

# Chapter 3

## Functionalized Nanomaterials, Classification, Properties, and Functionalization Techniques



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### 1 Introduction

Nanotechnology involves creating particles, more technically referred to as “nanoparticles (NP)” that are one billionth of a meter ( $10^{-9}$  m). Due to the quantum confinement effect, scaling down bulk material to nanoscale results in a variety of marvels. The application of nanotechnology has enabled the creation of compact, lightweight, malleable, and portable machinery and devices. Nanomaterials are already used in almost all industries, including those in farming, health care, aesthetics, fabrics, and energy storage devices [1–3]. These particles are produced using either by top-down or bottom-up approach, and they have exceptional qualities like low toxicity, chemical stability, surface functionality, and biocompatibility [4]. Due to the well-known fact that these nanoparticles’ physicochemical qualities are superior to those of bulk materials, their properties are further improved through functionalization, surface and structural engineering, etc. This causes the formation of more active sites, an enhancement in surface-to-volume ratio, and an increase in structural defects with a reduced ion diffusion distance which is carried over through many ways.

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C. M. Hussain and M. B. Ahamed (eds.), *Functionalized Nanomaterials Based*

*Supercapacitor*, Materials Horizons: From Nature to Nanomaterials,

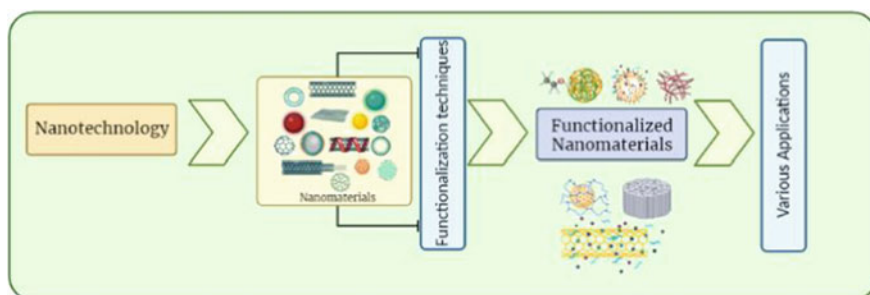
[https://doi.org/10.1007/978-981-99-3021-0\\_3](https://doi.org/10.1007/978-981-99-3021-0_3)

## 2 Functionalized Nanomaterials

The addition/combination of certain chemical groups and functional entities that are physically and chemically decorated to the nanomaterial surface by changing the surface chemistry helps in developing distinct active sites based on the needs (Fig. 1). To have a broad range of potential applications, the solubility, uniform dispersion of nanoparticles in a medium, as well as their interactions with other molecules must be examined. The functionalization of nanomaterials via surface modifications aids in the interaction of nanomaterials with their surroundings which can be purposefully designed to exhibit the desired properties [5]. Without modification, the surface of nanoparticles has lesser interaction (physical or chemical contact) with the matrix or any other substance under process.

Unmodified nanoparticles form agglomerations as a result of intermolecular interactions which hinder its dispersion into the solvent [6]. Functionalized nanomaterials not only improve existing properties but also contribute to the development of new ones. Other properties, such as cluster formation, colloidal stability, and dispersibility, are greatly influenced by functionalization. Furthermore, utilizing the suitable functionalization method, surface attributes such as corrosivity, hydrophilic/hydrophobic nature, and conductivity may be readily on hand [7]. As a result, the distinct properties of functionalized nanomaterials make them an appealing candidate for a wide range of applications.

Creating composite materials is one of them, as is synthesizing metal oxide nanoparticles with carbon, doping with heteroatoms using gases, liquids, and solids. In addition to being employed in various energy devices including DSSCs, batteries, supercapacitors, fuel cells, LEDs, etc., functionalized nanoparticles are also discovered to have less toxicity and are used as catalysts in biomedical applications and toxic removers in environmental applications [8, 9]. It has been discovered that functionalized nanomaterials can get over problems like aggregation caused by strong van der Waals forces at close proximity or overlapping of bandgap in nanoscale dimensions. These chemical alterations increase the probability that the solubility and processability of the nanoparticles for various applications will be enhanced.



**Fig. 1** Need for functionalized nanomaterials

### 3 Choice of Functionalizing Strategy

The functionalization strategy is chosen based on the specific needs of the application, and it varies depending on the type of NP. Typically NP are functionalized through covalent or non-covalent means. Covalent functioning involves the formation of a bond between the functional entities and the skeleton of the NP. For example, covalent functionalization of graphene has been shown to disrupt the  $\pi$ - $\pi$  conjugation and the properties associated with it, whereas non-covalent functionalization does not disturb the electronic or atomic structure of graphene. The electronic properties at the quantum level, as well as carrier concentration and mobility, are altered by adsorbents upon functionalization and are extremely useful for the application of photovoltaic devices.

Non-covalent functionalization involves the use of attractive forces such as van der Waals, hydrogen bonds, electrostatic force, and  $\pi$ - $\pi$  stacking interactions between the NP and additives. The surface functional groups modify the surface charge functionality and reactivity, increasing its stability and dispensability in different phases [10]. Different chemical and physical methods, such as exfoliation, intercalation, and hybridization, have been used to improve the functionalities and properties of NP.

### 4 Response to the Functionalizing Agents

Generally, adsorption of functional groups is classified into two types: physisorption and chemisorption. Physisorption involves the formation of non-covalent bonds with longer bond lengths as a result of weak interaction, whereas chemisorption involves the formation of strong bonds with shorter bond lengths. Chemisorptions caused by orbital hybridization produce the majority of covalent bonds. Doping is another aspect of physisorption caused by adsorbate on the material's surface. Substitutional doping can be achieved by introducing a hole or additional electrons into the material. Surface doping is the process of exchanging electrons at the surface with another heteroatom such as boron, nitrogen, aluminum, phosphorous, or sulfur via reactive binding sites. The atomic size of the adsorbate and its electronegativity has a large impact on doping [11, 12].

For example, carbon-based graphene functionalized with nitrogen has been found to effectively increase electronic conductivity, charge storage capacities, and agglomeration due to the presence of a lone pair of electrons and the protonation of some nitrogen groups such as pyridinic, pyrrolic, and pyridine. Modified graphene is often synthesized using the traditional Hummers method, in which oxygen is strictly adhered to the graphitic layer and oxidized, causing the van der Waals forces present within the graphite to move away from each other and, as a result, graphene oxide is formed. This chapter discusses the properties, synthesis strategies, and case studies of functionalized nanoparticles [13–15]. Figure 2 broadly explains the different modes of functionalization and their relative effects on the various properties of the materials.



