



# Progress in self-cleaning textiles: parameters, mechanism and applications

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Received: 2 April 2023 / Accepted: 30 September 2023 / Published online: 15 October 2023  
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**Abstract** With the growing concerns about the conservation of the environment and the minimal consumption of water, the self-cleaning approach for textile materials is gaining much popularity and interest day-by-day. There are various approaches for producing self-cleaning textiles surfaces, of which the application of nanoparticles is more effective. The self-cleaning property can be achieved by either creating super-hydrophobic surfaces or applying photocatalyst materials. Super-hydrophobic self-cleaning surface follows the principle of the behavior of liquid on surface roughness. On the contrary, under the exposure of light radiation, the photocatalytic self-cleaning surface follows the chemical redox reaction mechanisms to degrade the organic materials including microorganisms or stains. Several previous studies

were done to implement self-cleaning functionality to textile materials. Hierarchical surface roughness using nano-whisker or nano-spherical structure using  $\text{SiO}_2$ , carbon nanotubes or ZnO nanoflower produces super-hydrophobic self-cleaning surface with excellent water contact angle whereas different semiconductor nanoparticles including  $\text{TiO}_2$ , ZnO,  $\text{SnO}_2$  exhibit photocatalytic properties. There are various suggested methods of synthesis and fabrication methods to impart nanoparticles on textile materials. In this review paper, the progress and technological advances in the field of nanoparticles impregnated self-cleaning textiles materials are discussed with different fabrication methods and nanoparticles. Apart from various challenges and limitations,

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nanoparticles coated self-cleaning textile materials have a wide range of applications in different fields.

**Keywords** Self-cleaning textiles · Nanotechnology · Nanoparticles · Textiles · Lotus effect · Photocatalysis

## Introduction

Textile industry is experiencing many advantages using nanotechnology as compared to traditional processing. The technology is also hygienic and reduces production cost with increasing product quality. In fact, the textile industry may be one of the most benefited areas when it comes to the application of nanotechnology (Kaounides et al. 2007). In case of textile processing, nanotechnology is mostly influential in functional finishing. Nanoparticles, when applied to textile materials, exhibit higher durability and better comfort as compared to conventional processing. It also provides hygiene and maintains the breathability of textile materials (Munoz-Sandoval 2014). Functionalization of nanoparticles throughout the various textile manufacturing processes, such as dyeing, finishing, and coating, improves the performance of products and also adds functionality that was previously unattainable. Modification of the surface of textile products to impart and improve their functionality is also possible with the incorporation of nanomaterials (Hosne Asif and Hasan 2018).

Nanomaterials or nanoparticles are basically materials or particles with the dimension of nanometer scale. They have a large surface area to volume ratio which gives them unique characteristics to use for functional property enhancement and to interact strongly with the substrate (Wong et al. 2006; Jadoun et al. 2020). Different types of nanomaterials can be used in the finishing of textiles to impart different performances. Most of the nanomaterials provide multifunctional properties to textile materials. The basic parameters of nanomaterials or nanoparticles are their shape and size, as well as the morphological structure of the materials on which they are applied (Hong 2018). Because of their tiny size, the adhesion of particles to textile materials is easy as it is easy to penetrate into the substrate fibrous polymer. Thus, the finishing with nanoparticles enhances many functional performances, including water repellent

finish, antimicrobial treatment, self-cleaning finish, UV protective treatment, and wrinkle resistance, etc. Finishing of textiles with nanoparticles is also called ‘nanofinish’ (Patra and Gouda 2013; Salman et al. 2020).

Regardless of the fact that it is essential in our daily lives, we can’t imagine our lifestyle without textiles. In fact, textiles can be considered to be our second skin. Different indoor textile materials like curtains, sofa covers, even our daily wearable items and also the outdoor textiles including tents, awnings, canopies, etc. can easily attract dust and stain. Almost all types of textile materials go through different types of washing process several times for the purpose of cleaning these dust and stain (Pillai and Sundaramoorthy 2022). These washing cycles and chemical agents can damage textile materials either by creating dimensional distortion or by damaging the surfaces of the materials. The process of washing textile materials also requires a huge amount of consumption of water. For reducing this washing cycle and resulting damage to textile materials, researchers are now concentrating on the field of self-cleaning materials. Self-cleaning materials are attracting attention due to their economic and environmental sustainability besides functional activity that ultimately reduce the cost of labor and detergent with cleaning the surface in a short time, resulting in a minimal effect on the environment (Parkin and Palgrave 2005). Self-cleaning properties impart repellent or photocatalytic cleaning mechanisms which theoretically do not require any type of washing process. Self-cleaning textile surfaces can be produced by incorporating functional additives of organic and inorganic materials (Wang et al. 2015).

Conventional washing of textile materials requires a lot of water, resulting in huge consumptions of water per processing. The concept of self-cleaning functionality is very concerning and is important for reducing the consumption of water. In addition to self-cleaning materials, they not only clean the surface and degrade the stain, but also inhibit microbial growth.

There are many investigations that have been published in the field of self-cleaning properties of textile materials. However, there is a lack of review in the field of the nanoparticles impregnated self-cleaning properties of textiles published in the literature.

In this review paper, nanoparticles-induced self-cleaning properties of textile materials and their different aspects are discussed which include the approach of self-cleaning finishing and different factors affecting the performance of self-cleaning textiles. Different types of nanoparticles and their synthesis and fabrication on textile substrates are also discussed in this paper.

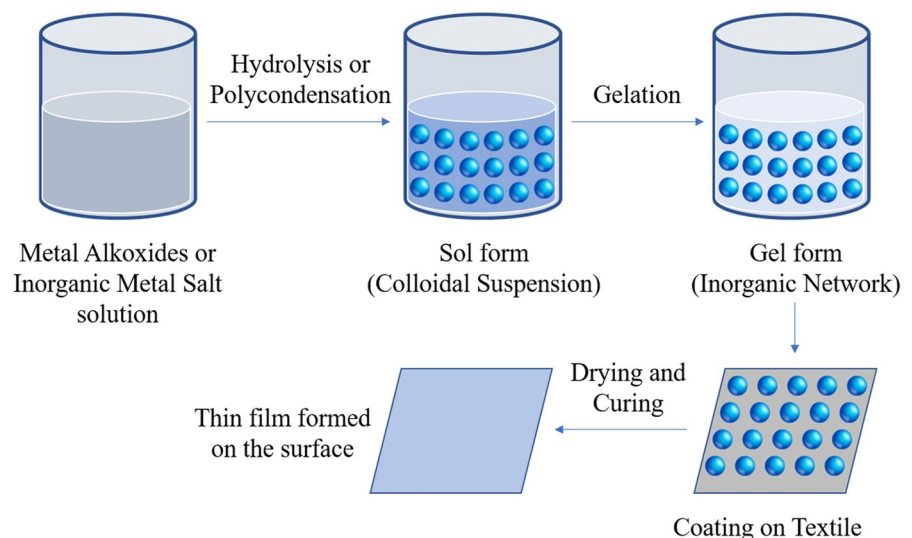
## Fabrication techniques of self-cleaning textiles

### Sol–gel technique

Among the various fabrication techniques used in the production of self-cleaning textile materials, the sol–gel technique is the most versatile and effective one. This is because of some of its important features, such as high efficiency, less cost, less chemical consumption, durability, and functionality of nanomaterials and being environmentally friendly (Gupta et al. 2008; Kathirvelu et al. 2008). A sol–gel technique involves basically the stepwise formation of colloidal suspension (called as sol) and gelation of the sol forming inorganic networks on the surface in a continuous liquid phase (called as gel). The resulted gel form was then directly applied to the substrates and further drying and curing with certain temperature, thin film of coating was formed. The formation of sol is initiated with some metal or metalloid elements that are bounded with ligands. These materials

are known as precursors which are generally metal alkoxides. The controlled addition of inorganic metal salts to aqueous medium can also act as a precursor (Brinker and Scherer 2013; Feinle et al. 2016). The mechanism of sol–gel reaction follows a series of hydrolysis of metal alkoxides and condensation of the hydrolyzed product (Fig. 1). Metal alkoxide precursors contain alkoxide groups ( $-OR$ ) in their structure that are replaced by hydroxyl groups ( $-OH$ ) when they are hydrolyzed in water. Subsequently, the hydrolyzed product was passed through condensation to form metaloxane ( $M-O-M$ ). The condensation mechanism is continuous to construct a large and porous three-dimensional polymer network and this polymeric structure extended to form a gel (Ismail 2016). Sundaresan et al. (2012) and Mishra et al. (2018) developed self-cleaning cotton fabric through the sol–gel approach of  $TiO_2$  nanoparticles using titanium tetra iso-propoxide as the precursor and distilled water and ethanol as solvent systems for the process. The process includes the preparation of nano-sols of  $TiO_2$  using the precursors and gelation of the prepared nano-sol. The bleached cotton fabric was dipped in the prepared sol, padded, dried, and cured. The resulted fabrics exhibited multi-functional properties including photocatalytic self-cleaning (Sundaresan et al. 2012; Mishra and Butola 2018). There were other studies that described the sol–gel process for synthesis of  $TiO_2$  nanoparticles using different precursors including titanium n-butoxide, titanium tetrachloride, titanyl oxysulphate in different solvent

**Fig. 1** Typical sol–gel process flow diagram



systems (Baiju et al. 2007; Periyat et al. 2007; Saalinraj and Ajithprasad 2017; Tao et al. 2018). Moafi et al. (2011) described the sol–gel synthesis of ZnO nanoparticles in which the research group employed zinc acetate dihydrate as the precursor and methanol as the solvent systems (Moafi et al. 2011). Hasanzadeh et al. (2022) modified the surface of polyester/viscose fabric with silica hydrosol following the treatment of coated sample with PDMS and APTES. Tetraethoxysilane was used as a precursor for the sol–gel synthesis of silica nanoparticles and the developed sample showed high degree of surface roughness and super-hydrophobicity with WCA at 151° (Hasanzadeh et al. 2022). The efficiency of sol–gel technique depends on some important factors which are the pH, temperature and time of reaction, nature and concentration of reagent and catalyst, molar ratio of water and precursor etc. A small summary of the studies is shown in Table 1 which represents synthesis of different nanoparticles using sol–gel method using different precursors for modification of cotton fabric with self-cleaning activity.

