helpful for removing the excess powder present on the LFP. There was a decrease in magnetic saturation due to the presence of silica shell coated on magnetic particles. But saturation was sufficient for removing the physical magnet. The formation of LFPs was due to physico-chemical process between the skin and surface. Physical property of powder and oily component helps in adhesion, in that way the silica-coated MNPs were designed to create lipophilic and microscopic interaction with oil and greasy molecule. And these powders showed a good contrast and clarity in LFPs. With the help of tape and gelatin film, and photographic method the LFPs were recorded. The prints were successfully collected from porous surface be that wall, paper sheet, medium-density fibreboard, and nonporous surfaces including plastic wall, water glass, and door handle made up of metal [20].

P-MNP@Ag Magnetic Nanoparticle

For synthesis of nanosilver, $AgNO_3$ needs to be added in water and heated, followed by the addition of sodium citrate. A continuous stirring needs to be provided by mechanical stirrer and then cooled at room temperature. For synthesis of $Fe_3O_4.FeCl_3.6H_2O$ in a flask, $Fe_3O_4.4H_2O$ and distilled water were added and to maintain pH ammonia was added and then a gel of black color appeared in large amount. Solution was heated and continuous stirring was given and the black color product obtained due to centrifuge was washed with the ethanol. And then Fe_3O_4 was dried under vacuum conditions at room temperature. Then for the final synthesis of S-MNP, Fe_3O_4 and distilled water were added and ultrasonicated, and to that 3-mercaptopropyl triethoxysilane (MPTES) with ethanol and acetate was added and on ice bath it was ultrasonicated. Then to Fe_3O_4 and ultra-sonicated water the above made solution was made and after that centrifugation was done, the precipitate was washed with ethanol and then dried under vacuum condition and ground to fine particles, and stored. To make P-MNP Ag a facile coprecipitation was formed, firstly synthesis of P-MNP-0.13. $NH_3.H_20$ was taken in flask and to that MPTES was added very carefully and the striation was provided. In the flask $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ were taken and distilled water was added and stirred. Then the hydrolyzed MPTES was added into flask to make pH to 9, striation was provided and

black precipitate opted out and they were washed with ethanol. They were collected and dried at room temperature, and were ground to fine particles. And like this the amount of MPTES was changed and different magnetic nanoparticles were synthesized: P-MNP-0.043, P-MNP-0.13, PMNP-0.36, and P-MNP-1.08. Then synthesis of P-MNP Ag. P-MNP-0.13 was dispersed in distilled water and stirred and then carefully drops of nano silver were added and then ultra-sonicated for 2 h. Once reaction is quenched it was centrifuged and precipitate was washed with ethanol and collected and dried in vacuum, and then the final product was converted to fine particles.

Fingerprints were developed on porous surfaces such as paper, artificial leather, filter paper, weighing paper, and non-permeable objects such as metal doorknobs, railings, plastic bottles, and plastic wash basin. P-MNP Ag has excellent development effects on plastic and paper. Due to smooth texture of P-MNP Ag than of S-MNP Ag, it was able to develop LFP on plastic and leather. P-MNP Ag showed very less background interference, and was highly sensitive and was able to show very fine secondary details of the LFPs on many of the surfaces with less time taken for development [26].

Fe_3O_4 Ag Nanoeggs

For the synthesis of Fe_3O_4 nanoparticles coprecipitation was used. Coprecipitation of ferric and ferrous chloride was added into the NaOH and stirring was provided. Then cooling was done in an atmosphere of nitrogen and black product which resulted was washed with ethanol, then fabrication of APTES-modified Fe_3O_4 nanocomposites was done by keeping Fe_3O_4 nanoparticle in ethanol and then APTES mixture along with CH_3COOH or $NH_3{\cdot}H_2O$ was added and mixture reacted vigorously under water bath. Precipitate was filtered and separated by permanent magnet and washing was done using ethanol. Then fabrication of Fe_3O_4 Ag nanoeggs was done. APTES-modified Fe_3O_4 nanoparticles were mixed with Ag nanoparticles and were kept for adsorption to take place. Excess amount of Ag was removed using magnet and after that particles were dispersed in ethanol. A shell of Ag-modified Fe_3O_4 magnetic nanocomposites was formed by reducing aliquots of AgNO3 with NaBH4 in magnetic separation and dissolved in distilled water.

The fingerprints were developed using adhering property of powder with moisture and oily components, and excessive amount of powder was removed by dusting or gently blowing on the surface. These modified Ag Fe_3O_4 nanoeggs were strongly attached to magnetic brush. They were able to produce less background development due to smooth surface of the Ag and that gave a good contrast between the LFPs and surface. Fe_3O_4 Ag nanoeggs powder was synthesized in different pH and it was found that fingerprints which were developed using the higher pH nanoeggs powder showed more intensity of powder and maximum background development was observed due to the bigger size of Fe_3O_4 Ag nanoeggs. Fe_3O_4@Ag nanoeggs

showed excellent ridge details with minimal background staining on glass, porcelain enamel, polyethylene pieces, and paper surfaces [27].

Conclusion

To develop latent fingerprint adherence and reaction are two properties for their development. So these magnetic nanoparticles get adhered to the moisture and oily substances present due to the sweat spores present on the fingers. The magnetic particle due to their fine texture and surface gets smoothly adhered to the surface and decreases the background development and gives high contrast development of latent fingerprints. And the excessive amount of powder can be recovered from the development area with the help of external magnet and like other nanoparticle hazardous to the person who is developing those fingerprints, these magnetic nanoparticles doesn't show such threat. These magnetic nanoparticles can be tuned or modified according to the concern of their response toward magnetic field. But the drawback is the cost of production of very minute quantity is very high. These magnetic nanoparticles can show very high contrast of latent fingerprint. In the field of forensic science to develop latent fingerprint, magnetic nanoparticle can play a crucial role, due to their property of producing high contrasting images and decreasing the background noise. Magnetic powder sowed its development on all kinds of surfaces, according to the type of surface the MNPs powder can be used and LFPs can be developed. Fingerprints on the surface will have a complex mixture of natural organic and inorganic particles, so lipophilicity and size of the particle are very crucial parameters to get a high visualization of latent fingerprints on the surface.

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Chapter 4
Silver and Gold Nanoparticles for the Development of Fingerprints

Abhinav Singh, Vandana Prasad, Sally Lukose, and Ashok Kumar

Introduction

Forensic technique is defined as the methodology adopted to assist and identify evidence to assist criminal investigations with more ease and success. These forensic techniques are also being opted to evaluate fingerprint evidence since fingerprints are considered as a primary tool in criminal investigations. Additionally, fingerprints provide valuable information about the accused, and play a key role in individualization and identification of the offender from a group of suspects. The fingerprints are not limited to criminal investigations or forensic detections, but also have significant value in various areas such as biometrics, as a substitute for signature in legal documents, police records, etc. The characteristics of fingerprints such as uniqueness, immutability, and persistence give very important evidentiary value in criminal investigations and law enforcement [34]. Three types of fingerprints are recovered from the crime scene. The ones which are easy to locate and visible to the naked eye are called "Patent" prints. Other fingerprints recovered from clay or wax surfaces are called "Plastic" prints. Prints not visible to the naked eye are called "Latent" prints, and are often left inadvertently by the offender at the crime scene [65]. Therefore, development of latent prints requires extra effort using various physical and chemical methods.

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Conventionally, latent prints have been developed using powder dusting, cyanoacrylate fuming, silver nitrate fuming, and small particle reagents methods [67]. Although, the results obtained using these conventional methods have low sensitivity, low selectivity, low contrast visualization, and are highly toxic to use. In the absence of an alternative method, these conventional development procedures are still being adopted for processing the latent fingerprints.

In addition, Ruhemann introduced the method for detecting latent fingerprints in the twentieth century [50]. The method was based on the reaction of ninhydrin with amino acids released from sweat pores, resulting in purple color fingerprints. Further, treating ninhydrin with other metal salt solutions like Zn, Cd, and Hg provides fresh fingerprints on white paper. The other reagents that work like ninhydrin and react with amino acids are 1,2-indanedione and 5-methylthio ninhydrin (5-MTN). The latent fingerprints developed using 5-MTN require high temperature and humidity for development similar to ninhydrin. Further, the color of latent fingerprints changes from purple to pink when 5-MTN is treated with a zinc salt [10].

The cyanoacrylate fuming method to develop latent fingerprints on non-porous surfaces results in white color prints. The white color-coated prints are developed due to the rapid polymerization on the residue of latent fingerprints. Further, metal oxides such as zinc oxide, iron oxide, etc., and sulfides like molybdenum disulfide, cadmium sulfide, and selenide powders are also used to develop latent fingerprints [51].

But, latent fingerprints produced by using gold and silver nanoparticles have a high detection rate and high sensitivity as gold particles are inert, preserving latent fingerprints for an extended time. The surfaces usually adsorb AuNPs electrostatically to detect latent fingerprints [3]. Also, the surface properties of the AuNPs can be modified, increasing their affinity to interact with the sweat components.

Nanoparticles are defined to have dimensions of 100 nm or less. Nowadays, nanoparticles are gaining popularity because of their attractive properties and unusual behavior. Many nanoparticles are synthesized by applying physical, chemical, and biological methods. However, the use of hybrid nanoparticles is also tremendously rising in dealing with bulk applications [3].

In the current scenario, the synthesis of metallic nanoparticles by physical and chemical methods is rising. The applicability of nanoparticles generally depends upon their process of synthesis. However, the use of synthesized gold and silver nanoparticles gaining more attention in forensic science, specifically in dactyloscopy (study of fingerprints).

To overcome the limitations of conventional techniques, fingerprints are nowadays developed using nanoparticles of different elements. The next-generation technology for developing latent fingerprints by means of nano-based techniques is called nanofingerprinting [47].

The use of nanoparticles for the decipherment of latent fingerprints is being used since the nineteenth century. Various nanocomposites have been developed for the detection of latent prints. The most commonly used variants are fluorescent nanoparticles such as quantum dots, carbon dots, rare-earth materials, metal nanoclusters,

etc. [26]. Although pre-processing of fluorescent nanoparticles is a complex process [13, 18], the primary nanomaterials that were opted for the development of latent fingerprints were gold and silver nanoparticles. The gold and silver nanoparticles are bio-compatible and show supreme physico-chemical properties in locating the latent prints as they adhere to the ridges of latent fingerprints (Choi, 2008) and preserve them for long periods of time [69].

The traditional practice of latent fingerprint development comprises various physical and chemical methods; however, regarding the stability and contrast of latent fingerprints, these methods remain inadequate to fulfill current needs. Therefore, recent research focuses chiefly on nano-based techniques to better identify latent fingerprints. Nanoparticles are being utilized in the form of nano-solution or nano-powder to identify latent fingerprints. One of the significant advantages of using nanomaterials in latent fingerprint detection is their large surface to volume ratio, which provides relatively greater active surface area than conventional techniques. Additionally, due to their unique optical properties, nanomaterials lead to excellent contrast for the fingerprint residue in daylight conditions without any addition of chemicals. Among all the other nanomaterials, silver and gold nanomaterials are trendsetters for identifying latent fingerprints in different conditions. In addition, the inert nature of gold nanomaterials demonstrates better stability of latent fingerprints, whereas silver nanomaterials display a better adherence property between fingerprint residue and the surface containing the fingerprint.

Gold Nanoparticles

In general, gold nanoparticles appear as spherical balls with an average size of about 2–3 nm. The unique properties of gold nanoparticles create an emerging platform for diverse applications. The nanogold-based system works effectively because of its adjustable functionality dependent upon nanoparticle shape and size [14].

Gold nanoparticles show variance in optical properties as per change in their size. In addition, gold nanoparticles (AuNPs) are inert, with high selectivity and sensitivity in fingerprint detection. AuNPs show conformational stability and low toxicity toward biological systems [73].

Further, AuNPs show various morphological characteristics in their structures. The synthesis of AuNPs is done by reducing gold in aqueous phase then the shape appears to be quasi-spherical [14]. The AuNPs are manufactured in various forms such as Nano-spheres, Nano-rods, Nano-shells, Nano-prisms, etc., that have effective applications in large number of fields. Some of the most common types of AuNPs are depicted in (Fig. 4.1).

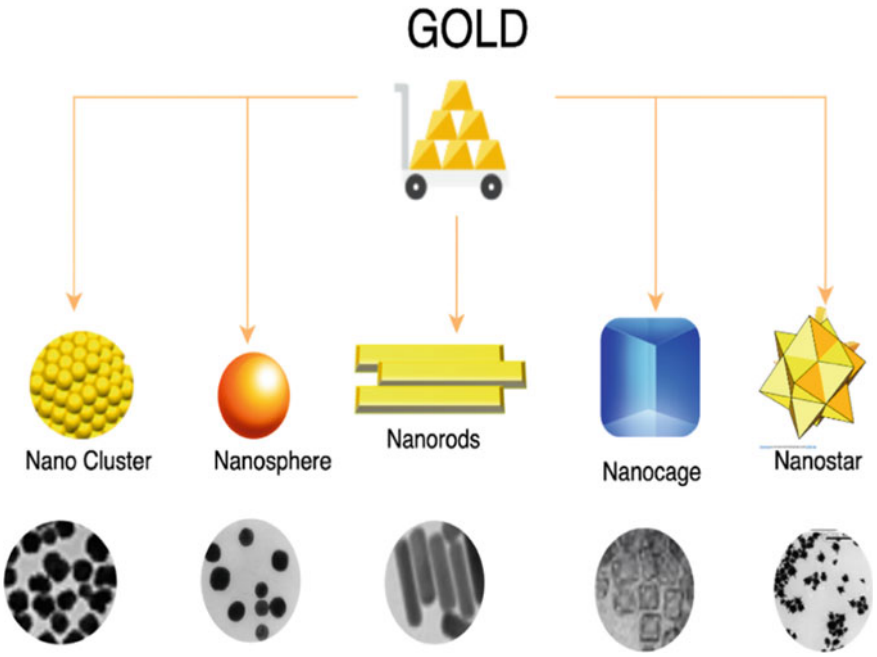

Fig. 4.1 Shapes of Gold nanoparticles

Silver Nanoparticles

Nanotechniques are an important emergent trend in many fields of science. Nanomaterials have attracted attention from many other disciplines including forensic science. Silver nanomaterials are being utilized in fields like fingerprint detection and illicit drug detection. Silver nanoparticles possess unique chemical and physical properties, which rely upon their particle size which is typically less than 15 nm [6]. One of the important properties of silver nanoparticles is surface plasma resonance showing absorption spectrum in UV–visible range, which depends upon the size and shape of the nanoparticles. A decrease in particle size leads to a blue shift, whereas an increase in particle size leads to a red shift in the absorption spectrum. Thus, absorption spectra can indicate particle size distribution of silver nanoparticles. A diagrammatic representation of the various shapes of the silver nanoparticles is given in Fig. 4.2.

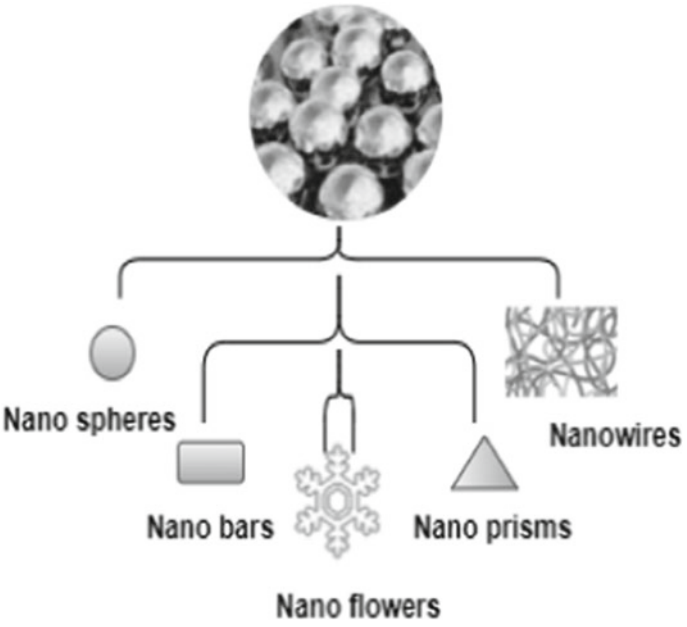

Fig. 4.2 Shapes of Silver nanoparticles

Synthesis of Gold and Silver Nanoparticles

The synthesis of gold and silver nanoparticles follows several protocols. The most common protocol is top-down protocol. In top-down protocol, physical and chemical processes are applied to bulky materials to degrade them into smaller pieces [68]. Whereas in the bottom-up protocol, the nanoparticles are synthesized using small precursors. These precursors are metallic salts or metallic seeds that combine to form nanostructures [2].

The affinity of nanomaterials to other materials depends upon their size and, more significantly, on their route of synthesis and the properties of nanomaterials vary according to their size [28]. Therefore, current research studies are more focused on the preparation methods for nanomaterials. There are myriad ways of silver nanoparticles' synthesis. The methods for synthesizing gold and silver nanoparticles are classified into three categories, i.e., Physical, Chemical, and Green approaches (Elahi, 2018). All these three methods for synthesis of nanoparticles produce numerous varieties in the morphological structure of nanoparticles [27]. A diagrammatic representation for the synthesis of gold and silver nanoparticles is shown in (Figs. 4.3 and 4.4) respectively.

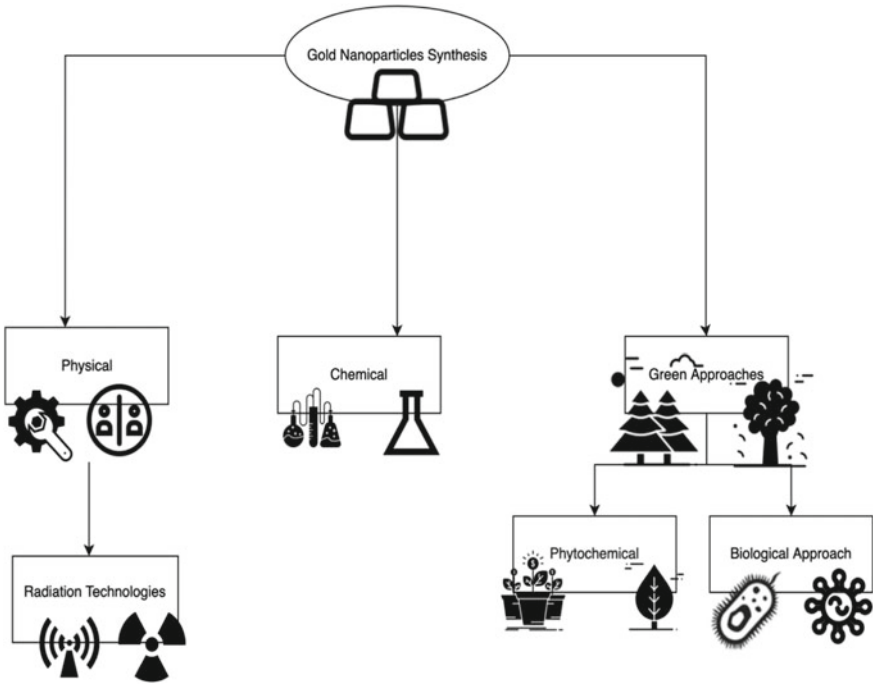

Fig. 4.3 Methods of Gold nanoparticles synthesis

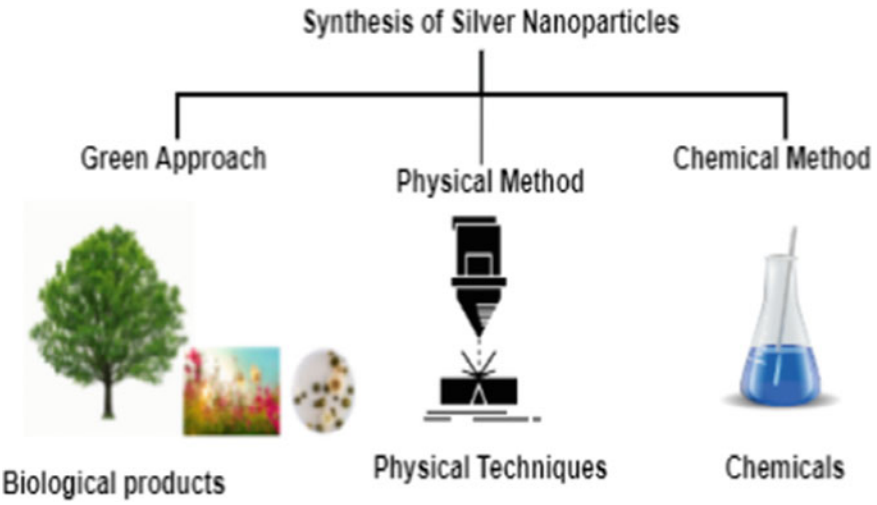

Fig. 4.4 Methods of Silver nanoparticles synthesis

Physical Methods for the Synthesis of Gold and Silver Nanoparticles

In the physical method, gold and silver nanoparticles are prepared via physical techniques like laser ablation, arc discharge, and vapor condensation. The laser ablation technique involves the reduction of bulk material into nano-size particles using a laser beam [72]. While arc discharge involves arc discharge method for the production of nanoparticles. Likewise, the vapor-condensation method comprises two steps; first, the bulk material is vaporized into a gaseous state, and then its condensed form results in nano-size particles. One of the main advantages of using a physical method is that it doesn't require any reducing agents. Hence, it provides nanoparticles of uniform structure with distinct dispersion [1, 72].

Mechanical energy transfer occurs when a material is treated with ionizing and non-ionizing radiations while the nucleation of nanoparticles occurs due to the reduction in a reaction. The most common methods are photochemical processes [66], use of ionizing radiation [38], and microwave radiation [16]. Some of the methods for the synthesis of AuNPs and AgNPs are discussed below.

Sonochemical Techniques

Nowadays, the use of radiation technologies to develop AuNPs and AgNPs is rising. The benefit of using radiation technology is that it is a time-saving procedure and shows a rapid reaction rate.

One of the well-known techniques for synthesizing nanoparticles by using ultrasonic radiation is the sonochemical method. The nanoparticles synthesized by this technique show a wide range of size variation which is helped by using surfactants and alcohol. As per the literature, the average size of gold nanoparticles deposited on chitosan powder developed by the sonochemical method was about 22 nm. Further, thiol-functionalized ionic liquid synthesizes highly regular small-sized AuNPs and AgNPs with uniform distribution.

Gamma Radiation in Aqueous Polyvinyl Pyrrolidone (PVP)

In this method gamma radiation plays a pivotal role in reducing Au^{3+} to Au^{0} and Ag^{+} to Ag^{0} as in this radiolytic route no external reducing agent is required [38, 57]. Therefore, this method has the capability to synthesize gold nanoparticles more effectively in a shorter span of time. The gamma radiation route for gold nanoparticles' synthesis reaction involves only precursor and stabilizing agents.

Microwave Techniques

For the synthesis of uniform colloidal AuNPs and AgNPs, the high-power microwave techniques can also be utilized. The AuNPs created using microwave techniques have a diameter between 12.04 and 13.39 nm [54]. The synthesis of colloidal AuNPs is so quick that nanoparticles are synthesized within a few minutes. While, AgNPs created using microwave heating technique possess spherical shape with an average particle size of about 10-20 nm [74].

At the initial stage of the reaction, the high-power microwave is applied to increase the temperature ramping rate. The increase in the temperature ramping rate facilitates homogeneous nucleation. Due to the homogeneous nucleation, the nanoparticles' sizes reduce, which also results in the uniformity of the nanoparticles. In this technique, atmospheric pressure is applied to synthesize colloidal AuNPs and AgNPs.

The role of pH in the development of AuNPs and AgNPs by microwave technique is crucial as higher pH solutions produce uniform-sized nanoparticles. Less reactive Au complexes also strengthen the stability of the nanoparticles. Hence, by providing high pH, and fast ramping temperature for extended time period, produces the AuNPs and AgNPs by microwave technique [54].

Chemical Methods

The chemical synthesis of nanoparticles requires strong and mild reducing agents. The nanoparticles synthesized using chemical methods have excellent size control, and their morphology depends on their matrix size [11]. Additionally, chemical reduction is considered as one of the most common and simplest methods for synthesizing gold and silver nanoparticles at ambient temperature [37].

Sodium borohydride ($NaBH_4$) [24], hydrazine [63], and citrate [73] are used to initiate the synthesis process followed by the nucleation of the nanoparticles. Pathways for the synthesis of AuNPs and AgNPs are not limited to a few chemicals only. Newer pathways could be explored owing to high stability and performance of gold and silver nanoparticles. However, sodium borohydride and hydrazine as reducing agents have worked effectively since long. Other chemicals such as formaldehyde, hydroxylamine, hydrogen peroxides, sulfites, hydrogen, acetylene, polyols, citric and oxalic acids, and sugars are also used as reducing agents in the synthesis of AuNPs [20].

The chemicals like trisodium citrate dihydrate, sulfur thiolates, phosphorus ligands, oxygen, nitrogen-based ligands, surfactants, and bromides are used as stabilizing agents for AuNPs.

Table 4.1 shows the different sizes of silver nanoparticles using various reducing agents [25, 28, 29, 31, 36, 44–46, 48, 60].

Few methods for the synthesis of gold and silver nanoparticles by reducing and stabilizing agents are mentioned below:

Table 4.1 Different sizes of silver nanoparticles using various reducing agents

S. no	Reducing agent	Size (nm) of AuNPs	Size (nm) AgNPs
1	Ethylene glycol	10-60 nm	17 nm
2	Tollens's reagent	–	10–12 nm
3	Hydrazine	20-130 nm	2–20 nm
4	Sodium borohydride	2-10 nm	5- 20 nm
5	Ammonia	–	10–12 nm
6	Sodium citrate	1-5 nm	2–10 nm

Table 4.2 Representation of structural study of nanoparticles synthesized using microorganisms

S. no	Microbes	Shape	AuNPs size (nm)	AgNPs size (nm)
1	*Sargassum wightii*	Planar	7–11	–
2	*Rhodococcus sp.*	Spherical	6–14	–
3	*Plectonemaboryanum*	Cubic	10–25	–
4	*E.coli*	Triangles	20–30	–
5	*Pseudomonas aerignosa*	–	15–30	–
6	*Candida utilis*	–	–	–
7	*Brevibacterium casei*	Spherical	10–50	10–50
8	*Neurospora crassa*	Spherical	32	20–50
9	*Yeast*	Irregular Polygonal	9–25	9–25
10	*Fusarium oxysporum*	Spherical	8–14	8–14
11	*Corynebacterium glutamicum*	Irregular	–	5–50
12	*Trichoderma viride*	–	–	2–4
13	*Bacillus licheniformis*	–	–	50
14	*Aspergillus flavus*	Spherical	–	8.9–1.61
15	*Verticillium sp.*	Spherical	–	25–33

Turkevich Method for the Synthesis of AuNPs and AgNPs

The Turkevich method is one of the most famous chemical techniques used to synthesize AuNPs and AgNPs. In this method, the solution of gold(III) chloride hydrate is boiled, followed by trisodium citrate dihydrate with continuous stirring. The solution turns wine red from light yellow with time. The AuNPs and AgNPs synthesized by using Turkevich method have a diameter of about 20 nm. Citrate ions play a crucial role in this method as they act as both reducing and stabilizing agents simultaneously [22, 62].

Nanoparticles of diameters ranging from 15 to 150 nm were synthesized by Frens who modified the Turkevich method by controlling the reducing and stabilizing

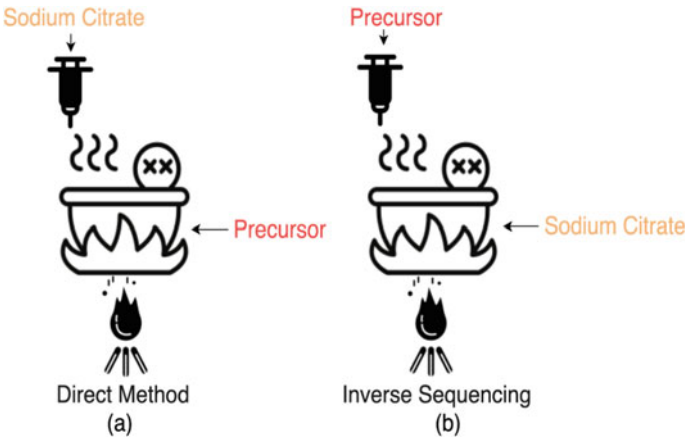

Fig. 4.5 **a** Direct method [62] **b** Inverse sequencing [15]

agent trisodium citrate. It was noted that high concentration citrate ions stabilized the smaller size AuNPs and AgNPs [15]. However, in a lower concentration of citrate, the small nanoparticles were aggregated into large nanoparticles [73]. Based on the theoretical and experimental values, It was noted that the size of nanoparticles could be controlled by sodium citrate based on the pH of the solution (Li, et al., 2011) as shown in (Fig. 4.5a).

Inverse Sequencing

The other method for the synthesis of small and narrow size AuNPs and AgNPs is reported by the inverse sequencing of the Turkevich method. In this process the sodium citrate solution was put onto a boiling system which was further followed by the addition of precursors [15, 43] as shown in (Fig. 4.5b).

The Brust-Schifrin Method

This approach was introduced in 1994 by Brust and Schiffrin and worked effectively to develop controlled size, thermally stable, and air-stable AuNPs and AgNPs.

The transfer of precursor ions from an aqueous solution to a toluene phase, the solution of tetrabutylammonium bromide(TOAB), was used as the phase transfer agent. Further, the process was reduced by using sodium borohydride ($NaBH_4$) in the presence of dodecanethiol. The addition of reducing agents results in developing a deep brown color compound indicating the synthesis of AuNPs and AgNPs [5].