Fig. 2 Different functionalization techniques versus respective impact on material properties

## 5 Properties of Functionalized Nanoparticles

### 5.1 Morphology and Porosity

NP can have varied dimensions ranging from 10 to 100 nm and its shape is discovered to be crucial in increasing their qualities for a variety of applications. However, aggregation of NP is a significant disadvantage that might be avoided by utilizing functional groups to modulate shape. It is discovered that the functionalized NP display more intriguing characteristics than the pristine nanoparticles in terms of morphology [16].

The porosity of the nanoparticles plays an important role in promoting host–guest interactions during targeted drug delivery in pharmaceutical or medical systems, as well as in energy storage systems like EDLC supercapacitors to enhance the storage of ions for excellent capacity. The surface-to-volume ratio of NP prepared with high porosity is significantly higher than that of bulk materials. The functionalization of pores present in NP is found to have a significant influence on the pore size, volume of the porous cavity, interconnected porous structure, specific surface area as well as the surface-to-volume ratio. Better porous property of NP improves the efficacy of nanoparticles in a wide range of applications, including drug delivery, catalysis, sensing adsorption, separation, and biomedical.

In general, materials are classified into three types based on their porosity: microporous (less than 2 nm), mesoporous (2–50 nm), and macroporous (>50 nm). This requirement is met by the functionalization of NP at the inner and outer surfaces of the pores and is accomplished by using steric hindrance or electrostatic repulsion to control the site selectivity of the functionalization [17]. Such regularity in allowing only certain type of molecules to enter the pores, promotes the controlled environments, and unwanted side reactions are avoided. This is particularly evident in mesoporous silica NP prepared with anionic functional groups attached to the outer surface of silica, which exhibit hydrophilicity and repel other submicron structures [18, 19]. This has been shown to inhibit specific adsorption while promoting biomolecular conjugation. The addition of specific cationic or anionic functional groups has been found to specifically interact with biomolecules such as lipids and plasma proteins, while inhibiting the adsorption of other unwanted groups. This clearly demonstrates that surface modification is critical in increasing surface area reactivity with the targeted molecules of interest.

Functionalization is further useful in the development of 3D carbon materials for supercapacitors loaded with multiple active sites and mesoporous structures at the micro- and nanoscale, which in turn helps to obtain high capacitance by reducing ion diffusion length. Controlling the pore size of the electrode material improves supercapacitive behavior significantly. This means that the electrode material's pore size should be significant compared to that of the solvated ions in the electrolyte solution. If the pore size is too small, ions will find it more difficult to accumulate at the pores on the electrode surface, reducing the capacitance of the double layer. Generally capacitance of a supercapacitor can be improved by creating electrode materials with a large active surface area which act as a network for efficient electron transfer. However, producing electrode materials with a high specific area would result in a large pore volume, which could eventually cause the density and volumetric specific capacitance to decrease. The shape of the pores influences the pore size distribution when selective ion adsorption occurs at the electrode surface, where ion size also has a significant impact [20]. Cone-, inverted cone-, and cylindrical-shaped pores are just a few of the many different types of pore shapes that have been reported thus far. The electrode materials prepared with these shapes of pores are reported to have nearly identical capacitance, resistance, and maximum charge storage capacities [21, 22].

## 5.2 *Optical Properties*

The functionalization of nanoparticles confers better optical properties, which broadens their applications in luminescent fields. Functionalization improves the recombination of localized electron–hole pairs for improved luminescent properties in pristine nanomaterials. This is especially noticeable in nanoparticles prepared through functionalization via heteroatom doping of nitrogen or metal doping, which results in a high fluorescence yield. The band structure can be tuned as a result of this functionalization, and the excitation independence behavior due to passivated surface states can be determined. The fluorescent properties are affected by the surface structure and electron distribution in nanoparticles, which is related to the energy gap between HOMO and LUMO. After surface passivation, the functionalization groups tend to attach or bind on the surface of nanoparticle, and the emission caused by surface energy traps becomes more stable [23]. For example, doping of heteroatom like nitrogen results in the formation of a new surface state (N-state) that traps electrons and increases the radiative recombination while suppressing the non-radiative recombination. Also, because of the increased probability of an electronic transition from ground state to lowest singlet state, nitrogen amino groups act as electron donors, indirectly increasing quantum efficiency. While functionalization has little effect on the band gap in graphene-based quantum dots, it does change their redox potentials by covalently attaching groups with lone pair of electrons such as carbonyl and amine groups. The development of these new sub-bands enabled optical transition in the near UV and visible ranges, resulting in positively and negatively charged surface sites.

In optoelectronic applications, achieving high color purity with narrow line width luminescence and warm colors is critical. This has been accomplished through the development of functionalized nanomaterials [24].

## 5.3 *Mechanical Properties*

The mechanical properties of functionalized nanoparticles are found to be better than pristine nanoparticles in terms of elasticity, rigidity, strength, stiffness, and hardness. This is heavily influenced by the concentration, type of functional groups as well as the interfacial bonding between the functional groups and the NP. In some cases, Young's modulus of covalently functionalized NP such as single-walled nanotube is significantly lower than that of pure. On the other hand, Young's modulus of the Cu–O-CNT composite is found to be increased with increasing functional group concentration. This is due to the fact that the appropriate amount of oxygenation improves the bonding between the CNTs and the Cu matrix, resulting in only minor structural changes to the nanotube backbone and an increase in elastic modulus. Especially, for CNT-based NP, the effectiveness of the CNT (single or double walled)

used also plays a role in determining differences in mechanical properties of the resulting composite [25].