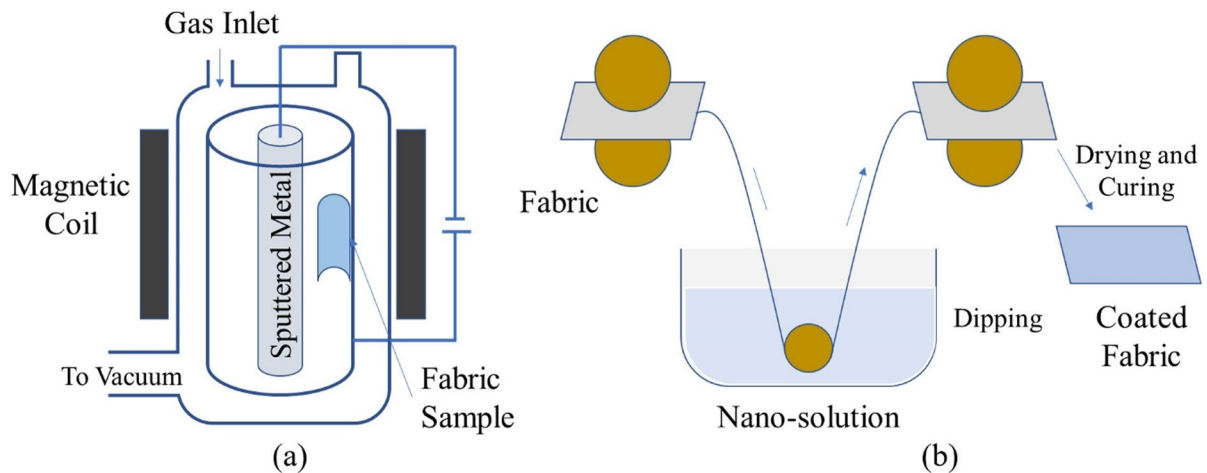
#### Plasma technique

Plasma treatment is a newer and special type of technique that can be used in the modification of textile surfaces. This technique is very efficient for textile materials as it does not require any wet chemical procedure, hence the process is dry with no water

consumption. Modification of a textile surface to impart some important properties is sometimes difficult to produce by conventional methods. Plasma treatment can be a better alternative for those modification techniques (Haji and Naebe 2020; Naebe et al. 2022). Plasma is the fourth state of matter, which consists of a cluster of particles like positive ions, electrons, free radicals, UV radiation and some neutral species. These are created by excitation of a gas medium in electromagnetic and/or electric fields. When fabric is exposed to plasma fields, the electrons and free radicals hit the surface and rupture the covalent bond by activating the surface (Haji and Kan 2021; Ahmed et al. 2022; Khatabi et al. 2022). Besides, different chemical functional groups and radicals can be generated on the plasma treated surface where the generation of functional groups is dependent on the gas used for the treatment. The gas medium may be air, oxygen, nitrogen, hydrogen, ammonia, inert gases, etc. These functional groups including –OH, –CO, –COOH etc. which can improve the surface properties of textile materials. Research also suggests that pre-treating the fabric with plasma can improve the affinity of the surface to nano-dispersion (Shishoo 2002; Busi et al. 2016). For plasma treatment of materials, a typical set-up includes the plasma reactor or electrodes, vacuum pump, gas inlet, matching networks, and power source (Fig. 2a). Fabric is placed on the anode in a gas medium. When voltage is applied in the system, the fabric surfaces

**Table 1** Precursors used for sol–gel synthesis of different nanoparticles

Nanoparticles	Precursor (s)	Medium	Crystallinity	References
TiO <sub>2</sub> NPs	Titanium n-butoxide	Isopropanol	Anatase and brookite	(Hu and Yuan 2005)
		Ethanol		(Yang et al. 2018)
	Titanium oxychloride	Water	Anatase	(Baiju et al. 2007)
	Titanium oxysulphate	Water	Anatase	(Periyat et al. 2007)
	Titanium iso-propoxide	Water, ethanol	Anatase	(Sundaresan et al. 2012)
		Water/ethanol (50:50)	Anatase	(Mishra and Butola 2018)
ZnO NPs	Titanium tetrachloride	2-Propanol	Anatase and rutile	(Saalinraj and Ajithprasad 2017)
	Zinc acetate dihydrate	Methanol		(Moafi et al. 2011; Shaban et al. 2016)
		Water		(Borda d' Água et al. 2018)
SiO <sub>2</sub> NPs	Zinc nitrate	Water		(Butola et al. 2018)
	Tetraethoxysilane	Water/ethanol (50:50)		(Yu et al. 2007; Hao et al. 2010)
		Methyl trimethoxysilane	Water	
Ag NPs	Silver nitrate	Water		(Xing et al. 2007)



**Fig. 2** Typical schematic diagram of **a** a DC magnetron sputtering plasma system (Rashidi et al. 2013) and **b** dip-pad-dry-cure techniques (Ortelli et al. 2015)

are physically and chemically modified by introducing functional groups covalently bond to the surface (Shahidi et al. 2015).

Busi et al. (2016) treated the fabric with a 2-hydroxyethyl methacrylate binder after plasma exposure with an argon-air gas mixture (cold plasma). The plasma-functionalized fabric was then impregnated in  $\text{TiO}_2$  nanoparticle solutions to produce self-cleaning properties (Busi et al. 2016). Acyanka et al. (2019) synthesized  $\text{TiO}_2$  nanoparticle on cotton fabric using atmospheric plasma and a suitable precursor where the fabric was first treated with a  $\text{TiCl}_3$  solution following plasma treatment using a humid air mixture containing  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$ . This produced hydroxyl free radicals ( $-\text{OH}$ ) which can easily oxidize  $\text{Ti}^{3+}$  to form nano  $\text{TiO}_2$  on the fabric surface resulting a better photocatalytic cleaning of organic dye (Acayanka et al. 2019). Abualnaja et al. (2021) applied low pressure plasma on PET fabric to impart self-cleaning properties. The fabric was treated in a plasma chamber in the presence of  $\text{O}_2$  which generated surface functional groups (negatively charged  $-\text{COO}$  and  $\text{O}-\text{O}$  substituents). The treated fabric was then padded in  $\text{Ag}/\text{TiO}_2$  nano-solution following drying and curing (Abualnaja et al. 2021). Irfan et al. (2021) reported the application of plasma in the activation of cotton fabric where the activated surface gained  $-\text{COOH}$  and  $-\text{OH}$  free radicals on their structure. The activated fabric was then coated with

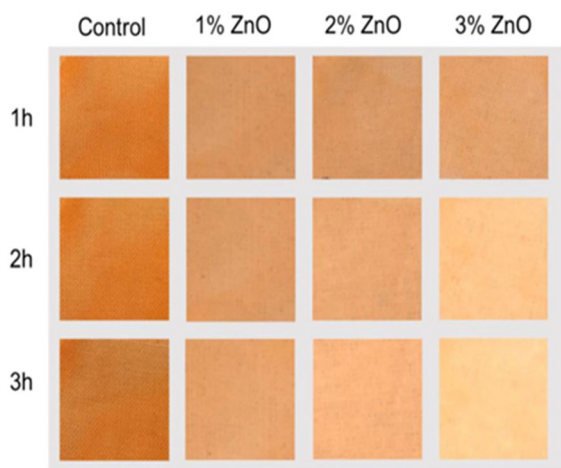
$\text{ZnO}$  nanoparticles and the self-cleaning function was assessed (Irfan et al. 2021). Other research also described the plasma techniques to produce self-cleaning textile materials with different nanoparticles and nanocomposites (Chemin et al. 2018; El-Naggar et al. 2021).

#### Pad-dry-cure technique

As there are various fabrication methods for developing self-cleaning textile materials (or applying nanoparticles to produce multifunctional textile materials), there are some major issues regarding these methods, such as the involvement of multiple steps, high energy consumption, and use of costly equipment and expensive materials. Yet, it is very challenging to develop and design a simple, low cost, energy efficient and time saving method (Ortelli et al. 2015; Wang et al. 2022). Pad-dry technique is one of the simple techniques like dip coating technique and the processes are almost similar. The difference is that in the pad-dry method, after dipping in the solution of nanoparticles, the treated materials are to be passed through the nip of the padding roller for the required wet pick-up following the drying of the materials at a certain temperature (Fig. 2b). If binder is added then curing is also be done for better cross-linking (Kaihong Qi et al. 2011; Chaudhari et al. 2012; Hebeish et al. 2013). Khan et al. (2018a and 2018b) developed multifunctional cotton fabric including



super-hydrophobic self-cleaning fabric through pad-dry-cure techniques. The fabric was first immersed in solution containing nanoparticles (ZnO and TiO<sub>2</sub>), repellent chemicals and binder. The treated fabric was then passed through padding rollers for certain wet pick-up following drying and curing at certain temperature for better performance. The nanoscale surface roughness was generated on the surface, which increased the water contact angle (up to 160°) and reduced the contact area between the surface and the water droplet (Khan et al. 2018b). Ahmad et al. (2019) developed photoactive cotton fabrics using TiO<sub>2</sub> nanoparticles solutions through pad-dry-cure techniques for UV protection and self-cleaning properties (Ahmad et al. 2019). Wang et al. (2022) developed multifunctional self-cleaning textiles using ZnO nanoparticles through dip-pad-dry-cure methods. The developed materials have photocatalytic property (Fig. 3) as well as better and uniform surface roughness which made the materials super-hydrophobic. Due to the hydrogen bonding between cotton fabric and ZnO nanoparticles, the adhesive force is very good, which ensures the durability of the coating (Wang et al. 2022). There are some variables of the methods on which the effectiveness of the applied coating solution depends, namely the concentration of the nanoparticles, the concentration of the binder, the speed of the padder and the number of pads (Asim and Naem 2022).