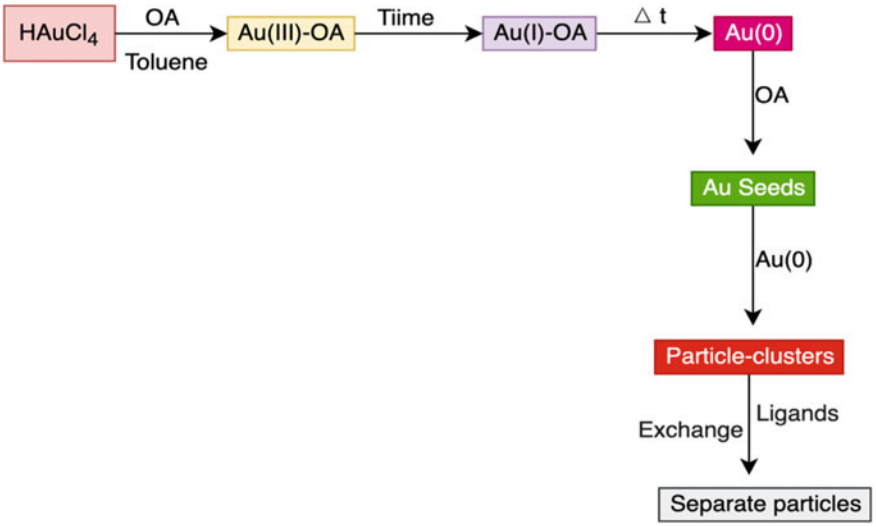

Fig. 4.6 Chemical reaction pathway for Seed growth methods [55]

Seeding Growth Method

This approach is a quick, low-cost process and easy for the synthesis of AuNPs. This approach synthesizes gold nanoparticles' diameters ranging from 5 to 40 nm. The size of the particles in this process is controlled by changing the ratio of seed particles and metal salts. The primary source for seeding up OH- is trisodium citrate, whereas the reducing agent used was sodium borohydride ($NaBH_4$) [55]. The chemical reaction is represented in (Fig. 4.6).

Green Approach

Due to the growing demand for eco-friendly nano-techniques, the green process has become a favored over chemical methods. Biological products act as reducing agents to reduce silver ions to metallic silver. Presently, mostly microbes and plant extracts [37] are being used for the green approach. The microbial process comprises micro-organisms like fungi, yeast, bacteria, and algae to reduce silver ions to metallic silver. Additionally, microbes secrete different proteins around the nanomaterials, protecting them from agglomeration.

Plant extracts have gained significant attention for the synthesis of silver nanoparticles because they are readily available and contain a variety of functional groups that act as reducing agents. Mainly leaves, stems, roots, seeds, fruits, flowers, and bark of the plants are used to prepare silver nanoparticles. The major reducing components

in plant parts are amino acids, alkaloids, vitamins, proteins, flavones, and enzymes that promote the reduction of Au^{3+} to Au^0, and Ag^+ to Ag^0.

Additionally, phytochemicals also provide a "green approach" for the synthesis of AuNPs and AgNPs. One of the best examples of synthesizing the nanoparticle by green approach is the Microwave-Induced-Plasma-in-Liquid process (MWPLP). MWPLP consumes less energy and does not require toxic reducing reagents [30].

The phytochemical compounds extracted from soybean have a low molecular weight that helps to initiate the nucleation. In contrast, the proteins with high molecular weight are highly efficient in reducing gold nanoparticles and stabilizing them [14].

The phytochemical constituents such as aldehydes, alcohols, fats, and volatile oils have functional groups like amino, thiol, hydroxyl, carboxyl, etc., that act as reducing agents in generating gold nanoparticles. Nanoparticles reduced by phytochemicals are stabilized using arabica gum.

Biological Approach

The synthesis of gold nanoparticles using "microorganisms" such as bacteria, fungi, etc., creates an eco-friendly approach to nanoparticle synthesis. Synthesis of AuNPs and AgNPs by biological approach is vigorously rising and is receiving considerably more attention than other approaches [42]. The shape, size, and synthesis locations of AuNPs and AgNPs depend upon the culturing temperature of the microorganisms. The shapes of AuNPs and AgNPs synthesized by microorganisms include planar, spherical, cubic, octahedral, triangular, hexagonal, pyramidal, etc.

Monodisperse AuNPs are synthesized at extreme conditions. The *Rhodococcus sp.* bacteria is treated at high temperature in an alkaline medium to synthesize monodisperse AuNPs. The filamentous cyanobacteria synthesize the AuNPs with different shapes from gold thiosulphate and gold chloride complexes [41]. Although, nanocrystals and nanoalloys are synthesized by *Lactobacillus sp.* [42].

Some fungi, such as *Fusarium oxysporum, and Thermomonospora sp.,* are reported for the extracellular synthesis [41], whereas, *Verticillium sp.* is reported for the intracellular synthesis of gold and silver nanoparticles [35]. Some properties of AuNPs and AgNPs synthesized by microorganisms are depicted in the Table 4.1 [36].

Characterization of Gold and Silver Nanoparticles

Characterization of nanoparticles deals with determination of the nanoparticles' structure, morphology, and other properties so that the suitability of these particles for certain applications can be determined. There is a wide range of instruments used for characterizing nanoparticles. The optical properties of silver & gold nanoparticles were initially characterized by UV–visible spectroscopy, and the absorbance spectra

were used to furnish preliminary details about the nanoparticle formation, shape, and size. Whereas the morphological study of nanoparticles can be ascertained using electron microscopy (SEM and TEM) and X-ray diffraction (XRD) methodology.

TEM and SEM images provide detailed information about average particle sizes and surface morphology. XRD analysis provides detailed information about the crystalline structure of the nanoparticles where particular absorbance peaks of the element can be used to determine the lattice structure of the nanomaterials. Figure 4.7 displays some SEM and TEM images of silver and gold nanoparticles illustrating their morphology. Figures 4.7a, b show SEM images of spherical AuNPs and AgNPs. Figure 4.7c shows a TEM image of uniform AuNPs particle shapes. section, while Fig. 4.7d shows a TEM image of AgNPs showing variable particle shapes.

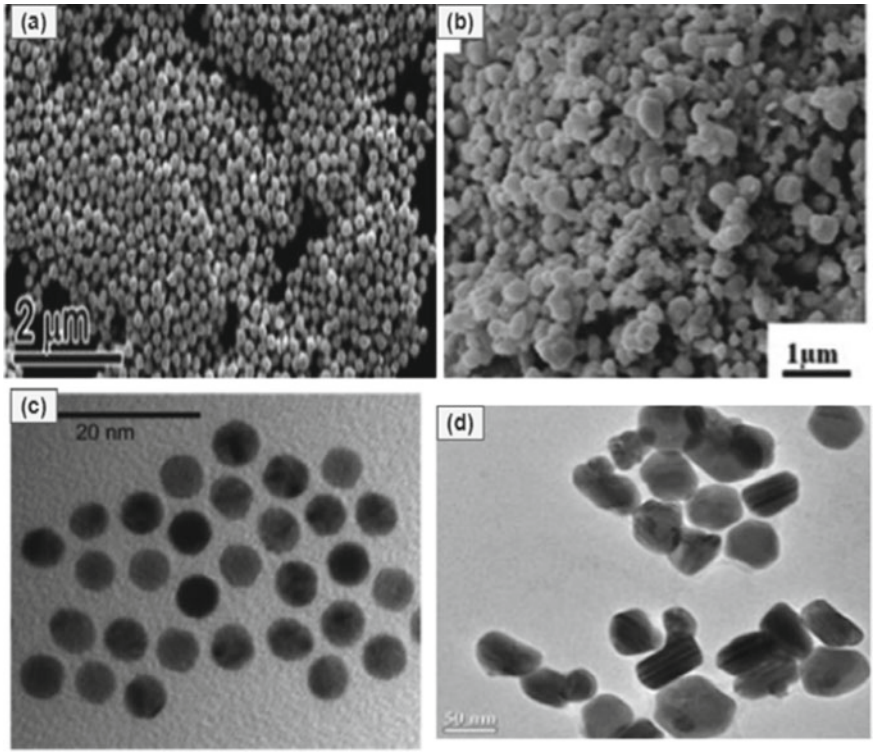

Fig. 4.7 SEM images of surface morphology **a** AuNPs [17] **b** AgNPs [19]; TEM image of structural morphology of **c** AuNPs [49] **d** AgNPs [56]

Application of Gold Nanoparticles in Latent Fingerprint Development

The use of gold nanoparticles for the development of latent fingerprints was applied for the first time in 1989 [52]. However, at that time the use of gold nanoparticles for the detection of latent fingerprints was not that much explored in the field of forensic science. After decades, the use of nanoparticles for the development of latent fingerprints came into limelight in the year 2006. In the time span between 2006 and 2016 nanoparticles such as aluminum oxide, silicon dioxide, starch-based carbon, and Eu^{+3} -doped Al_2O_3 were used in the development of latent fingerprints. All these nanoparticles were capable of detecting the latent fingerprints on porous and non-porous surfaces. But nowadays, the results obtained using AuNPs present the finer details of ridges [47] and the inert nature of the AuNPs allows the development of better-quality fingerprints [39].

- **Gold Nanoparticles in Fingerprint Imaging**: Owing to their unique optical property, gold nanoparticles possess a light tuning ability from red to blue in a wide spectral range. Depending on their size, the color of gold nanoparticles changes; smaller particles lead to a blue shift, while larger particles lead to a red shift. In general, this light tuning property of gold nanoparticles could be characterized using mass spectroscopy (MS). Besides this, gold nanoparticles also possess a laser ionization property under UV-laser, which could generate rapid heating.

These dual properties of gold nanoparticles are implemented to better identify the latent fingerprint on various surfaces [61]. Firstly, the objects bearing fingerprints are immersed in a gold nanoparticle solution. Secondly, latent fingerprint underlying substrates are placed under a sputter coater chamber for about 120 s—the method developed a dual-color of latent fingerprints with pink ridge details and blue grooves. The dual nature of latent fingerprints not only furnishes the detailed information of the individual but also molecular information for criminal investigation as shown in Fig. 4.8.

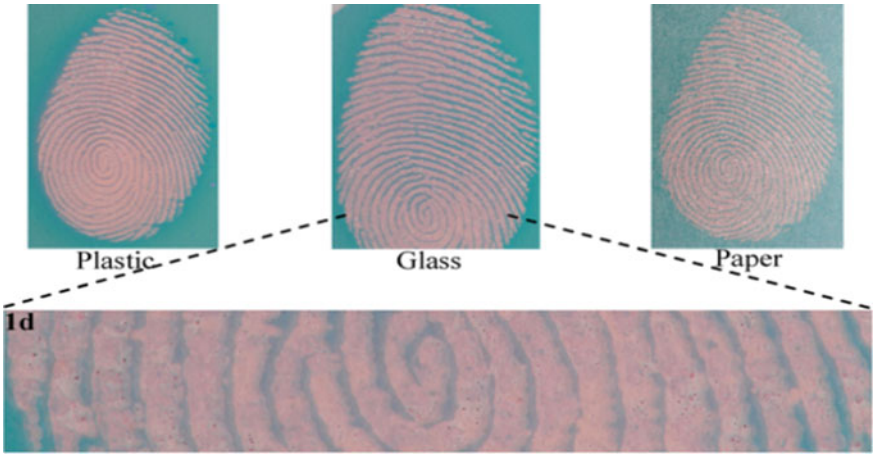

Fig. 4.8 Dual-color development of latent fingerprints with pink ridge details and blue grooves on plastic, glass, and paper surfaces [61]

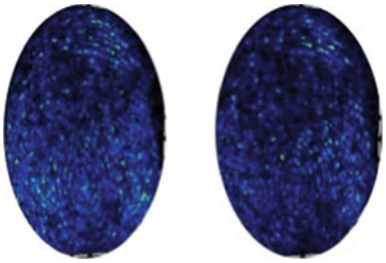

Fig. 4.9 Latent fingerprints enhanced using MS and imaging technique on fingerprints containing traces of drugs [45]

Fig. 4.10 Latent prints developed using photothermal semiconductors from various objects [9]

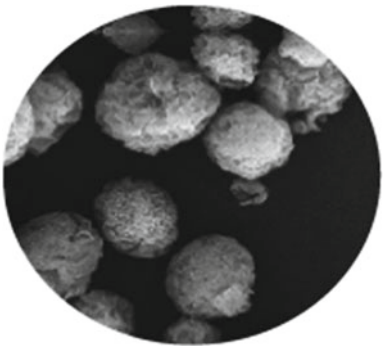

Fig. 4.11 Au montmorillonite nanoparticles under SEM [71]

Fig. 4.12 Latent prints developed using Gold nanoparticles as montmorillonite powder

Fig. 4.13 Latent prints developed using gold nanoparticle amalgamation with bio-adhesive chitosan [23]

The structural analysis of gold nanoparticles is characterized by UV–visible spectroscopy and TEM. The largest wavelength of absorbance spectra of gold nanoparticles is near 592 nm. While TEM image of gold nanoparticles reveals a pseudospherical shape of nanoparticles with an average diameter of about 20 nm in size. This approach is effective in stabilizing the latent fingerprints for about 11 months [61].

- **Gold Nanoparticles as Enhanced Targets (Au-NPET) for Mass Spectroscopy Analysis and Imaging on Toxic Fingerprints**: The static nature of gold nanoparticles allows to investigate various materials originating from biological samples. Gold nanoparticles with mass spectroscopy are highly efficient in giving information about ridges, patterns, and individual characteristics. Further, gold nanoparticles with mass spectroscopy also extract the chemical information present on the fingerprints. The properties of gold nanoparticles allow the extraction of both exogenous and endogenous information present on the fingerprint. Moreover, MS imaging with gold nanoparticles is so effective that it can also extract the information of fingerprints even from the surfaces on which toxic materials like drugs, psychoactive substances, steroids, etc., are also present [45].

- **Gold Nanoparticles as Efficient Photothermal Semiconductors for Imaging of Latent Fingerprints:** The optical imaging of the latent fingerprints is the technique developed to extract information from the latent fingerprints. But the information extracted using this method requires more attention as the process of optical imaging suffers from interference from different fluorescent sources and various background color conditions. A thin layer of gold nanoparticles develops interesting electrical and semiconducting properties. Moreover, the gold nanoparticles absorb light at wavelengths that produce photoacoustic and photothermal effects. Latent fingerprints show more affinity toward the photothermal properties of gold nanoparticles [34].

- **Gold Montmorillonite Nanocomposite Powder as an Alternative for Fingerprint Development:** A strong microwave (MW) radiation is used to prepare nanoclusters of gold in the montmorillonite (MMT) assisted synthesis method. The nanocomposites prepared by this method show strong red fluorescence, high emission, highly stable chemical properties, and very little toxicity.

The gold montmorillonite nanocomposites are characterized by their size, optical properties, and microstructure using UV–visible spectroscopy, fluorescence spectroscopy, infrared spectroscopy, TEM, SEM, and XRD. The preparation of these

nanocomposites is eco-friendly and their use in fingerprint examination process is a user-friendly, time-saving, and low-cost option.

The use of gold montmorillonite nanocomposites powder is considered as an alternative for fluorescent developing powder. The fingerprints developed using this technique enhance the quality of fingerprints and can develop fingerprints from various surfaces such as glass, stainless steel, painted metal, paper weight, etc. The results obtained from gold montmorillonite powder are precise and show fine ridge details in the forensic investigation or individual identification tasks. Moreover, the intense red color fluorescence works effectively on the multicolor backgrounds 2017 [71].

- **Gold Nanoparticles and Bio-adhesive Chitosan Amalgamation for Enhancement of Latent Fingerprints**: The detection of latent fingerprints with the amalgamation of gold and bio-adhesive chitosan by using lipophilic and polycationic polymer enhances the fingerprints and makes it possible to identify the ridges and pattern with clarity. Being a natural polymer, the use of chitosan is very cost-effective and it shows high efficiency for the enhancement of fingerprints. The forced amalgamation of gold nanoparticles with lipophilic chitosan present onto the lipid residues is a more effective method for the visualization of latent fingerprints [72].

- **Gold Nanoparticles and Multi-metal Deposition:** Apart from the single-metal deposition (SMD) process, a multi-metal deposition (MMD) method has also been used to develop latent fingerprints [59]. The multi-metal deposition works effectively with the gold nanoparticles which help improve the persistence of the latent fingerprints. MMD techniques involve the use of two solutions consisting of 0.5% (w/v) of hydroquinone solution at pH 3.8, and a modified version of the first solution which comprises 0.5% (w/v) of hydroquinone solution with 0.2% of silver acetate at the same pH of 3.8.

For the development of latent fingerprints, the surface bearing print is immersed in the aqueous solution of gold nanoparticles. The contrast enhancement of the latent fingerprints is done by regulating the pH of gold nanoparticle solution. The characterization of the fingerprint is then done by using a spectrophotometer, SEM, TEM, and XRD.

Application of Silver Nanoparticles in Latent Fingerprint Development

The optical properties of silver nanoparticles have found a significant role in developing latent fingerprints. The inorganic component of the fingerprint residue shows more affinity toward the silver nanoparticles due to electrostatic attraction between

them leading to higher sensitivity in detection. In the following we summarize the use of silver nanoparticles for developing latent fingerprints on a variety of surfaces.

- **Silver Nanoparticles as a Physical Developer (Ag-PD Method)**: The silver nanoparticles were first identified in the year 2001 to have an affinity toward fingerprint residues. The silver physical developer method consists of oxidation and reduction reactions, where Fe^{+} ion reduces Ag^{+} ions to (Ag^{0}) silver nanoparticles. Silver nanoparticles formed are about 1–200 nm in size. The interaction of Ag^{0} with fingerprint residue produces a silver image of the latent fingerprint on a paper surface. This method is effective on different substrates like adhesive tape, latex gloves, raw wood, and on different kinds of papers such as photocopier paper or newspapers [60, 61]. Besides, the Ag-PD method was more effective toward moist items, resulting from its sensitivity toward the inorganic constituent of fingerprint residue as given in (Fig. 4.14). However, the process presents some limitations, like it requires multiple steps and the use of expensive chemicals to develop a latent fingerprint, which makes it cumbersome and time-consuming.
- **Silver Nanoparticles as Eco-friendly Gum-based Reagent:** Biocompatible reagents, can facilitate the formation of eco-friendly silver nanoparticles helpful in developing latent fingerprints. Natural gums possessing charged groups can provide an electrostatically charged background to silver nanoparticles. When in contact with the inorganic component of fingerprint residue, the charged silver nanoparticles are electrostatically attracted to the residue which enables the development of latent fingerprints. In one study natural gum solution of cashew resin was prepared in the presence of acetylated reducing agent [65]. The silver nanoparticles were characterized using UV–visible spectroscopy, AFM, and TEM. The morphological study by AFM & TEM confirmed that silver nanoparticles exhibited spherical shape with an average particle size below 200 nm. The method was reported more effective at 0.5 gm/mL concentration of nanoparticles in developing

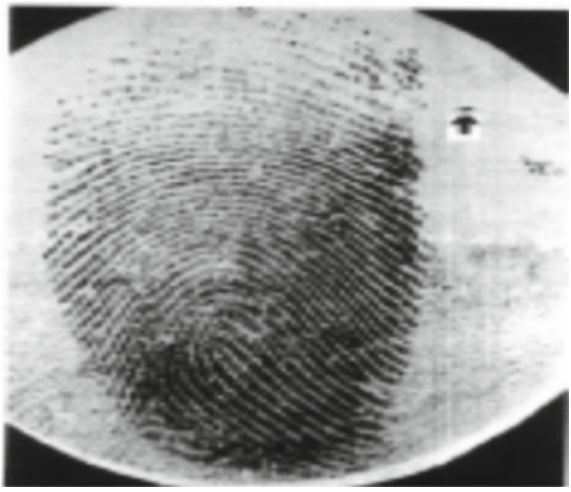

Fig. 4.14 The ridge characteristics are shown by the silver physical developer (Ag-PD) method [7]

Fig. 4.15 Development of latent fingerprint by eco-friendly gum-based silver nanoparticles [4]

latent fingerprints on a paper surface. An additional, advantage is that the cytotoxic effect of silver nanoparticles is reduced by natural gum coating (Fig. 4.15).

- **Silver Nanoparticles as a Fingerprint Imaging Ink:** The silver ink method is a non-destructive method to develop latent fingerprints on a non-porous surface. The silver imaging ink is prepared using silver acetate, ammonium hydroxide, formic acid, and water and ethanol as solvents. When applied on a non-porous substrate containing a latent fingerprint, the silver-amino coordination ions and formic acid contained in the ink react in situ in the fingerprint furrows. When the ink dries, dark silver nanoparticles form on the furrows of fingerprints. The whole process of application of ink to visualization of latent fingerprints can be completed within 10 min [8].
- **Silver Nanoparticles in Magnetic Nanomaterials:** The phenomenon of magnetism has drawn great attention in the field of forensic science, especially in latent fingerprint identification, since magnetic nanoparticles act as a labeling agent on the fingerprint constituents. The significant advantages of magnetic nanomaterials include recyclability, non-toxicity, and high sensitivity. When magnetic nanoparticles are combined with silver nanoparticles, it results in a novel magnetic nanomaterial. A novel magnetic nanomaterial can be created using iron oxide (Fe_3O_4) as a magnetic nanoparticle encapsulated with silver nanoparticles. They were synthesized by the facile co-precipitation method. The Fe_3O_4 nanoparticles were first covalently bonded with coupling agent (3-mercaptopropyl) triethoxysilane and, in the second step, encapsulated with the silver nanoparticle [65]. To

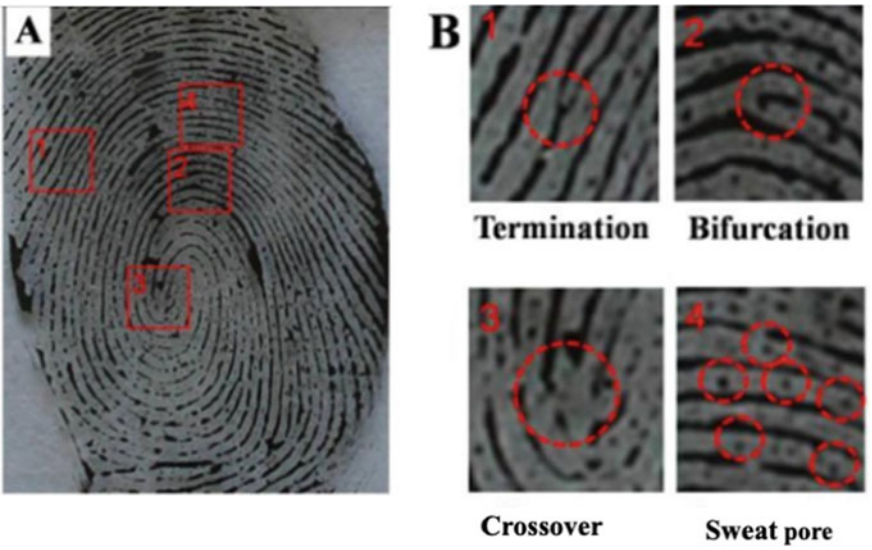

Fig. 4.16 Development of latent fingerprint by silver imaging ink at 1.2 M concentration **a** fingerprint pattern **b** ridge characteristics [70]

characterize the morphology and properties of magnetic nanoparticles, IR, SEM, XPS, VSM, TEM, and XRD methods were used. SEM and TEM images revealed the smooth surface of nanoparticles with an average particle size of about 120–150 nm. XPS and VSM results showed that Fe_3O_4 is firmly covered with silver nanoparticles and has strong magnetic permeability. XRD analysis resulted in the cubic spinel structure of magnetic nanoparticles. Distinct ridge characteristics were observed by novel silver magnetic nanomaterial on paper surface in comparison to conventional powder methods as shown in (Fig. 4.17) [65].

- **Silver Nanoparticles as Nano Powder:** The most commonly adopted method for latent fingerprints development by investigators is the powder method. Considering that, it is the easiest method used since the nineteenth century. The powder methods depend on the particle sizes, as smaller particles adhere more easily to substrate surfaces. Powders with nano-sized particles are used to enhance the adherence property to develop latent fingerprints. Silver nanopowders can be synthesized by silver nitrate as a precursor in the presence of oleylamine stabilizing agent. Developed fingerprints using the silver nanopowder display distinct ridge characteristics over the conventional powder methods. The SEM images show that particles of silver were more concentrated on the ridge area than on the valley region, which results in excellent quality of latent fingerprint on a non-porous surface without background staining [15].

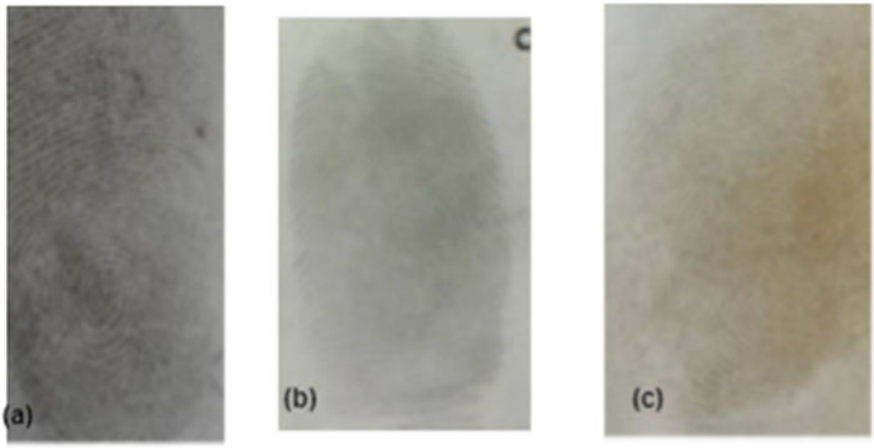

Fig. 4.17 Development of latent fingerprint on paper surface using **a** Novel silver-based magnetic nanomaterial **b** Silver nanoparticles **c** Gold nanoparticles [64]

- **Silver Colloidal Nanoparticles in a "Nanosolution":** A nanosolution can be defined as a colloidal suspension of nanoparticles. Due to affinity toward fingerprint components and favorable UV–visible optical properties of silver nanoparticles, a colloidal suspension of silver 10–15 nm sized nanoparticles in a nanosolution can be used to develop latent fingerprints on a porous paper surface. A colloidal suspension of silver nanoparticle is prepared using a wet chemical method in the presence of silver nitrate as a precursor and sodium borohydride as a reducing agent. The mechanism of latent fingerprint development by silver nanoparticles is depicted in (Fig. 4.18). The silver nanoparticle solution containing particles is applied to develop a latent fingerprint as a spraying solution [14].

Besides this, a comparative study on the development and stability of latent fingerprints was also reported for the proposed method. The conventional silver nitrate method of latent fingerprint development was compared with the silver nanoparticles. The latent fingerprint displayed an excellent quality of ridge detail at 0.1 M concentration of silver nitrate, but at 0.01 M and 0.001 M, faint ridge characteristics were observed. Whereas distinct ridge characteristics were observed at different concentration of silver nanoparticles. Latent fingerprints developed by silver nanoparticles showed good stability, which lasted more than a month compared to the silver nitrate method (Fig. 4.19) representing the comparative details on the development of latent fingerprints using silver nitrate and silver nanoparticles.

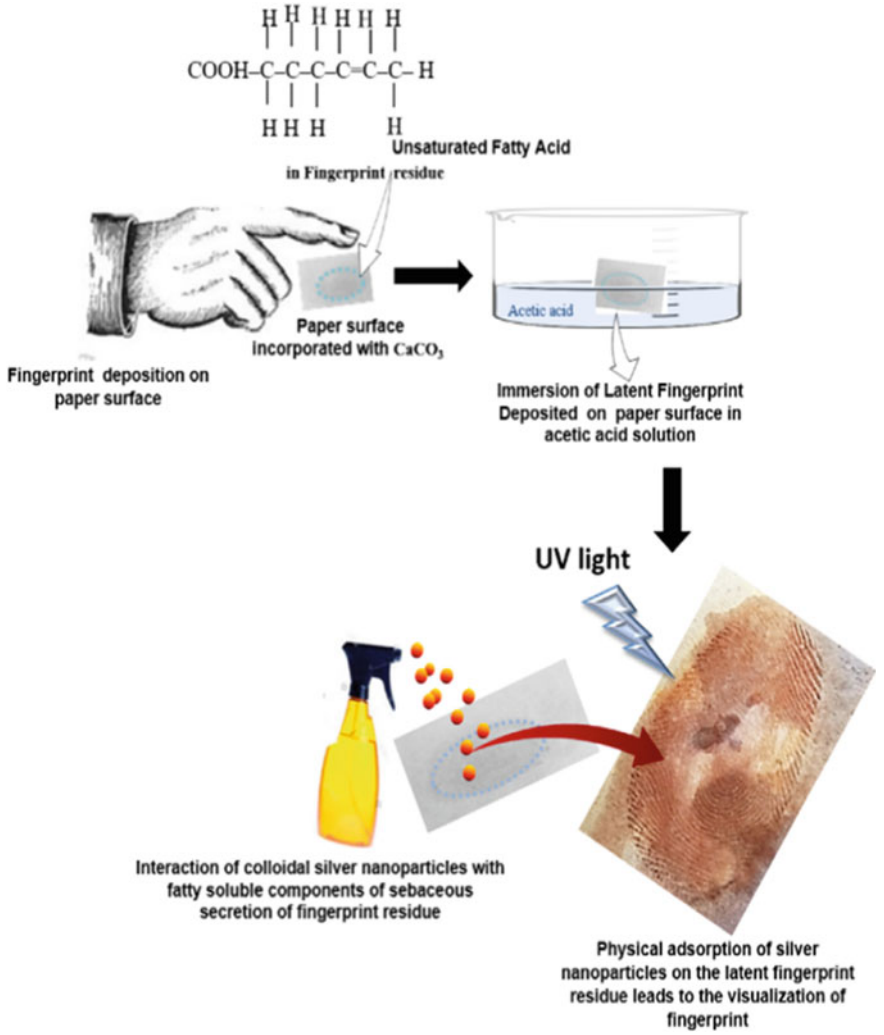

Fig. 4.18 The mechanism of latent fingerprint development by silver nanoparticles using a nano solution [48]

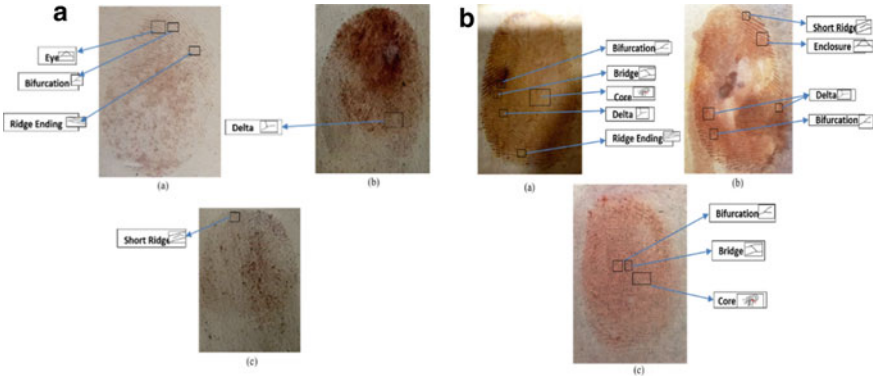

Fig. 4.19 Comparative study of latent fingerprint development using silver nitrate (on the left) and silver nanoparticles (on the right) at different concentrations **a** 0.1 M **b** 0.01 M, and **c** 0.001 M showing better performance by silver nanoparticles [48]

Conclusion

This chapter provides an overview of the current nano-fingerprinting techniques with a focus on applications of gold and silver nanoparticles in latent fingerprint development and identification of ridge characteristics. Their important optical property of UV–vis fluorescence (absorption in UV range and emission in visible range) provides a visible display of latent fingerprints when illuminated with UV light. Gold and silver nanoparticles show an enhanced quality of latent fingerprints on various surfaces. Latent fingerprints developed with gold nanoparticles demonstrate excellent stability, with prints persisting for more than 11 months. On the other hand, silver nanoparticles show good visibility and resilience of developed latent fingerprints, which display stability for more than 50 days. Although the performance of gold nanoparticles is superior as compared to silver nanoparticles, the use of silver nanoparticles is more cost-effective. A schematic representation of latent fingerprints development methods using different AuNPs, and AgNPs is provided in Fig. 4.20. Hence, AuNPs and AgNPs can be considered as very effective nano-based technique used for the identification of latent fingerprints at the crime scene.