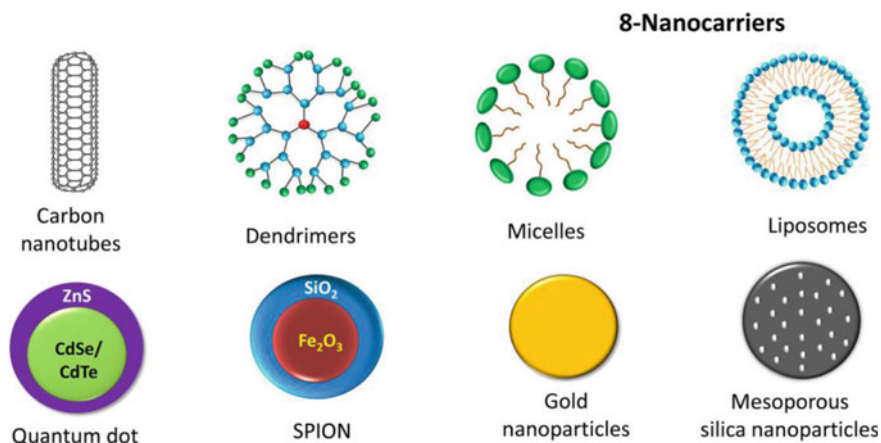
The effectiveness of bonding is demonstrated in the graphene oxide sheet prepared with functionalized  $\text{SiO}_2$ , in which the f- $\text{SiO}_2$  NP acted as cross-linking points to connect the GO sheets, resulting in improved mechanical properties. However, increasing the f- $\text{SiO}_2$  content above 10 wt% causes aggregation, which causes enhanced stress, resulting in reduced mechanical properties such as Young's modulus, tensile strength, and toughness. The improved mechanical property below 10 wt% is due to strong interfacial interactions such as hydrogen bonds and covalent interactions between graphene oxide sheets and f- $\text{SiO}_2$ , which in turn resulted in effective load transfer during deformation process. This is quite opposite in a simple oxygenated graphene nanoparticles where the mechanical robustness is found to be reduced than the defect-free graphene [26].

## ***5.4 Reduced Toxicity***

There are more chances for NPs to have non-specific side effects than there are in the bulk, which is why they are discovered to be harmful as well. This is substantially mitigated by the use of functionalized nanoparticles [27]. The toxicity of nanoparticles must be taken into consideration because it is a significant issue for applications such as using nanoparticles as nanodrug carriers and removing heavy metal components from the environment. It has been discovered that functionalizing nanoparticles reduces the generation of reactive oxygen species and enhances the biocompatibility, pharmino-kinetics, and assembly of biomolecules [28]. This is also because there are several opportunities for nanoparticles to aggregate and cause adverse side effects with biological, environmental, and cell surfaces. Particularly when functionalized with polymers, nanoparticles can be contained inside the polymer layer, acting as a protective layer. In the case of drug delivery, this can lessen the direct interaction of the nanoparticle with the antioxidant molecules or core molecules. Ultimately, this restricts the flow of oxygen to the polymer's core surface, reducing the oxidation process that results in the breakdown of NP and undesired side effects. It has been discovered that functionalized magnetic NP can deliver drugs more effectively and with less toxicity [29] (Fig. 3).

## ***5.5 Electronic/Electrochemical Properties***

It has been observed that the introduction of functional groups can be used to adjust electrochemical properties, including tuning of energy levels, surface area, shape, porosity, and stability. The functionalized graphene dots are particularly effective at transferring electrons for proton reduction in photocatalysis applications. Additionally, it has been discovered that the graphene dots functionalized with amine groups



**Fig. 3** Types of nanocarriers. Adapted with permission from reference 30

have significant inherent solubility. The surface functionalization of carbon dots is anticipated to increase performance by improving detection sensitivity and designing new composite functional materials or donor–acceptor arrays [30].

High diffusion profile, high collision rate, high loading capability, and preserving electroactive species from degradation are some of the improved qualities that these functionalized NP are discovered to display in electrochemical sensing applications. Also, doping the nanoparticles with heteroatoms like boron, nitrogen, and phosphorous is observed to subsequently speed up the charge transfer kinetics of the electroactive species at the electrode surface, particularly in the case of electrochemical sensors. The use of functionalized nanoparticles as electrodes in supercapacitors favors the migration and penetration of electrolyte into the electrode materials, thereby improving the electronic conductivity and enhancing the kinetics of electrochemical reactions while reducing charge transfer reactions.

Pd–Ni nanoparticles supported in functionalized multi-walled carbon nanotubes were created in order to boost the electroactivity of glucose sensors, and this increase in electroactivity is visible through an increase in the intensity of anodic peak current for glucose detection. The electrochemical sensing property has also been observed to have high sensitivity, improved stability, high selectivity, low detection limit, fast current response, and great repeatability [31].

When compared to pristine TiO<sub>2</sub> NP, amino-functionalized ones showed stronger crystallinity. After functionalization with TiO<sub>2</sub> nanoparticles, it is discovered that the conduction band and valence band energy levels have been elevated to greater levels, and larger open-circuit voltage values have also been noted. Further, NP's ambient stability has been improved upon functionalization, enabling a greater resistance to the infiltration of moisture [32].