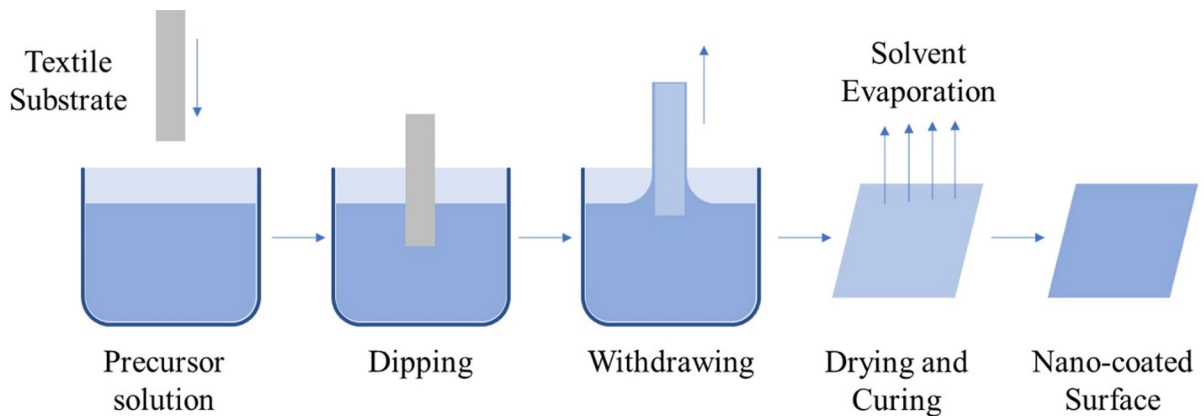


**Fig. 3** Photodegradation of a Orange II dye stains on ZnO-coated fabric produced through dip-pad-dry techniques. Reproduced with permission (Wang et al. 2022). Copyright © 2022, Taylor & Francis

## Dip coating technique

Dip coating techniques are one of the most common and easy methods for application of nanoparticles on textile substrates. The term ‘dip coating’ holds for the general procedure in which the substrate whose surface is to be modified is to dip in the required nano-solution or dispersion. The process is simple, low cost and can produce high quality coating films of large and complex shapes. Besides, the method has some advantages like reproducibility, non-hazardous and suitable for deposition of coating materials in a large area at low temperature (Dastan et al. 2016; Tang and Yan 2017). The technique involves the deposition of wet liquid films coating on substrate’s surface. The substrate is first immersed in the liquid coating medium following withdrawal of the substrates after a certain time. During and after withdrawal, a coherent liquid film is produced which is deposited on the surface. For a certain property and better impregnation, the process is performed several times to impart more deposition layers. The coated material is then consolidated by drying and for further fixation of coating materials, curing or sintering is done (Puetz and Aegerter 2004; Brinker 2013; Afzal et al. 2014). Figure 4 represents the process flow diagram of dip coating process.

Afzal et al. (2014) in their research, fabricated a new type of self-cleaning fabric which is super-hydrophobic and photocatalytic at the same time using dip-coating techniques. They used self-assembled monolayers of *meso*-tetra(4-carboxyphenyl)porphyrin on TiO<sub>2</sub>-coated cotton fabric followed by hydrophobization using trimethoxy(octadecyl)silane (Afzal et al. 2014). Latthe et al. (2019) studied the self-cleaning superhydrophobic coatings by dipping the fabric in hydrophobic silica nanoparticles dispersed in hexane. The super-hydrophobicity and self-cleaning properties of the surface are controlled by the coating temperature, dipping time, withdrawal speed and deposition layers (Latthe et al. 2019). Pal et al. (2021a, b, c) fabricated a durable and fluorine free cotton fabric through dip coating in TiO<sub>2</sub> nanoparticles. The coated fabric exhibits super-hydrophobicity and efficient self-cleaning properties (Pal et al. 2021c). The process is typically a batch process and the fabric should be cleaned before dip coating.

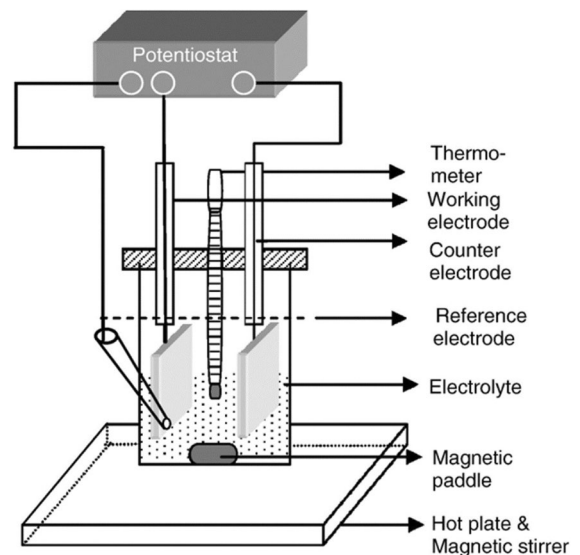


**Fig. 4** Typical process flow diagram of dip coating process. Reproduced with permission (Neacșu et al. 2016). Copyright © 2016, Elsevier

### Chemical and electrochemical deposition

Chemical and electrochemical deposition techniques have a significant impact on designing and developing self-cleaning surfaces. Techniques can be applied to produce surfaces with rough micro and nanoscale structure such as lotus leaves and self-cleaning photocatalytic surfaces (Dalawai et al. 2020). Fabrication of nanoparticles on materials' surfaces by processes such as sol-gel, lithography techniques, or layer-by-layer assembly is expensive, requires high temperature, and consumes a lot of time. These limitations can be overcome by introducing robust techniques like chemical and electrochemical depositions. There are various deposition techniques for the fabrication of nanoparticles to produce self-cleaning textiles. Among them, electrochemical deposition is more convenient. The advantages of electrochemical deposition over other methods include less time and chemical consumptions, low-temperature process, better particle controllability, large-scale industrial application, cheapness, and simplicity (Oliveira et al. 2016). There is a major limitation of the electrochemical method. For nanoparticle deposition, the fabric surface should be conductive either by incorporating metal wires and nanoparticles or by coating the surface with conductive polymer (Kim et al. 2017).

Typical electrochemical cell constructed using two electrodes or three electrodes namely working electrode, counter electrode and additional reference electrode. These three electrodes are meant to be



**Fig. 5** Typical set up (a) for electrochemical deposition. Reproduced with permission (Wellings et al. 2008). Copyright © 2008, Elsevier

immersed in an electrolyte solution where the nanoparticles are deposited on the surface of the working electrode (Fig. 5). The counter electrode is made up of Pt or graphite and the reference electrode may be of Ag/AgCl as described in the paper (Wellings et al. 2008). Ekanayake et al. (2022) developed superhydrophobic self-cleaning polyester fabric through electrochemical deposition. The fabric is prepared conductively using carbon black by means of screen

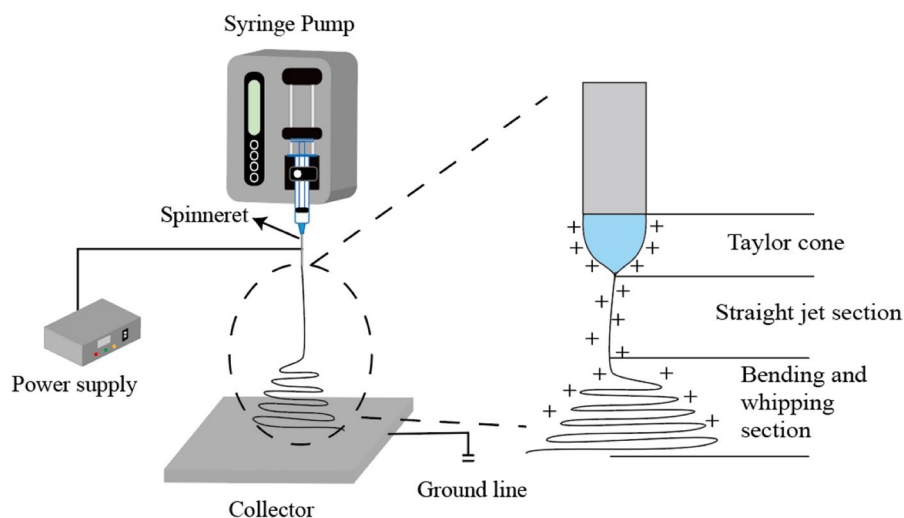
printing. The fabric is then used as working electrode in three electrode electrochemical cell system. The three electrodes were immersed in a  $\text{Zn}(\text{NO}_3)_2$  solution and when voltage is applied, the ZnO nanoparticle films were deposited on the surface of the fabric. The ZnO deposited fabric was then treated in stearic acid solution to make super-hydrophobic (Ekanayake et al. 2022). There are also other researches done on depositing ZnO nanoparticles on fabric surface through electrochemical deposition techniques (Dai et al. 2013; Oliveira et al. 2016). Study done by Qing suggest that the micro- and nano-scale rough surface can produce well super-hydrophobicity but can stop functioning when exposed to oil. To solve this problem, the researchers fabricated the surface through electrodeposition methods which includes the subsequent coating of the super-hydrophobic surface with fluorinated metal oxide nanoparticles (Qing et al. 2017). Other research showed the electrochemical deposition of  $\text{TiO}_2$  nanoparticles, CuO nanoparticles, etc. (Yin et al. 2016; Verma and Kumar 2019). Anderson et al. (2016) developed robust techniques to deposit nanoparticles on a cotton surface known as electroless chemical deposition. The process is inexpensive and produced high quality materials that can effectively degrade organic substances (Anderson et al. 2016).

#### Electrospinning/electrospray coating technique

There are several established methods of fabrication of nano-coatings on textiles substrates. However, a

common shortcoming of most of the processes is the low surface-to-volume ratio, which ultimately limits the overall activity of the nanoparticles. The electrospinning process is a versatile method for fabrication and formation of nanofibers that overcomes this limitation. The method is simple and feasible that produces nanofibers with a very thin diameter (Jeong and Lee 2019). Electrospinning techniques involve the forces created by the electrical field for the production of continuous filaments or webs from polymers, melts, or other viscoelastic liquids. The fibers are dispersed on a collector and form nonwoven web or uniaxial and bi-axial nanofibers assembly (Teo and Ramakrishna 2006). Basic setup of electrospinning system consists of three parts; a feeding system, a grounded collector and high voltage power supply (Fig. 6). In the feeding system, precursor solution from a container is forced to pass through a spinneret (usually a blunt needle) with the help of a pump. High voltage from a power source is applied on the needle which charged the precursor droplets. Electrical fields from the opposite direction force the droplets to elongate, resulting in a conical shape of the droplets (Taylor cone) (Sas et al. 2012). When the force of electrical field overcome the surface tension of the droplet, a thin jet of the precursor is ejected. But due to the instability of the jet, it moves randomly, which is collected by a grounded metallic collector (Nuraje et al. 2013). These forms a web of fine fibers having nanoscale size with high surface area and porosity. By controlling the parameters, different morphological