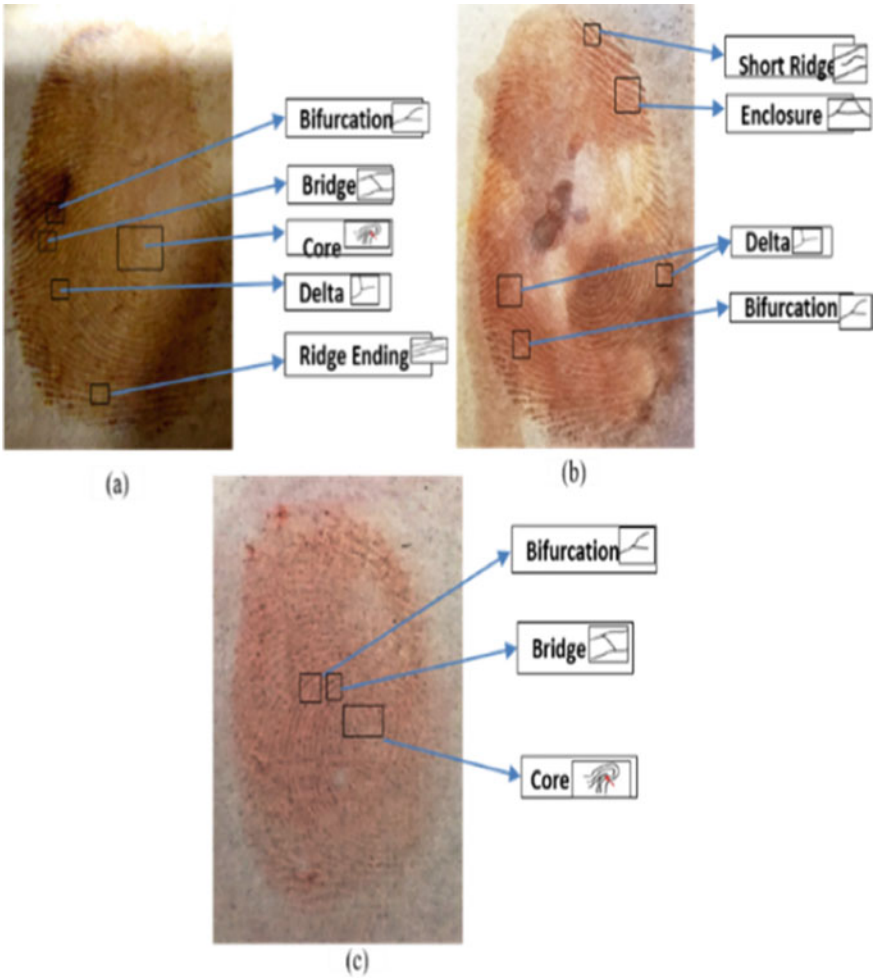

Fig. 4.20 Shows the illustration of different color of latent fingerprints developed using different forms of AuNPs and AgNPs

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Chapter 5
Aluminum Oxide Nanoparticles or Development of Fingerprint

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Introduction

Nanotechnology is one of the most rapidly developing areas of technological advancements, providing hope for many branches of modern industry, as well as medicine and pharmacy. Properly engineered nanoparticles of metal oxides are expected to be employed in the near future to impregnate clothing and medical items, to attack viruses and bacteria, in new drug delivery systems or cancer therapy, as well as for cell labeling and biosensing [1, 2]. It is possible to argue that the certainty of detection is the most effective deterrent to crime. Similarly, fingerprints are the most reliable technique for establishing identity. The detection and development of latent fingerprints at the scene of a crime is thus one of the most powerful instruments available in casework investigations. When the papillary ridges leave a deposit of perspiration on a surface with which the finger has come into contact, fingerprints are formed. Different chemical reagents can selectively fix the elements of sweat mary, making the latent impressions visible [3, 4].

In the present study, we have recognized the Neutral Aluminum Oxide G (TLC Grade) as a new material for the visualization of latent fingerprints. Aluminum oxide or Alumina is a cheap, non-toxic material and is easily available. Of the three variants of the alumina namely, acidic, basic, and neutral, the neutral alumina is used in this

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work. Gypsum is added as the binder in the commercially available neutral alumina G for TLC applications. The structure of the neutral alumina is complicated. However, it is thought to have the structure portrayed. The aluminum atoms are connected with oxygen atoms which can form hydrogen bonds with water and other hydroxyl compounds [5–7]. It has been reported that many attempts have already been made at determining the biocompatibility of nanometric alumina for plant species, bacterial cells, animals, and humans [8] found that aluminum oxide nanoparticles show a minor inhibitory effect on seed germination and root elongation in plants such as maize, cabbage, and carrot, which is no longer seen after coating the nanoparticles with phenanthrene. In their opinion the phytotoxicity of aluminum oxide nanoparticles is due to the presence of reactive hydroxyl groups, which were blocked after covering the nanomaterial surface with phenanthrene [9] showed that the phytotoxic activity of nanometric Al_2O_3 is significantly lower compared to nanoparticles of zinc and zinc oxide. For instance, aluminum oxide-based nanoparticles were also used for the investigation of LFP detection because these are good labeling agents and minimize the background interference. Modifiers such as natural dyes, organic groups, and metal ions on aluminum oxide nanoparticles were reported to improve LFP detection. Such materials also present the advantages of less background interference, high visibility, and better adherence on oily compounds of fingerprint residue with different substrates [10, 11]. The polar nature of the alumina surface attracts other polar compounds by electrostatic or hydrogen bonding interactions or through Van der Waals forces of attraction. Moreover, alumina as a Lewis acid, can form coordinate bonds with lone pair containing hetero atoms such as nitrogen and oxygen (amino acids and hydroxyl compounds for example) present in the natural secretions of fingers. It is well known that the natural secretions of palm contain 98% water and many amino acids. Both these emanations can interact well with the alumina. The interactive groups on the surface of neutral alumina in contact with aqueous solvent are mostly hydroxyl groups as analogous to the interaction between hydroxyl groups and silica gel. On the other hand, the polar surface of the alumina can form electrostatic interactions with the polar amino acids. Scheme 1 illustrates some of the possible interactions between the neutral alumina and fingerprint secretions such as amino acids and hydroxyl compounds. To our knowledge, no reports have been published so far on the application of alumina as a fingerprint powder. In this context, we have employed the neutral alumina G to visualize latent fingerprints and presented the results here. We hope these findings will be useful to forensic fingerprint experts in handling the latent fingerprints [12]. Among the investigated methods, the membrane-based approach holds promise for wastewater treatment and heavy metal ion removal. Due to its ease in preparation, superior properties, and enhanced separation efficiency, membrane-based materials are extensively employed for the wastewater treatment process [13] (Fig. 5.1).

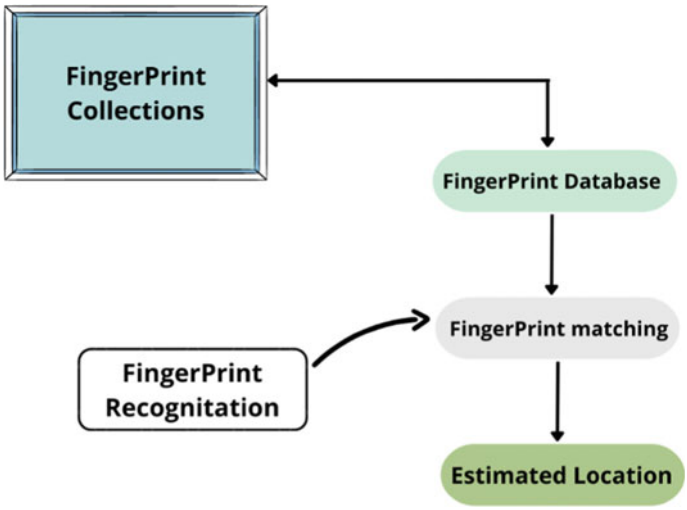

Fig. 5.1 Flow chart for latent fingerprint detection

Nanotechnology Used in Forensic Science

The rapid advancement in nanotechnology sets new paradigms in science and technology, but simultaneously increased apprehensions about the health risks of nano-objects. Recently, various types of nanoparticles used in several areas of forensic including paint, inks, security document, and to develop the latent fingerprint [14, 15]. The technological advancement in the field of forensic science has also changed the character of particulate characteristics, increasing the proportion of manometer-sized particles "nanoparticles" and expanding the variety of chemicals. Forensic science has a broad range of sub-specialties which use techniques adapted from the natural sciences to obtain criminal or other legal evidence. Nanotechnological advancements in the field of forensic science have involved the use of nanoparticles in the discovery of various aspects which are used in the investigations to reveal out the truth behind the screens. Although most of the investigations dealing with forensic science involve the use of certain ailments which sometimes leads to the outcome of moderate results therefore the newly discovered technique involving nanoparticles is the discovery of latent fingerprinting and the use of nano ink [14, 15]. The effective method of fingerprint becomes visualized by ascertaining in-organic constituents that are present in the prints. This method is in contrast to the chemical enhancement methods that have been applied to visualize latent fingerprints. This micro X-ray fluorescence method has several advantages over conventional chemical method for detecting latent fingerprints. Micro X-ray fluorescence is a non-destructive method that does not affect the analysis and the stability of the inorganic residues during image formation of fingerprints. During analysis of the fingerprint, result revealed that some of the residues contain silicon, aluminum, and calcium [16]. Still this

method required instrument and trainer to conduct such analysis. However, the latest nanotechnology-based techniques can help to analyze the evidences on the spot at the scene of crime that not only save the time of analysis but also reduce the chances of error. Nowadays, in the forensic investigation process, different types of nanopowders have been applied to reveal the latent fingerprints on various surface [17]. Colored compounds such as ninhydrin carbon black for a white background and aluminum flakes for black background are normally used for the visualization of latent fingerprints. The drawback of this conventional method is that it does not give a proper and clear result since the powders adhere to the background along with the print. The newly synthesized nanopowders and nanomaterials are used for fingerprint development to overcome this drawback [18]. Also, nanotechnology can be effectively used for the collection, investigation, and analysis of fingerprints at the crime scene. To connect any human being with crime or to prove them innocent, forensic investigators always choose physical evidence like fingerprints [19]. This technique has two main advantages, one is that the analysis and residues are not affected as it is a non-destructive technique, and second is that adulterations and errors are reduced as spot detection is possible. Apart from this, many nanopowders are being used for the visualization of latent fingerprints. Nanotechnology is the future of forensic investigation that makes fingerprint analysis and identification easy and more effective [20]. Nanotechnology can serve as a boon to overcome these drawbacks. As a part of this, micro X-ray fluorescence can be used to envisage the latent fingerprint [21] (Fig. 5.2).

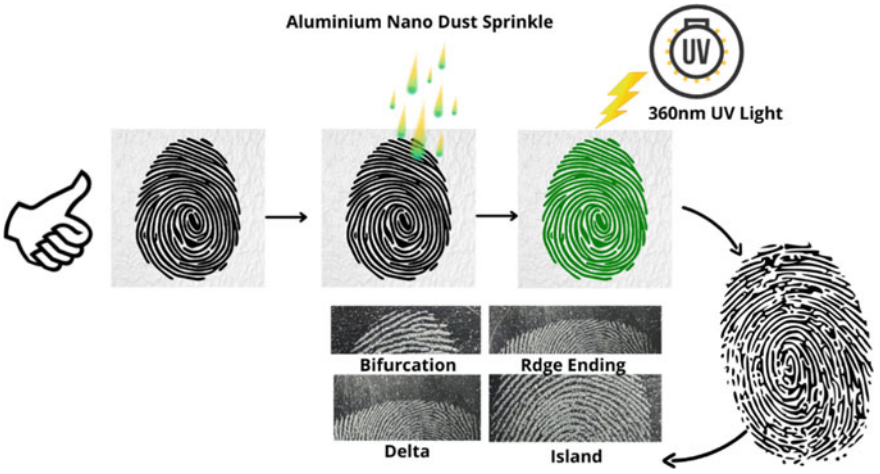

Fig. 5.2 Stability and reusability analysis in the UV and fluorescent color doped and silicon on the different surfaces (Adapted and Modified from [53])

Principle of Fingermark Detection

Fingerprints are one of the most useful types of physical evidence in identifying people and providing universal proof of identity. Because the ridge patterns are generated deep in the skin, they are unique to each individual. They're also universal and leave marks on objects that have been handled with bare hands. Fingerprint evidence can be divided into three categories. Fingers tainted with blood, paint, oil, grease, or other substances (positive image) or material such as dust removed from the surface by touch can leave visible markings (negative image). Visible fingermarks are usually easy to spot. Contact with pliable substances such as putty, candle wax, or wet paint can result in indented or plastic marks. The most common and troublesome type of fingerprint evidence is latent prints, which are present but not apparent. Visualizing latent fingermarks necessitates the use of optical, physical, or chemical techniques. The fingermark is a complicated blend of natural body fluids (mainly sweat from many types of glands) and environmental contaminants. Latent fingerprints may include secretions from three types of glands: eccrine, apocrine, and sebaceous. The deposit is largely made up of water (99%), with tiny concentrations of inorganic and organic substances (up to 1%). Only eccrine glands can be found on the palms of the hands and the soles of the feet. Eccrine fluids are thus present in every latent fingermark to some extent. Eccrine glands produce inorganic secretions as well as amino acids and sugars. Sebaceous glands are associated with hair roots and are located throughout the body, except on the palms, or soles of the feet. Sebaceous secretions are often found in latent fingermarks [22]. A variety of techniques have been used to enhance the visibility of latent fingermarks. The combination of optical methods (absorption, diffuse reflection, luminescence, UV absorption, and reflection) [23], physical methods (powdering, small particle reagents, vacuum metal deposition), physical/chemical methods (physical developer, multi-metal deposition, iodine, cyanoacrylate), and chemical methods (ninhydrin and its analogues, metal complexation after ninhydrin treatment, DFO, 1,2-indanedione and genipin), allows for the development of fingermarks deposited on various surfaces [24]. Powdering is a somewhat insensitive physical process. Latent fingermarks dry down, lose stickiness, and become less sensitive to fingerprint powders as they age. As a result, this procedure will only discover relatively new, high-quality latent fingermarks. As a result, fingerprint powders are usually used on big or permanent surfaces at crime scenes. Treatment with an aqueous suspension of an insoluble powder followed by rinsing with water can detect latent fingermarks on wet, non-porous surfaces. The small particle reagent (SPR) is made up of powdered molybdenum disulfide and a detergent combined with tap water [22].

Determination of Latent Finger-Marks

Although nanotechnology has the ability to provide foundation for adaptable and sensitive approaches to latent fingermark detection, treatments based on nanoparticles still display only faint or partially developed markings, leaving many fingermarks on various surfaces unreported. Weak adhesion between the nanoparticles and the fingermark residue may play a major role in such circumstances [25–27]. Finding them and comprehending their meaning is the most difficult task. Fingermarks come in a variety of forms. Only a few of them are visible with the naked eye. The great majority are so-called latent fingermarks, which must first be created before being seen, recorded, and utilized in an inquiry. Various approaches for the development of latent fingermarks have been proposed so far. Powder dusting, small particle reagent (SPR), cyanoacrylate and iodine fuming, ninhydrin and its analogues, physical developer (PD), vacuum metal deposition (VMD), multi-metal deposition (MMD), single metal deposition (SMD), and others are the most commonly utilized [4]. One should bear in mind that the composition of human sweat and sebum is an individual feature. Moreover, it changes with an individual's age, health condition, diet, and so on. The fingermark already [28] deposited on the surface also changes with time. The mark's volatile components vanish. The mark's volatile components vanish. Light exposure, temperature, and humidity influence the composition [29]. Fingermark components in porous surfaces dissipate with time. The changes in fingermark surface composition are caused by distinct components moving at different speeds [28]. To manage the abovementioned diversity many different methods have been proposed to develop various types of latent fingermarks over the years. The classic, latent fingermarks development methods, have been already reviewed in several papers [30]. As a result, in recent years, nanoscientists have used increasingly sophisticated approaches to leverage the effects of nanoparticles such as Au-NPs (gold), CdS (cadmium sulfide), and ZnS (zinc sulfide) on the development of latent fingerprints in order to better detect fingerprints. As a result of nanotechnology, new fingerprint procedures with enhanced qualities such as improved selectivity, improved background contrast, and higher sensitivity can be developed. The rate of change will be determined by the residue's initial chemical composition as well as the surrounding environment. The successful formation of a latent fingermark can be influenced significantly by the aging process. Despite these concerns, most fingermark detection systems have been designed based on the components of human skin secretions, with little regard for the potential for contamination [31].

Analytical Methods for Latent Fingermark Detection

All fingermark detection approaches try to establish a contrast between a latent fingerridge mark's features and the background on which it is found. Because the bulk of

current approaches relies on this contrast being in the visible part of the electromagnetic spectrum, they have issues when background interferences like printed images or patterns are present. Some of these issues can be solved with traditional methods. Techniques of visible or fluorescence imaging (e.g., alternate forensic light sources with appropriate barrier filters). Some of the more complex difficulties have lately been addressed using visible and fluorescent chemical (hyperspectral) imaging techniques. Images are acquired at numerous separate wavelengths across the spectrum using these approaches. This method can be used to find and choose wavelengths that provide the best ridge contrast for fingermark images, or multivariate image analysis techniques can be used to improve contrast if this method fails [32, 33]. Most carbon compounds have a large number (typically more than 10) of narrow, well-resolved bands in their vibrational spectra, which indicate vibrational modes of discrete functional groups in these molecules. Vibrational spectra are thus significantly more powerful than UV–visible approaches when it comes to detecting and distinguishing between distinct compounds. Although various investigations based on infrared analysis of the chemical elements of fingermarks have been conducted, this inherent property of infrared (and Raman) spectra has not been used in the forensic imaging of fingermarks to date [34, 35]. A focal plane array (FPA) detector is used in infrared chemical imaging and is made up of thousands of discrete detectors (or pixels) set arranged in a grid pattern (Digilab, Nicolet, Bruker instruments). A different design (the Perkin Elmer Spectrum Spotlight instrument) uses a relatively modest number of detectors (16) in a zigzag pattern to scan the material spatially utilising an automated microscope stage. The equipment, in both versions, takes images with thousands of pixels and a spectrum at each pixel. Because of the wavelengths of light involved, the highest spatial resolution feasible is on the order of 5 micro meter, hence the smallest effective pixel size in infrared chemical pictures is usually around 5 micro meter. [35].

Exogenous and endogenous substances are distributed in a certain manner in latent fingerprints (LFPs). They may carry more forensic information than just the subject's identity; they may contain proof of interaction with explosives or misuse substances. To disclose the whole information contained in LFPs, chemically specialized surface analysis procedures are necessary. Derivatization or the insertion of fluorescent or other tags is frequently required for such approaches. MS imaging gives chemical composition information on surfaces that is spatially specific. Desorption electrospray ionization (DESI) MS, unlike previous MS imaging technologies, provides chemical imaging capabilities through mass spectra collected without sample preparation from typical samples in their natural environment [36–39].

For chemical examination of materials, chemical imaging combines molecular spectroscopy with digital imagery (2, 3). Forensic scientists profit from fluorescence chemical imaging and visible absorbance chemical imaging (color analysis) because they expand their skills. Chemical imaging is a non-destructive approach that requires little to no sample preparation, reducing the risk of contamination and enhancing sample analysis efficiency. On both organic and inorganic species, chemical imaging quickly offers high spatial/spectral resolution data as well as qualitative and quantitative chemical information [40, 41].

The mapping of the spatial distribution of fluorescence lifetimes of a specimen is possible with frequency domain fluorescence lifetime imaging (FLIM). It's been used widely in biology. This paper describes a theoretical analysis for determining the fluorescence lifetime of latent fingermark samples, followed by a feasibility investigation of employing FLIM in the frequency domain to detect latent fingermarkings. On two separate surfaces, preliminary experiments are carried out with latent fingermarks coated with a fluorescent powder [42, 43].

Fluorescent Dye-Doped Nanopowders

The previous decade saw substantial advancement in the field of polymer-based composite materials, which are now widely used in all fields where great mechanical qualities, low weight, and ease of manufacture are important. The diverse uses in the aviation and automobile industries, as well as civil engineering works, demonstrate their ubiquity. However, in addition to their strong mechanical qualities, polymer-based composite materials may also have very appealing luminous properties, which could open up entirely new areas of application. Light-emitting polymers have been studied for a long time and have been proven to work. Luminescence and laser properties have been studied since the dawn of laser technology. There are three major study paths that have been pursued over nearly five decades: (1) active organic dye-doped materials, (2) electroluminescent polymers, and (3) rare-earth substance doped polymers. Polymers activated with rare-earth ions are typically introduced as metal–organic (M–O) complexes or as dopants in inorganic nanocrystals, which are dispersed in the volume of the polymer host, forming a composite material with luminescent properties determined primarily by the features of RE3+ doped active crystals.

The fingerprints were created using a standard fluorescent powder and a powder brushing technique on porous (banknotes, tree leaves, and cup paper) and nonporous (glass slide, ceramic and aluminum foil, glass bottle, highlighter, and rule) surfaces [44]. The fingerprints were wiped with soap and subjected to dry air without touching anything for 10 min before being pressed on the surface of various substrates at room temperature to ensure consistency. Fingerprints were acquired and aged for at least 12 h before being put on specified substrates and allowed to air for at least 14 days in a Petri dish [45–48].

Stability and Reusability Analysis Al_2O_3.

For the recognition of latent fingerprints, a harmless, environmentally friendly nanopowder was produced. Eco-friendly binders such as aluminum oxide nanoparticles covered with a naturally colored dye (eosin yellow) and hydrophobic seed extract were used to make the nanopowder. The seed extract of *Cyamopsis tetragonoloba*

Table 5.1 The sources of fingerprint by sweat

S. No	Source of fingerprint sweat	Constituents	
		Inorganic	Organic
1	Sebaceous	Chlorides, Metal ions	Glycerides, Fatty acids, Wax ester, Squalene, Sterol esters, Sterols
2	Eccrine	Sulfates, Phosphates, Ammonia, Water	Amino acids, Proteins, Urea, Uric acid, Lactic acid, Sugars
3	Apocrine	Iron, Water	Sugars, Creatinine, Choline, Carbohydrates, proteins, Sterols

(guar bean) behaved as a hydrophobic material, repelling water molecules and allowing the small powder particles to attach to the latent fingerprints' oily contents. The use of nanopowder in the development of latent fingerprints not only enables clear visibility on a variety of porous and nonporous surfaces, but also recognizes faded latent fingerprints [49].

Heat and mass transmission in these devices, which typically have channel or capillary width of less than 1000 mm, can be orders of magnitude higher than in traditional batch reactors, allowing for fine chemical reactivity control. Under these conditions, flow chemistry benefits from highly quick reagent stream mixing, as well as extremely precise reaction time (residence time) and temperature control. Chemists can now perform chemical transformations with a level of selectivity that is generally impossible to achieve in a standard stirred batch reactor. Furthermore, in microreactors, combustion and explosion dangers are minimized, resulting in extraordinarily harsh process conditions, such as in a safe and controllable manner, reactions in the explosive or thermal runaway domain can be harnessed. Hazardous reagents can be made on demand, reducing operator exposure and eliminating the requirement for storage or shipping of such compounds [50–52]. Some nanoparticles are stable and reusable, while others are unstable and not reusable (Table 5.1).

Conclusion

This chapter describes the preparation and application of various equipment for latent fingerprint (LFP) detection in the realm of forensic technology. Nanomaterials are often used in SALDI-TOF–MS (surface-assisted laser desorption/ionization time-of-flight mass spectrometry) fingerprinting with bloodstains and drug analysis. The talk focused mostly on the important nanoparticles and fluorescent nanomaterials that have been used for the generation and identification of latent fingerprints, with little emphasis on preparation processes. Al_2O_3 nanoparticles were made using the multi-fetal deposition (MMD) approach to improve fingerprint detection. In crime scene

investigation, the use and qualities of fingerprints are discussed. Metal oxide nanoparticles (titanium dioxide, silica dioxide, zinc oxide, iron oxide, and europium oxide) were dispersed in aqueous and organic solutions to demonstrate LFP production, ridge characteristics, and reduced background interference. Due to greater visibility of fingerprint images, ridge patterns, and sweat pores, LFP detection is better than other materials for crime scene investigations. Nanoparticles of fluorescent silica, a variety of non-porous and porous substrates, fluorescent mesoporous silica nanoparticles, aggregation-induced emission luminates molecule integrated nanomaterials, and rare-earth upconverter nanomaterials were demonstrated to be more successful in detecting LFPs than commercially available materials. When exposed to ultraviolet (UV) light, fingerprint pictures must have good images and better contrast to improve their quality. Furthermore, functionalized amphiphilic aluminum nanoparticles have shown high attraction to chemical components of fingerprint residues due to strong electrostatic and hydrophilic interactions. Many nanomaterials have been used to utilize nanotechnology in the field of LFP detection in forensic technology until 2020. As a result, nanotechnology has a lot of promise in terms of developing LFPs, criminal identification, and effective crime-fighting tools.

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Chapter 6
Iron Oxide Nanoparticles for Development of Fingerprints

O. Icten

Introduction

Forensic science is a significant field that depends on physical, chemical, and biomedical information to explain criminal offenses. Comprehensive scientific analysis of materials found at the crime scene is required to determine the cause of death and identify the suspects [34]. The fingerprints are the most critical evidence internationally accepted among physical evidence in criminal cases [23]. In general, there are three different fingerprints at the crime scene: visible, plastic, and latent fingerprints [12]. Visible or patent marks occur with fingers contaminated with foreign substances like blood, paint, oil, grease, and visible fingerprints are usually easy to detect. Plastic fingerprints are marks formed by contact with substances such as soap, clay, paste, wax, and glue. As the name suggests, latent fingerprints are marks that cannot be seen with the naked eye and are formed by the transfer of secretions in the pores of the hands' ridge skin of the fingers to the touched surface [50]. Finger ridges have many sweat pores, and when the finger touches a surface, the sweat released from these pores forms on the surface, leaving a pattern that is a mirror image of the ridge patterns [10]. And accordingly, since the sweat released by the finger ridges is colorless, they also produce colorless marks on surfaces, called latent fingerprints [11]. As latent fingerprints have unique patterns and do not change with age, they are significant evidence for identification [62].

Consequently, the identification of latent fingerprints is an essential issue which is necessary to be addressed. It has become the study area of many disciplines such as chemistry, legal medicine, material science, engineering, optics, computer science, etc., not just for a single discipline. Figure 6.1 shows the number of publications produced from Web of Science on latent fingerprint detection per research area. It is thought that the increase in studies on latent fingerprint detection would be thanks

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to the collective studies of different disciplines. Depending on the extensive work of scientists, new specific developments such as the design of the functional fingerprint powder or sensitive imaging device will contribute to the explanation of criminal crimes.

Many researchers are working on various methods, including powder dusting [53], cyanoacrylate fuming [8], small particle reagent method [7], silver nitrate method [51], ninhydrin method [17], and 1,8-Diazafluoren-9-one method [9] for visualizing latent fingerprints in criminal investigations [56]. The single method or the combination of two or more methods can be benefited to visualize latent fingerprints, and the method to be chosen also depends on the morphology, texture, and color of the applied surface [10]. Among these methods, powder dusting, which is one of the oldest applied methods, is widely used because of its easy preparation and use, being efficient and inexpensive technique, and harmless to fingerprints [19, 47, 55, 56].