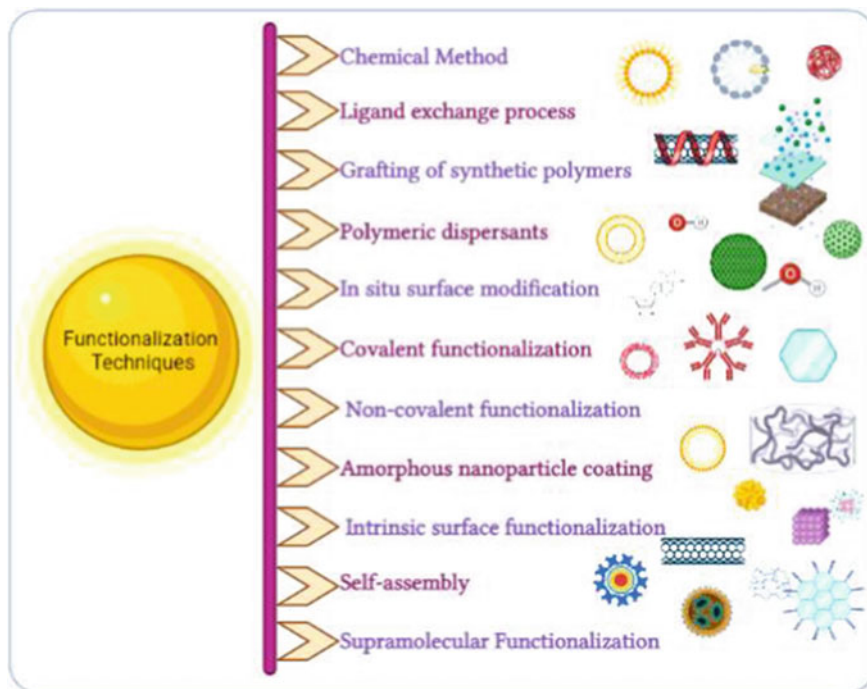


Additionally, the  $sp^2$  carbon network is weakened, producing defects and increasing back-scattering in the system, due to the adsorbates formation of covalent bonds with the CNT surface. The functionalized carbon-based NPs are shown to have higher carrier densities and electrical conductivities. In particular,  $N_2$  doping and surface modification limit the aggregate formation and shield the nanoparticles from bulk oxidation in ambient circumstances. Further, it can reinforce carbon systems and raise the carrier density of those systems, which will improve their electrical conductivity during catalysis. For example, nitrogen's substitution in MWCNTS enhances the electrical conductivity rather than only impeding their aggregation.

The concentration of functionalized groups on the NP determines how many electronic states there are at the Fermi level whereas significant suppression of the transmission channels below Fermi energy is covalent functionalization. The type of functional groups used has a significant impact on the electrical characteristics of the nanoparticles. In particular, it is discovered that  $O_2$  atoms function as carrier traps, decreasing carrier density and increasing back-scattering in the system, whereas  $N_2$  dopants virtually double locally, increasing transmission through the nanotube and lowering back-scattering in the nanoparticles matrix. The total density of states of NPs at the Fermi level is increased by the presence of functional groups like  $O_2$ . By creating novel states related to electron injection through functionalization, new conduction channels can be opened in the nanoparticles [33].

## 6 Functionalization Techniques

By altering the solvents, surfactants, and reaction temperature, functionalization may be done via covalent or non-covalent interactions, allowing for control of desired and unique functionalities. Because of this sort of functionalization, nanomaterials become hydrophilic and easily soluble in organic solvents. Functionalization occurs in non-covalent interactions by means of hydrogen bonding, ionic bonding, or hydrophobic contact. The electronic arrangement and characteristics of the atoms on the surface are unaffected in this form of interaction [34]. To improve the properties of nanomaterials such as solubility, biocompatibility, and the inclusion of new active sites, several functionalization pathways such as chemical techniques, ligand exchange processes, and synthetic polymer grafting are employed. Nanomaterials can be functionalized with a variety of ligands via various strategies such as physical or chemical routes to confer novel properties that cannot be exhibited as in bulk counterparts. Functionalized nanomaterials are majorly categorized according to their functionalizing agent and nanomaterial composition [35]. The following section explains various forms of functionalization techniques (Fig. 4).



**Fig. 4** Functionalization techniques

## 6.1 Chemical Functionalization

Chemical functionalization method involves a chemical process that occurs at the nanomaterial's interface in a medium. This method is mainly developed to functionalize unmodified nanomaterials in order to improve their solubility, reactivity, and hydrophobic interaction. Among various chemical techniques for the functionalization of nanomaterials, treatment with metal alkoxides, ethoxides, and silane coupling agents is widely used [36]. To remove surface contaminations acid treatments are employed. Besides alkali treatments, treatments with hydrogen peroxide, and heat treatments are the most popular chemical treatment procedures [37–39].

## 6.2 *Ligand Exchange Process*

Ligand exchange process is second widely employed method which mediates a dynamic interaction mechanism that exchanges ligands bound to the surface of nanoparticles. During the synthesis process, certain organic compounds or polymers are utilized to stabilize the nanoparticles. Nanomaterials may be broadly decorated by numerous ligands using this technique, depending on the needs. The additional components get attached to the nanoparticles' surface, improves their shape and size. Polyvinyl alcohol, polyvinyl pyrrolidone, oleylamine, oleic acid, cetyl trimethyl ammonium bromide, and ascorbic acid molecules are considered to act as capping agents, ligands, or surfactants depending on their chemical composition and functionality [40].

As an organic protector, the capping ligand materials deposited on the nanoparticle surfaces deter reactant molecules from approaching the surface of the nanomaterials. A few nanometers thick ligand layer is sufficient to shield the nanoparticles and prevent the transit of electrons among the nanoparticles before the occurrence of recombination [41]. But one major drawback of the choice of bulky organic ligand is that these material-deficit functionally active groups can participate in charge transfer between the nanoparticles. In order to maximize the transferring of charges and reduce the recombination loss, synthesis ligands must be removed from the nanoparticle surface [42]. This can be consummate by substituting the bulky ligands with more appropriate ones. To obtain better conductivity and charge separation, the incorporated or substituted ligand should be readily altered by annealing or any vacuuming. Because, in some cases, the presence of capping ligands might inject complexity into the system, such as unpredictable random charge transfer and non-covalent interaction between nanomaterials [43].

## 6.3 *Grafting of Synthetic Polymers*

A further popular surface modification technique that improves kinetics and changes the shape or form of nanomaterials is grafting of polymers. The three different polymer grafting functionalization techniques are grafting-to, grafting-from, and grafting-through. The final stage polymer is directly bonded to the suitable nanoparticle exterior using the grafting-to process. The grafting-from procedure produces polymer chains from a surface starting point. During the grafting-through procedure, a small monomer copolymerizes with another monomer on the surface of the nanomaterial [44]. Due to the fact that these low molecular weight monomers can interact with the active regions on the surface of the aggregated nanoparticles by permeating them. Also, by doing this, the nanoparticle surface will become hydrophobic, which is a crucial need for the blending of any metal oxide matrix or filler. On the other hand, introducing any kind of groups on the nanoparticle surfaces results in effective grafting.

Other methods of surface functionalization include *in vivo* passivation and the deposition of polymeric emulsifiers on the surface of the nanoparticle. Furthermore, synthetic methods including coating with amorphous nanoparticles and intrinsic surface engineering are used to functionalize nanomaterials.

#### ***6.4 The Adsorption of Polymeric Dispersants***

To prevent aggregation, surfactants or capping agents like oleylamine, oleic acid, etc. are incorporated in the reaction system. On the flip, hydrophilic nanoparticles are dispersed in organic solvents which are polar using cationic and anionic additives. The polymer chains are exposed to steric opposite charges by the dispersants, which raise surface charge and enhance nanoparticle miscibility. Numerous polycarboxylic chemicals and their derivatives are used as anionic surfactants to scatter different kinds of metal oxide nanoparticles [45].