**Fig. 6** Schematic diagram of electrospinning device and process (Zhou et al. 2022)





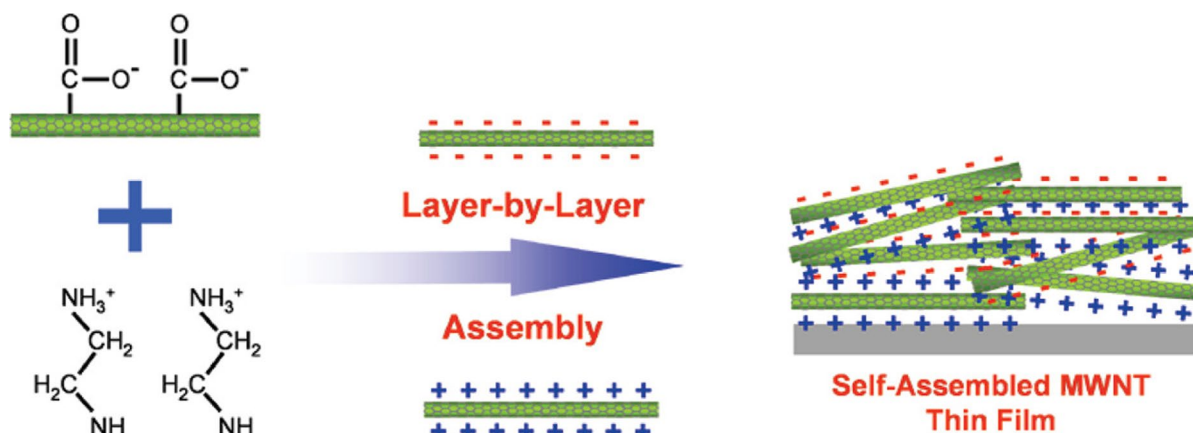
structures of the fibers can be obtained (Zohoori and Davodiroknabadi 2013; Yoon et al. 2017).

Bedford et al. (2010) created photocatalytic self-cleaning fiber using co-axial electrospinning cellulose acetate and TiO<sub>2</sub> nanoparticles. Cellulose acetate was used as the core phase and as the sheath phase a dispersion of nanocrystalline TiO<sub>2</sub> was used. After a deacetylation process, the cellulose acetate turns pure nanocellulose and the TiO<sub>2</sub> nanoparticles attached with the fiber with photocatalytic properties (Bedford and Steckl 2010). Khan et al. (2017) studied the self-cleaning effect of electrospun poly(1,4-cyclohexane dimethylene isosorbabide terephthalate) nanofibers that were embedded with ZnO nanoparticles due to the high photocatalytic properties of ZnO (Khan et al. 2018a). Yuan et al. (2019a, 2019b) developed multifunctional fabric through electrospinning which resulted fabric with disinfecting and self-cleaning properties. The group modified the PAN fabric with polymeric carbon nitride (PCN, a two-dimensional metal-free semiconductor) nanosheets through electrospinning method following a high-pressure steaming. After the electrospinning process a white nonwoven was collected on the grounded collector (Yuan et al. 2020). Karagoz et al. (2021) investigated the advantages of using PMMA nanofibers with ZnO nanorods and Ag nanoparticles to develop protective mats through the electrospinning process. Nanofibers prepared on a non-woven fabric by direct electrospinning from solutions. The mats obtained exhibit multifunctional properties such as antibacterial, antiviral, and photocatalytic self-cleaning properties (Karagoz et al. 2021).

#### Layer by layer assembly

Among the fabrication process of nanoparticles, one of the facile and simple but effective processes is layer-by-layer (LBL) assembly techniques. The method involves the deposition of coating solution on substrates several times to form a multilayer coating, as it gained its name. This method has a wide variety of applications with different structures, functionalities, and properties. In addition, the method is very simple with suitability to coat on various surfaces that are more durable (Patrocínio et al. 2014; Atwah and Khan 2022). The mechanism of LBL assembly follows the electrostatic attraction between oppositely charged molecules on the

surface of the materials and nanoparticles. The principle involves the alternating adsorption of cationic and anionic species. The process is initiated with the generation of charge over the substrate surface. The charged substrate is then immersed in the colloidal coating solution having the opposite charge resulting the first monolayer on the substrate. After the substrate is rinsed, it is immersed again in the solution which has the alternative charge of the previous. The process has to be repeated several times and a multilayer coating film is produced on the surface of the substrate. The coating films are strongly bonded with each other due to the strong electrostatic interaction (Ugur et al. 2010; de Villiers et al. 2011; Lin et al. 2018). The colloidal charged species can be nanoparticles, dyes, proteins, and other supramolecules although, in general, some polyelectrolyte is also used (Dubas et al. 2006). Xue et al. (2020) developed a superhydrophobic flame-retardant cotton fabric by imparting carbon nanotubes through LBL deposition. The research groups employed poly(ethylenimine) solution to functionalize the cotton surface that generates positive charge on the substrates. After being rinsed with deionized water, the unbound contamination was removed. Then the charged substrate was treated in CNTs dispersion to form first monolayer. CNTs layers were attached with the negatively charged surface through ionic bond. The substrate was then again immersed in poly(ethylenimine) solution following the treatment of CNTs. The process was repeated to form 'n' number of layers of coating films and after the treatment, the surface got roughened and produced a super-hydrophobic surface (Xue et al. 2020). Another research group developed self-cleaning denim fabric using TiO<sub>2</sub> nanolayers. They first modified the surface with cationic agent following the treatment of TiO<sub>2</sub> nano solutions and repeated the process. After obtaining 10 layers of deposition, the fabric exhibited acceptable self-cleaning properties (Uğur et al. 2017). Desisa et al. developed super-hydrophobic cotton fabrics using the nanocomposite of TiO<sub>2</sub>/SiO<sub>2</sub> through the LBL technique. They found that the materials produced through these techniques were soft, very durable after washing, and resistant to water and stain (Desisa et al. 2022). Xiong et al. (2019) fabricated cotton fabrics with SiO<sub>2</sub> nano solutions using LBL technique. They modified the surface



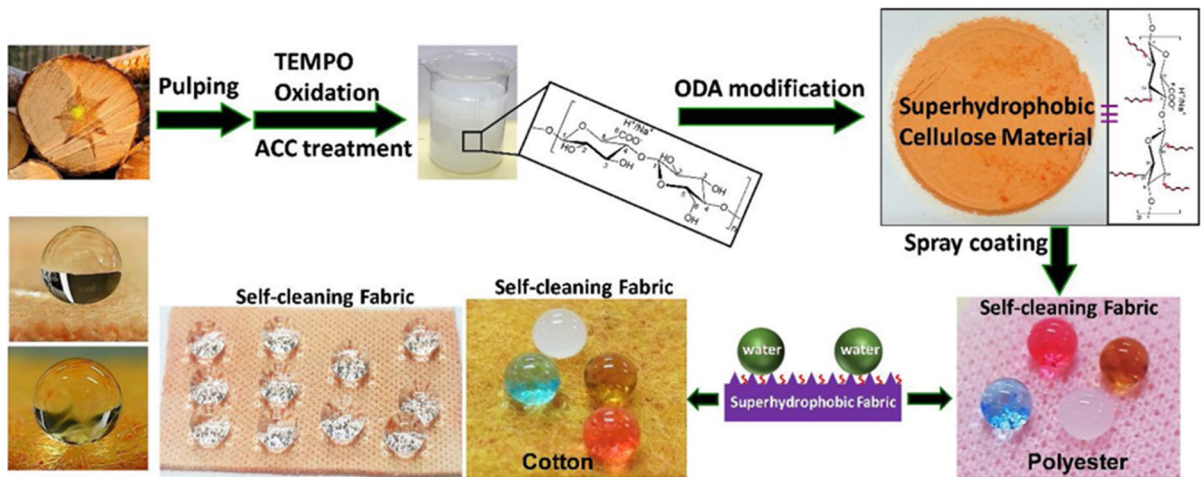
**Fig. 7** Layer-by-layer self-assembly techniques for CNTs. Reproduced with permission (Lee et al. 2009). Copyright © 2009, American Chemical Society

with poly(ethylenimine), which attached to the cotton fabric through H-bonds and charged the surface positively and then treated in  $\text{SiO}_2$  nano solutions. The materials showed multifunctional properties including super-hydrophobic self-cleaning properties, UV-protection, and anti-fouling properties (Xiong et al. 2019). Figure 7 indicates the the layer-by-layer self-assembly techniques for CNTs.

#### Spray coating technique

Spray coating technique involves coating the substrates simply by spraying the coating solutions. Nanocoating solutions or dispersions are sprayed on the surface of the material for multifunctional properties. The process is very simple and economical compared to other fabrication techniques. First, the coating solution is prepared using the constituents that are nanoparticles, the binder, and sometimes the dopants. The solution is then sprayed on the material surface by means of air or gas blow through nozzle system. After coating, the materials are dried and then cured for better bonding. In case of spray coating techniques, the thickness of the coating is an important factor (Latthe and Rao 2012; Li et al. 2014; Rana et al. 2016). For better performance, sometimes the surface of the materials is functionalized through pretreatment with different techniques like chemical

etching or plasma treatment etc. Jeong et al. (2016) developed a superhydrophobic and transparent coating of silica nanoparticles on cotton fabrics. The group fabricated the fabric surface using hydrophobized silica nanoparticles through the spray coating method. Silica nanoparticles were dispersed in three different alcohols and the dispersions were sprayed using an airbrush spray. The treated fabric surfaces exhibited better surface roughness with both micro- and nano-scale hierarchical structure (Jeong and Kang 2017). Cheng et al. (2018) fabricated super-hydrophobic cotton fabric using ZnO nanoparticles dispersed in alcoholic solutions. They incorporated the solutions on the fabric through spray-coating method and the fabrics exhibited a better oil/water separation (Cheng et al. 2018). Zahid et al. (2018) have fabricated cotton fabrics for photocatalytic antimicrobial and self-cleaning properties using a spray coating system. They coated the surface with Mn-doped  $\text{TiO}_2$  nanoparticles through an airbrush spray system. The treated materials exhibited better photocatalytic degradation of organic dyes and were resistant to several washing cycles while maintaining the physical properties (Zahid et al. 2018). Roy et al. (2020) developed super-hydrophobic self-cleaning-healing fabric by spray coating methods. They sprayed a simple coating solution of cellulose nanofibers on polyester and cotton fabrics using a pen gun and nitrogen



**Fig. 8** Process flow diagram of applying cellulose nanofibers (CNFs) on PET fabric through spray coating. Reproduced with permission (Roy et al. 2020). Copyright © 2020, Elsevier

as blowing gas (Fig. 8). For better bonding capability the fabrics were pre-treated in oxygen plasma and the obtained fabric surfaces showed a better super-hydrophobicity with high water contact angle (Roy et al. 2020). During spraying, the distance between the spray nozzle and the fabric and the blowing pressure were controlled. The method is quite facile as it is not specific to precise substrates as well as the method is also easy to apply to a large surface area. Furthermore, the method is fast, material efficient, easy to use, and produces films with the required properties (Steele et al. 2009; Men et al. 2011). Multilayer coating films can be produced by spraying the coating solutions for several times on the substrates. It is also possible to develop multiple layers of coatings with different coating solutions containing polycation and polyanion on the substrates similar to layer-by-layer assembly method (Yao and He 2014).