Many different powders are employed to visualize fingerprints like black, white, fluorescent, and magnetic powders according to the surface type that the latent fingerprints are found [19]. Magnetic materials, especially nanomaterials, have superior

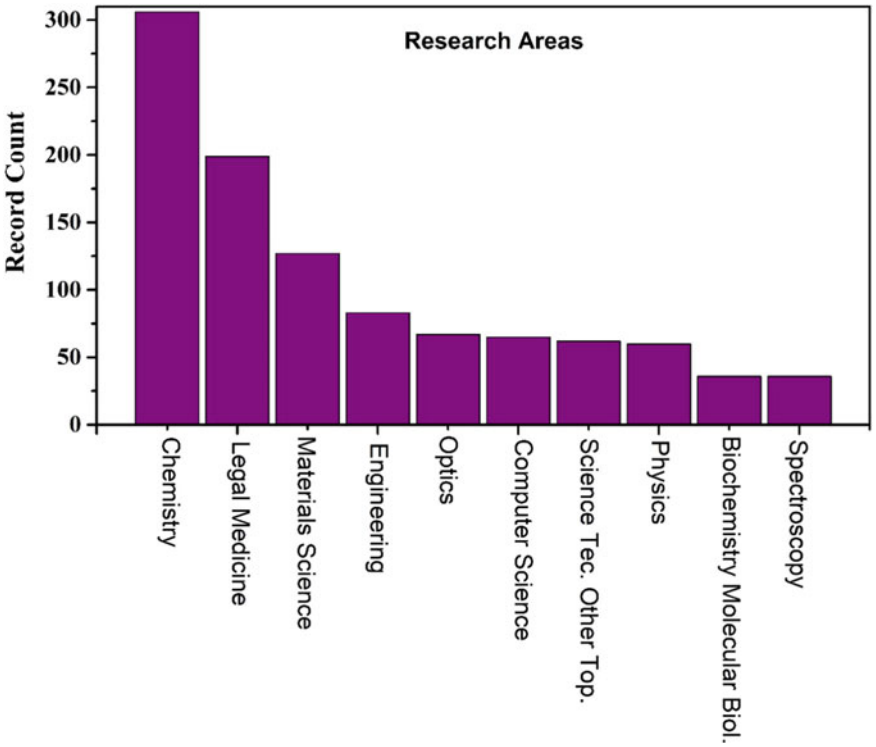

Fig. 6.1 Number of publications on latent fingerprint detection per research area. Produced from Web of Science, webofscience.com, 2022. Web of Science—Clarivate. https://apps.webofknowledge.com (accessed 13 January 2022)

morphological, optical, magnetic properties, and biocompatibility, and therefore, they offer some superiorities when used as a powder for visualizing latent fingerprints compared to other methods. First of all, since magnetic nanomaterials have high saturation magnetization, excess powders can be recovered and reused by applying an external magnetic field. Another superiority is that magnetic nanomaterials have low DNA toxicity and, accordingly, they extract the DNA information and provide the suspect's biological information. The last advantage is that magnetic nanomaterials can expose the details of fingerprints even with a minimal amount owing to their high sensitivity as a result of their small size [55].

The literature shows that the magnetic nanomaterials used to detect latent fingerprints are generally based on iron oxide nanoparticles thanks to their high magnetization, biocompatibility, and low toxicity [34]. Therefore, studies including iron oxides should be reviewed in detail to develop new and functional magnetic-based fingerprint powders considering the advantages mentioned above of magnetic nanomaterials.

Iron Oxide Types, Properties, and Synthesis Methods

Iron Oxide Types and Properties

There are 16 identified types of iron oxide structures that consist of iron and oxygen atoms. Iron oxide is found as the form of rust in nature, as is known, and the most commonly used iron oxide structures are hematite (α-Fe_2O_3), magnetite (Fe_3O_4), and maghemite (γ-Fe_2O_3) [2]. Hematite, which has a blood-red color, is the most stable type of iron oxide at ambient conditions, and it is the end product of iron oxide transformations. Magnetite possesses the highest magnetization among transition metal oxides. Maghemite is a phase formed by the oxidation of magnetite or by heating other iron oxides [54]. The crystal structure of the three types of iron oxides generally consists of arranging the closely packed oxygen anions and iron cations at tetrahedral and octahedral sites (as shown in Fig. 6.2).

Hematite (α-Fe_2O_3)

Hematite, which is used as the starting material for magnetite&maghemite syntheses, has a hexagonal crystal structure. In the hexagonal structure where oxygen ions are closely packed, Fe^{+3} ions occupy 2/3 of the octahedral sites (Fig. 6.2a). Hematite has high corrosion resistance and n-type semiconductor properties (bandgap: 2.3 eV), and therefore, it is commonly utilized in catalysts, pigments, and gas sensors applications. However, hematite is generally not preferred in biological, biomedical, or fingerprint applications as magnetic support or core due to its low magnetization value [61].

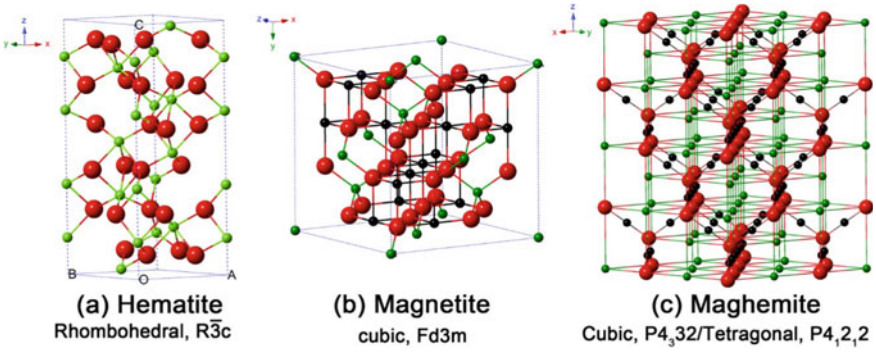

Fig. 6.2 Crystal structure of hematite (**a**), magnetite (**b**), and maghemite (**c**) (Fe^{2+}:black, Fe^{3+}:green, and O^{2-}: red). Copyright © 2015 Taylor and Francis. All rights are reserved and reprinted with permission [61]

Magnetite (Fe_3O_4)

Magnetite, consisting of the Fe^{+2} and Fe^{+3} cations together, has the highest magnetization among other iron oxide forms. Magnetite is composed of face-centered cubic unit cells, and while closely packed oxygen ions form the face-centered cubic structure, iron ions occupy 8 tetrahedral sites and 16 octahedral sites, consisting of inverse spinel crystal structure (Fig. 6.2b). Fe^{+2} ions are located in octahedral sites, and Fe^{+3} ions are occupied in equal numbers of tetrahedral and octahedral sites because of their particular crystal field energies. The length of the cubic unit cell in the crystal structure is 0.839 nm. In stoichiometric magnetite, the ratio of Fe^{+2} to Fe^{+3} is 1/2, but Fe^{+2} ions can be changed with some divalent ions such as Co, Mn, Zn, etc. [39]. Magnetite could be both an n- and p-type semiconductor (bandgap: 0.1 eV). Thanks to their magnetic properties and biocompatibility, magnetite particles are used in many different biomedical applications like targeted drug delivery, biosensor, magnetic resonance imaging (MRI), bioseparation, magnetic hyperthermia [1, 29, 45] apart from water purification, high-density magnetic data storage, reusable catalysts applications [35]. In addition, it attracts great attention in forensic science and is widely used due to its superior properties [25, 31, 47, 64].

Maghemite (γ-Fe_2O_3)

Maghemite is isostructural with magnetite, and it exists in a higher oxidation state due to cation vacancies in the unit cell. Maghemite has a cubic structure, and 32 O^{-2}, 21 1/3 Fe^{+3} ions, and 2 1/3 vacancies are located in each cell unit. Fe^{+3} cations are located in tetrahedral and octahedral sites of the closely packed cubic structure formed by arranging oxygen ions (Fig. 6.2c). Since magnetite can turn into maghemite by oxidation, Fe^{+2} cavities are seen in the crystal structure. Although maghemite has a ferrimagnetic structure, Fe^{+2} vacancies cause a decrease in magnetization saturation.

For example, while this value is approximately 92 emu/g for pure magnetite, it could be 70 emu/g for maghemite [52]. Maghemite is an n-type semiconductor (bandgap: 2 eV) [6, 61], especially preferred in recording and data storage applications in addition to applications using magnetite because it is chemically stable [46].

As a result, compared to maghemite and hematite, magnetite-type iron oxides are getting more attention in forensic science applications because they have advantages such as high magnetization, homogeneous particle size distribution, superparamagnetic properties, and biocompatibility [18, 25, 31, 47, 64]. These excellent properties of iron oxides vary greatly depending on the preparation methods since the synthesis method is a significant factor in the determination of particle size and distribution, shape, morphology, and surface chemistry. Thus, it would be appropriate to decide on the proper synthesis method according to the application area [54]. Some of the synthesis methods that are widely used are given in the following section.

Synthesis Methods of Iron Oxide Nanoparticles

To date, various methods such as co-precipitation, solvothermal synthesis, thermal decomposition, microemulsion, sonochemical or sonolysis synthesis have been utilized to prepare iron oxide nanoparticles [2, 61]. Among these synthesis methods, co-precipitation [16, 25, 31, 33, 40, 55, 57, 64] solvothermal synthesis [47], thermal decomposition [58] techniques are applied to synthesize iron oxide nanoparticles (Fe_3O_4) for preparing fingerprint powders. However, it is seen that the co-precipitation technique is the most preferred process compared to other methods, but still, three methods will be briefly described in this chapter.

Co-Precipitation

The co-precipitation method is the most common technique to synthesize iron oxide nanoparticles [30]. In this method, Fe_3O_4 nanoparticles are obtained by the reaction of the solution prepared by mixing the Fe(II) and Fe(III) salts in a molar ratio of 1:2 in a basic solution at room temperature or higher temperature. The reaction equation is given below to synthesize Fe_3O_4 nanoparticles [18, 43].

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe(OH)_2 + 2Fe(OH)_3 \rightarrow Fe_3O_4 \downarrow + 4H_2O$$

This reaction is usually carried out in inert gas such as nitrogen to prevent the oxidation of Fe(II), and nucleation of Fe_3O_4 is easy at pH lower than 11, but nucleation growth of Fe_3O_4 is easy at pH higher than 11. The properties of the synthesized Fe_3O_4 nanoparticles depend on the type and ratio of iron salts, the pH of the medium, the reaction temperature, the mixing rate, and the presence of surfactant [61]. The co-precipitation technique is more economical than other methods, and the reaction temperature at which synthesis takes place is lower than solvothermal and

hydrothermal methods. In addition, the synthesis takes place in water, which provides a high amount of product and this method is the most effective way to synthesize iron oxide nanoparticles with high saturation magnetization [28, 38, 61].

As an example of a study using the co-precipitation method, Lee et al. prepared the powder for latent fingerprint detection, including Fe_3O_4 nanoparticles and 10,12-pentacosadiynoic acid (PCDA: imaging material). Fe_3O_4 nanoparticles were synthesized by co-precipitation method by using Fe(II) and Fe(III) salts, polyethylene glycol (PEG) as a surface-active agent, and ammonia hydroxide for adjusting to pH:9. In this study, especially the ratio between magnetic particle and initial monomer was determined. If the magnetic particles were overused, the color determination would be difficult due to the dark color of the magnetic particles. Otherwise, when the number of magnetic particles in the matrix was few, the magnetization of the total material would be passive. In this context, the most visible latent fingerprint view was obtained with a weight ratio of PCDA/Fe_3O_4:20 and the size of the Fe_3O_4 nanoparticles in the 10,12-pentacosadiynoic acid matrix was determined as approximately between 15–40 nm by TEM analysis [31].

Solvothermal Synthesis

The solvothermal method is based on mixing the suitable organic solvent with reactants containing iron sources and surfactants and then reacting in a sealed reactor at high temperatures. In this method, the various solvents such as ethylene glycol, diethylene glycol, ethylenediamine hydrazine, and the different surface-active agents like sodium citrate, oleic acid, polyacrylic acid, etc., are utilized in order to prevent aggregation formation [44]. More than one organic solvent can be mixed to control the morphology of the product in the same synthesis procedures [32]. The solvothermal method is especially preferred for preparing magnetic nanoparticles with homogeneous size distribution and high crystallinity, whose size can be controlled.

For instance, Fe_3O_4 nanoparticles as a core material in the Fe_3O_4@YVO_4:Eu^{3+} fingerprint powder were prepared by the solvothermal method in the study carried out by Pan et al. In this study, Fe_3O_4 nanoparticles possessing the spherical morphology and diameter of 150 nm were synthesized by reducing Fe(III) with polyethylene glycol and then Fe_3O_4 nanoparticles as a core material were combined with shell material (YVO_4:Eu^{3+}) through the sol–gel process. The new Fe_3O_4@YVO_4:Eu^{3+} fingerprint powder indicated excellent magnetic and fluorescent properties [47]. As another example, Das et al. synthesized Fe_3O_4 nanospheres at 200 °C by solvothermal method before the preparation of Fe^{3+} sensitive Fe_3O_4/ZnS hybrid material for visualization of the latent fingerprint [14].

Thermal Decomposition

Another method used to synthesize iron oxide nanoparticles is the thermal decomposition technique based on the decomposition of organometallic or metal salt precursors such as iron(III) acetylacetonate, iron(III) oleate, iron pentacarbonyl, Prussian blue, ferrocene iron oxyhydroxide at high temperatures [42, 44]. Synthesis in the thermal decomposition technique is performed in the presence of solvents like benzyl ether and ethylenediamine, and also various surfactants (oleylamine, oleic acid, etc.) can be added to the reaction medium to obtain monodisperse nanoparticles [61]. Parameters such as precursor type, precursor/surfactant ratio, surfactant concentration, solvent type, and reaction temperature are pretty effective in determining the features of iron oxide nanoparticles in the thermal decomposition method [27, 37].

There are limited studies using iron oxides synthesized by the thermal decomposition method to prepare fingerprint powders. In the sample study performed by Wei et al., Fe_3O_4 nanoparticles with approximate 16 nm size were synthesized by thermal decomposition of $Fe(oleate)_3$ at 300 °C and under a nitrogen atmosphere. Then, $Fe_3O_4@SiO_2$-$CsPbBr_3$ bifunctional powder, which was highly effective at detecting latent fingerprints, was obtained by combining Fe_3O_4 nanoparticles with a silica shell and fluorescent $CsPbBr_3$ structures [58].

Iron oxide nanoparticles prepared by different methods need to be characterized by diverse techniques in order to comprehensively determine their properties. Occasionally, it may be necessary to use more than one method to explain a single property in detail. Table 6.1 is given commonly used techniques with explanations for characterizing iron oxide nanoparticles, and this table will help decide which analysis technique to use after synthesizing the iron oxide nanoparticles according to the feature to be determined [2, 42].

Modification of Iron Oxide Nanoparticles for Fingerprint Detection

The previous section states that magnetic particles have superparamagnetism, high specific surface area, biocompatibility, and stable physical/chemical properties. However, there are still some barriers such as aggregate formation, no excessive loading due to the absence of active groups on the surface, and low affinity, limiting magnetic nanoparticle applications [13, 34]. Furthermore, it is often challenging to control nanoparticles' size, shape, and stability in various solvents. Iron oxide nanoparticles also have high surface energy due to their high surface/volume ratio, so the iron oxides form aggregates to minimize this surface energy. Also, uncoated iron oxides are highly chemically active and easily oxidized (especially Fe_3O_4), resulting in a magnetization decrease [60]. Considering such obstacles, it is crucial to modify the iron oxides to maintain their stability and provide new properties.

Table 6.1 Analysis techniques and identified properties for iron oxide nanoparticles

Analysis techniques (or instruments)	Identified properties (Commonly)
Powder X-ray diffraction (p-XRD)	Phase identification, crystallite size, phase quantification, crystallinity, etc
Scanning electron microscopy (SEM)	Size and morphology
Transmission electron microscopy (TEM)	Size and morphology details in high resolution
Atomic force microscopy (AFM)	Shape heterogeneity, size, and size navigation
Fourier transform infrared (FTIR)	Chemical bonds (for example, to prove surface modification)
X-ray photoelectron spectroscopy (XPS)	The elemental composition and chemical state of the surface
Surface Area & Pore Size Distribution Analyzer (using various methods)	Surface area, pore size, and volume
Zeta Sizer	Zeta potential and size
A vibrating sample magnetometer (VSM)	Magnetic properties
Inductively coupled plasma mass spectrometry or Inductively coupled plasma atomic emission spectroscopy (ICP-MS or ICP-OES)	The atomic composition
Thermogravimetric (TG) analysis	Weight losses in a sample (for example, the amount of organic matter in the sample)

Different surface modifications can be made using organic or inorganic materials for the desired purpose. Considering the studies in the literature, it is seen that materials such as organosilanes, surfactants, and polymers are utilized to modify magnetic nanoparticles. Silica structures formed by hydrolysis of organosilanes have been used for surface modification of iron oxide nanoparticles for many years. Silica coating reduces the interaction between iron oxide nanoparticles, prevents aggregate formation, and provides solution stability. Furthermore, silica coating would provide the formation of biocompatible and hydrophilic structures and enable further modifications such as biological molecules or the various ligands due to the presence of many silanol groups on the silica surface [60, 61]. Ding et al. utilized silica interlayer to combine the Fe_3O_4 nanoparticles, which were synthesized by co-precipitation, with fluorescent carbon dots. As shown in Fig. 6.3a, it was confirmed by TEM analyses that the total size of the $Fe_3O_4@SiO_2$ in the core–shell structure was 50 nm after coating of spherical Fe_3O_4 nanoparticles with a diameter of approximately 30 nm. While negatively charged carbon dots were prepared using gelatin and ethanediol, positively charged $Fe_3O_4@SiO_2$ nanoparticles were prepared with polydimethyl diallyl ammonium chloride (PDDA). A novel bifunctional composite powder ($Fe_3O_4@SiO_2$-$CD_{(n)}$) was developed through the electrostatic interaction of negatively charged carbon dots and positively charged $Fe_3O_4@SiO_2$ nanoparticles using a layer-by-layer assembly route. Due to the $CD_{(n)}$ modification, the particle size of $Fe_3O_4@SiO_2$-CD(n) was approximately 120 nm. As shown in Fig. 11.3b,

the excess carboxyl and hydroxyl groups, the negative charges on the surface of Fe_3O_4@SiO_2-CD(n) covalently or electrostatically interact with fingerprint residues, resulting in highly selective detection of the latent fingerprints [16]. Wei et al. reported a similar study involving the modification of iron oxide nanoparticles with silica. Direct coupling of magnetic Fe_3O_4 nanoparticles with fluorescent $CsPbBr_3$ structures is challenging to prepare bifunctional magnetic fluorescent Fe_3O_4@SiO_2-$CsPbBr_3$ powders, and therefore an intermediate layer such as silica is needed. In addition, the silica layer increases the interaction between the Fe_3O_4@SiO_2-$CsPbBr_3$ powders and fingerprint residues. For these reasons, Fe_3O_4 nanoparticles in spherical morphology were coated with silica, approximately thickness of 30 nm, and then amine groups were formed on the surface by (3-aminopropyl)triethoxysilane (APTES) to bind the $CsPbBr_3$ to the silica-coated surface effectively. The Fe_3O_4@SiO_2-$CsPbBr_3$ powder performed excellently in visualizing fingerprints on various surfaces such as glass slide, banknote, back plastic, black cardboard, leather, and a periodic table of elements and the excess powder was recovered from the surfaces with the external magnetic field [58].

Another critical factor in identifying latent fingerprints on surfaces is lipophilicity, which refers to a structure's ability to attract fats, oils, lipids, and non-polar substances. Since fingerprint residues are composed of lipophilic structures like lactic acid, cholesterol, urea, free fatty acids, etc., providing the lipophilic interaction between the powder and the fingerprint will improve the visualization [15, 40, 41]. Lipophilic magnetic powders can be easily prepared by modification. For example, the lipophilic magnetic fingerprint powder was developed by Mobaraki et al. by using co-precipitation and sol–gel methods, respectively. For this purpose, firstly, Fe_3O_4 nanoparticles were prepared by the co-precipitation method, and their surfaces were coated with SiO_2 through hydrolysis of tetraethyl orthosilicate (TEOS). Then, the surface of Fe_3O_4@SiO_2 was modified with trimethoxymethylsilane ($MeSi(OMe)_3$) to provide a lipophilic feature for the selective and effective detection of latent fingerprints. Fe_3O_4, Fe_3O_4@SiO_2, and Fe_3O_4@SiO_2@Me samples were applied to different surfaces to see the lipophilic effect. Among them, the Fe_3O_4@SiO_2@Me was more affinity for greasy surfaces thanks to the methyl groups on the surface. In addition, it was shown with various images that Fe_3O_4@SiO_2@Me was an effective fingerprint powder material on porous and non-porous surfaces [40].

Fe_3O_4 nanoparticles have superior properties such as high magnetic moment, biocompatible, and accessible synthesis conditions [28], but their properties can be further improved by combining them with different nanoparticles [48]. Silver, gold, and platinum nanoparticles can be appropriate modification agents due to their specific surface properties to show new properties compared to the single component structure [59, 64].

Silver nanoparticles attract attention in latent fingerprint detection studies because they have the ability to adhere to fingerprint residues effectively [51]. For instance, Zhan et al. produced the Fe_3O_4-core@Ag-shell nanoeggs as fingerprint development agents and also compared them with different commercial structures such as Fe_3O_4, carbon, and aluminum powders. In this study, iron oxides prepared according

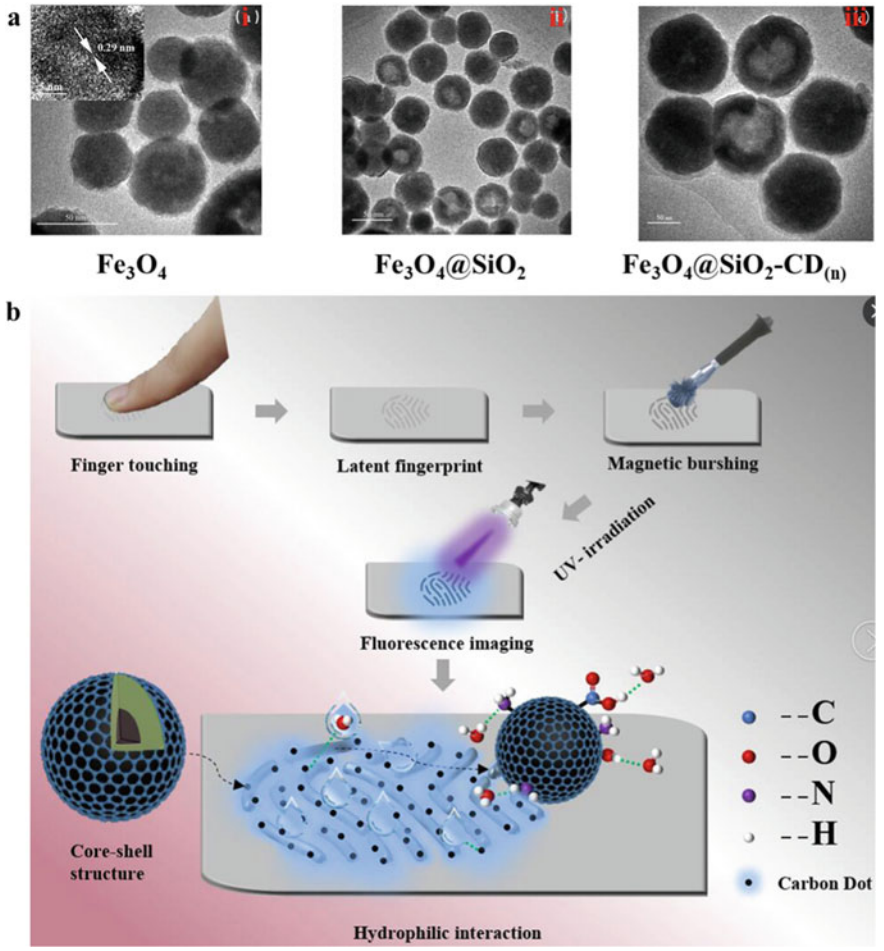

Fig. 6.3 TEM images of Fe_3O_4, $Fe_3O_4@SiO_2$, and $Fe_3O_4@SiO_2$-CD(n) with scale bare of 50 nm (**a**) and schematic illustration of the interaction between $Fe_3O_4@SiO_2$-CD(n) and fingerprint residue (**b**) [16]

to the co-precipitation method were modified with 3-mercaptorpropyl trimethoxysilane (MPS), and then the silver nanoparticles were reduced on the surface of MPS-modified iron oxides. The $Fe_3O_4@Ag$ nanoeggs, possessing a saturation magnetization of 31.6 emu/g and size of 280 nm, were highly monodisperse and stable against aggregation. $Fe_3O_4@Ag$ nanoeggs produced better latent fingerprint images on glass surfaces than commercial products due to their smaller size. Furthermore, the effects of parameters such as the amount of Fe_3O_4 nanoparticles, pH, hydrolysis, and condensation of MPS on the development of the latent fingerprint visualization were investigated in this study. As a result, the authors reported that multifunctional magnetic nanoparticles would be highly effective in detecting latent fingerprints and

open up new opportunities [64]. Another example for silver modification was carried out by Wan et al., who developed the novel magnetic nanomaterials consisting of Fe_3O_4 core encapsulated by the nanosilver (MNP@Ag). The magnetic nanomaterials exhibited advantages such as high sensitivity and clearly showing secondary details [55].

Gold nanoparticles are also employed in detecting latent fingerprints due to their significant features, such as selectivity, sensitivity, and long-term stability [49]. Li et al. demonstrated that the Fe_3O_4@SiO_2-Au obtained after modifying the surface of Fe_3O_4@SiO_2 nanoparticles with gold nanoparticles was more effective than commercial copper powder and gold nanoparticles for visualizing latent fingerprints [33].

As described in the previous sections, fingerprint powders formed by the combination of magnetic iron oxide particles and fluorescent structures will provide advantages for visualizing latent fingerprints [25]. For example, Pt nanoclusters, widely used as catalysts, also possess superior optical properties [24, 26]. In a study performed by Huang et al., Fe_3O_4@Glutathione-Pt nanoclusters (Fe_3O_4@GSH-Pt NCs) were synthesized by combining positively charged polyethyleneimine coated iron oxides nanoparticles and negatively charged glutathione-Pt nanoclusters through electrostatic interaction. Because of the magnetic property of iron oxides in composite, the developed fingerprint agent could visualize latent fingerprints on diverse light-colored objects without suspended particles in addition to the black surface and also prevent the suspended particles from being inhaled into the lungs because Pt nanoclusters have a negative effect on human health. Fe_3O_4@GSH-Pt NCs, which had a size of about 110 nm, possessed a quantum yield of 8.139% and a saturation magnetization of 23.9 emu/g, which revealed the characteristics of latent fingerprints by emitting visible red fluorescence under 465 nm light. The authors reported that the functional material was excellent at detecting latent fingerprints on a dark desktop, and it would be appropriate to detecting latent fingerprints [25]. As an example study related to PEI modification, Huang and Liu coated the surface of Fe_3O_4 nanoparticles with PEI to obtain hydrophilic particles before synthesizing Fe_3O_4@Pt nanoclusters. PEI modification will not only prevent the formation of aggregates but will also form a three-dimensional structure on the surface of iron oxide nanoparticles for the deposition of platinum nanoclusters [24].

Quantum dots (QDs) are widely used chemicals in fingerprint visualization because they have excellent optical and electronic properties depending on their size. QDs can visualize latent fingerprints with UV light without needing an extra reagent because of their effective luminescence properties [23]. Fe_3O_4 nanoparticles were combined with CdTe quantum dots and utilized to detect latent fingerprints in the study by Wang et al. Firstly, Fe_3O_4 nanoparticles prepared by the co-precipitation method were coated with silica by an inverse microemulsion method, and then amine groups were formed on the surface by hydrolysis of γ-aminopropyl triethoxysilane. Silica-coated magnetic cores containing amine groups were covalently bonded to glutathione (GSH) modified CdTe quantum dots through coupling NH_2 and COOH groups. The core–shell structure of the synthesized final sample (Fe_3O_4@SiO_2-CdTe) and its dimensions of approximately 50 nm were determined by TEM analysis. The

fingerprint powder interacted better with fingerprint residues and moisture in the air because of the carboxyl groups on the surface of Fe_3O_4@SiO_2-CdTe, preventing dust flying and improving the detection sensitivity [57].

Thanks to the surface modifications to be carried out to magnetic particles, the functionalized materials can provide some detailed information about the suspect, like drug use and smoking, as well as latent fingerprint information. Although there are many studies including micron-sized magnetic particles related to antimorphine or antibenzoylecgonine and anticotinine antibodies functionalized particles, for identification of the criminal's drug use or smoking [4, 5, 20–22], antibody modified nanoparticles based studies are pretty limited.

Applications of Iron Oxide Nanoparticles for Detection of Latent Fingerprints

Table 6.2 summarizes the fingerprint powders containing iron oxide nanoparticles developed in recent years. As can be seen from this table, iron oxide nanoparticles are generally modified with various non-magnetic materials such as quantum dots, gold, silver, platinum, florescent structures, etc., and then they are used to visualize latent fingerprints from different surfaces. In general, it is seen that Fe_3O_4 nanoparticles, which are smaller than 100 nm, are used in the preparation of these functional fingerprint powders. As expected, nanotechnology influences by making positive contributions to detecting latent fingerprints in forensic science as it affects every field. Nano-sized magnetic particles display a higher surface area/volume ratio than micron-sized particles, allowing the visualization of all the details in latent fingerprints to be determined [34]. The performance of the powders used to reveal fingerprints also depends on the applied surfaces [47]. For instance, fluorescent powders are very effective in visualizing fingerprints from dark-colored surfaces, but they do not show excellent sensitivity on multi-colored and shiny surfaces. Since iron oxide powders also have a black or brown color, they cannot create enough contrast differences on dark surfaces, so they are generally not preferred alone for visualizing fingerprints from dark surfaces [53, 54]. However, eliminating such problems is possible by synthesizing multifunctional composites that can be more effective in visualizing latent fingerprints [47].