#### ***6.5 In Situ Surface Modification***

During any nanoparticle synthesis, *in situ* surface modification approaches are used. *In situ* surface modification techniques include reverse micelle procedures, thermal breakdown of organometallic compounds, and polyol approaches [46, 47].

#### ***6.6 Covalent Configuration***

The term “covalent modification/functionalization” of nanomaterials refers to the covalent bonding of several chemical species to nanoparticles. The attachment of certain polymers, biomolecules, and inorganic/organic compounds to the surface of nanomaterials via this complexation technique is a potential strategy for enhancing distributions, colloidal stability, and adaptability. Covalent functionalization is frequently used to alter common nanomaterials like nanoclays, 2D nanomaterials, and metal oxide nanoparticles since it suggests a very strong coupling and a stable surface. The application of nanomaterials in a wide range of cutting-edge industries, including biosensors, catalysis, bio-imaging, packaging, cosmetics, environmental remediation, and agriculture, is considerably increased by this form of functionalization [48].

## **6.7 Non-covalent Configuration**

Non-covalent configuration/functionalization involves the formation of relatively weak bonds between guest molecules and the nanomaterials. Electron donor–acceptor ligand systems, polymer hydrogen bonding, and interactions according to van der Waals are the most common methods of non-covalent functionalization. Such functionalization is highly helpful in close proximity and simple to access at ambient temperature since it is mostly reliant on weak forces like hydrogen bonding and van der Waals interactions. These feeble forces are predicted to have an impact on the solvation of nanomaterials as well as hydrophobic and hydrophilic surface interactions. Non-covalent functionalization has the potential to enhance bioactivity, miscibility, sensitivity, binding affinity, catalytic action, and other properties. The implications of the big interfaces are comparable despite the fact that the energy produced during non-covalent bond formation is substantially smaller than that released during covalent contact [49, 50].

## **6.8 Amorphous Nanoparticle Coating**

Inorganic materials like amorphous silica and polymers can be used to form a covering of amorphous nanoparticles on the surface of metallic nanomaterials. Additionally, by allowing therapeutic ligands to be attached on their surface, coating the surface of nanoparticles, particularly with polymers, provides capabilities to the nanomaterials. Moreover, the decorating of nanomaterials with amorphous entities is possible by covering organic monomer, organic polymer, and inorganic metal oxide materials with different entities. Silica or polymers are arranged amorphously on nanoparticles to increase stability and create a conducive environment for later functionalization [51].

## **6.9 Intrinsic Surface Functionalization**

The atomic-level change of a nanomaterial's crystal referred to as intrinsic surface functionalization may be achieved largely by defect engineering and heterogeneous integration. The structural, electrical, and catalytic characteristics of nanomaterials are altered by the addition of electron-donating and electron-accepting elements including S, O, N, B, P, and other metals [52].

## 6.10 *Self-assembly*

The phrase “self-assembly” refers to an important method in supramolecular chemistry. Self-assembly is the spontaneous construction of specified components into ordered superstructures that may be used for a variety of purposes by nanoscale particles or materials [53]. The same mechanism that permits supramolecular organization also stabilizes molecular assemblies, but it has an effect on the number of connections, the presence of structural complementarities, and recognition phenomena. Mechanisms involved in self-stabilization include ionic stabilization, van der Waals forces, dipole–dipole interactions, and hydrophobic associations. Further, static and dynamic self-assembly are the other two types of self-assembly processes. External impacts are absent in a static process, and structure self-assembly is driven by energy minimization; however, external influences are present in a dynamic process, and the self-assembling system will adapt to its surroundings [54].

At the molecular, meso-, and macro-levels, self-assembly emerges. The spontaneous clustering of molecules under steady state into balanced, physically well-defined clumps connected by non-covalent connections is known as molecular self-assembly [55]. The self-assembly of a mesoscopic entity, like nanomaterial engineering, is referenced to mesoscopic self-assembly. Intramolecular and intermolecular self-assemblies are two further types of molecular and nanoscale self-assembly. In intramolecular self-assembly, molecules self-assemble from a random coil into a well-defined stable structure; on the other hand, intermolecular self-assembly refers to molecules’ capacity to form supramolecular ensembles.

## 6.11 *Supramolecular Functionalization*

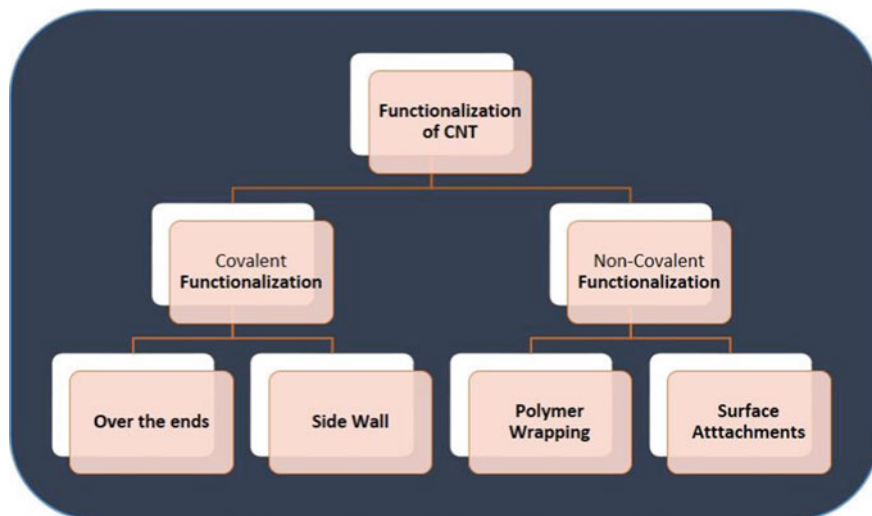
To create functional materials from molecular and nanounits, a unique notion combining procedures associated with nanotechnology together with supramolecular chemistry approaches is required. The molecular structures and nanostructures are inextricably linked. Solvents, temperature, pH, and physical factors such as light intensity all have an impact on the arrangement of molecules into a stable nanoassembly [56]. Besides, few structures are transitional that may be modified further. Unlike simple self-assembling processes, functionalization is often based on non-symmetrical processes that mandate extensive knowledge of nanostructures and their communications utilizing analytical methodologies [57].