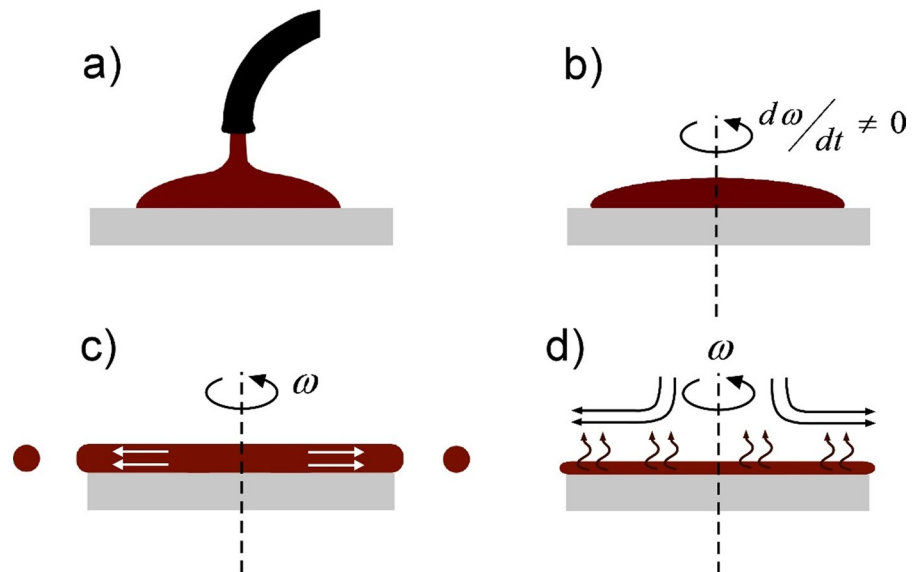
### Spin coating technique

The method of spin coating is a widely used technique for the electronics industry to coat the surface of the materials with thin films of less than 10 nm thickness. The method is less popular and very challenging in the field of coating textile materials. These are due to the high porosity of the textile materials as well as the hydrophilicity. However, recently, several studies have been performed on spin coating on

textile substrates with different materials. The method is becoming popular because of its simplicity and ease of use. Selectively, the method is very useful for coating the sample with a small area which makes it less practical in large scale production (Dissanayake et al. 2020; Lukong et al. 2022). The performance of the spin coating is dependent on some parameters such as rotational speed, type of materials, concentration of coating solution and binder, evaporation rate etc. (Danglad-Flores et al. 2018). The coating of substrates by the spin coating method involves some basic steps mentioned in Fig. 9. After the sample is placed on the rotating disc, a small amount of coating solution is dispensed on the center of the surface of the substrate. Due to the centrifugal force produced by the higher speed of rotation, the coating solvents spread over the surface, resulting in a thin film of coating. Finally, the coated materials are dried or cured at a certain temperature which evaporates the solvent and makes crosslinking of the coating paste with the substrate (Bornside et al. 1989; Tyona 2013; Heeravathi and Christy 2020).

Shaban et al. (2016) fabricated cotton fabric for photocatalytic self-cleaning textiles using ZnO nanoparticles through spin coating method. The ZnO nanoparticles coating solution was prepared using zinc acetate dihydrate as a precursor, 2-methoxyethanol as a solvent, and monoethanolamine as a stabilizer. The coating solution was applied on cotton fabric at 1100

**Fig. 9** Different “stages” of spin coating. **a** Dispensation, **b** Acceleration, **c** Flow dominated and **d** Evaporation dominated (Hellstrom 2007)



rpm for 60s following the evaporation of solvents and annealing. Multilayer ZnO NPs were obtained by coating with the nanoparticles for several times. The fabrics developed through this process exhibited a high degree of decomposition of organic dye (methyl orange) (Shaban et al. 2016). The research team also produced super-hydrophobic self-cleaning fabrics with antibacterial properties on a non-photocatalytic surface. The resultant fabric surface showed high water contact angle with antimicrobial properties. The team also investigated the effect of different parameters like concentration of precursor, pH, number of coating layers and doping ratios on structures, morphologies and water contact angle of the coated substrate (Shaban et al. 2018). Another study was carried out by Rilda et al. (2016) on the fabrication of nanoparticles of  $\text{TiO}_2$  and  $\text{SiO}_2$  on cotton textiles using spin-coating technique. The method involved the application of  $\text{TiO}_2$ : $\text{SiO}_2$  nanoparticle clusters on cotton fabric with acrylic crosslinking agent. Different clusters were formed by varying the molar composition of Ti and Si. The self-cleaning performance of the treated cotton was evaluated by the degradation of methylene blue dye (Rilda et al. 2016).

#### Chemical etching technique

For the generation of Super-hydrophobic surface, it is well known that two primary factors play important role; surface roughness and presence of low surface

energy materials (Saleh and Baig 2019). This required surface roughness can be produced on the textile surface without the use of external materials, such as nanoparticles and it is possible to produce roughness through surface modification using chemicals (Liu et al. 2016). This chemical surface modification process is known as chemical etching of the surface. The primary purpose of chemical etching is to produce protrusions and holes on fiber surface for the generation of micro- and nano-scale surface roughness. Applying low surface energy materials after the etching can produce a super-hydrophobic surface (Ganesh et al. 2011; Wei et al. 2020). The study also showed that chemical etching creates functional groups on the etched surface which is very effective for imparting low surface energy materials on the surface.

Xue et al. (2013) produced surface roughness on PET (polyethylene terephthalate) fabric through chemical etching technique. The etching of PET fabric was carried out using NaOH solution through soda-boiling or soda-decating process. The etching process introduced surface roughness as well as generated functional groups like hydroxyl groups ( $-\text{OH}$ ), carboxyl groups ( $-\text{COOH}$ ) etc. by breaking down the ester groups of PET. The treated or etched fabric was then diffused in fluoroalkyl silane, which acted as the low surface energy material. Fluoroalkyl silane compounds created covalent bonds with the surface through those generated functional groups. The developed product had high mechanical durability

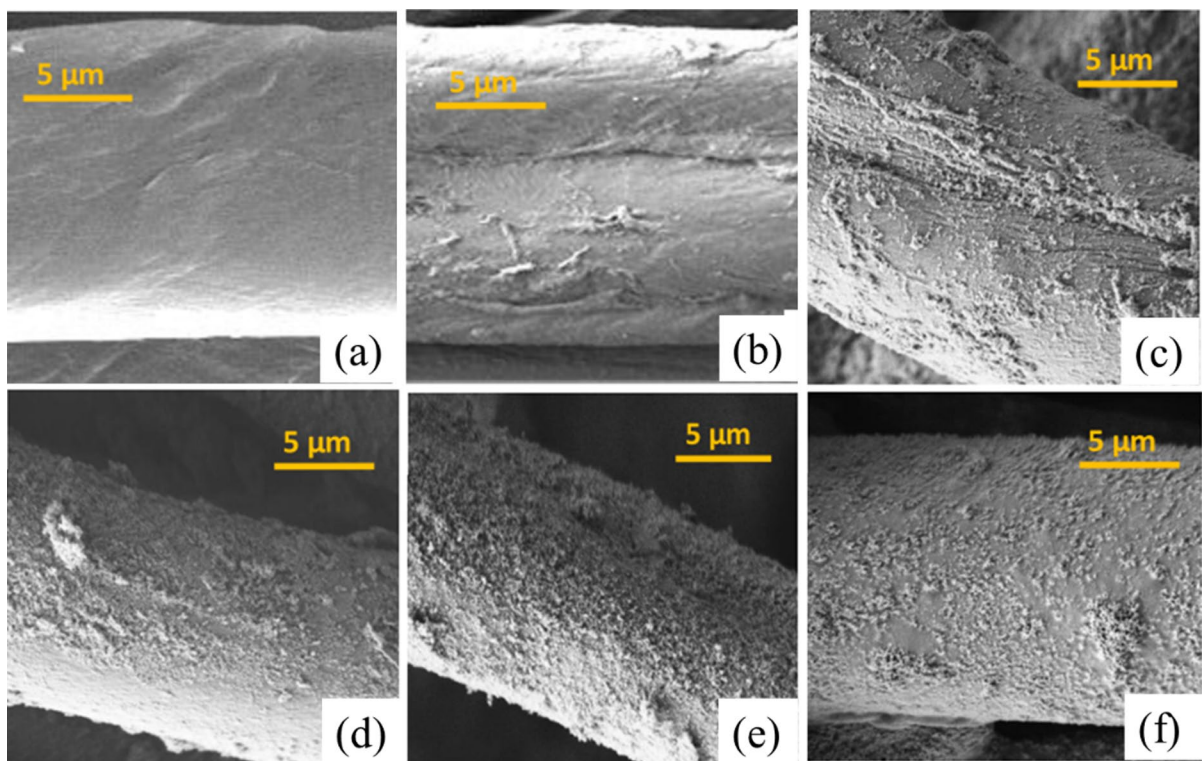


with super-hydrophobic self-cleaning surface (Xue et al. 2013). The researcher and his team also developed washable and wear resistant superhydrophobic self-cleaning surface following the same procedure with polydimethylsiloxane (PDMS) coating (Xue et al. 2014). A facile and fluorine free method was studied by Nguyen-Tri et al. (2019) to produce super-hydrophobic cotton fabric. The etching process was carried out with NaOH that increased the rugosity of the cotton as a result of extraction of low molecular weight materials and lignin. The induced functional groups helped to absorb  $\text{SiO}_2$  nanoparticles with tetraethyl orthosilicate (TEOS) which produced a super-hydrophobic self-cleaning cotton surface (Fig. 10) (Nguyen-Tri et al. 2019). Saleh et al. (2019) developed super-hydrophobicity on stainless steel woven fabrics for technical application with sulfuric acid treatment and applied silane compounds (Saleh and Baig 2019). Another study also reported that it is

also possible to etch the surface with enzyme (Cheng et al. 2019).