Pan et al. prepared bifunctional core–shell magnetic fluorescent microspheres consisting of iron oxide cores with an average size of 150 nm and YVO_4 crystals with a size of about 20 nm. Latent fingerprint images, visualized with Fe_3O_4@YVO_4:Eu^{3+} on a glass slide and the magnified images of the fingerprints are displayed in Fig. 6.4a, b. Related to fingerprints, loops, terminations, bifurcation, and wrinkle can be observed in Sects. 6.1–4, respectively. The resulting high-resolution patterns can identify fingerprints that are inconvenient to detect. Furthermore, Fig. 6.4c shows the photograph of latent fingerprints applied on glass visualized with commercial magnetic powder, YVO_4:Eu^{3+}, Fe_3O_4@YVO_4:Eu^{3+} materials. Compared to

Table 6.2 Overview of iron oxide-based samples for detection of latent fingerprints

Year	Iron oxide-based samples	Description	Applied surfaces	References
2022	Fe_3O_4@mesoSiO$_2$@YVO$_4$:Eu^{3+}	Magnetite-mesoporous silica-europium(III) doped yttrium vanadate	– Glass – Porcelain – Marble – Aluminum foil – Blue nitrile gloves – Hop pocket – A4 paper – Carton – Paper cup – Coins – Train ticket – Shopping receipt – Credit card – Paper currency	[63]
2022	Fe_3O_4@YVO$_4$:Eu^{3+}	Magnetite-europium(III) doped yttrium vanadate	– Glass slides – Plastic sheets – Aluminum foil – Print paper	[47]
2022	P-MNP@Ag	Prepared novel magnetic nanomaterial (Fe_3O_4)-silver	– Paper – Plastic – Metal – Leather	[55]

(continued)

Table 6.2 (continued)

Year	Iron oxide-based samples	Description	Applied surfaces	References
2021	Fe_3O_4@SiO_2-$CsPbBr_3$	Magnetite-silica-cesium lead bromide bifunctional powder	– Glass slide – Black cardboard – Back plastic – Periodic table of elements – Banknote – Leather	[58]
2021	Fe_3O_4@SiO_2-CD(n)	Magnetite-silica–carbon dots powder	– Plastic sheet – Painted wood – Ceramic tile – Aluminum alloy – Printed paper – Cardboard – Coin – Transparent glass	[16]
2020	Fe^{3+}:Fe_3O_4/ZnS	Fe^{3+} sensitized zinc sulfide grafted magnetite core–shell luminomagnetic hybrid	– Glass slide – Copper foil – Aluminum foil – Debit card – Green leaf	[14]
2020	$ZnFe_2O_4$-RGO	Zinc ferrite- reduced graphene oxide	– Glass – Marble – Plastic sheet – Mobile screen – Stainless steel	[3]

(continued)

Table 6.2 (continued)

Year	Iron oxide-based samples	Description	Applied surfaces	References
2019	Fe_3O_4@SiO_2@Me	Magnetite-silica with methyl moieties nanopowder	– Wall – Sheet of paper – Engineered wood – Sofa – Wooden handle of a knife – Plastic wall electricity switch – Ceramic – Glass of water – China plate – Metal door handle – Telephone set	[40]
2019	Fe_3O_4@Pt@PE	Magnetite-platinum-phycoerythrin composite	– Impermeable objects	[36]
2019	Fe_3O_4@SiO_2-NH-CO-CdTe-QDs	Magnetite-amino functionalized silica-glutathione modified cadmium telluride quantum dots nanoparticles	– Glass slide – Black plastic – Ceramic – Black paper – Banknote – Period table – Leather	[57]
2018	Fe_3O_4@GSH-Pt NCs	Magnetite-glutathione-platinum nanoclusters powder	– Dark wood desktop – Glass plates – Metals – Plastics	[25]

(continued)

Table 6.2 (continued)

Year	Iron oxide-based samples	Description	Applied surfaces	References
2017	Fe_3O_4@Pt NCs	Magnetite-platinum nanoclusters powder	– Glass – Black plastic mouse – Dark brown wood stool – Piece of black paper – Black leather bag	[24]
2016	PCDA-Fe_3O_4	10,12-Pentacosadiynoic acid (PCDA)-magnetite powder	– Paper – Aluminum foil – PET film – Glass	[31]
2013	Fe_3O_4@Ag	Magnetite core -silver shell nanoeggs	– Glass	[64]
2013	Fe_3O_4@SiO_2-Au	Magnetite-silica-gold powder	– Glass – Polyethylene bags – Paper	[33]

commercial magnetic powder and bare $YVO_4:Eu^{3+}$, $Fe_3O_4@YVO_4:Eu^{3+}$ material provided more detailed fingerprint strip information such as fine lines and wrinkles. The obtained results showed that it could be one of the promising fingerprint agents in personal identification [47].

In a recent study carried out by the same research group, a mesoporous silica layer was formed between core Fe_3O_4 and shell $YVO_4:Eu^{3+}$ to increase the fluorescence efficiency because Fe_3O_4 nanoparticles could absorb the fluorescence emitted by fluorescent $YVO_4:Eu^{3+}$. The synthesized $Fe_3O_4@mesoSiO_2@YVO_4:Eu^{3+}$ powder possessed an overall size of nearly 590 nm and exhibited excellent luminescence properties with a saturation magnetization of 26.5 emu/g. In addition, they showed that the fluorescence intensity of the sample could be adjusted with the amount

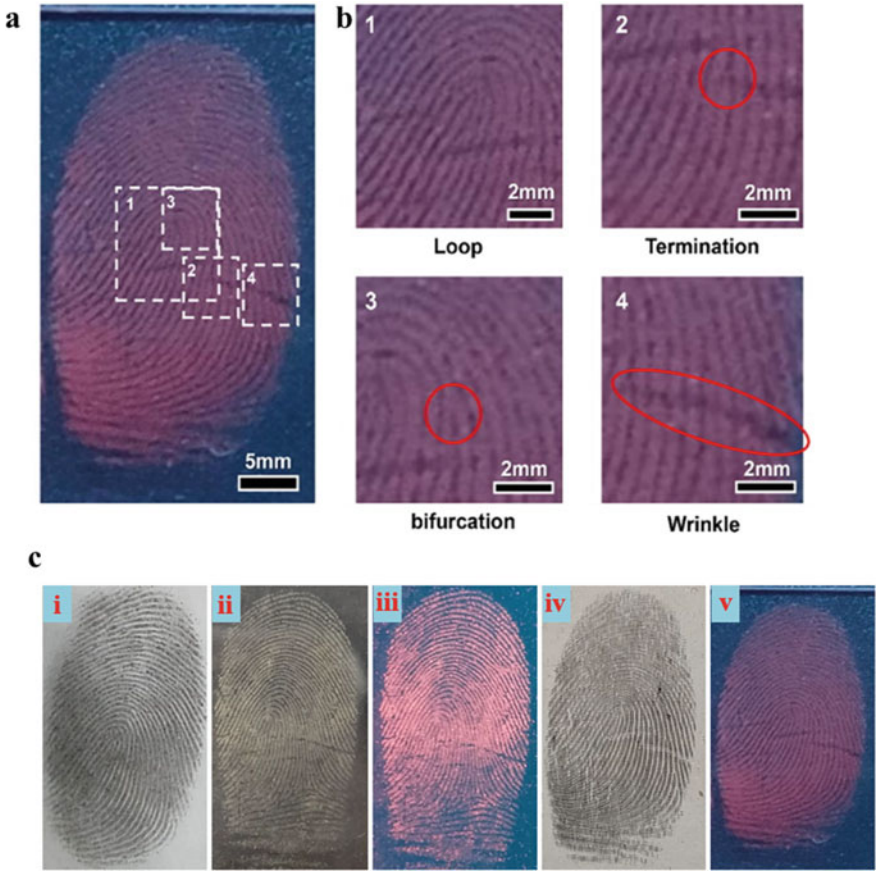

Fig. 6.4 Latent fingerprint images on a glass slide visualized with $Fe_3O_4@YVO_4:Eu^{3+}$ (**a**), the magnified images of the fingerprints (**b**), and latent fingerprints obtained by commercial magnetic powder (i), $YVO_4:Eu^{3+}$ (ii, iii "under UV light"), and $Fe_3O_4@YVO_4:Eu^{3+}$ (iv, v "under UV light") powders. Copyright © 2022 Elsevier. All rights are reserved and reprinted with permission [47]

of doped Eu^{3+}. Fe_3O_4@mesoSiO$_2$@YVO_4:Eu^{3+} powder clearly visualized ridge patterns of latent fingerprints on glass by using 254 nm UV light. Furthermore, the developed powder was applied to some impermeable surfaces such as glass, porcelain, marble, and aluminum foil and different permeable substrates such as blue nitrile gloves, hop-pocket, A4 paper, and carton for detection of latent fingerprints. As a result, Fe_3O_4@mesoSiO$_2$@YVO_4:Eu^{3+} powder demonstrated excellent adhesion on all applied surfaces and high contrast and sensitivity in detecting fingerprints [63].

As another application related to the combination of magnetic particles and fluorescent structures, Lee et al. developed the magnetic iron oxide (Fe_3O_4) supported 10,12-pentacosadiynoic acid (PCDA) powder for viewing latent fingerprints. After Fe_3O_4 nanoparticles were prepared by the co-precipitation method, these nanoparticles were thoroughly ground with PCDA in the presence of a solvent. When the synthesized powder consisting of magnetite and PCDA was applied to the surface containing the latent fingerprints, the magnetic powder mixture would remain constant along with the ridge patterns of the fingerprints in the presence of the magnetic field. Blue-colored polydiacetylenes were formed by irradiating magnetic powders fixed on fingerprints to UV light. With heat treatment applied to the blue color image, the fluorescence state was realized with the conversion from blue to red (Fig. 6.5a). Because of the fluorescence property of PCDA, the ridge patterns of the latent fingerprint were detected with the aid of a fluorescence microscope (Fig. 6.5b). In addition, high-quality images obtained using the same technique allowed the visualization of some specific patterns such as bifurcation, crossover, termination, and lake (Fig. 6.5c). As a result, the combination, which was the aligned pale brown monomeric state, the blue polydiacetylene state due to UV irradiation, the red and fluorescent state because of heat treatment and magnetic property, allows the latent fingerprints to be displayed [31].

In another study, Lv et al. prepared multifunctional nanocomposites (Fe_3O_4@Pt@PE) containing iron oxide, platinum nanoparticles, and fluorescent phycoerythrin to detect latent fingermarks. According to the obtained results, the new nanocomposite indicated the relevant details of fingerprints and clearly showed latent fingerprints [36].

Unlike previous applications, Wan et al. demonstrated the synthesis of the novel magnetic nanomaterial, including silver and Fe_3O_4 nanoparticles (P-MNP@Ag) by the facile co-precipitation method for the first time. MPTES ((3-mercaptopropyl)triethoxysilane) monomer hydrolyzed into ammonia solution and precipitated together with Fe(II) and Fe(III) ions to form the P-MNP by the co-precipitation method, and then, silver nanoparticles were modified on the P-MNP by reduction with sodium borohydride. Also, the same sample coded with S-MNP@Ag was synthesized step by step with surface modification for comparison. Latent fingerprints on various surfaces such as metal, plastic, paper, and leather were visualized with bare magnetic powders, S-MNP@Ag, and P-MNP@Ag. Silver, gold, real silver, and real gold were applied to the same surfaces for comparison, and among the fingerprint agents, P-MNP@Ag and S-MNP@Ag were more effective at visualizing latent fingerprints on plastic and paper. Because of the larger size of the S-MNP@Ag particles, they accumulated more in the tiny grooves, resulting in more blurred images.

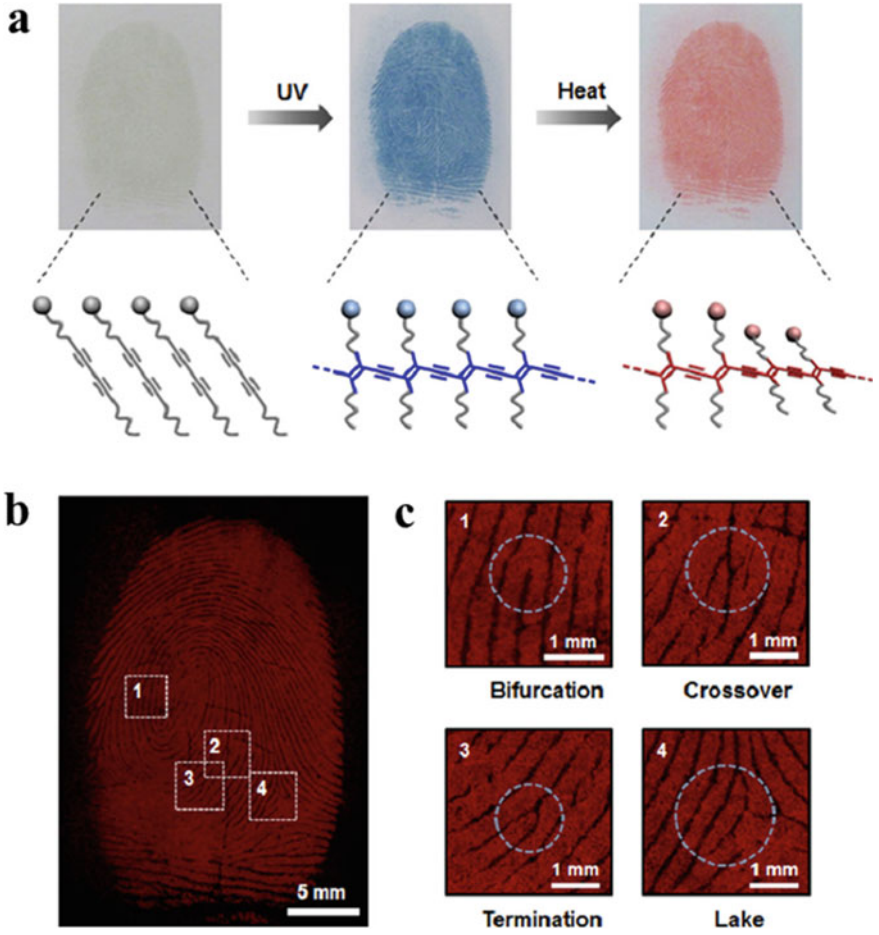

Fig. 6.5 Latent fingerprint images visualized using PCDA-magnetite powder and schematic illustrations of monomer and polymer after UV radiation and heat treatment (**a**), fluorescent images of latent fingerprints obtained using PCDA-magnetite powder on paper (**b**), fingerprint fluorescence images at different magnifications related to patterns. Copyright © 2016 American Chemical Society. All rights are reserved and reprinted with permission [31]

Bare magnetic powders were not very effective in latent fingerprint on leather visualization due to the micropores of the leather. In addition, the newly developed magnetic material (P-MNP@Ag) was used to visualize fingerprints in the crime scene. Fingerprints of criminal suspects were verified by comparison, and the new magnetic material was also suitable for practical applications [55].

Another interesting study was carried out by Das et al. The hybrid microstructure Fe^{3+}:Fe_3O_4/ZnS fingerprint powder, including nano-sized iron oxide (Fig. 6.6(i)), was prepared by hydrothermal method to provide the combination of luminescence and magnetic properties. Unlike other studies, ZnS was utilized as a rare-earth free

luminescence shell due to its wide bandgap, excitonic binding energy, and intrinsic luminescence. Fresh and aged latent fingerprints were examined with the developed functional Fe^{3+}:Fe_3O_4/ZnS powder, and the details in the fingerprints were clearly visualized despite the passing time, as seen in Fig. 6.6(ii). Also, the distance between the yellow ridges and the black furrows was still discernible despite the passing of time, as shown in the graph of vibration intensity. Fe^{3+}:Fe_3O_4/ZnS powder was applied to different porous and non-porous surfaces under room light and UV excitation. Latent fingerprints were clearly identified under 350 nm UV light without any background contrast, and ridge patterns of latent fingerprints were revealed using the hybrid material, as shown in Fig. 6.6(iii) [14].

As described in the previous sections, the powders used to visualize fingerprints should create a color contrast difference on the applied surfaces. Particle sizes and shapes of fingerprint powders are essential factors determining the visualization of patterns obtained from fingerprints. In the study carried out by Gürbüz et al. the size distribution of the magnetic fingerprint powders (Fe_3O_4) was examined in detail in addition to the effect of the porosity of the surfaces for the visualization of the latent fingerprints. Although micron-sized particles could be obtained in this study, it would be appropriate to describe it as a sample study in this section since the effect of size distribution on fingerprints was extensively investigated. Fingerprints applied to the different surfaces indicated that the background staining increased because of the easy trapping of fine particles in the pores of the surfaces as the amount of fine particles rose. The sample containing negligible fine particles was found to be poor

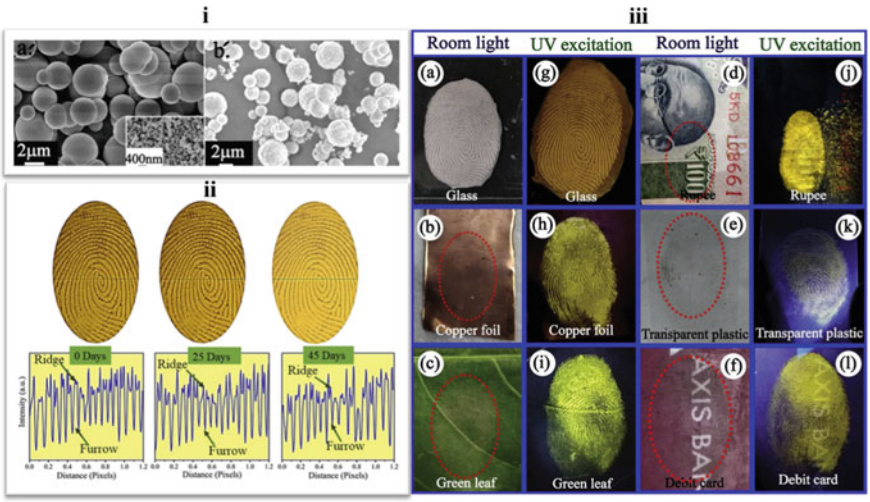

Fig. 6.6 FESEM images of ZnS (**a**'), Fe_3O_4 (a'inset) and Fe^{3+}:Fe_3O_4/ZnS (b') (i), the aged fingerprint images with graphs of intensity variation (ii), latent fingerprint images visualized with Fe^{3+}:Fe_3O_4/ZnS on different porous and non-porous surfaces under room light (**a**–**f**) and UV excitation (**g**–**l**) (iii). Copyright © 2020 Elsevier. All rights are reserved and reprinted with permission [14]

at visualizing fingerprints. Additionally, all samples effectively visualized both old and fresh fingerprints on non-porous glass and porcelain surfaces, but they showed poor visualization for developing fingerprints on paper [19].

The study by Amrutha et al., in which $ZnFe_2O_4$ nanoparticles prepared via green method were used instead of Fe_3O_4 nanoparticles as the magnetic support, can be given as another application example. RGO (reduced graphene oxide) was synthesized by reducing graphene oxide using Emblica officinalis fruit extract and then combined with $ZnFe_2O_4$ nanoparticles. The obtained $ZnFe_2O_4$-RGO nanocomposite was employed to detect the latent fingerprints from various surfaces such as glass, stainless steel, marble, mobile screen, plastic sheet and compared to commercial magnetic and titanium dioxide powders. The $ZnFe_2O_4$-RGO powder was found to be quite effective in visualizing tread ridges patterns in fingerprints [3].

Conclusions

This book chapter summarizes the advantages of iron oxide nanoparticles employed to prepare magnetic powders for detecting latent fingerprints, the most widely used synthesis methods of iron oxides and modifications, and their practical applications in recent years. When magnetic materials, especially nanomaterials, are used as powder for visualizing latent fingerprints, they offer some superiorities, such as recovery and reuse of powder via an external magnetic field, providing the suspect's biological information due to extraction of DNA information, and visualization of all the details in the fingerprint as a result of their small size. Among the iron oxide structures, magnetite-type iron oxides (Fe_3O_4) are getting more attention in forensic science applications because they have advantages such as high magnetization, homogeneous particle size distribution, superparamagnetic properties, and biocompatibility. These excellent properties of Fe_3O_4 vary greatly depending on the preparation methods since the synthesis method is a significant factor in the determination of particle size and distribution, shape, morphology, and surface chemistry. It has been seen in the literature that the co-precipitation method is the most common technique to synthesize Fe_3O_4 nanoparticles with high saturation magnetization. However, Fe_3O_4 nanoparticles should be modified with organic or inorganic materials to maintain their stability and provide new properties since there are some obstacles such as aggregate formation, no excessive loading due to the absence of active groups on the surface, and low affinity. Application examples have shown that iron oxides can be modified with various non-magnetic materials such as quantum dots, gold, silver, platinum, florescent structures, etc., and then they are used to visualize latent fingerprints from different surfaces.

According to the result obtained from this chapter, a magnetic powder containing iron oxide nanoparticles exhibit excellent adhesion on all applied surfaces, high contrast, and sensitivity in detecting fingerprints compared to commercial and non-magnetic powders. Hence, I believe that this chapter will contribute to developing

new and functional magnetic-based fingerprint powders, considering the advantages mentioned above of magnetic nanomaterials.

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Chapter 7
ZnO Nanostructures for Latent Fingerprints

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Introduction

The research, examination, and analysis of evidence at the scene of the crime that provides strong correlations to criminals and easy capture is referred to as forensic technology. Before court trials, forensic evidence is an important aspect for verifying the suspects through investigations done at locations of criminal activity. Fingermarks are the most essential clue materials that are often unintentionally left by criminals. Personal identification in forensic investigations necessitates the creation and improvement of fingerprints. They are one of the earliest and most widely acknowledged forms of physical evidence for determining a person's identification, and they can establish a direct link to the suspect. The skin surface pattern of one human finger distinguishes a fingerprint from another human finger. Fingerprints are formed by the contact of sweat residues to the surfaces, which are secreted from the pores of human fingers. In humans, various glands like eccrine, apocrine, sebaceous, etc., naturally secret amino acids, fatty acids, sugars, and proteins with sweat from fingers, which are responsible for the formation of fingerprints on surfaces. Forensic experts typically meet three sorts of fingermarks as evidence: visible, latent/invisible, and plastic. Latent fingerprints are the most difficult to develop of the three types of fingerprints since they are undetectable to the naked human eye and the surface on which they are present further complicates their development. Many methods or procedures are available for the production of latent fingerprints, including optical detection (absorption, reflected diffusion, luminescence), physical approach (powdering, small particle

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reagent, vacuum metal deposition), and chemical method [1]. Optical technologies are non-destructive and use electromagnetic radiations to make latent impressions visible whereas physical approaches entail the interaction of latent fingermark residues with various powder formulations. There is a chemical transformation of a particular sweat component into a colorful derivative in the chemical approach [2]. The method chosen is determined by the color, condition, nature, and texture of the surface where the latent fingerprint is deposited.

Conventionally AFM (Atomic Force Microscopy) was used to observe thickness, adhesion, and migration of residues; The dispersion of eccrine and sebaceous material throughout fingerprints was studied using FTIR imaging; The presence of eccrine/sebaceous emulsions was confirmed using confocal Raman spectroscopy, and chromatography/mass spectrometry was used to look at squalene quantitation and Various types of mass spectrometry (MS) can be used to detect endogenous and exogenous substances in a fingerprint chemical analysis. Various chemical imaging techniques (like mass spectrometric imaging; MSI) have been used in fingerprints to (a) photograph the ridge pattern; and (b) chemically analyze the fingerprints deposit to deduce info about the donor that is not contained in the ridge pattern. As a result, in forensic science and linked areas, innovative methods for fingerprint development have always been a priority, and much work has been done to improve their efficacy [3].

Nanotechnology is the branch of science concerned with the study of materials on a nanoscale size with a range from 1 to 100 nm. In the last two decades, nanotechnology is widely used in criminal investigations and latent fingerprint detection. Nanoparticle-based visualization is a unique technology for developing latent fingerprints. Nanoparticles have a larger surface area, smaller size, electrical, and thermal conductivity, which allows them to interact more effectively with the sweat residues present on the surfaces. Van der Waal forces cause the existence of an incomplete structure on the surface of nanoparticles that has a high affinity. Over the last decade, huge numbers of publications are reporting the use of nanomaterials in the field of latent fingerprint detection, and most researchers are using nanomaterials as a new dusting powder to detect latent fingerprints [4]. Gold (Au), silver (Ag), titanium dioxide (TiO_2), zinc oxide (ZnO), iron oxide (Fe_3O_4), europium oxide, molybdenum disulfide, and cadmium sulfide nanoparticles have all been used to effectively produce latent fingerprints [1]. To improve fingerprint pictures, micro-sized metal oxide powders were mixed with color additives such as dyes, pigments, and luminous compounds.

This chapter presents a literature review on the role of ZnO nanomaterials and their composites for latent fingerprint detection. Also, it provides an overview of the different methods for latent fingerprint detection using nanomaterials with their advantages and disadvantages. The chapter also discusses the advances and challenges of the ZnO-based nanomaterials in the field of latent fingerprint detection.

Metal Oxides for Latent Fingerprints Development

Metal oxide nanomaterials have gained much attention in each possible application in the world due to their high stability, electrical, optical, and structural properties. Metal oxides nanomaterials like Zinc oxide (ZnO), Titania (TiO_2), Silica (SiO_2), Aluminum oxide (Al_2O_3), Copper oxide (CuO), etc., are widely used in the field of biomedical applications, cosmetics, pharmaceuticals, water treatment and many more due to their wide bandgap, high surface area, and good photocatalytic activity [5]. For latent fingerprint detection, metal oxide nanomaterials powders such as TiO_2, ZnO, Fe_3O_4, europium oxide nanoparticles, and SiO_2 have been utilized [6].

Powder dusting is a commonly used technique to develop latent fingerprints on different surfaces. In this method, powder particles show interaction with the fingermark residue and adherence to residue gives a contrast between the fingerprint ridges and the background [7]. As the nanopowders are in nanoscale size, they show very good adherence to fingermark residue like amino acids, lipid content, and other secreted products in comparison to microsized powders. For this reason, metal oxide nanomaterials are widely used in the development of latent fingerprints due to their small diameter which gives better resolution. Metal oxide nanomaterials show excellent chemical stability in the air and spectral absorption in the UV region. So, for all these properties, different metal oxides and their composites are used in the field of latent fingerprint detection. Most of the metal oxide nanomaterials are used as a dry powder for the development of fingerprints. Direct use of dry nanopowder for fingerprint detection can cause serious health and safety issues due to airborne nanoparticles arising from the dusting of dry powder on a crime scene [4]. To overcome this issue, a safer way to use nanopowder in suspension form is by dissolving powder into a solution or aqueous suspension. Bergeron et al. [8] synthesized TiO_2 nanoparticles and suspended them in methanol solution to evaluate the detection of fingerprints in blood. The results demonstrated good ridge detail from several hours to days. Amin et al. [9] used different kinds of metal oxides nanoparticles—zinc oxide, ferric oxide, titania, and cerium oxide nanoparticles for the development of fingermarks. For this purpose, they treated sebaceous's secreted rich fingermarks and evaluated using a smartphone camera and microscope. They found that titania and cerium oxide nanoparticles showed blurry ridge detail, whereas zinc oxide and ferric oxide gave only limited ridge details.

In the last few years, nanomaterials-based composites are widely used to develop latent fingerprints to increase their adherence as well as resolution and decrease their background staining. Sodhi et al. developed eosin y dye coated Al_2O_3 NPs for fingerprints detection on various surface—paper, glass, plastic, and wood. The results showed good and identifiable fingerprints compared to conventional powders. In another study, Theaker et al. [10] synthesized rhodamine B and 6G doped SiO_2 NPs to identify fingerprints on the glass surface. On the other hand, Choi et al. [11] used fluorescent perylene diimid dye doped TiO_2 NPs for fingerprint detection on the black polyethylene and glass surfaces. These nanopowder-based compositions

have been shown to have low background staining and high resolution in comparison to conventional powders for the detection of latent fingerprints.

ZnO Nanostructures for the Fingerprint Detection

Zinc oxide (ZnO) nanomaterials are widely used in the various field like photocatalyst [12, 13], luminescence [14], pH sensing [15], biosensors [16, 17], antibacterial activity [18, 19], and wastewater treatment [5]. In forensic research powders of nanoscale dimensions are gaining popularity for fingerprint detection. In the field of forensic science and technology, zinc oxide nanoparticles powder is used as reagent for tiny particles to enhance detecting fingerprints methodologies. This method works best for identifying fingerprints on wet and non-porous surfaces, and it also shows a distinct color contrast between the white metallic oxide NPs and the surface of the backdrop [6]. ZnO NPs exhibit good physicochemical characteristics, as well as significant binding activity for interacting with amino acid residues, lipids, and proteins on fingerprint deposit materials at ambient temperature, with a bandgap energy of 3.37 eV. [20]. Latent fingerprint identification with ridge properties was done using ZnO powder and UV irradiation. Under UV light irradiation, in the presence of moisture, and the absence of ZnO nanoparticles powder the LFP was normally glowing for a time [21]. The produced fingerprints on any of the surfaces showed no background interference. For more than a century, ZnO has been widely utilized as a white pigment. It has also been claimed to be used as a basis for colored pigments. It's employed in nanopowder formulations because of its sticky characteristics and interaction with the lipids and proteins found in latent fingermark residues [2].

Different techniques were used to make zinc oxide nanoparticles, including wet chemical, sol–gel, green leaf extract, microwave, and hydrothermal processes, and the nanoparticles were characterized using XRD, SEM, EDX, and UV [22]. Guzman et al. produced zinc oxide nanoparticles that have crystallite sizes ranging from 25 to 30 nm. Wurtzite structure was found in all of the prepared nanoparticles [23]. SEM investigation revealed a variety of morphological characteristics, ranging from a flowery arrangement to a spherical form. Fingerprints were easily spotted on the surface of steel and aluminum, and black glasses using a UV light. Fingerprints on wood surfaces could not be detected. When the UV lamp was used, though, a faint trace could be seen. The presence of the footprint was confirmed by the trace, but the image was not defined, making it impossible to reveal [23].

Luminescence Tests

According to Guzman et al. [23] the fingerprints are captured on two distinct surfaces (steel and aluminum). The fingerprints were examined under white light before being exposed to UV–Vis light. The luminescent process occurs when UV–Vis light is

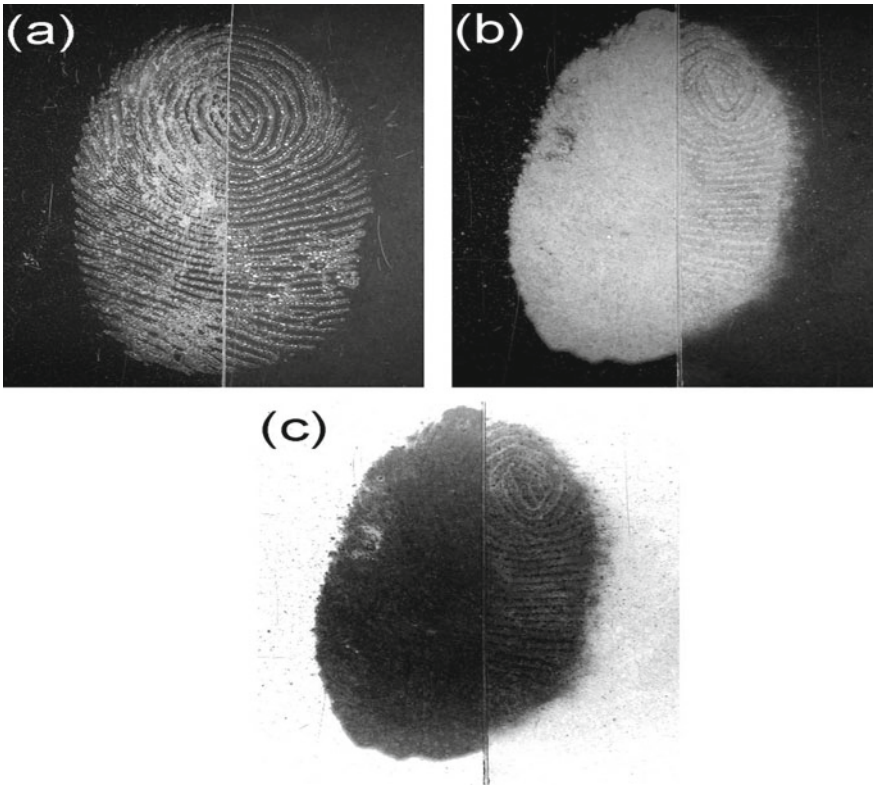

Fig. 7.1 Fingerprints developed by Au/Zn deposition (left halves) and ZnO deposition (right halves) on aged samples that were stored for **a** 1 day and **b** 45 days before development, and **c** inverse images of fingerprints from (**b**). Reproduced from Yu et al. [24]

used to activate the nanoparticles. The colors released by the three ZnO samples made it possible to see the latent fingerprint grooves and folds on the surfaces. Another scientist group, Yu et.al reported that ZnO deposition developed more clear fingerprints in comparison to Au/Zn VMD techniques with the aged sample which is expressed in Fig. 7.1 [24].