## 7 Methodical Designing of Advanced Functional Nanomaterials: A Broad Split-Up

The introduction of functionalized nanomaterials has opened up innumerable possibilities for constructing high-performance membranes with customized features. Functionalizing nanoparticles have emerged as a new class of high-performance materials that have provided a viable foundation for modernizing traditional membranes. To meet the various applications, the use of functionalized nanocomposites is a possible option. With required state-of-the-art performance, the materials made of functionalized nanomaterials as additives exhibit their enormous promise in a variety of emerging sustainable technologies. Among various materials, few groups of materials are way more functionalized at maximum to acquire advanced properties. To name a few, titanium dioxide ( $\text{TiO}_2$ ), copper oxide ( $\text{CuO}$ ), zinc oxide ( $\text{ZnO}$ ), carbon nanotubes (CNT), iron oxide ( $\text{Fe}_3\text{O}_4$ ), silicon dioxide ( $\text{SiO}_2$ ), graphene oxide, and various carbon-based functionalized nanomaterials are widely used in the development of various nanocomposite-based applications [58–65].

Carbon exists in three hybridization states and may combine with other carbon atoms or nonmetallic elements to produce a wide range of structures, from small molecules to massive polymeric complexes. Carbon nanoallotropes are classified into two primary categories depending on the predominant covalent link in the structure; the first group consists mostly of  $\text{sp}^2$  hybridized carbon atoms that are positively packed in hexagonal crystal lattices that resemble honeycombs. Graphene and graphene-like structures such as CNTs, quantum dots, and fullerenes are common forms of this group, whereas the second category is an aggregation of mainly  $\text{sp}^3$ -bonded carbon atoms that may not be classified as graphene derivatives. Fullerenes are hollow spherical nanostructures comprised of carbon atoms that have been  $\text{sp}^2$  hybridized.

To meet the crucial demand for innovative materials for nanocomposite applications, graphene and CNT have the capacity to change the material's properties, which can be used in a wide range of applications and a relevant schematic is given in Fig. 5. Many researchers have recently reported significant advances in the utilization of carbon-based nanoparticles, namely, carbon nanotubes (CNTs) and graphene oxide (GO), in nanocomposite membranes for a variety of existing and upcoming research disciplines [66]. CNTs and GO are promising nanomaterials for the development of next-generation membranes with selectivity, high flux, and low fouling characteristics.



**Fig. 5** Modification of CNT nanoparticles

### ***7.1 Functionalization of CNT***

The characteristics and performance of CNT-reinforced nanocomposites are heavily reliant on the homogeneous dispersion of individual carbon nanotubes inside the polymer matrix surface, as well as the interfacial contact between the CNT and matrix phase. However, the smaller diameter, along with a greater aspect ratio and much larger surface area, complicates CNT dispersibility within the matrix when compared to other traditionally used metal oxide fillers [61]. Because the commercial CNT resides in the cluster due to van der Waals interactions, dispersion of these nanotubes in the polymer phase is particularly difficult. Another common restriction is a lack of interfacial contact with the polymer matrix. Because of the aromatic nature of the connection, carbon atoms on CNT walls are often chemically stable. CNT interacts with the surrounding matrix mostly by van der Waals' force of interactions, which is unable of delivering enough load transmission across the nanotube and the matrix interface [67]. Massive efforts have been put into sophisticated strategies to change the surface property in order to overcome the aforementioned concerns. According to the interactions between the carbon atom on the CNT and active molecules, functionalized techniques may be generally separated into covalent and non-covalent modifications.



## 7.2 *Functionalization of Graphene and Graphene Oxide*

All of the remarkable features and properties of graphene and its derivatives' give a glimpse of a supremacy over other nanostructured carbon allotropes. Because of its unusual structure, graphene dispersion in water and organic compounds is extremely difficult to achieve. Furthermore, graphene has a zero bandgap and is exceedingly inert to most chemical processes, limiting its potential applicability in the domain of energy applications. Despite the fact that graphene and its derivatives have acquired importance in technological growth, its ease of agglomeration severely limits their applicability in a variety of composite and nanocomposites domains. Despite CNTs, graphene and GO are often functionalized using one of three methods: covalent functionalization, non-covalent functionalization, and elemental doping [66]. As a result, graphene functionalization reduced aggregation and enhanced graphene processability, widening its breadth of applications in numerous sustainable development domains. Furthermore, functionalization aids in the modification of inherent properties such as electrical property, which allows for the control of bandgap and conductivity for the usage of novel nanoelectronic devices [68].

## 7.3 *Functionalization of Metal and Metal Oxide Nanoparticles*

Metal and metal oxide-supported nanoparticles, primarily Au, Ag, Cu, ZnO, CuO, TiO<sub>2</sub>, etc. are in the spotlight of current nanotechnology due to their superior physicochemical characteristics as well as their exceptional conductivity and antibacterial activity. Metal's unique size-dependent feature makes it a more promising material than other large-scale materials. Metal nanoparticles are classified into four types: metal-based nanomaterials, metal oxide-based nanomaterials, doped metals, metal sulfides, and metal-organic frameworks.

Metallic nanoparticles are produced and chemically modified using different functional groups. This method allows them to be combined with ligands or of any antibodies. All these metal and metal oxide-based nanomaterials can modify the surface of a material to provide functionalities and stabilize it. The functionalization with metals and metal oxide nanoparticles are widely used because of its easy processing methods and expansion. Moreover, all these materials are highly stable, less toxic, and low cost. As a result, it offers a surprising range of potential applications in the field of energy storage and conversion technology [69–71].