#### Lithographic patterning technique

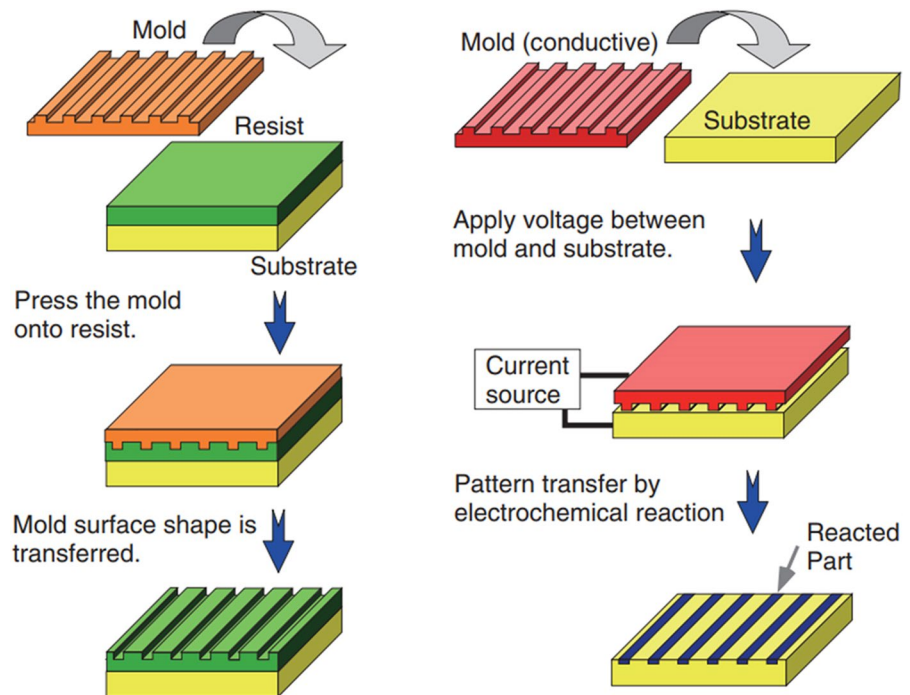
Lithographic patterning is described as one of the versatile and easy methods of creating a distinctive grade micro/nanostructure over a large surface area (Zhang et al. 2008). Lithography is basically a patterning technique in which a negative or positive impression of the design is made on a master surface and the master pattern is used as a template. The design is either used as a template or transferred to a substrate from the master (Fig. 11). Multiple copies can be made from a single master of the design. The method is similar to the production of stamp that is the design is first developed on a material like photoresist as template and then like inking the stamp on the substrate to produce the pattern (Roach et al. 2008). There are generally



**Fig. 10** SEM images of **a** untreated cotton surface, **b** chemical (NaOH) etched cotton surface and etched cotton sample with **c**  $\text{SiO}_2$  (8%)+TEOS (10%), **d**  $\text{SiO}_2$  (10%)+TEOS (10%),

**e**  $\text{SiO}_2$  (12%)+TEOS (10%) and **f**  $\text{SiO}_2$  (12%)+TEOS (15%) (Nguyen-Tri et al. 2019)

**Fig. 11** Typical nanoimprint (left) and nanoelectrode lithography (right) (Yokoo and Namatsu 2008)



two types of lithographic techniques as photolithography and soft lithography. Photolithography may be subdivided into several categories such as ultraviolet, X-ray, electron beam, etc. as well as laser or particle etching is also possible (Ganesh et al. 2011). There is another patterning method in nanotechnology which is nanosphere lithography. This technique involves the deposition of polystyrene or silica nanoparticles in a closed packed lattice array with controlled drying of the nanoparticles containing solutions. After modification of the surfaces, the aligned nanoparticles array generates super-hydrophobic surfaces (Kim 2008). Park et al. (2012) developed dual-triangular patterned hierarchical structures by simply combining microsphere lithography and reactive ion etching (RIE) and nanosphere lithography and RIE. Two-dimensional  $\text{SiO}_2$  microscale and nanoscale rods were first fabricated using polystyrene beads. The structure was then modified with low surface energy materials such as fluoroalkyl silane which exhibited super-hydrophobic properties (Park et al. 2012). Reports are also available about the patterning techniques of carbon nanotubes for developing

super-hydrophobic surfaces (Lau et al. 2003). Fernández et al. (2017) employed nanoimprint lithography (NIL) to create super-hydrophobic self-cleaning surfaces on silicon and polyethylene terephthalate (PET). The method is advantageous over other fabrication methods (Fernández et al. 2017). The advantages of lithographic patterning techniques include that the fabrication of the template is very easy and can be used several times and it is possible to design the surface of the materials with various designs. The main drawback of the method is that it requires a long molding cycle with high costs (Ghanashyam Krishna et al. 2013; Zhang et al. 2016). Lithographic patterning technique allows the precise control over the dimensions (width, height, and separation distances) and shape of the structure.



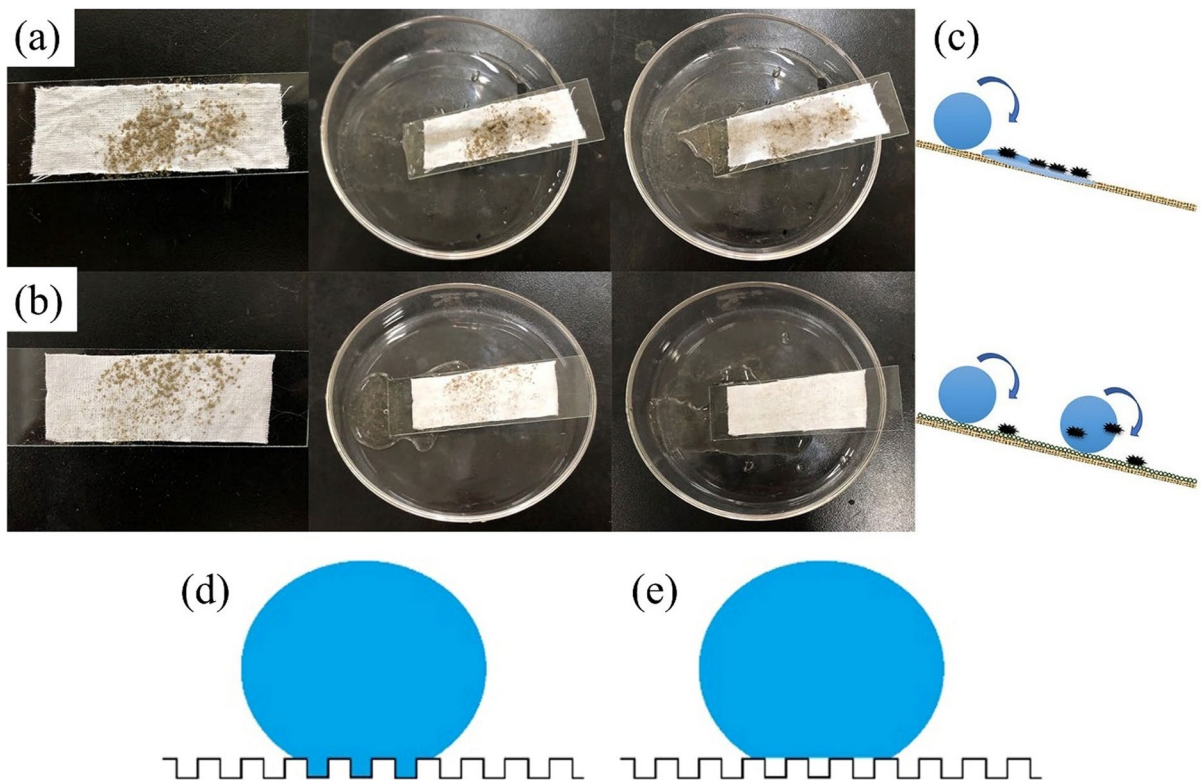
## Super-hydrophobic self-cleaning textiles

### Mechanism of super-hydrophobic self-cleaning activity

The mechanism of self-cleaning activity on materials surfaces follows two major phenomenon, that are the development of super-hydrophobic surfaces through hierarchical structures and application of photocatalyst on super-hydrophilic surfaces permission (Banerjee et al. 2015; Xu et al. 2016). The super-hydrophobic coated surfaces are capable of removing the impurities by forming near-spherical droplets of water which ultimately roll-off from the surface and remove the impurities. The photocatalysis method is based on the fabrication of surfaces that absorb and decompose organic matter (Nishimoto and Bhushan 2013).

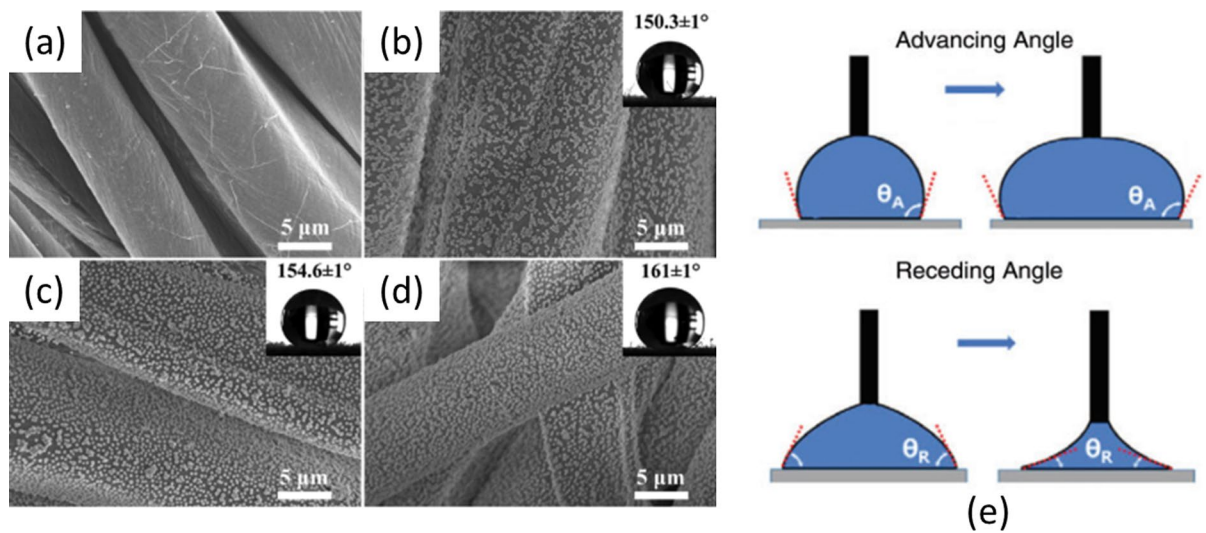
Super-hydrophobic self-cleaning surface finishing is adopted from the concept of ‘Lotus effect’

or ‘Butterfly wings’ or ‘Rice leaves’, which is based on the capability of cleaning itself by repelling water and dirt particles (Bixler and Bhushan 2012). Super-hydrophobic surfaces with high contact angle and low contact angle hysteresis show self-cleaning properties (Tung and Daoud 2011a; Bixler and Bhushan 2012). Generally, hydrophobic surfaces contain a water contact angle of more than  $90^\circ$ , but if a surface has to be super-hydrophobic, the water contact angle should be equal or greater than  $150^\circ$ . Researchers have engineered the technology of super-hydrophobicity by biomimicking the properties for functional finishing of materials for self-cleaning performance. Lotus leaves have two types of structure which affect their properties, micro-scale bumps and nano-scale whiskers. These intrinsic hierarchical structures are produced by convex cell papillae which are coupled with arbitrarily oriented waxy chemicals. Due to these structures with low contact angle hysteresis, the water