Nanoparticles of Zinc Oxide for the Formation and Analysis of Latent Fingermarks

Powder dusting is a good way to find latent fingermarks on smooth, non-porous surfaces. The fingerprints formed with the ZnO nanoparticles are crisp, distinct, and visible to the naked eye. Both colorless and colorful surfaces can be used to make

fingerprints. In the created fingerprints on any of the surfaces, there was no background interference. For more than 100 years, ZnO is being used as a white pigment. It's also been stated that it's used as a basis for colored pigments. It's employed in nanopowder formulations because of its sticky characteristics and interactions with lipids and proteins found in latent fingermark residues. According to Bumbrah et al. [2], In the fingerprints left on these surfaces, fine ridge features may be seen. Tinfoil and the trackpad of a tablet offer the best results. Additionally, utilizing our ZnO nanoparticles-based formulation, old latent fingermarks ranging between 0 and 24 h Additionally, utilizing our ZnO nanoparticles-based formulation, old latent fingermarks ranging from 0 to 24 h were generated on tin foil, coverslip, and the screen of the cell device (Fig. 7.2).

On moist, non-porous surfaces, the ZnO nanoparticle composition can also be employed to generate latent fingermarks. Aluminum foil and glass slides with latent fingermarks were soaked in water for 10 min to 24 h and kept undisturbed. These surfaces were carefully removed from the water and air-dried before the formation of latent fingermarks using a ZnO nanoparticles-based formulation after the predetermined period. On wet aluminum foil and a glass slide, latent fingermarks were developed fresh (10 min) and aged (24 h) (Fig. 7..3).

All of the eccrine LFPs are obtained from a single donor after he has cleaned his hands well with soap and gently wiped them. The fingers are then pushed against various surfaces, both porous and non-porous, with medium pressure. According to PXRD studies, the crystallite size of barbituric acid used as fuel is smaller, hence this product was chosen as a labeling agent in the powder dusting approach. The prepared

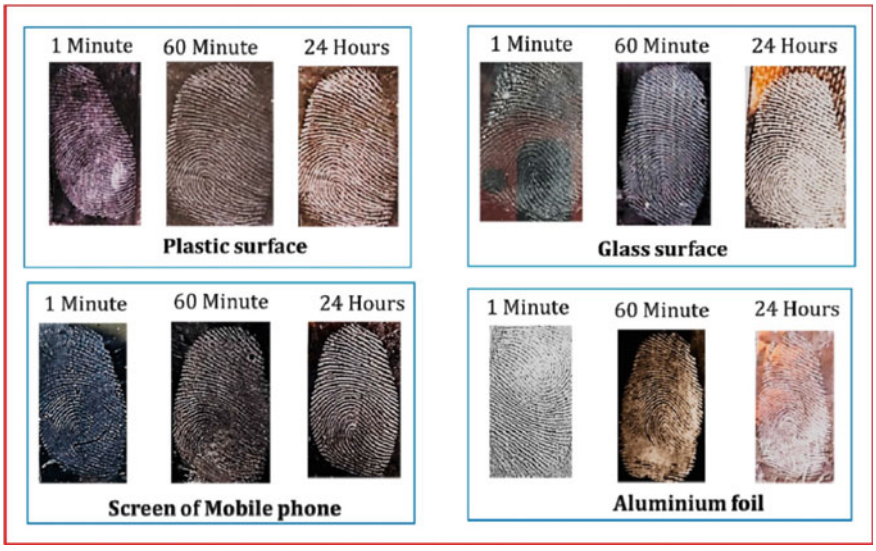

Fig. 7.2 Developed latent fingerprints (LFPs) using ZnO nanoparticles. Reproduced from Bumbrah et al. [2]

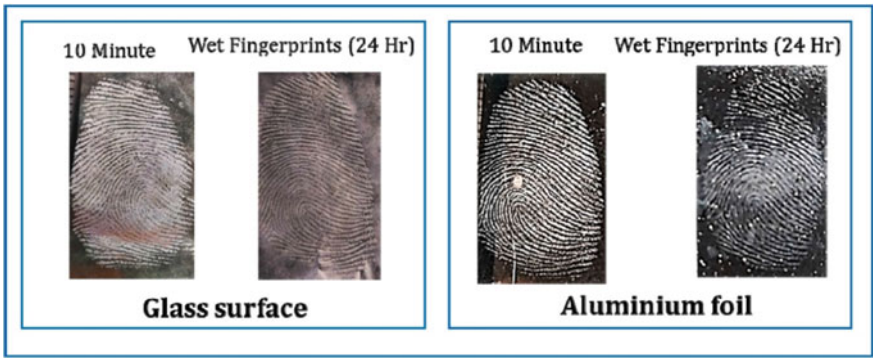

Fig. 7.3 Wet fingerprints are produced using ZnO nanoparticles for up to 24 h. Reproduced from Bumbrah et al. [2]

ZnO NPs are useful for detecting FPs on non-porous surfaces such as blades, metal scales, and staplers. The crystallite size of ZnO NPs produced with barbituric acid is smaller. As a result, it's utilized to identify and enhance latent fingerprints on a variety of permeable and non-permeable surfaces. The fingerprint photos were crisp, with great contrast and no background interference, and even revealed minute characteristics that aid in individualization. As a result, the produced ZnO NPs are employed in both white LED production and forensic applications [25].

ZnO was used to identify both new and old fingerprints on a variety of non-permeable and permeable substrates. They also tried powder brushing and small particle reagent techniques with a new type of $ZnOeSiO_2$ oxide nanoparticles for improved LFP detection. This nanopowder has been employed for fingerprint detection investigations on unusual non-permeable materials, semi-penetrable substrates, and parched substrates. This metal nanopowder has also been employed on sweaty, non-porous surfaces and used in tiny particle agent wet powdering operations to increase and improve visibility for LFP identification on sweat and non-porous surfaces such as glasses, polyethylene, and aluminum foil. On non-permeable substances, this nanopowder yielded fine information and excellent fingerprint images with very little backdrop staining. When contrast to inexpensive white powders, $ZnOeSiO_2$ metal oxide has several advantages, including non-toxicity, low price, enhanced latent fingerprint detection results, and superior visuals for fingerprint recognition. The SiO_2 NPs were immiscible through organic and aqueous media and caused vascular homeostasis impairment, and sperm production damage in human hepatocytes, despite the importance of toxicity studies of ZnO and SiO_2 nanoparticles for latent fingerprint detection [6].

ZnO-Based Composites for the Fingerprint Detection

Metal oxide nanoparticles are becoming more and more attractive as labeling agents for latent fingermarks development. For the latent fingermarks detection with various substrates, metal oxides such as TiO_2, Al_2O_3, ZnO, SiO_2, and CeO_2 were utilized as labeling agents. Carbon-based metal oxides nanomaterials, such as C-silica dioxide, carbon dots/SiO_2, and carbon-based silica nanohybrids, have also been used to create LFP detection. ZnO is a semiconductor having strong photoluminescence qualities, cheap cost, good chemical stability, non-toxic, ease of manufacture, and chemical abundance among them [26, 27].

Zinc oxide-quantum dots (ZnO-QDs) have been used to alter the interior of the particles. The long-term luminescence of ZnO quantum dots has previously been established. The use of ZnO-QDs instead of lanthanide complexes reduces the cost of the formulation and makes it water-compatible (many lanthanide complexes break down in water) [28]. From the standpoint of end-user safety, the water-based suspension is critical. Silica particles coated with carbon quantum dots have recently been shown to be latent fingerprints producing agents, however chemical surface modification or no time-gated imaging was used [29]. The addition of lipophilic phenyl groups on the surface of ZnO-SiO_2 nanoparticles promotes particle adsorption on the latent fingerprint ridges without background staining. Particles in suspension were used to demonstrate natural latent fingerprints deposited on non-porous and semi-porous surfaces such as aluminum foil, drink cans, and magazine cover paper.

Furthermore, utilizing the novel substance, latent fingerprints placed on the sticky side of the adhesive tape can be developed. The water-based suspension is both user and environmentally friendly since it does not need the use of volatile organic solvents throughout the creation process. The use of time-gated imaging for fingermark visibility is enabled by doping the particles with ZnO-QDs that have a long-term fluorescence [28].

Development of Fingerprints

As shown in Fig. 7.4, ZnO-La^{3+} NPs were dispersed to latent fingerprints using a brush on a non-porous and semi-porous surface. The noncovalent/hydrophobic interaction between ZnO-La^{3+} nanopowder and fingermark residue as shown in Fig. 7.5 allows viewing of latent fingerprints on various objects which indicates very good adhesive property [30].

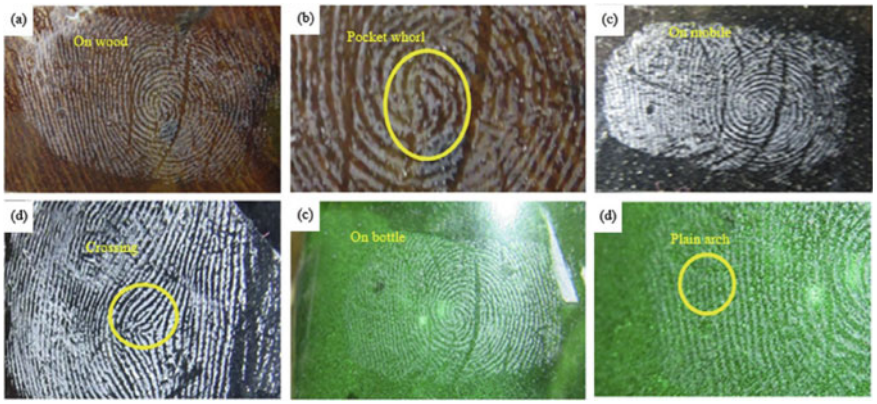

Fig. 7.4 LFP images and its ridge types visualized by staining optimized ZnO:La^{3+} (2 mol %) on various objects. Reproduced from Shivananjaiah et al. [30]

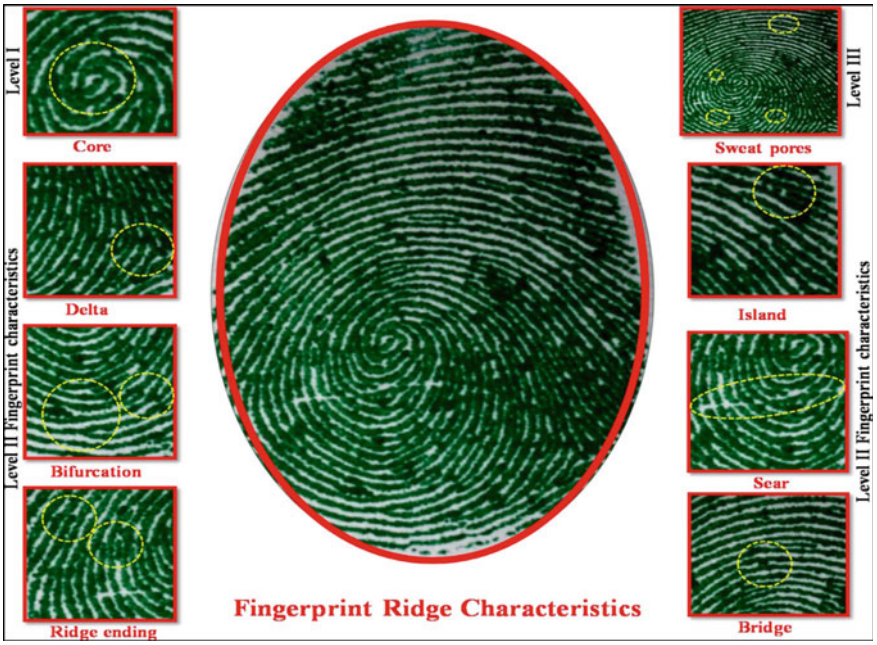

Fig. 7.5 Detailed fingerprint ridge characteristics of Cu doped ZnO nanoparticles taken on the glass surface under UV lamp (365 nm) showing level I, level II, and level III fingerprint ridge characteristics. Reproduced from Naik et al. [31]

Powder Dusting Method for the Latent Fingerprints Detection

Recently Naik et.al reported LFPs of Cu-doped ZnO nanoparticles on the surface of glass depicting three levels with clearer ridge patterns and all the levels were indicated by yellow circles comprising level 1-core, level 2-ridge ending, bifurcation, sear, delta, bridge, island, and level 3-sweat pore (Fig. 7.5). Therefore, the ability to provide such minute details stated Cu doped ZnO NPs as an efficient candidate for latent fingerprints detection [31]

Due to its nanosize and unusual synthetic technique, the latent fingermarks created with this powder displayed outstanding ridge features with less background staining/painting and superior outcomes than those previously described [32].

For seeing latent fingermarks on various non-porous materials, a simple, quick, and successful method was developed. The ZnO–SiO_2 nanopowder was discovered to produce crisp and sharp photographs of latent fingerprints on the non-porous surface with low background staining, exposing superb ridge features important in criminal investigations. The produced nanopowder provided excellent visualization of third-level ridge features. Because of their ease of synthesis with low-cost precursors and minimal toxicity, ZnO–SiO_2 nanopowders have an advantage over other commercial white powders. It's important to utilize it as both a dry powder and an SPR suspension for wet non-porous surfaces. On dark-colored surfaces, however, ZnO–SiO_2 performed better than on light-colored surfaces [33]. There is some work reported for the use of ZnO nanostructures and their composites enlisted in Table 7.1.

Advances and Challenges

There are several points, which should be fulfilled by a novel nanomaterial for the development of good latent fingerprints. The first one is that the nanostructure should be in the range of 1 to 100 nm for better adherence with fingerprints residues. The second one is to have a smooth surface that can be readily functionalized to target selective fingerprint residues. The other one is to have a good optical property that enhances fingerprint visualization post-development. Another important point about nanomaterials is that they should be cost-effective, low toxic, and must show good luminescence. Moreover, the use of nanomaterials as a dry powder is strictly not recommended for fingerprint detection and must be avoided as they show very serious health concerns to the operator.

However, it is observed that there is not much paper reported on the development of latent fingerprints using ZnO nanostructures. For the last few years continuous research was done to modify zinc oxide nanostructures by doping, composites, and by adding luminescent components to improve the resolution and quality of latent fingerprints. However, there are still many challenges, which have to be overcome,

Table 7.1 Role of different ZnO nanostructures and their nanocomposites in the development of latent fingerprint

S.no	Nanoparticle	Dopant	Detection method	Shape	Size(nm)	Synthesis method	Remarks	Ref
1	ZnO-SiO_2		Powder Dusting, SPR		32.9	Heating	Excellent quality was discovered, with extremely obvious third-level ridges and higher visibility than commonly available White powder	[33]
2	ZnO		Powder Dusting	Spherical	3–5	Precipitation	The findings in this study present a concise technique for enhanced encryption that might have a wide range of applications in the disciplines of information security	[34]
3	ZnO		Powder dusting	Hexagonal	5–23	Combustion	When compared to commercially available white powders, the detection of latent fingerprints was determined to be outstanding	[25]
4	ZnO		Powder Dusting	Semi Spherical	10–30	Precipitation	When the nanoparticles were exposed to UV light on aluminum, black glass, black paper board, and steel fingerprints were easily spotted	[23]
5	ZnO		Powder Dusting		14.75	Precipitation	For its smaller size, ZnO was shown to be a superior choice for detecting latent fingerprints	[1]
6	ZnO	Nitrogen	Powder Dusting	Spherical	40–50	Hydrothermal	Photoluminescence activity, chemical characteristics, and latent fingerprint detection were all outstanding in the nanocomposite powder	[26]

(continued)

Table 7.1 (continued)

S.no	Nanoparticle	Dopant	Detection method	Shape	Size(nm)	Synthesis method	Remarks	Ref
7	ZnO		Powder dusting	Spherical	> 100	Green	Organically produced nanostructures were used to create fingerprints. On dark non-porous surfaces, zinc oxide powder had good clarity and contrast	[35]

such as difficulties in achieving nanoscale composite particles, low emission of luminescence, and problematic functionalization [7]. Many dyes, fluorescent, and other luminescent entities can be incorporated with ZnO nanostructure for better illumination. Some points need to be optimized for the development of good fingerprints and also should be compatible with common forensic instruments like cameras, light sources, and filters.

Conclusion

In this chapter, we first discussed the latent fingerprints which cannot be seen by the naked eye, and then we described the use of metal oxide nanomaterials in the development of the latent fingerprints. The discussion mostly focused on the role of zinc oxide nanostructures and their composites in the detection of latent fingerprints. For instance, ZnO nanopowder, lanthanum-doped ZnO, ZnO-SiO_2 composites, etc., showed very good resolution and visualization of latent fingerprints. Additionally, we discussed the process of fingerprint development and the factors which are required for a novel nanomaterial to obtain a better illumination of the fingerprint. Hence, zinc oxide nanostructures and their composites show good potential for the development of fingerprints and may improve their quality in the future for the identification of suspects and controlling crimes.

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Chapter 8
Green Synthesized Nanoparticles for Development of Latent Fingerprints

Khushboo Gautam, Dipak Kumar Mahida, and Ankita Patel

Introduction

The evolution of forensic sciences results in significantly better community safety, which is among one of the fundamental basics of human necessities as well as a pillar of growth in the economy. Fingerprints are extremely important pieces of tangible evidence in crime scene investigations [1, 2]. Amidst their individuality and long-term uniformity, fingerprints have also been enormously essential platinum bio-metric traits for qualities for personal authentication in crime scene investigation for over a century. If a hand comes into contact with an object, it leaves a lasting impression in the form of ridges. At the scene of a crime, latent fingerprints (LFPs), also known as hidden fingerprints, are fingerprints that are not apparent to the human eye. The majority of crime scene investigations include the identification of fingerprints. Fingerprinting reveals several fundamental concepts. In forensic science, latent fingerprint recognition has entrenched itself as one of the main approaches to personal identification [3].

The powder method, cyanoacrylate fuming, iodine fuming, ninhydrin, and the silver nitrate technique are all common methods for the formation of latent fingerprints. Non-metallic and metallic powders are used for the formation of latent fingerprints on crime scenes. Due to "their anticipated physical, chemical, and biological capabilities," scientists are now paying close attention to nanostructured metal oxide and plant-based green nanoparticles that are free from toxicity and environmentally friendly [4–7]. Nanoparticles become essential in the development of sustainable economic advancements to human beings and the ecosystem.

Green-based nanoparticle (also known as biogenic nanoparticles) synthesis is a green chemistry technique that bridges the gap between nanotechnology and forensic—Nanotechnology [7]. The importance of a green synthesis perspective to

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nano particles' growth prospects cannot be overstated. The field of nanoscience should lead to the production of reliable, environmentally acceptable nanoparticles, as well as widespread recognition in nanotechnology worldwide. With the advancement of technology, there is indeed a necessity to develop environmentally friendly biosynthetic procedures that don't use toxic chemicals. The advancement of efficient, harmless, and ecologically friendly "green chemistry" processes, likely including species ranging from microorganisms to fungus and even green plants, should help the production and integration of nanoparticles [8, 9]. Green synthetic methods have advantages over traditional methods that use harmful chemical agents. The most important aspects to consider in green nanoparticle synthesis are solvent medium selection and the selection of eco-friendly non-toxic reducing and stabilizing agents. Nanoparticles help detect and expand latent fingerprints.

To obtain latent fingerprints, many green and green-based nanoparticles have been developed. Green nanoparticles boost the overall and particular properties of fingerprints, as well as other intricate details such as the position of pores [10, 11].

Methods for the Synthesis of Nanoparticles

Nowadays; Physical, chemical, and biological methods could all be used for nanoparticle synthesis. Various methods available in different classes are indicated in Fig. 8.1

The sol–gel method, spray pyrolysis, chemical vapor synthesis is among the most often utilized chemical procedures. Organic and inorganic oxidizing agents are used

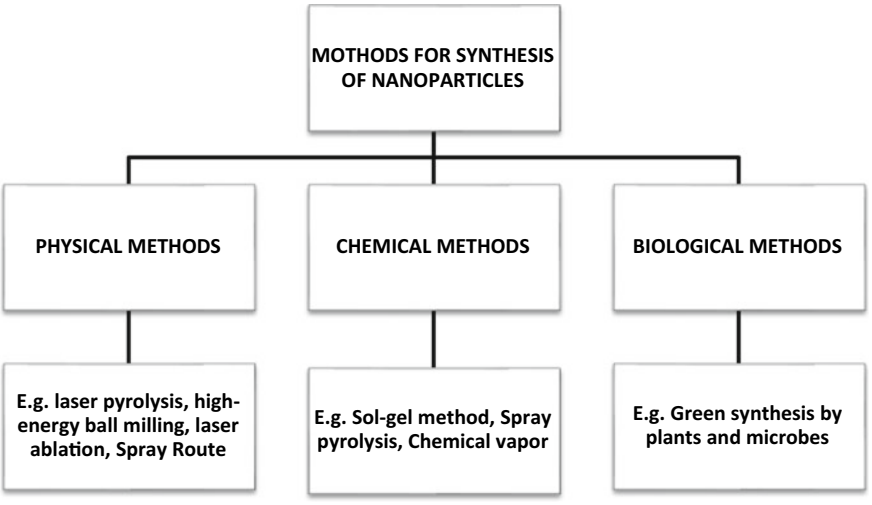

Fig. 8.1 Methods for Synthesis of nanoparticles

in chemical oxidation for instance citric acid, baking soda, glycyrrhizin, azelaic acid, hydroquinone, sodium borohydride ($NaBH_4$). These reactions are usually accomplished while in suspension, as well as the outcome possesses colloidal properties [12]. If there is no solvent interference throughout the developed nanoparticles and the dispersion of manufactured nanoparticles is constant, such physical methods are more favorable than chemical methods. This physical approach could be used as a nanoparticle generator for long-term inhaling toxicological studies as well as a calibrating tool for nanoparticle measuring devices [13–15].

Even though chemical and physical methods could be used to produce nanoparticles; it is becoming easier to embed biological components. The environment would also have evolved several mechanisms for the generation of nanoparticles and inorganic and organic materials with size in microns that have helped throughout the creation of a comparatively recent and most fascinating research area focused on nanomaterial biosynthetic pathways. In biomolecules, oxidizing agents are broadly disseminated. The biological method of generating nanoparticles could be synthesized based on four types of kingdoms out of five, like Monera, Protista fungi, and Plantae [16, 17].

Synthesis of Green Nanoparticles

There are 3 most important qualities for green synthesis: (i) selection of eco-friendly solvent, (ii) a suitable reducing agent, and (iii) a safe chemical for stabilization. Several synthetic techniques have been used to create nanoparticles, with the most common being physical, chemical, and biosynthetic. Chemical methods are sometimes expensive and need the utilization of dangerous and poisonous chemicals, which pose a variety of environmental hazards [18, 19]. Green nanoparticles are synthesized using flora and microbes such as bacteria, actinomycetes, and fungus, which is a safe, biocompatible, and eco-beneficial green technique. [20]. Greener nanoparticles such as cobalt, iridium, bimetallic alloys, copper, silica, silver, gold, palladium, platinum, and magnetite have been reported to be synthesized by photosynthetic living organisms such as plants, algae, and diatoms, as well as some biocompatible agents and heterotrophic human cell lines. The utilization of those living organisms, as well as environmental-friendly substances, for the production of nanoparticles, has up to now completely investigated due to their diversity and long-term survivability [21] (Fig. 8.2).

Bottom-up approaches: A bottom-up method is the creation of nanoparticles from excessively small size units such as molecules and atoms, which then evolve into a particle with gradual dimensions via a range of chemical and biological processes [3].

Top-down approaches: Top-down process consisting of the method of nanoparticles synthesis by utilizing a size reduction method, in which lithographic procedures such as crushing, spitting, and milling are used to reduce acceptable bulk material to tiny units [22].

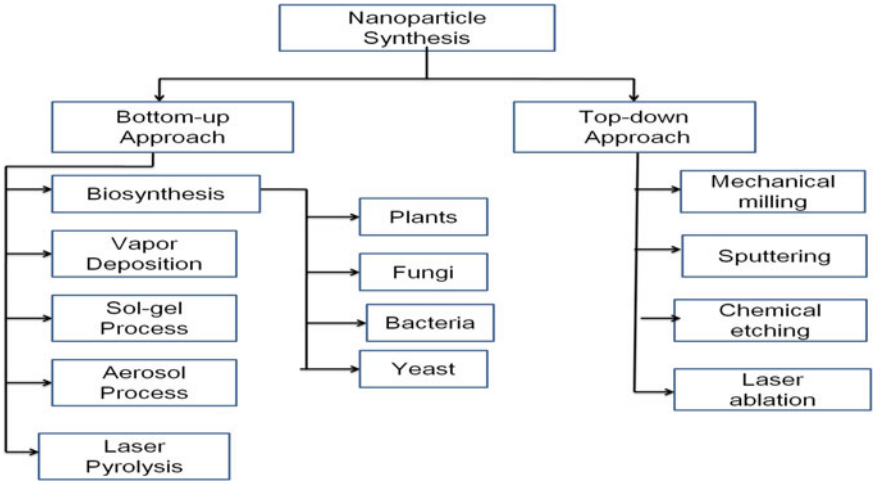

Fig. 8.2 Biological and physicochemical methods for nanoparticle production [22]

Green Synthesis Constituent

As such, green synthesis is recognized as a significant technique to lessen the damaging consequences connected along with standard methods of nanoparticle synthesis procedure extensively applied in pharmaceuticals and laboratories. Some of the green synthesis constituents are green reducing agents, green capping agents, green stabilizers, and green support materials [6, 9].

Green Reducing and Capping Agents

Generally reducing reagents are used in the creation of metal nanostructures. They have mainly converted metal salts into metallic materials, while surfactants are polymers utilized in the wet chemical synthesis to protect nanoparticles from aggregation by steric repulsion. Capping agents are essential as stabilizers in colloidal synthesis because they prevent nanoparticles from overgrowing and clumping. The capping agents help to keep the interface between nanoparticles and their manufacturing medium stable. Phyto-based reducing and capping agents, microbial materials, and some other hydroxyl and carboxyl group-containing green chemicals are considered green reducing and capping agents [6, 9].

Green Stabilizers and Support Materials

As green stabilizers and support materials, there is many biological polysaccharides are used likewise cellulose, dextran, starch, glucose, heparin, chitosan, and

others have been employed as nanoparticle stabilizers. Due to the absence of harmful chemicals, synthesizing nanoparticles with the use of those biological materials as capping agents is both energy efficient and ecologically beneficial. Some investigations employed standard protocols with the addition of water-soluble starch as a stabilizing agent, while others looked at increasing nZVI transport in soil using potato starch [23].

Green Synthesis Methods

Green synthesis techniques are based on the traditional 12 chemistry principles and help to ensure the long-term growth of chemical processes. They take longer, have lower chemical and final product toxicity, cause less environmental and human worry, and lessen the danger of global warming [24]. Both well-known chemical compounds and wholly new materials have been created using more environmentally friendly approaches. Simultaneously, conventional components (e.g., cement, ceramics, adsorbents, polymers, bioplastics, and biocomposites) may be improved or manufactured using more environmentally friendly processes [24]. Greener synthesis relies on pure physical procedures such as hydrothermal processes, ultrasound-assisted, ball milling, or microwave heating as well as solventless and biosynthetic approaches, which are usually combined with using natural resources. Non-hazardous solvents investigated in conjunction with material development include ionic liquids, plant extracts, and other micro-organisms [24]. Nanoparticles are made in two methods that are both environmentally friendly: Preparation of green reducing and capping agents, as well as green nanoparticle assembly methods green reducing and capping agents are extracted from various plant parts in general. These techniques either make it simpler to combine green materials or those that require not so much energy or natural resources than classic techniques for nanoparticles synthesis, or they do both. Researchers in green synthesis are especially interested in low-energy, quick, and cost-effective assembling systems with few stages. Simple methods offer the benefit of being more readily scaled up for large-scale production [6, 9]. A common strategy for constructing green nanoparticles is to employ a simple hydrothermal procedure to increase crystallization in nanoparticle materials [25].