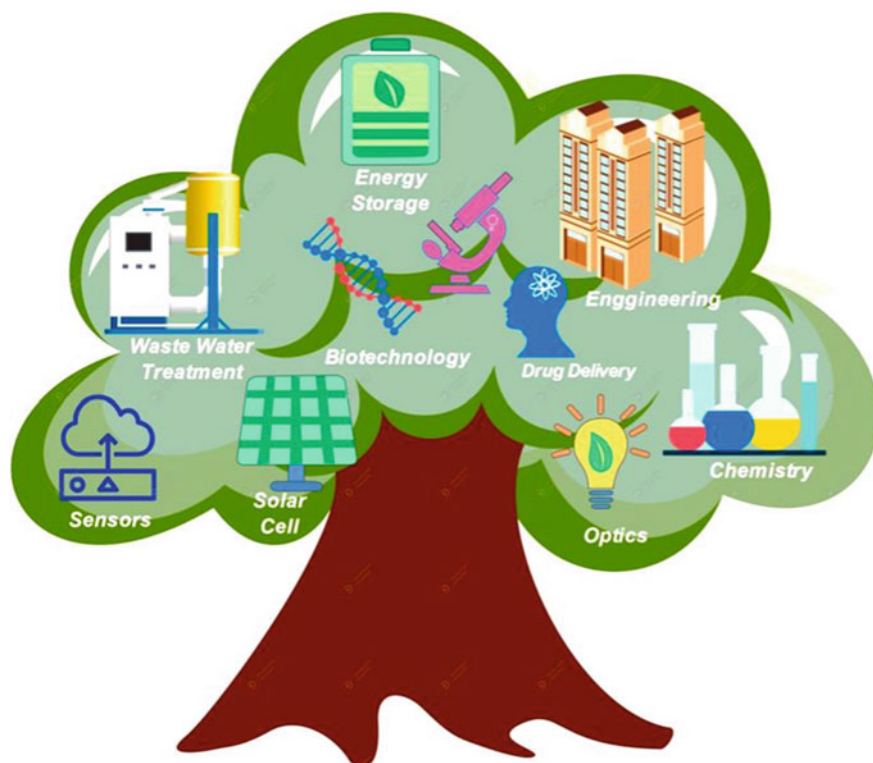
## 7.4 *Functionalization of Silica-Based Nanomaterials*

The functionalization of silica-based nanomaterials is highly employed and approached which enables their utility in numerous advanced applications by making them compatible with a wide variety of polymer molecules. In general, a typical method, namely, the silanol organ functionalization method, has been used to functionalize mesoporous nanosilica and zeolite. However, functionalization of zeolite differs slightly from that of mesoporous silica in that it occurs only on the zeolite's external surface. The channel dimension of zeolite is extremely narrow, limiting access to the internal surface for the majority of the reactants [72]. There are two commonly used methods to functionalize both of these nanomaterials which are co-condensation and post-synthetic grafting.

It is important to understand these two techniques because of its easy methodological strategy. Co-condensation is an advantageous method for functionalizing mesoporous silica nanomaterials because they crystallize more easily which is a one-pot synthesis. The main disadvantage of the co-condensation functionalization method is that it affects the final product's high crystallinity [73]. This procedure involves the addition of one or more organosilane and silicon sources, namely, tetraethylorthosilicate, so that functionalization occurs concurrently with the formation of the framework. The co-condensation method results in high functionalization and uniform deposition of functional units on the entire inner pore surfaces, with no pore blockage or shrinkage [74]. Furthermore, the particle morphology of the functionalized mesoporous silicate is easily controlled by this process, whereas the post-synthetic approach refers to the further alteration of pre-shaped nanomaterials prior to functionalization. For surface functionalization of silica nanoparticles by grafting, a well-known silylation technique is most typically used. Using this functionalization technique, nearly all functional groups such as amino, thiol, sulfonic acid, and carboxylic acid have been introduced on the material surface [75]. Nonetheless, the method's main disadvantage is the uneven distribution of functional entities on the pore surface. Typically, a large number of functional groups are adorned around the outer surface of nanomaterials and the entrance of pores.

## 7.5 *Polymeric Nanomaterials*

The commercial polymeric nanoparticles' inertness limits their development for long-term uses in a variety of sectors. The surface of the polymer must next be modified to improve its printing, wetting, and adhesion capabilities. This may be accomplished by coating polymeric surfaces and nanostructures with a range of polar and functional groups. Several surface functionalization approaches have been developed during the last several decades, most of which follow the following paths: first, main reactive functional groups are attached to the polymer chain's surface. Second, active/bioactive substances, oligomers or polymers, hydrophobic and hydrophilic



**Fig. 6** Illustration of various applications of functionalized nanomaterials

monomers are used to modify the reactive surface in order to achieve particular surface properties that meet the demands of the end use [76].

As discussed so far, functionalization is essential to extract the virtues of nanomaterials to the whole extent. These functionalized nanomaterials hold applications in all the technological advancements. The tree chart given in Fig. 6 indicates the few appliance sectors of these systems. Among different fields, energy storage systems such battery and supercapacitors are the most practical applications in these era. The following portions discover the effect of functionalization of the supercapacitor materials.

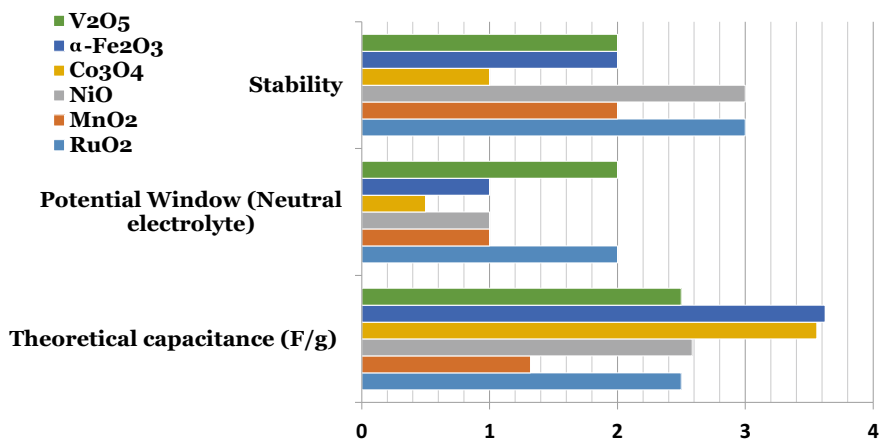
## 8 Role of Functionalized Nanomaterials in Supercapacitors

Supercapacitors (SC) are extremely promising energy storage devices that use two types of electrode materials with surface adsorption to store charges and the other one Faradic redox reaction to store charges. The first type of SC is known as an

electrochemical double-layer supercapacitor (EDLS), whereas the second type of supercapacitor is known as a pseudocapacitor. Carbonaceous nanomaterials such as CNTs, activated carbon, graphene oxide, and graphene are often employed in the EDLS for electrode fabrication. However, several types of conducting polymers, metal oxides, and hydroxides are employed as electrode materials in pseudocapacitors. The adjustment of bandgap, structural adaptability, charge carrier mobility, and electrical conductivity are the most important elements in improving the electrochemical energy storage mechanism of SCs. The usage of modified nanomaterials as EDLS and pseudocapacitive electrode materials was discovered to boost energy and power density while also providing outstanding electrochemical performance by enhancing the available free charge carriers [77].