**Fig. 12** Self-cleaning process on **a** pristine cotton fabric (non-hydrophobic) surface, **b** PFOTES-TiO<sub>2</sub>@coated cotton fabric (superhydrophobic) surface and **c** their principle (Sheng et al.

2021), Behavior of water droplet on **d** Wenzel wetting model and **e** Cassie–Baxter wetting model (Darmanin and Guittard 2015)



**Fig. 13** SEM images of **a** pure cotton textiles **(b–d)** water contact angles of SiO<sub>2</sub>/PDMS coated cotton textiles. Reproduced with permission (Chen et al. 2021). Copyright © 2021,

American Chemical Society and **e** representation of advancing and receding angle. Reproduced with permission (Ko et al. 2015). Copyright © 2015, Elsevier

droplets bead up and roll off from the surface with the contaminants producing the self-cleaning functionality of Lotus leaves (Nosonovsky and Bhushan 2008; Bhushan et al. 2009; El-Khatib 2012; Saad et al. 2016b). Different research works have been

performed to generate nanostructure surface roughness on textile materials to mimic the natural lotus effect which have the physical self-cleaning properties (Xue et al. 2009; Bae et al. 2009). The super-hydrophobicity of substrates surface

**Table 2** Superhydrophobic modification of cotton with different nanoparticles

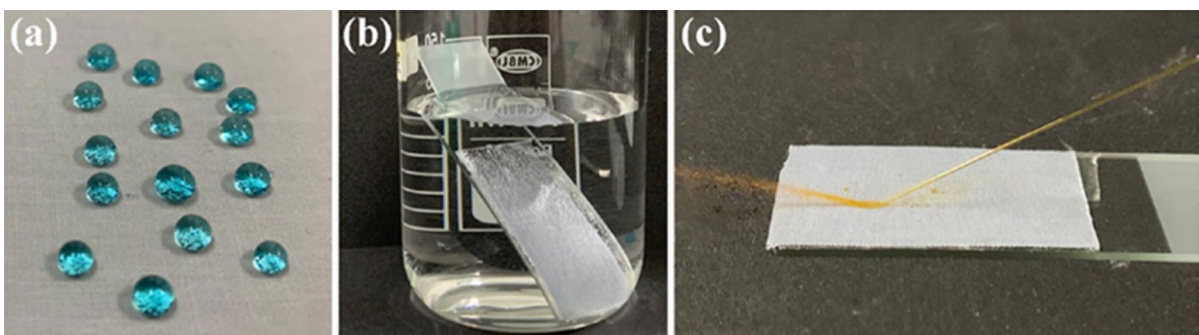
Nanoparticles	Application method (s)	Water contact angle	Wash durability	References
TiO <sub>2</sub> NPs	Dip coating	156.7°±1.9°		Pakdel et al. (2021)
	Pad-dry-cure	160°		Yang et al. (2019a)
	Spray coating	163°±2°		Sutar et al. (2020)
	Simple immersion	169°±2.1°	Up to 20 washes	Tudu et al. (2020)
SiO <sub>2</sub> NPs	Dip coating	151°–170°		Xue et al. (2009)
	Pad-dry-cure	156.5°	Up to 5 washes	Hao et al. (2010)
	Dip-pad-dry-cure	145°		Yu et al. (2007)
	Dip-pad-cure	151.9°		Xu et al. (2011a)
ZnO NPs	Dip coating	161°		Ghasemi et al. (2018)
	Dip-pad-dry	153°		(Boticas et al. (2019)
	Pad-dry-cure	152°	Up to 35 washes	Patil et al. (2019)
CNTs	Dip coating	154°		Li et al. (2010)
	Layer-by-layer assembly	165.94°±1.29°	Up to 100 washes	Xue et al. (2020)
Cellulose nanofibers	Spray coating	152°±3°	Up to 20–21 washes	Roy et al. (2020)
Ag NPs/silane	Two step dip coating	148°±2°	Up to 15 washes	Pal et al. (2022)
Ag NPs	Simple immersion	152°–154°	Up to 10 washes	Gao et al. (2021)

with hierarchical roughness can be explained by two possible wetting theories. When the liquid droplet is in contact with the surface and rests on it, two principles states can be appeared (Ensikat et al. 2011). The first theory is known as the Wenzel state, which suggests that, when a surface has no roughness, the liquid can wet the surface, and the contact angle increases with increasing surface roughness. These produce a homogeneous solid–liquid interface. The second theory is known as the Cassie–Baxter state, which suggests that the gaseous phase (or air) may entrap inside the cavities of the surface roughness. Thus, the liquid droplet creates a solid–air–liquid interface. It is investigated and found that, to be a self-cleaning surface, the surface must follow the Cassie–Baxter state (Bhushan et al. 2009; Fernández et al. 2017). Figure 12 indicates the self-cleaning process on non-hydrophobic and superhydrophobic cotton fabric surface and the behavior of water droplet generalized in Wenzel wetting model and Cassie–Baxter wetting model. Table 2 represents the use of different nanoparticles used for the development of super-hydrophobic self-cleaning cotton surface.

#### Assessment of super-hydrophobic self-cleaning surface

As the methods of constructing the self-cleaning textile materials follow two main phenomena: the super-hydrophobic approach and the photocatalytic approach. Therefore, the evaluation of the self-cleaning surface can also be done according to these two approaches.

For super-hydrophobic self-cleaning approach, the assessment of the self-cleaning performance is done by measuring the water contact angle (WCA) and sliding angle (SA) or roll-off angle of water droplet that falls on the surface. Water contact angle is basically greater than  $90^\circ$  in hydrophobic surface, but for being super-hydrophobic, the water contact angle should be greater than  $150^\circ$  (Tudu et al. 2020). The most common and simple method of determining the contact angle between liquid droplets and solid surfaces is through digital image processing and the images are then analyzed to measure the angle (Fig. 13a–d) (Eral et al. 2013). To determine the efficiency of super-hydrophobicity, the contact angle of water droplet is measured by Young–Laplace fitting method using Goniometer. For a liquid drop that beads up on homogeneous surface, the drop can assume to be axisymmetric, and the drop shape can be explained by the Young–Laplace equation also called Axisymmetric Drop Shape Analysis (ADSA). Although the method was limited to measuring the contact angle when the droplet is symmetric with visible apex (Rotenberg et al. 1983). Later, the method was improved by research to determine the contact angles for droplets with no visible apex and also for sliding droplets (Andersen and Taboryski 2017). The sliding or roll-off angle is measured when the droplet starts to slide which is known as critical angle (Joshi et al. 2012; Vasiljević et al. 2013). In this method, first, the liquid droplets are placed over the nanoparticles treated fabric surface. Contact angle hysteresis was developed by measuring the advancing and receding contact angles (Fig. 13e) (Abidi et al. 2012). The contact angle measured can explain the



**Fig. 14** Super-hydrophobic self-cleaning activity of nano-silica functionalized cotton fabric surface. Reproduced with permission (Chen et al. 2021). Copyright © 2021, American Chemical Society

super-hydrophobicity of the treated surface and the sliding angle explain the self-cleaning mechanism. A certain type of impurities (soil, dirt, carbon powder, dye, etc.) is placed on the surface, and then a water shower is employed. Due the super-hydrophobicity with high contact angle and very low sliding angle, the shower take away the impurities from the surface without wetting the surface (Cao et al. 2020).

### Nanoparticles used for super-hydrophobic self-cleaning textiles

#### Silica (SiO<sub>2</sub>) nanoparticles

Silicon dioxide nanoparticles, also known as ‘silica nanoparticles (SiO<sub>2</sub> NPs), are one of the most promising nanoparticles which can impart super-hydrophobicity hence self-cleaning properties to textile surfaces (Fig. 14). Nano-silica has some special properties like low toxicity, easy handling, surface functionality, thermal stability etc. which makes the particles a preferable choice for super-hydrophobic self-cleaning finishing (Athauda and Ozer 2012; Abou Elmaaty et al. 2021). Silica nanoparticles contain a huge amount of surface hydroxyl groups, due to which the nanoparticles can create a strong covalent bond with cotton textiles. These hydroxyl groups are responsible to produce hydrophilicity to textile materials. Thus, silica nanoparticles have to be modified before or after application with water repellent agents or cross-linkers. Additionally, the nanoparticles can produce surface roughness that is durable against washing. Furthermore, there are some kinds of silane compounds that can improve the functionality of silica nanoparticles (Bae et al. 2010; Roe et al. 2012; Riaz et al. 2019; Pal et al. 2021a; Chen et al. 2021).

Previously the super-hydrophobic surfaces were prepared using the fluorine containing materials like fluorinated silane groups which are often used as hydrophobic agents as they have less surface energy, are highly oleophobic, chemically resistant, and stable under temperature. But the fact is that, these compounds are toxic to human body because of the emission of fluorine-compounds (Zhang et al. 2018; Maia et al. 2022). Thus, researchers have investigated alternative silane compounds free

from fluorine which resulted in discovering different types of non-fluorinated silane hydrophobic compounds or hydrophobic modifier. Silica nanoparticles in combination with these multifunctional silane compounds can make super-hydrophobic self-cleaning surface with better durability (Roe et al. 2012; Janowicz et al. 2020).