Plants Used for Green Nanoparticles

Plants produce a range of compounds that are environmentally friendly, easy to get, and need little maintenance. Because photosynthetic organisms are long-term suppliers, they might be widely exploited in the production of green nanoparticles. The green chemistry approach, which is the most current feasible way for combining material science toward biotechnology in the area of nanobiotechnology, is an alternate method for chemically synthesizing biocompatible nanoparticles. Because biological bodies contain more components for the production of nanostructures, nanobiotechnology has more benefits than conventional techniques. The

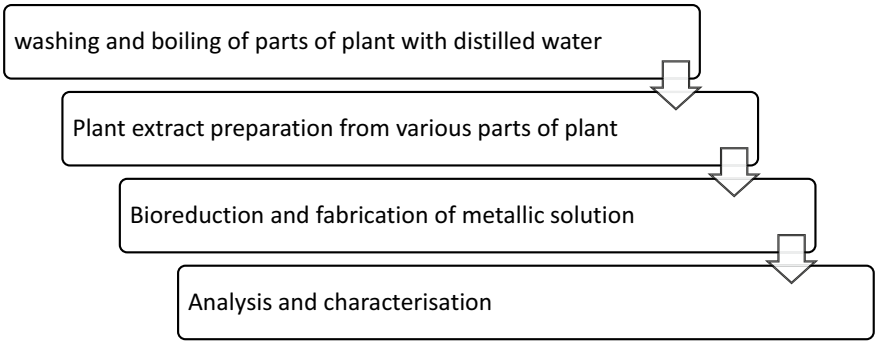

Fig. 8.3 Route of synthesis procedure for nanoparticles

enormous variety of such living creatures must be researched to synthesize bionanomaterials. The engineering of gene encoding and atomic cloning that helps in the metals bioreduction makes it easier to make nanomaterials [21]. Because of their exceptional ability to detoxify and accumulate heavy metals, plants contain a large number of them. Some metals are also very poisonous at even very low quantities, which may be used to solve pollution concerns in the environment [27]. Plant extract nanoparticle synthesis is more advantageous than other biological synthesis techniques, such as microorganisms, since it may be achieved via more sophisticated procedures, such as maintaining microbial colonies [21]. In the past, only prokaryotes were used to generate soluble benign metal salts from insoluble hazardous metals for biosorption and bioreduction. Plants and other eukaryotes do, however, have the capacity to convert metal ions to metal nanoparticles [21]. The route of synthesis procedure for nanoparticles is shown in the flowchart [28] (Fig. 8.3).

Advantages of Using Plants for Nanoparticles Synthesis

(1) Plants are reachable, safe, and innocuous to handle, and have a multiplicity of metabolites which can be much helpful in reduction [19].
(2) Plants have sufficient higher kinetics for synthesis than other biosynthesis approaches [25].

Many researchers have conducted different studies on the synthesis of nanoparticles from various plant species. Some major metal nanoparticles with their suitable plant species are listed below in the Table 8.1 [22].

Table 8.1 List of various metal nanoparticles with their suitable plant species

Sr. No	Nanoparticles	Suitable plant species
1	Ag	*Saccharum officinarum, Helianthus annus, Cinnamomum camphora, Oryza sativa, Aloe vera, Capsicum annuum, Medicago sativa, Zea mays, Magnolia Kobus, Cinnamon zeylanicum*
2	Au	*Geranium sp., Azadirachta indica, Aloe vera, Diospyros kaki, Magnolia Kobus, Terminalia catappa, Coriander sp., Trifolium sp., Salix alba, Coffea arabica, Croton quadratus Geisel, Bacillus marisflavi, Croton spersiflorus, Citrus Limonum, Aeromonas hydrophila*
3	Pd and Pt	*Musa paradisica, Cinnamomum camphora, Terminela chebula, Gardenia jasminoides, Pinus resinosa, Ocimum sanctum, Anogeisus latifalia, Glycine max, Ocimum sanctum, Curcuma longa, Cinnamomum zeylanicum, Pulicaria glutinosa, Doipyros Kaki, Cantharanthus rosesus, Annacardium occidentale, Camellina sinensis, Anogeissus latifolia, Chlorella vulgaris, Azadirachta indica*
4	Cu	*Aloe vera, Cuscuta reflexa, Lawsonia inermis, Tamarindus indica, Citrus limon, Berberis sp.*
5	ZnO	*Azadirachta indica, Vitex negundo*
6	TiO_2	*Annona squmosa L., Jatropha curcas, Catharanthus roseus, Moringa oleifera, calotropis gigantea, Cucurbeta papo*

Development of Latent Fingerprint by Green Synthesized Nanoparticles

In recent years, many researchers have focused on the utilization of nanoparticles in the development of latent fingerprints. Parallelly, Researchers are concentrating their efforts on developing effective green chemistry methods for the synthesis of metal nanoparticles. They looked at finding an environmentally acceptable method for producing well-characterized nanoparticles. Various metal and metal oxide nanoparticles (which can be synthesized through green methods) such as gold (Au) nanoparticles, silver (Ag) nanoparticles, copper oxide (CuO) nanoparticles, iron oxide (FeO_2) nanoparticles, titanium dioxide (TiO_2) nanoparticles, zinc oxide (ZnO) nanoparticles, europium oxide (EuO) nanoparticles, silica (SiO_2) nanoparticles are used in various studies for the development of latent fingerprints.

Au Nanoparticles for Latent Fingerprint Development

Shankar et al. conducted the first work on gold nanoparticles production in 2003, utilizing geranium leaf extract as a reducing and capping agent. The terpenoids included in leaf extract were responsible for the reduction of gold ions to gold

nanoparticles, and this reaction was carried out for 48 h. According to morphological investigations, these nanoparticles were generated in a variety of morphologies, including triangular, spherical, decahedral, and icosahedral [29]. In addition, they created gold nanoparticles in 2.5 h using Azadirachta indica leaf extract. The neem extract, which contains a lot of terpenoids and flavanones, was presumably absorbed on the nanoparticles' surface and kept them stable for 4 weeks. Morphological analyses found that nanoparticles were spherical and mostly planar in form, with the majority being triangular and some being hexagonal [21].

Tang et al. used certain unique features of gold nanoparticles with imaging mass spectrometry to see and image latent fingerprints at the molecular level. The optical pictures of latent fingerprints are revealed by two opposing hues (blue and pink) coming from separate surface plasmon resonance (SPR) bands of Au nanoparticles. The laser desorption/ionization feature of Au nanoparticles enables the direct analysis and imaging of endogenous and foreign chemicals contained in latent fingerprints without disrupting the fingerprint patterns. The simultaneous observation and recording of latent fingerprints' molecular pictures not only provide proof of individual identification but also help to resolve overlapping fingerprints and identify dangerous compounds [30].

Ag Nanoparticles for Latent Fingerprint Development

Ecofriendly bio-organisms present in plant extracts serve as a capping agent and reducing agent in the manufacture of shape-controlled and stable silver nanoparticles. The use of polymers and surfactants to modify silver nanoparticles exhibited strong microbiological activity against Gram-negative and Gram-positive bacteria. Silver nanoparticles were synthesized by some researchers using a methanolic extract from the *Eucalyptus hybrida* plant [22].

For developing invisible fingerprints on moist, porous materials like paper and cardboard, the silver physical developer is the typical reagent. A black silver precipitate forms along the fingermark ridges when silver is deposited on the water-insoluble residues of latent fingerprints. This method is based on an electroless deposition reaction in which Fe_2 + ions convert Ag+ ions to metallic silver, a reaction that is likely facilitated by the fatty composition of the latent fingerprint substance. A procedure known as "colloidal gold" or "multi-metal deposition" is being utilized to improve latent fingerprints using gold nanoparticles fixed by citrate ions in an aqueous media, followed by Ag-PD (MMD). The gold nanoparticles stick to the fingermark residue and help the Ag-PD solution to precipitate metallic silver. At low pH, anionic interaction between negatively charged gold colloidal particles and positively charged particles of the fingermark deposit explains gold adhesion to the fingermark substance [31].

CuO Nanoparticles for Latent Fingerprint Development

CuO nanoparticles were successfully synthesized utilizing green tea leaves extract and an ultrasonicator-assisted procedure. The catechins included in green tea leaf extract operate as a stabilizing, reducing, and capping agent. Sound waves pass through liquid mediums, resulting in alternating high-pressure (compression) and low-pressure (rarefaction) cycles. During rarefaction, high-intensity sonic waves create small vacuum bubbles or voids in the liquid, which then collapse violently (cavitation) during compression, creating very high local temperatures and increasing the intensity of effective collision, which aids in the formation of CuO nanoparticles. Green tea extract-coated CuO nanoparticles were synthesized using an ultrasonicator-assisted efficient and innovative approach.

The powder dusting approach was utilized to visually identify latent fingerprints on diverse surfaces using green tea extract-coated CuO nanoparticles powder. Because of its unique qualities, such as its stable nature, non-corrosive nature, scalability, cost-effectiveness, and eco-friendliness, green tea extract-coated CuO nanostructures are beneficial for the improved formation of latent fingerprints on diverse non-porous surfaces [1].

Iron Oxide (FeO_2) Nanoparticles for Latent Fingerprint Development

Iron oxide nanoparticles were modified using thiol, silane, and triethoxysilane which are customized iron oxide nanoparticles were created using pH-varying suspension solutions for the generation of latent fingerprints on various substrates, with acidic pH resulting in greater fingerprint formation than higher pH [33]. Iron oxide nanoparticles synthesized using tea extract were utilized for the development of latent fingerprint successfully [32].

Green Synthesized Nano Over Conventional Methods for Latent Fingerprint Development

Earlier traditional powders such as ninhydrin, black powder, grey powder, orange powder, fluorescent powder, synthetic color powder, etc., were used for the development of latent fingerprints. Such approaches led to substantial improvements on a wide range of substances; however certain advancements became required to improve its effectiveness while also reducing the cost. Traditional powders include toxic elements that could be highly lethal. The following is an explanation of where and how fingerprints develop using traditional powder.

The being is first recognized, and then the fingerprint powder is dispersed upon it. The traditional powder clings to the oils and some components of perspiration are left in a fingerprint, allowing the impression to be decoded. However, it is not uncommon for just half or imperfect prints to be interpreted. Moreover, traditionally, powders don't always provide enough comparison, making it tough for an investigator to observe and evaluate the generated impressions. To circumvent this limitation, researchers throughout this work attempted to generate hidden impressions using non-toxic, readily available powders. For this purpose, green syntheses nanoparticles are utilized because they are environmentally benign and easy to use [35].

Nonetheless, traditional approaches made it impossible to retrieve fingerprint information through surfaces like latex and cotton, which plays a critical role in forensic investigations [36]. Presently, the implementation of a novel medium for the conveyance and identification of latent fingerprints became a vital concern such as, to ensure a higher exchange and identification of latent fingerprints from various surfaces concurrently opted nano fibrillated cellulose as just the endorsed content to begin preparing fluorescence nano fibrillated cellulose/carbon dots paper by synthesizing fluorescent carbon dots upon that substratum of nano-fibrillated cellulose across thermal annealing. Nano-fibrillated cellulose has a wide base, permeable characteristics, customizable physical and chemical properties, and specific strength as a sorbent [34].

Furthermore, cumin, coriander, black pepper, cardamom, and cinnamon as green synthesis nanoparticles in leaves or seed form were employed for the development of latent fingerprints. Vitamin C, pectin, flavonoids, antioxidants, phytochemicals, polyphenols, tannins, gallic acid, glucoside, and quercetin, are abundant in the fruits of *Phyllanthus emblica Linn.* These are the novel marker for detecting latent fingerprints on a wide variety of substrates [36].

Besides, in the era of using nanoparticles for latent fingerprint development, the synthesis procedures also matter. For the synthesis of nanoparticles, different conventional techniques have been used for several years, but many researchers have recommended that green approaches are more successful for the creation of nanoparticles because they have fewer chances of failure, are cheap, and are easier to distinguish. The hazardous metabolites produced by physical and chemical ways of manufacturing nanoparticles have exposed the environment to a range of stresses. Plant-based nanoparticle synthesis is a simple process that includes mixing a metal salt after extracting plant residues and finishing the reaction in a few minutes to an hour at room temperature [37]. Green nanoparticle generation technologies are simple to expand and cost-effective. Green-synthesized nanoparticles are currently preferred over conventionally supplied nanoparticles because of their better qualities. Additional substances are hazardous to the environment and human concerns due to the lack of clarity and ambiguity of composition may enhance particle reactivity and toxicity, as well as cause undesired adverse health impacts [38].

Conclusion

Forensic science includes several disciplines and focuses on several sources of evidence that aid in determining a criminal's identity. The fingerprint is among the most important sources of evidence when it comes to determining a criminal's identity. Because fingerprints are one-of-a-kind, they portray the person. No two people have the same fingerprints. Besides enhancing the properties of fingerprints with appropriate techniques, DNA can be extracted from them. The nanoparticle development approach improves the quality of latent prints. Forensic scientists have been given a new direction when nanoparticles are used in latent fingerprinting. Whenever utilized as a developing method in latent fingerprinting, these nanosized particles offer various benefits over traditional ones. These nanoparticles may readily be used to disclose fingerprints on a wide variety of substrates, and they have a wide range of possibilities for further precise finger ridge etching. It's due to nanoparticles' superior Vincent over commercially available traditional powders that have been developed to develop fingerprinting materials.

Future Scope

Be numerous advantages described previously, there is a requirement to create green chemistry methodologies in comparison to traditional chemical nanofabrication and traditional method of development of latent fingerprinting processes. The green synthesis-based method to synthesizing nanoparticles has been revealed to be environmentally benign, cost-effective, versatile, accessible, and stable. In the last two decades, versatile biological nanoparticles have made great progress in medicinal applications, particularly in fingerprints. Green synthesis has a promising future because of its low cost and long-term sustainability. In comparison to chemical nanoparticles, toxicity issues for biological nanoparticles have indeed been found below. Isolation and purification of nanoparticles would be another crucial consideration that should be investigated further [39–41].

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Chapter 9
Fluorescent Nanomaterials in Visualization of Latent Fingerprint

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Introduction

Forensic science discipline is the amalgamation of all fundamental sciences applications including the research, examination, and identification of various obtained pieces of evidence from crime scenes side which predict direct or indirect link links between suspects with crime [17, 19]. The forensic examination report is necessary in the law of court for judgment in various criminal cases. Biological and non-biological matrices are important evidence in different crime scenes. Various sophisticated instrumentation technologies are used for the examination of this kind of sample [11]. Fingerprints are authenticated evidence for individual identification in the forensic examination which is a strongly admitted injustice system due to latent fingerprints marks having exceptional ridge configuration of each person which does not alter with age and other related factors [14, 28]. In the current arena, fingerprints are commonly used for individual identification in various government offices such

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as biometric systems, thumb impressions on legal documents, and UIDAI numbers issued by the government [8, 15].

Nevertheless, in most of the crime scene latent fingerprints are undetectable by traditional routine methods and have issues like poor contrast, and need extra effort to the identification of latent fingermarks without varying their reliability [40]. These traditional methods include ninhydrin reagent, iodine fuming, cyanoacrylate fuming, powder dusting, and silver nitrate spring techniques are routinely used in the development of various class of fingermarks on porous and non-porous surfaces [20]. These routine methods have multiple challenges belonging to surface unpredictability, contrast, sensitivity, and toxicity of materials [24]. The fluorescence nanomaterial is used for the enlargement and detection of the latent fingerprint on porous and non-porous surfaces which has very optimum sensitivity, minimum processing time, cost-effective, and a longer lifespan than the synthesized material [6].

Fingermarks are living behind at the crime scene site in types three includes; impression, visible, and latent fingerprints [31]. Amongst these, latent fingerprints are found commonly at crime scene sites, these fingermarks are not visible to the naked eye. Various examination methods are reported in the literature for the recognition of fingermarks on various surfaces having different background interference [10].

Over the last two decades, many research communities have explored numerous methods to report for effective detection of the latent fingermarks with great efficacy in crime scene examination for individual identification [34]. Generally, fingerprints are left at a crime scene site but in most cases, they can't be developed clearly by a routine traditional technique, appropriate fingermarks analysis and identification will be difficult to achieve [5]. In literature, numerous chemical, physical, and optical methods are reported for the examination of fingermarks on those surfaces having tedious background interference [26, 39].

Fluorescent Nanomaterials

Fluorescence is the type of optics spectacle in which the absorption of a light photon and emission of an alternative photon with a longer wavelength later some time relaxation called fluorescence of light [9]. Jablonski diagram explained phosphoresce and fluorescence phenomenon with movement of electron in singlet ground state to singlet excited state and triplet excited state, simply coined as photo-physical processes [3]. The optics-related materials have elevated with great potential and concern subsequently their inception and introduction to the technology and applications in forensic-related applications [7]. Fluorescent nanomaterials have excellent ophthalmic properties mostly used in various fields including the detection of explosive residue, examination of toxicological exhibits, bio-sensing technology, analysis of gunshot residue, and visualization of latent fingerprint marks [23]. Figure 9.1 illustrates the phenomenon of phosphorescing and fluorescence.

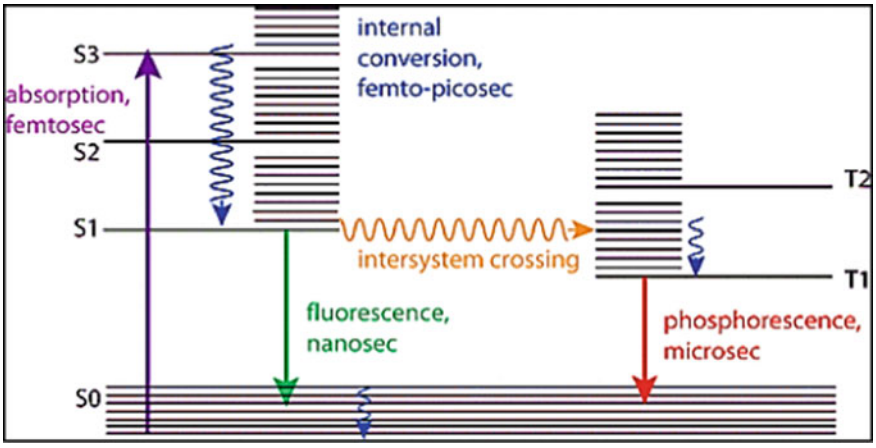

Fig. 9.1 Jablonski diagram with photo-physical routes. Reproduced with permission reference from ref [4]. Copyright 2010 American Chemical Society

Fluorescent Nanomaterial in Latent Fingerprints Development

Wang et al. demonstrated the synthesis of the $NaYbF_4$:Tm up-conversion nanomaterials and showed its efficacy for the development of latent fingermarks on porous and non-porous surfaces. The synthesis of $NaYbF_4$:Tm up-conversion nanomaterials is by two-phase solvothermal methods. Morphological features were determined by XRD, TEM, UV–VIS, and FT-IR sophisticated instrumentation techniques. $NaYbF_4$:Tm nanomaterial is directly used for the visualization of the latent fingermarks by powder dusting protocol, visualization of the latent fingermarks by taking photographs under electronic transition from excited state to ground the state of 980-nm near infrared light via near infrared -to-visible and near infrared -to- near infrared imaging modes [37].

Pushpendra et al. demonstrate a novel protocol for the synthesis of luminescent rare-earth ion-doped up-conversion of $Gd_{0.95}Eu_{0.05}PO_4$ nanorods for the enlargement of fingermarks on porous and non-porous surfaces with various background selection for studies. The $Gd_{0.95}Eu_{0.05}PO_4$ nanorods were synthesized by a modest co-precipitation method using $GdPO_4$ and $Eu(NO_3)_3;5H_2O$ in ethylene glycol. The synthesized $Gd_{0.95}Eu_{0.05}PO_4$ nanorods were examined by sophisticated instrumentation techniques including PXRD, TEM, EDS, and FESEM. $Eu(NO_3)_3;5H_2O$ showed emission spectra at 394 nm emitted spectrum. PXRD pattern showed a monoclinic phase of the synthesized nanorod with high crystallinity and TEM examination showed rod-shaped morphology [32].

Two types of pieces of evidence are found at the crime scene site including visible and non-visible evidence [16]. Biological and non-biological matrices are

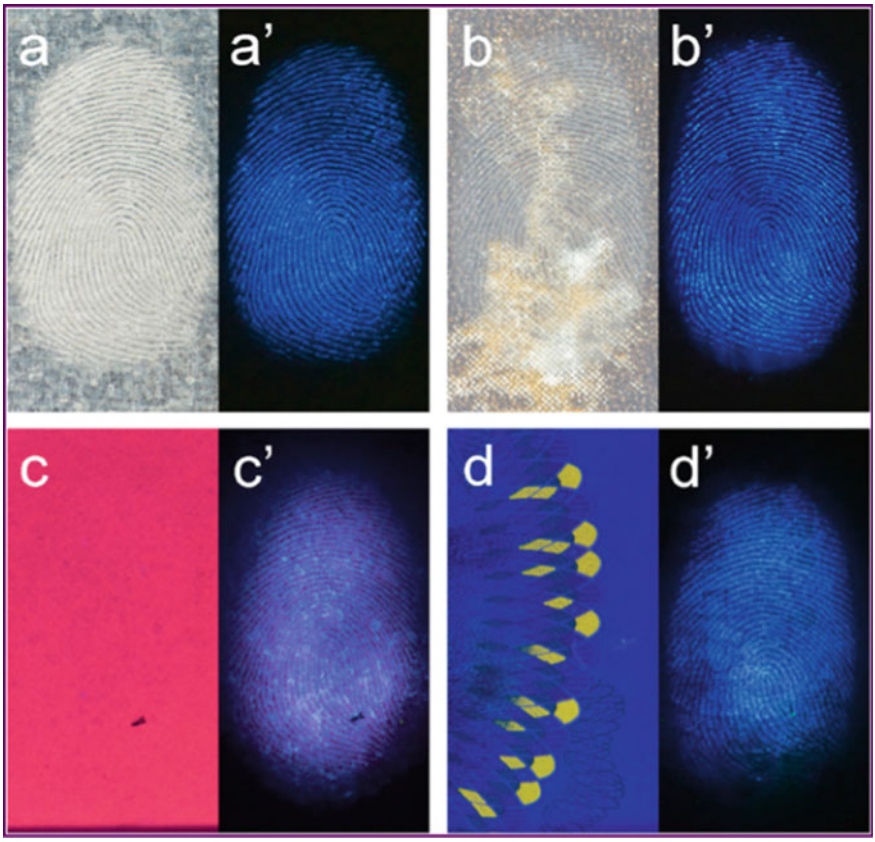

Fig. 9.2 Visualization of latent fingermarks using $NaYbF_4$:Tm UCNMs on porous and non-porous surfaces. Reproduced with permission reference, [37], Copyright 2020, Elsevier

types of visible evidence. Whereas, fingermarks and footprints are types of non-visible evidence [25]. Wang et al. synthesized YVO_4:Eu and $LaPO_4$:Ce, Tb-based nanoparticles and demonstrated the applicability of these manufactured nanoparticles. In Fig. 9.1, latent fingerprints are developed and visualized on a glass surface using YVO_4:Eu nanocrystals, followed by $LaPO_4$:Ce, Tb nanobelts in addition to red-green fluorescent nanomaterial. Developed fingerprint images showed a clear difference between ordinary powder and fluorescent powder [36].

Algarra et al. demonstrate the synthesis and application of synthesis of fluorescent hybrid material (PPH-S-CdSe) based nanomaterial and studied its application for visualization of fingerprint marks on various surfaces. Synthesized fluorescent hybrid by sophisticated instrumentation techniques includes XRD, TEM, X-ray photoelectron spectroscopy, and fluorescence spectroscopy. PPH-S-CdSe nanocomposite showed red emission at 576 nm [1]. Bride et al. gave Near-Infrared to Near Infrared (NIR-NIR) up-transformation nanoparticles made up of β-NaYF4:2% Tm,

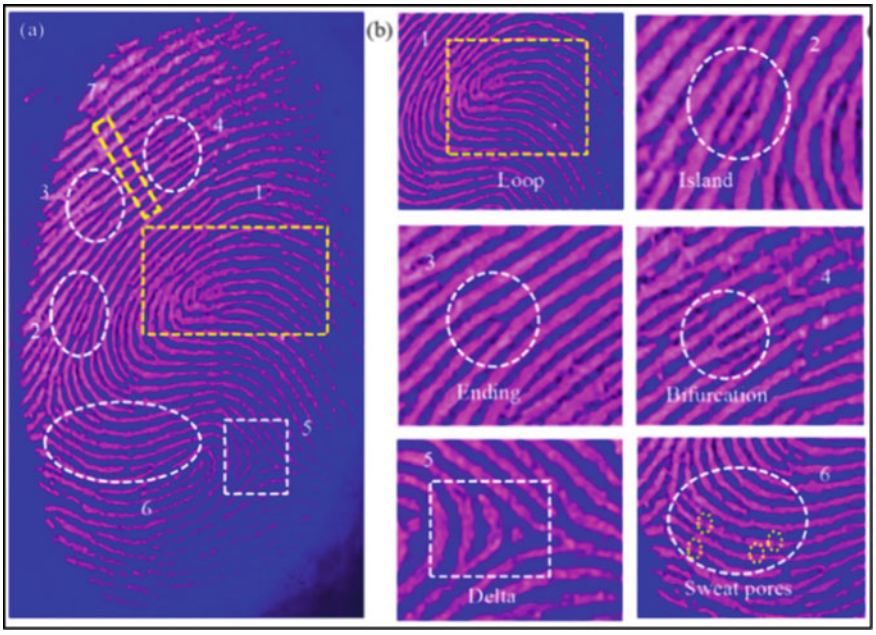

Fig. 9.3 Development of fingerprints bty$Gd_{0.95}Eu_{0.05}PO_4$ nanomaterial and visualized under 395 nm UV light in the detailed examination of the minutia. Reproduced with permission reference [32], Copyright 2021, Elsevier

48% Yb and evaluate its applicability for the visualization of fingerprints on those having tedious background interference. NIR-NIR 976 nm light is used to produce 800 nm luminous fingerprint pictures. Developed fingerprint images showed a very high-resolution distinctive number of minutiae [2].

Li et al. designed and fabricated two-mode luminescent UCNPs@SiO_2@TEuTbB nanomaterials for anti-counterfeiting. Structural morphology-related studies of synthesized nanoprobe have been investigated by sophisticated instrumentation techniques like XRD, FT-IR, XPS, SEM, TEM, and fluorescence spectral techniques. The observed morphology of the synthesized nanomaterial is spherical with a particle size of 100 nm. UCNPs@SiO_2@TEuTbB emit red color fluorescent in UV light which is used for recognition of the fingerprint marks on various surfaces [22]. Young Park et al. illustrate the synthesis of the Gd_2MoO_6:Eu^{3+} nanocomposite by doping the Eu^{+3} in a monoclinic Gd_2MoO_6 nanoprobe. The crystalline nature and phase-type and lattice parameters of Gd_2MoO_6:Eu^{3+} nanophosphors are examined thoroughly by the X-ray diffraction (XRD) spectral techniques [29].

Pavitra et al. synthesis of the new fluorescent nanocomposite of Mn^{4+} ions doped Ba_2LaNbO_6. Sophisticated instrumental analysis of the synthesized Ba_2LaNbO_6:Mn^{4+} using different techniques including XRD, TEM, and UV–VIS spectral techniques. These nanomaterials are used for the visualization of latent fingermarks on numerous non-porous surfaces under 365 nm light. Observed minutes

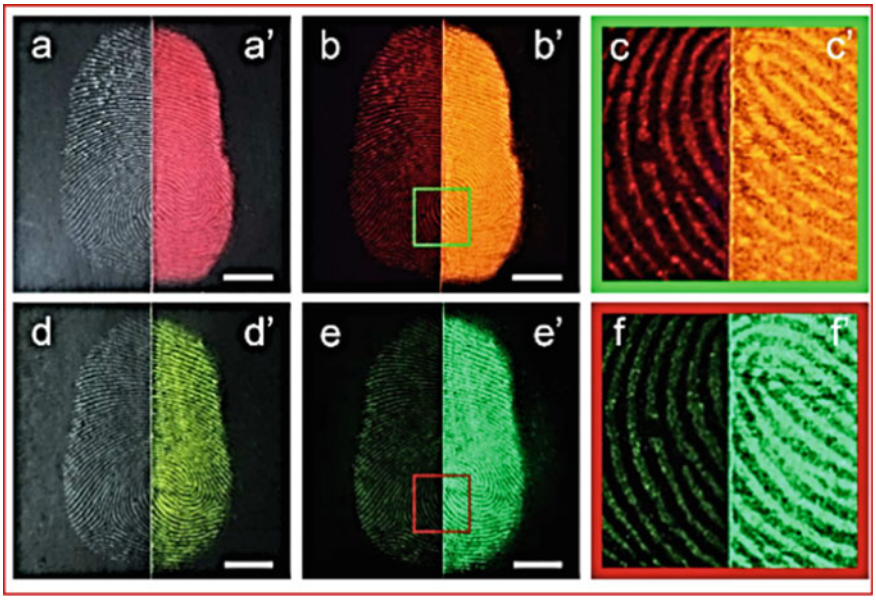

Fig. 9.4 Visualization of Latent fingermark with YVO_4:Eu nanocrystals $LaPO_4$:Ce, Tb nano-belts fluorescent powders. Reproduced with permission Ref. [32], Copyright 2015, American Chemical Society

are envisaged including bifurcation, core, bridge, termination, and sweat pores [30]. Suresh et al. demonstrate the synthesis of a deep red color of SiO_2@LaOF: Eu^{3+} core–shell nanocomposite that has been fabricated via facile solvothermal and thermal methods. Synthesized nanostructure is characterized by XRD, SEM, and TEM instrumental techniques. SiO_2@LaOF: Eu^{3+} nanocomposite has spherical morphology with 593 nm particle size. Synthesized nanomaterial having a fluorescent property that used visualization of latent fingerprints with high selectivity includes circumstantial meddling which showed distinct fingermarks ridge features [35].

Naveen Kumar et al. demonstrate the synthesis and application of the red luminous Eu^{3+} doped SnO_2 quantum dot. Investigating the Eu^{3+}:SnO_2 QDs remained appraised for detection of the various types of fingermarks on those surfaces that have a quite difficult background interference which was developed by the powder-dusting protocol. The resultant hidden fingerprint showed excellent compassion, distinct distinction, and clear ridge details. The examination of the non-cytotoxicity of the Eu^{3+}:SnO_2 QDs has been examined by accompanying a toxicity examined on normal fibroblast cell lines (L929). The obtained outcomes of the non-cytotoxic luminescent Eu^{3+}:SnO_2 QDs exhibit minimum toxicity [27].