### 8.1 Case Studies

As a comparative picture, few common metal oxide SC electrodes have been collected and effects of different functionalization modes are analyzed. Functionalization such as of synthesis techniques, dopants, metallic coating, composites with other metal oxides, and surfactant additions provide different effects on the performance and physical chemistry of the host materials. Extensive analysis on each of these parameters can occupy a volume of discussion. Further, the famous SC electrode candidates such as  $\text{RuO}_2$ ,  $\text{MnO}_2$ ,  $\text{NiO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{V}_2\text{O}_5$  are compared for their theoretical capacitance, potential window (in neutral electrolyte), and stability on cycling conditions have been plotted as a comparative chart (Fig. 7). Functionalization on each of these materials significantly affects the above-mentioned parameters as seen in Table 1.



**Fig. 7** Comparative illustration between significant parameters of popular supercapacitor electrodes

**Table 1** Effect of functionalization on the different technical aspects of the supercapacitor electrode materials

S. no	Electrode	Functionalization		Capacitance (F/g)	Stability (Cycles)	Salient features/remarks	Refs.
		Materials	Method				
1.	Co <sub>3</sub> O <sub>4</sub> /rGO-120-12	rGO	Hydrothermal	1152	10,000	Capacity retention	[78]
2.	Co <sub>3</sub> O <sub>4</sub> -MnO <sub>2</sub>	Carbon substrate and MnO <sub>2</sub> composite	Chemical deposition	616	10,000	83.1% capacity retention	[79]
3.	Ag-Co <sub>3</sub> O <sub>4</sub>	Ag	Grown on Ni foam	1323	2000	Capacity retention	[80]
4.	CoMoO <sub>4</sub> @CoS	Core-shell composite		3380	6000	81% capacity retention	[81]
5.	CuCo <sub>2</sub> O <sub>4</sub>	Electro-deposition		1473	5000	-	[82]
6.	Co <sub>3</sub> O <sub>4</sub> @graphene sheets	Graphene		3840	-	No loss in capacity	[83]
7.	MnO <sub>2</sub> /carbon	Carbon fiber fabric	Green hydrothermal	467	5000	Flexible electrode, 99.7% capacity retention	[84, 85]
8.	MnO <sub>2</sub> /CNT	Double-walled CNT array	Electro-deposition	793	5000	99.7% capacity retention	[86]
9.	MnO <sub>2</sub> /CNT on Ni foam	CNT-Ni	Chemical vapor deposition	325.5	5000	Binder free, carbon degradation	[87]
10.	MnO <sub>2</sub> /exfoliated graphite	Thermally exfoliated graphite	Hydrothermal	500	5000	Large conductive area	[88]
11.	MnO <sub>2</sub> -PANI	PANI	Polymerization	626	1000	Stability	[89]
12.	MnO <sub>2</sub> -Au	Au	Hybrid composites	1145	1000	High performance	[90]
13.	MnO <sub>2</sub> -Cu	Cu	MnO <sub>2</sub> coating on Cu	1024	2000	96% capacity retention	[91]
14.	MnO <sub>2</sub> -NCA	Ni, Ti	Electro-deposition	632	20,000	95% capacity retention	[92]

(continued)

Table 1 (continued)

S. no	Electrode	Functionalization		Capacitance (F/g)	Stability (Cycles)	Salient features/remarks	Refs.
		Materials	Method				
15.	MnO <sub>2</sub> -Co <sub>3</sub> O <sub>4</sub>	Co <sub>3</sub> O <sub>4</sub>	Core-shell on Ni substrate through hydrothermal	560	5000	95% capacity retention	[93]
16.	MnO <sub>2</sub> /NiCo <sub>2</sub> O <sub>4</sub>	NiCo <sub>2</sub> O <sub>4</sub>	Hydrothermal	2827	3000	1.6% loss	[94]
17.	RuO <sub>2</sub> /C	Carbon	Thermal decomposition	537.7	1000	Cycling stability	[95]
18.	RuO <sub>2</sub> /Au-C	Au, Carbon		558			
19.	RuO <sub>2</sub> -CNT	CNT foam		502.78	8100	106% capacity retention	[96]
20.	RuO <sub>2</sub> /CuO/MWCNT	Nanocomposites	Hydrothermal	461.59	-	Efficient electrochemistry	[97]
21.	Zr-ZnO	Zr	Doping	518	5000	94% capacity retention	[95]
22.	SnO <sub>2</sub> : RuO <sub>2</sub>	RuO <sub>2</sub>	1:3 ratio by SIL-AR method	185	2500	-	[96]
23.	SnO <sub>2</sub> -NiO	NiO	1:7 ratio by sol-gel and sonication	464	1000	87.24% capacity retention	[97]
24.	Fe-SnO <sub>2</sub> -CeO <sub>2</sub>	Fe, CeO <sub>2</sub>	Co-precipitation	348	5000	-	[97]

## 9 Conclusion

Functionalized nanomaterials are superior than their pristine versions due to the improved physical, chemical, optical, and other targeted performance-oriented properties. This review extensively focuses on the significance of functionalization, different methodological aspects available for the process, and their respective improvements in the end results of the nanomaterials. Figure 2 provides a broad overview on the impact of different functionalization strategies on the various properties of nanomaterials. Each strategy imposes a specific change in the matrix and the process involves in few limitations as well. For example, inclusion of polymer reduces the rigidity of the nanomaterials whereas inclusion of dense composites reduces the flexibility of the nanocomposites. Hence, the choice of functionalization technique requires deep survey suitable for that particular system. The present review gives an insight into the choice, impact, and different modes of functionalization technique. Finally, a short literature review has been compiled for the popular supercapacitor electrode materials and impact of different functionalizers on its SC performances.

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