Ghubish et al. synthesized novel red photoluminescence Eu^{+3} ion-doped calcium hydroxy stannate [$CaSn(OH)_6$:Eu^{+3}] in trisodium citrate by sol–gel protocol. The synthesized nanocomposite is characterized by FT-IR, photoluminescence, EDS, SEM, transmission electron microscopy, and X-ray diffraction. The synthesized Eu^{+3}

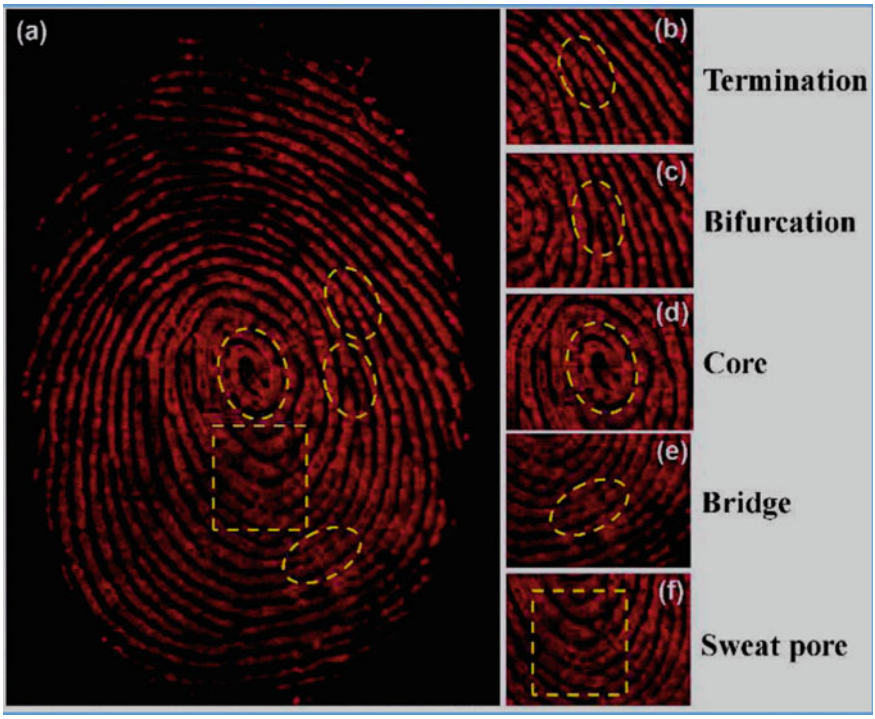

Fig. 9.5 Visualization of BLN:0.25Mn^{4+} nanophosphors under 365 nm visualization of level 1 to level 3. Reproduced with permission Ref. [29], Copyright 2019, Elsevier

ion-doped calcium hydroxy stannate nanocomposite produced a high-intensity fluorescence peak at 616 nm and these nanoparticles were used for visualization of latent fingermarks with a very high tenacity, excellent distinction, better selectivity, great efficiency, and little contextual interference on porous and non-porous surfaces [13].

Rohini et al. fabricated red-emitting ZrO_2:Eu^{3+} nanophosphors greener techniques by an ultrasonication-assisted protocol with *Aloe vera* gel as a bio-surfactant. *Aloe vera* gel, time, and reaction pH are architecting tools for controlling the morphology and size of the nanocomposite. The growth mechanism of the hierarchical ZrO_2:Eu^{3+} arrangements initiates with an accumulation followed by orientation attachment in ultra-sonication via. Ostwald ripening method. ZrO_2:Eu^{3+} showed photoluminescence properties and demonstrate for latent fingerprints on numerous surfaces by traditional powder dusting protocol. Developed fingermarks images exhibit all three types of ridges feature. Proposed methods have excellent contrast, high sensitivity, and negligible background hindrance as compared to regular powder dusting methods [33].

Femila Komahal et al. proposed synthesis of SiO_2@$ZnAl_2O_4$:Eu^{3+} nanocomposite by solvothermal protocol, the complete protocol of the proposed synthesis is illustrated in Fig. 9.7. Scanning electron microscopic examination of fabricated

Fig. 9.6 Schematic protocol for the synthesis of SiO_2 core–shell $SiO_2@ZnAl_2O_4:Eu^{3+}$ nanocomposite, Reproduced with permission reference, [18], Copyright 2018, Elsevier

$SiO_2@ZnAl_2O_4:Eu^{3+}$ nanocomposite particles has a spherical shape with non-agglomeration. This nanoprobe exhibits photoluminescence intense red emission peak observed at 612 nm which corresponds to the $^5D_o \rightarrow {}^7F_2$ transition of the Eu^{3+} ions. Synthesized $SiO_2@ZnAl_2O_4:Eu^{3+}$ nanocomposite accustomed imagine latent fingermarks Powder dusting method on porous and non-porous surfaces under UV light with very high sensitivity, reproducibility, high selectivity, cost-effectiveness, and showed all three levels ridge details in developed fingerprint, developed finger on various surfaces and rides details examination showed in Fig. 9.8 [18].

Wang et al. demonstrate an oleic acid-based mediated solvothermal route efficient amalgamation of NaYF4:Yb, Er luminescent nanocomposite with the highest fluorescence intensity under near-IR radiation. The fluorescence intensity and particle size depended upon synthesis parameters including reaction temperature, reaction time, and oleic acid gratified which are briefly illustrated in Fig. 9. Synthesis of NaYF4:Yb, Er nanomaterial undergoes excitation at 980 nm near-infrared irradiation to emit green light. NaYF4:Yb, Er nanomaterial demonstrate development of the latent fingerprints on three types of porous and non-porous surfaces including the first surface with a single background like transparent glass, white ceramic tiles, and black marbles, second surface with various circumstantial color patterns such as marbles with unlike multifaceted surface patterns and third surface with sturdy background interference auto-fluorescence includes note papers, Chinese paper money, and

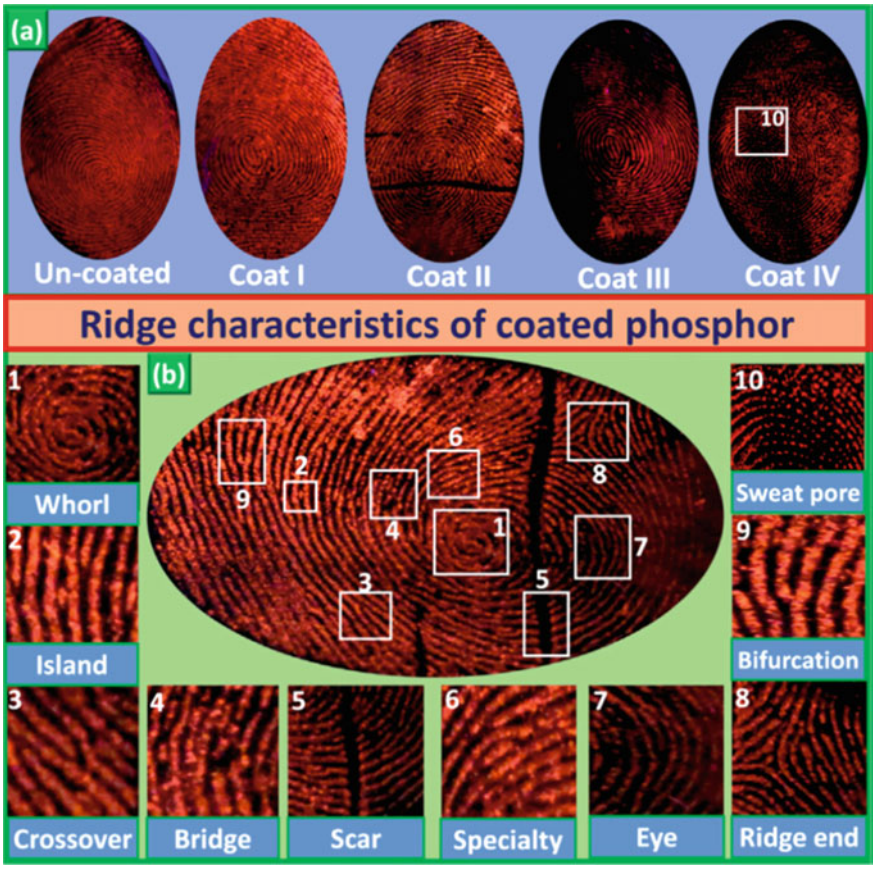

Fig. 9.7 Latent fingerprints visualized by $SiO_2@ZnAl_2O_4:Eu^{3+}$ on various surfaces and ridges details examination on aluminum foil under UV 254 nm light. Reproduced with permission reference [18], Copyright 2018, Elsevier

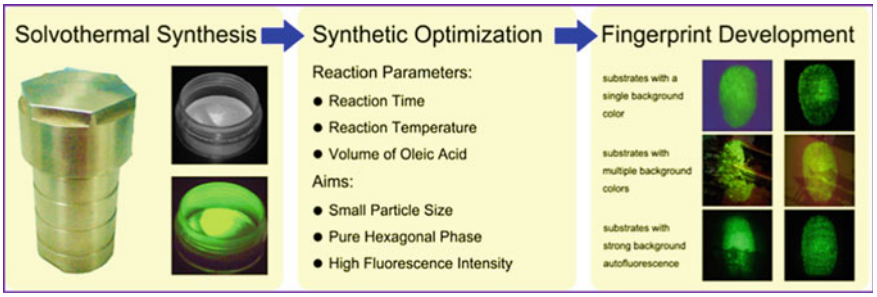

Fig. 9.8 General ideal of the proposed studies from synthesis to applications, Reproduced with permission reference [36], Copyright 2015, American Chemical Society

plastic plates. Developed fingerprints display excellent sensitivity, distinct contrast, little background interfering, and minimum auto-fluorescence interfering [36].

Li et al. synthesis of $La_2(MoO_4)_3:Eu^{3+}$ nanoparticle red fluorescent microcrystals by using sodium citrate mediated hydrothermal route. Morphology of the manufactured nanomaterials premeditated by XRD, SEM, and TEM having hemispheres morphology. Synthesized microcrystals emitted intense emissions at 616 nm. $La_2(MoO_4)_3:Eu^{3+}$ nanocomposite is used for the visualization of various types of entire fingermarks on numerous surfaces. Synthesized $La_2(MoO_4)_3:Eu^{3+}$ exhibits distinct dissimilarity and minimum background involvement [21].

Ghubish et al. synthesized $CaWO_4:Tb^{3+}$ co-doped Li^+ with facial co-precipitation methods. Morphology of the synthesized nanomaterial was examined by XRD, high-resolution TEM, EDX, UV–visible, fluorescence, and FT-IR spectrophotometric methods. $CaWO_4:Tb^{3+}$ nanocomposite exhibits green emission at 540 nm. $CaWO_4:Tb^{3+}$ fluorescent composite is used for the detection of level I, II to III details with the high contrast of latent fingerprint marks on various surfaces [12].

Discussion

Latent fingermarks are generally observed in most crime scenes traditionally powder dusting methods method used in the improvement of latent fingermarks on porous and non-porous surfaces with various background interference patterns. In the last two eras, the scientific community focused on the development and designing of new efficient materials for the development of hidden fingerprints on various porous and non-porous surfaces. Though, the routine powder-dusting protocol has appearances of minimum compassion, less dissimilarity, high background noise, and excellent autofluorescence interference.

So, the researcher focused on the development of novel fluorescent nanocomposites such as $NaYbF_4$:Tm, $Gd_{0.95}Eu_{0.05}PO_4$, YVO_4:Eu, $LaPO_4$:Ce, Tb, β-NaYF4:2% Tm, 48% Yb, $Gd_2MoO_6:Eu^{3+}$, $Ba_2LaNbO_6:Mn^{4+}$, SiO_2@LaOF: Eu^{3+}, Eu^{3+}:SnO_2 QDs, $CaSn(OH)_6:Eu^{+3}$, $ZrO_2:Eu^{3+}$, $SiO_2@ZnAl_2O_4:Eu^{3+}$, NaYF4:Yb, Er, $La_2(MoO_4)_3:Eu^{3+}$, and $CaWO_4:Tb^{3+}$ for effective detection and development of the latent fingerprints. Developed fluorescent nanomaterials showed excellent results in the visualization of latent fingermarks which have fluorescent properties with very high responsiveness, distinct contrast, high responsiveness, excellent effectiveness, and low contextual interference, on numerous substrates including non-infiltrating materials, semi-infiltrating materials, and infiltrating material.

Fluorescent nanomaterial is synthesized by doping of transition metals like La, Eu, Tm, Yb, Gd, and Lu metal oxides. The percentage of doping of transition into metal oxide is about 5 to 7 percent. Examination of synthesized nanomaterial by sophisticated instrumentation techniques like EDX, XRD, SEM, TEM, and photoluminescence (PL). These materials showed the fluorescent property at 300 nm to

700 nm emission after excitation. Transition metal ions doped fluorescent nanomaterial produced by sol–gel methods, hydrothermal methods, and co-precipitation protocol.

Conclusion

Latent fingerprints possess a significant role in crime scene examination. There are several reports on the development of a novel and effective material for examination of the latent fingermarks on various surfaces. Here we illustrate the practicality of synthesized fluorescent nanomaterial in the detection of fingermarks. Transition metals like La, Eu, Tm, Yb, Gd, and Lu are doped with other nanomaterials which showed excellent fluorescent properties. The usefulness of the synthesized fluorescent nanomaterials studies for the evolution of fingermarks on various porous and non-porous surfaces has been illustrated in this chapter. Fluorescent nanomaterial includes a metal oxide, and rare earth element doped transition metal oxides are useful fluorescent material in latent fingerprint detection. This fluorescent nanomaterial has low background interference, less toxicity, high efficacy, high sensitivity, and excellent contrast.

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Chapter 10
Visualization of Latent Fingerprint Using Conjugated Polymer Nanoparticles

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Introduction

According to Edmond Locard's exchange paradigm for forensic science, every touch leaves a trace. A multiplex combination such as (lipids, sebum, perspiration, and pollutants) is produced from the skin of a human which is transferred to the substrate when a human figure touches it, resulting in the development of a fingerprint. Ever since the late nineteenth century, fingerprints have already been utilized often as persuasive and effective evidence for human identification due to the individuality and durability of the ridge in the pattern of skin [1, 2]. Latent images of fingerprints (LFPs) found at the place where a crime has been committed are regarded as most important tangible solid evidence in forensic examination and the criminal justice system (CJS) due to the uniqueness and individuality of the pattern of ridges fingerprints [3, 4]. They are thus special and essential in solving any criminal case and correctly determining a suspect's involvement [5–8]. For the production of cyanoacrylate fuming, low-pressure metal installation, fluorescent dyeing, magnetic powder application, tiny particulate solution, and LFP powder sprinkling or dusting method, etc., are the most known methods [9–11]. Because of this, it is difficult to recover fingerprints that are good enough for unequivocal identification, especially when working with metallic surfaces [12, 13]. This chapter explains how to create fingerprints on various

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surfaces using polymer nanoparticles. Nanoparticle made of polymers is one of the types of nanomaterials that are employed in the development of fingerprints, but there is no direct use of nanoparticle made of polymers; the use of polymer nanocrystal is the second phase; the initial stage implies the utilization of conjugated nanoparticle made polymer for various chemicals. In many ways, fluorescent conjugated polymer materials outperform conventional fluorescent materials, such as tiny molecular fluorescent dyes and semi conductive quantum dots. As a result, conjugated polymers are frequently employed in bio imaging, sensing, and photoelectric devices [14–16]. In comparison to other small molecule fluorophores, conjugated polymers have a variety of advantages, such as low toxicity, high emission, great photo bleaching resistance, ease of synthesis at a low cost, superior mechanical stability, and processability [17–22]. These nanocrystals were widely used for identification of fingerprint because to the high-quality images, improved transparency, with perfect features of ridges, improved contrast of background surfaces, stronger selectivity, and result into the increased particle sensitivity with stronger selectivity.

History of Fingerprint Identification

The history of fingerprint identification as we know it now began in the late nineteenth century, and the establishment of identification agencies entrusted with preserving correct information on persons classified not by identity but by some physical characteristic. Modern nations were only bureaucratic enough in the nineteenth century to assume to keep structured criminal records that reached beyond a particular parish or municipality [23]. Fingerprints are formed up of ridges and furrows on the finger's surface, with a central core around which swirls, loops, and arches are curled to guarantee that each print is distinct [24]. An arch is formed when grooves enter a finger through one side, rise in the center to create an arc, and then escape from another. Ridges enter from one side of a finger, bend, and then escape from the same side in the loop pattern. Pattern of ridges develops in a circular pattern around a central spot on the finger in the whorl pattern. The imperfections known as minutiae, which are the distinguishing feature of finger scanning technology, are found in the ridges and furrows. Local ridge features that occur at either a ridge bifurcation or a ridge terminating are known as minutiae points. The point at which a ridge ends is known as the ridge terminating. A bifurcation is a point where a single ridge divides into two. Since no two fingers have been demonstrated to be identical, minutiae and patterns are extremely significant in fingerprint analysis [25]. As previously stated, fingerprint identification is extremely crucial in many sorts of criminal cases since it allows us to identify the primary suspect. As previously stated, fingerprints are unique to each individual. In the beginning, different old methods were used to develop such fingerprints, the most common is the powder method, in which several different powders are applied in the establishment of fingerprints at the site of crime [26]. However, powder methods have a number of flaws, and in order to overcome these flaws, new

techniques have been developed so that fingerprints as evidence are not contaminated [27]. Different sorts of chemicals are used in this innovative process to create fingerprints. One of them is the utilization of polymer nanoparticles to make the visualization of latent fingerprints impression; this polymer has a fluorescence property that causes fingerprints to become visible when exposed to various substances.

Nanotechnology Used in Forensics

Scientific proof that is evidence detection on weapons, samples related to biology, and residues or particles using nanotechnology is a rapidly developing field of forensic science that helps law enforcement identify offenders [28–31]. Innovations used in forensic are mostly focused on physiology and anatomy in order to collect solid evidence toward convicts [32–34]. Therefore, forensic research is growing with nanotechnology to collect evidence rapidly at the scene of crime (SOC) and their environment and in a criminal court, submit this after laboratory examination [35, 36]. As a result, nanotechnology is used to increase nanosensors for acquiring evidence at the scene of crime identifying whether or if chemicals, such as natural and explosive gases, were marked as evidence from the activity of terrorist which is involved in this [37, 38]. Forensic scientists have traditionally used bulk chemicals and microsubstances to detect evidence, for example explosives, traces, DNA, fingerprint impression, and gunshot residues (GSR) [39–41]. Therefore, the utilization of nanomaterials in many applications is gradually replacing conventional methods. This chapter discusses the use of nanoparticles in the production of latent fingerprints impression for person recognition in forensic investigations, there are many suspects, and the best strategy for identifying them is to employ fingerprints [35].

Techniques of Preparation and Production

Polymeric Nanoparticles

The study of polymer nanoparticles (PNP) has developed quickly over the past few decades. It has grown in significance in a number of fields, such as electronics, optoelectronic, conducting materials, sensors, biotechnology, pollution prevention, and environment management [42–47]. Preformed polymers can be used to create PNPs, or you can directly polymerize monomers using classical polymerization or poly-reactions [48]. PNP can be manufactured from pre-manufactured polymers using techniques such as solvent evaporation, salting-out, dialysis, and supercritical fluid technology, which includes rapidly expanding a supercritical mixture or rapidly expanding a supercritical mixture into a liquid solvent [49, 50]. In contrast the production of PNP by direct polymerization of various single units, i.e., monomer

by using a number of polymerization techniques, like interfacial polymerization, surfactant-free emulsion, mini-emulsion, and micro-emulsion [51].

Pdots

The nanoprecipitation technique previously described was used to prepare the Pdots. A conjugated polymer weighing 500 mg and PSMA weighing 50 mg were fully soluble in 10 mLtr of THF for the manufacture of Pdots. Under intense sonication, The polymer/THF combination was quickly diluted into 10 mL of ultrapure water with 3 ml of concentrated. From the nitrogen bubbling THF was removed on the hot plate. Filtration with a 0.22 m membrane filter allowed for the removal of a minor portion of aggregates [52, 53].

Preparation of CPDs

To create CPDs(carbonized polymer dots), a first-step solvothermal process was employed. 20 mL of toluene and 0.20 g of p-phenylenediamine (PPD) were placed in a Teflon-lined autoclave and cooked for 10 h at 160 °C with a constant temperature in drying oven. After the red precipitate was extracted and cooled at room temperature, the precipitate at the bottom of the autoclave was carefully collected and repeatedly washed with toluene. In order to make it easier to refer to them, CPDs-160, CPDs-180, and CPDs210 were given the respective designations [54] (Fig. 10.1).

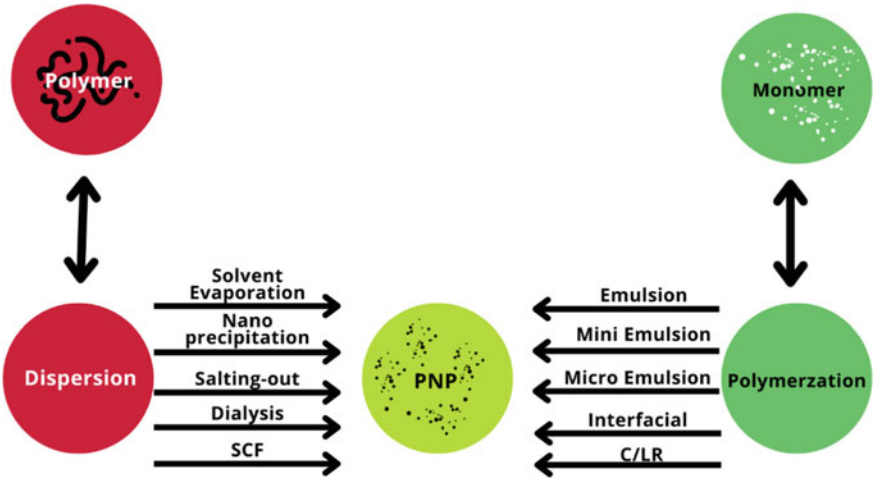

Fig. 10.1 Diagrammatic representation for the preparation of polymer nanoparticles by using various techniques

Use of Polymer Particles for Fingerprint Development

Conjugated Polymer Nanoparticles

Conjugated polymers (CPs), which are bright materials with exceptional light-harvesting capabilities and a range of appealing for use in biological and chemical detection, cell imaging, and photodynamic treatment, ocular characteristics have gained increasing attention [55–59] (Fig. 10.2).

Nanoparticles of Conjugated Polymer in an Aqua-Colloidal Suspension

An approach for creating fingerprints using conjugated polymer nanoparticles is suggested. Fluorescent poly (p-phenylene vinylene) (PPV) nanocrystals create a sustainable colloidal suspension after heat elimination of the polymer precursor (pre-PPV) in an aqueous system with the aid of a surfactant. The diluted colloidal solution may be used for fingerprint impression development by submerging the fingerprint sample for a brief moment in time, extracting it, and then rinsing the sample with deionized water to remove any extra PPV nanoparticles [60]. In terms of toxicity and/or cost, in aqueous solution, PPV nanoparticles have an edge them. Recently, multiple publications have appeared describing the use of conjugated polymers (or dots) as fingerprint-forming agents with excellent or good results [61–63]. Due to the lack of significant components (such as reactant, catalyst, or additive) or advanced processes used, the manufacture of colloidal solutions of PPV nanoparticles will be less expensive. While prior previous systems needed spraying or brushing techniques and the compounds were not reused, the current emerging approach is simpler and more affordable because it simply requires an immersive experience procedure; in some cases, further post-treatment or transmission steps involving fingerprints were required to achieve LFP visualization [60].

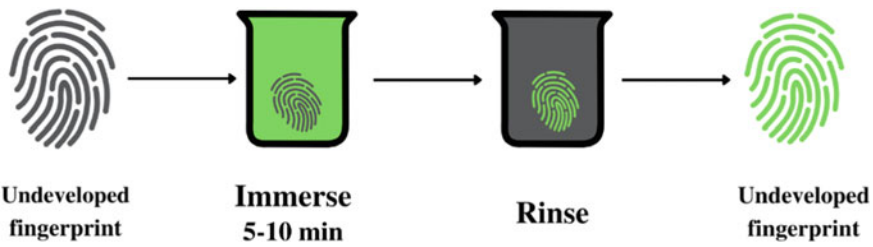

Fig. 10.2 Fingerprint development using polymer nanoparticles in aqueous colloidal solution

Cyanoacrylate Fuming with Conjugated Polymer Nanoparticles

A fingerprint development strategy involving the use of PPV nanoparticles (NPs) and the cyanoacrylate fuming method. To begin, a series of fluorescent PPV NPs with various emission colors are synthesized in aqueous colloidal solution using a modified Wessling approach in combination with in-situ self-assembly. A sequence of modified PPV precursors (pre-PPV-N) can be obtained in parallel by varying the reaction conditions. The simultaneous heat removal and self-assembly of PPV NPs with various emission colors occurs in the presence of surfactant, then using colloidal PPV NPs solutions, superglue-fumed fingerprints are created on various substrates [60]. To begin with, the color-tuning process for nanoparticles is straightforward, requiring only a change in the reaction duration of the substituent step and no further changes. Second, because the finished products are in aqueous solution, they may be used right away, which is good for the environment. Our strategy is, on the whole, cost-effective [64, 65].

Conjugated Oligomer with Silica Nanoparticles

Conjugated oligomers, which have a well-defined molecular weight and are less complex versions of CPs with the same conjugated backbone, have grown in popularity recently [66–69]. Comparatively speaking, conjugated oligomers are simpler to make, purify, and work with than conjugated polymers. Additionally, several special fluorescent properties related to the distinctive structure of oligomers show promise applications in detecting, imaging, antibacterial agents, drug/gene delivery, and controlled release [70–74]. A silane-modified conjugated oligomer was integrated into a silica matrix using a reverse micelle method, producing particles with ultra-bright blue fluorescence and quantum yields of up to 97 percent. The NPs were dispersed in a variety of solvents and showed little variation over a broad pH and temperature range. Silica NPs are widely employed in the materials and biological industries due to their controllable size, optical clarity, ease of modification, straightforward manufacture, and low toxicity. Conjugated polymers and oligomers experience aggregation-induced quenching when they are transformed from solution to nanoparticle form or a solid film (ACQ) [75]. This effect is assumed to be brought on by the aggregation-induced depopulation of excitons. The ACQ problem reduces the efficacy of such materials' emissions and restricts their applications in solid states. As evidence that the effects of ACQ were contained within the particles, photoluminescence quantum yields of fluorescent NPs with conjugated oligomer concentrations as low as 0.025–0.05 mol percent were as high as 97 percent. The resulting hybrid NPs could be used as a dusting agent to find latent fingerprints [75].

Polymer Dots for Latent Fingerprint Detection

In latent fingerprint imaging, the Pdots give exceptional sensitivity and reliability. For fingerprint identification, there are two basic groups of fingerprint matching procedures [76]. The minutiae-based method, which is the most extensively used recognition methodology, detects minutiae points first and then maps their relative arrangement on the finger to match ridge characteristics. Pattern matching, on the other hand, examines two photos to determine how similar they are. The spray approach may be used to detect LFP using radical fluorescence polymer dots. The fluorescence matrix has been altered in this way by mixing two types of polymers with ninhydrin [1]. The fluorescent matrix is used for latent fingerprint detection and colorimetric measurements on any porous or non-porous substrate [1]. These polymer dots are used to enhance the fingerprint ridge's detail and offer advantages including improved selectivity and low inherent interferences. These types of polymer dots have shown great potential as fingerprint detecting agents due to the robust interaction in LFP detection that produces clear fingerprint images. These polymer dots paved the way for a new forensic science study field focused on the detection of LFP [35].

Latent Fingerprint Imaging Using Carbonized Polymer Dots

Carbon-based nanomaterials (CNMs) which are fluorescent, such as graphene quantum dots, carbon nanoparticles, and carbon dots (CDs) have gained popularity due to the consequence of their exceptional optical characteristics, better stability, minimal toxicity, excellent photo-induced e-transfer characteristics, and straightforward synthetic processes [77–79]. CNMs are useful for many different applications, including photocatalysis, light-emitting devices, and bioimaging, among others [80, 81]. The majority of modern CNMs emit intense blue to green light when stimulated by UV(ultraviolet) radiation or light. However, red fluorescent CNMs are extremely difficult to make, and the scarcity of red-emitting CNMs greatly limits their use and advancement [82]. Researchers have made various attempts to create novel fluorescent agents and more efficient techniques for manufacturing LFPs [83]. Recently, bright nanoparticles have been effectively used to detect LFPS, in particular rare earth fluorescent nanomaterials. It is anticipated that CNMs will be employed to visualize LFPS as a sort of economical, extremely luminescent-stable, and environmentally beneficial nanomaterial [54].

Fingerprint Collecting and Development Process

The same methods were used to prepare regular fingerprint specimens for the development of latent fingerprint impression. The contributor should carefully wipe their hands before rubbing their hand away from greasy regions of the body such as the retro auricular region to avoid leaving fingerprints on the material (the adhesive side of the tapes, the aluminum foil, or the cover glass) [60]. With a soft brush, the powdered nanoparticles were applied to the imprinted surfaces to collect the LFPs produced by various nanoparticles, and the extra powder was removed with a moderate air flow [84]. Two different kinds of approaches were needed for the identification of LFP with nanoparticles. Interactions that are taking place are electrostatic and hydrophobic interactions. Because of electrostatic attractions with LFPs, distinct functional groups of amine and carboxylic acid are present in sweat pores, patterns of end ridges, and residues of fingerprint impression. Additionally, the hydrophobic, i.e., repulsion of water mechanism includes the fatty acids of LFPs and the negative charge of nanomaterial. These kinds of procedures showed high sensitivity and higher resolution without the foremost part of interferences in the ridges of LFPs with number of nanoparticles [84, 85]. The ability to quickly discern fingerprints under UV irradiation enables the identification of the culprit due to the characteristics of powdered materials' emissions. To enhance the detection of latent fingerprints and help identify offenders, aluminum foil and carbon-based compounds are frequently used [60].

Conclusion

A number of conjugated polymer nanoparticles with different fluorescence colors were studied and characterized in an aqueous colloidal solution. It was discovered that they were round, nanometer in size, and had the ideal wavelengths for scattering and absorption that can be used as reagents in the creation of fingerprints. The fingerprints were produced by "in-situ" fuming of superglue and then stained with fluorescent dye. This chapter discusses the many characteristics of fingerprints and their production procedures, with a focus on a novel and cost-effective technology that employs polymer nanoparticles and Pdots, which may be employed on a variety of surfaces at various crime scenes. Polymer nanoparticles have varying fluorescence qualities, which can aid in the better viewing of fingerprints and their patterns. Polymer nanoparticles are also employed in a variety of chemicals and shapes. It is inexpensive and easy to create latent fingerprints by using polymer nanoparticles.

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