The roughness of the nano-silica can be developed by creating coral-reef structure demonstrated by Anjum et al. (2020) and other researchers. The coral-reef-like fibrous structure of wrinkled nano-silica produce more hierarchical structure with better textured surface. These developed surface roughness exhibits more super-hydrophobic self-cleaning properties by minimizing the water/solid interface with higher water contact angle (Table 2) (Anjum et al. 2020; Yang et al. 2022). Apart from mimicking natural super-hydrophobic self-cleaning functionality, some research also studied the photocatalytic activity of nano-silica applied on materials surfaces. Due to the electronic properties and a very wide band gap energy, pure crystalline nano silica does not show any photocatalytic activity. But any structural defects if introduced, nano silica can exhibit photocatalysis to some extent like other transitional metal oxides and the self-cleaning activity to organic materials when exposed to radiation (Tarpani et al. 2016; Abou Elmaaty et al. 2021; Romolini et al. 2021).

#### Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) have obtained the interests of researchers due to their remarkable physical properties. CNTs exhibit metallic or semiconducting properties depending on their dimensions and structures which make them potential materials in the field of self-cleaning surface (Wei et al. 2001). The application of carbon nanotubes (CNTs) on textile substrates not only produces self-cleaning activity but also create sensory and photothermal properties due to its electro-conductive characteristics. It is known that the super-hydrophobic self-cleaning surfaces can be produced by the surface roughening similar to the lotus leaf surface on nature. By arranging the nanorods or nanowires vertically, this surface roughness can also be obtained. Carbon nanotubes when applied to textile surfaces with controlled assembling, construct the superhydrophobic nanoscale surface roughness (Xue



et al. 2020). Due to this hierarchical construction on the surface, the water contact angle can be increased to above  $150^\circ$  making it super-hydrophobic (Liu et al. 2007; Sethi et al. 2008). Different studies also describe that fluorinated CNTs exhibit better super-hydrophobicity and self-cleaning properties compared to pristine CNTs without affecting the surface (Hsieh et al. 2008).

In some other studies, it is also understood that the CNTs containing composite structures also produce functional properties with mechanical durability. Attempts to combine wax from lotus leaves with CNTs are also taken to produce self-cleaning surface (Jung and Bhushan 2009). Ma et al. (2018) produced a porous hydrophobic polymer composite which had self-cleaning properties. In his study, he employed poly(vinylidene fluoride) as a matrix, having a low surface energy and a hybrid structure of MWCNTs/graphene as the filler. These composite structures produced rough surface by creating multi-scaled raspy structures (Ma et al. 2018). Another research was done by Guo et al. (2017) to produce super-hydrophobic self-cleaning surface which reported different functional properties of CNTs composites containing poly(dimethyl siloxane) (PDMS) and poly(dimethyl diallyl ammonium chloride) (PDDA) on polyethylene fabric (Guo et al. 2017). From Table 2, it is seen that the water contact angle, hence super-hydrophobicity of cotton materials increased due to the fabrication of CNTs.

#### Copper (Cu) and copper oxide (CuO) nanoparticles

In previous many research, Copper showed its wide range of significance in the field of electrical and thermal conductivity with satisfactory antibacterial property. Research has also been done to investigate the self-cleaning mechanism of copper nanoparticles (CuNPs) (Suryaprabha and Sethuraman 2017). Application of CuNPs on materials surface produces surface roughness which exhibits super-hydrophobic self-cleaning characteristics. The rough surface structures with extreme water contact angle are responsible for the cleaning of impurities such as dirt with the water droplet when they roll off of the surface (Sasmal et al. 2014). The super-hydrophobic surface requires both the micro and

nanoscale bumps and most of the textile materials have microscale roughness due to microfiber on their structure. Therefore, it is essential to introduce some nanoscale roughness. Different researches have been done to impart nano-roughness on the textile surface by applying CuNPs (Hong et al. 2018; Han and Min 2020). However, CuNPs have not attracted so much attention in case of superhydrophobic self-cleaning surface preparation. It is basically used as dopant with other photocatalytic nanoparticles like  $\text{TiO}_2$  or ZnO to improve their functionality (Fu et al. 2011; Harya et al. 2018). Rather, the oxide form of copper, which is copper oxide (CuO), is being studied for the same purpose of self-cleaning. CuO nanoparticles (CuONPs) with large surface area exhibit strong physicochemical characteristics in a variety of applications. As it is eco-friendly, less toxic in nature, and has good electrical properties and is cost-effective, CuONPs are widely used in various sectors, including the removal of organic pollutants with photocatalysis (Xu et al. 2007; Perelshtein et al. 2009). CuO nanoparticles roughen the surface of fabric generating micro/nano structure which ultimately produce hydrophobic surface. Further treatment with low surface energy materials (silane compounds) converts the hydrophobic fabric into super-hydrophobic fabric (Agrawal et al. 2020; Pal et al. 2021b).

#### Titanium dioxide ( $\text{TiO}_2$ ) nanoparticles

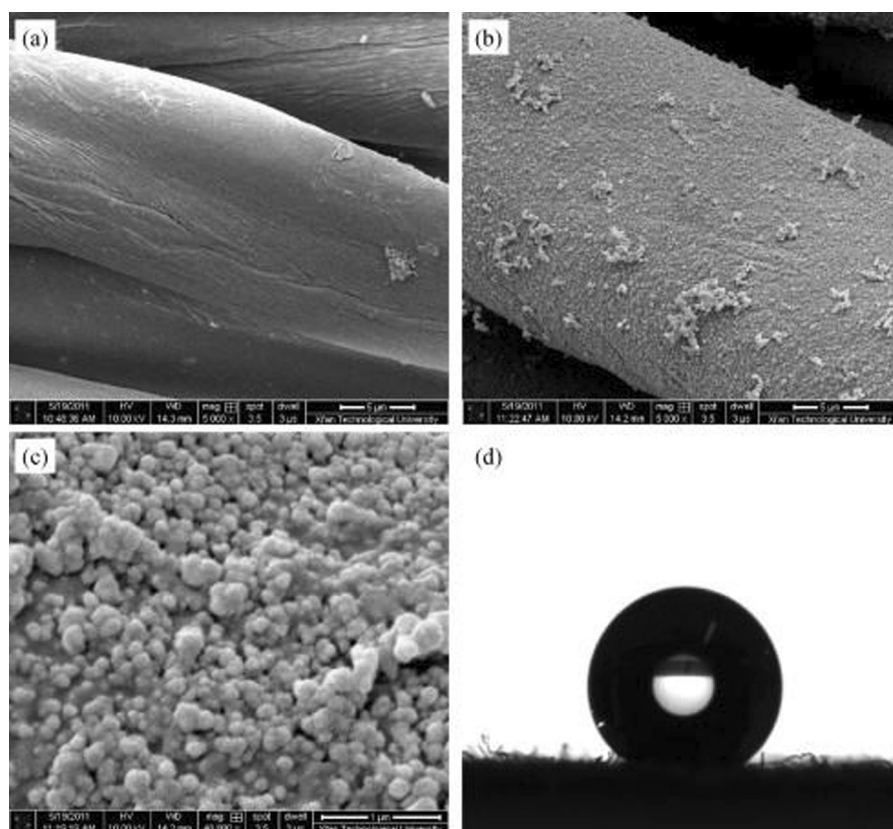
Titanium dioxide is generally famous for its significant photocatalytic properties. Though  $\text{TiO}_2$  exhibits strong photocatalytic activity, the nanoparticles were also used for the development of superhydrophobic self-cleaning surfaces as they can produce nano-roughness on surfaces (Table 2). Additionally, for developing super-hydrophobicity by imparting surface roughness, it is recommended to decrease the surface tension of the materials with the use of some low surface energy materials (Pakdel et al. 2021). Yang et al. (2019a, 2019b) modified the surface of cotton fabric to develop super-hydrophobicity by using  $\text{TiO}_2$  nanoparticles. The researchers employed sol-gel technology for coating the fabric surface which produces pure anatase form of  $\text{TiO}_2$ . The coated surface was then modified with (Heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane

which contains low energy hydrophobic groups that can actually enhance the super-hydrophobic properties of the treated fabric surfaces (Yang et al. 2019a). Tudu et al. (2020) modified the cotton fabric with  $\text{TiO}_2$  nanoparticles through dip coating process. The team applied perfluorodecyltriethoxysilane (PFDTs) in various amount to stabilize the  $\text{TiO}_2$  nanoparticles on cotton fabric and at optimum concentration of PFDTs, maximum functionality of  $\text{TiO}_2$  was obtained with higher water contact angle. Several other properties like UV blocking and antimicrobial properties were also obtained (Tudu et al. 2020). Pakdel et al. (2021) investigated the super-hydrophobicity for the removal of oily contaminants by using N-doped flower like  $\text{TiO}_2$  nanoparticles on cotton fabrics. The removal of oily substances is one of the issues for super-hydrophobic surfaces. The researchers applied fluorine free PDMS polymer as low surface energy materials which increase the removal of oily contaminants (Pakdel et al. 2021).

### Zinc oxide (ZnO) nanoparticles

Among different inorganic nanomaterials, ZnO is used widely in areas like photocatalysis, water splitting, UV protection, supercapacitor etc. Due to its low-cost, bio-compatibility in nature and better stability, it is very much efficient in developing super-hydrophobic surface by producing hierarchical surface roughness (Zhu et al. 2017b). The surface roughness of nanoparticles treated fabric surface can be modified by varying the structures and chemical reaction. Basically, ZnO nanoparticles are applied as one-dimensional nanowires or nanowhiskers with various height and pitch for producing surface roughness (Mardosaitė et al. 2021). Yang et al. (2019a, 2019b) developed super-hydrophobic multifunctional cotton fabrics by using ZnO nanoparticles in combination with dodecafluoroheptyl methacrylate (DFMA) as low surface energy materials through low cost thiol-ene click reaction which has the capability of self-cleaning and oil-water separation (Yang et al. 2019b). There are various fabrication methods that

**Fig. 15** SEM images of **a** cotton fiber, **b** silver treated cotton, **c** magnifying image of **a**, **d** water droplet on the silver and HDTMS treated cotton. Reproduced with permission textiles (Xue et al. 2012). Copyright © 2012, Elsevier





can be applied to produce super-hydrophobic cotton with higher water contact angle and good fastness property (Table 2).

### Silver (Ag) nanoparticles

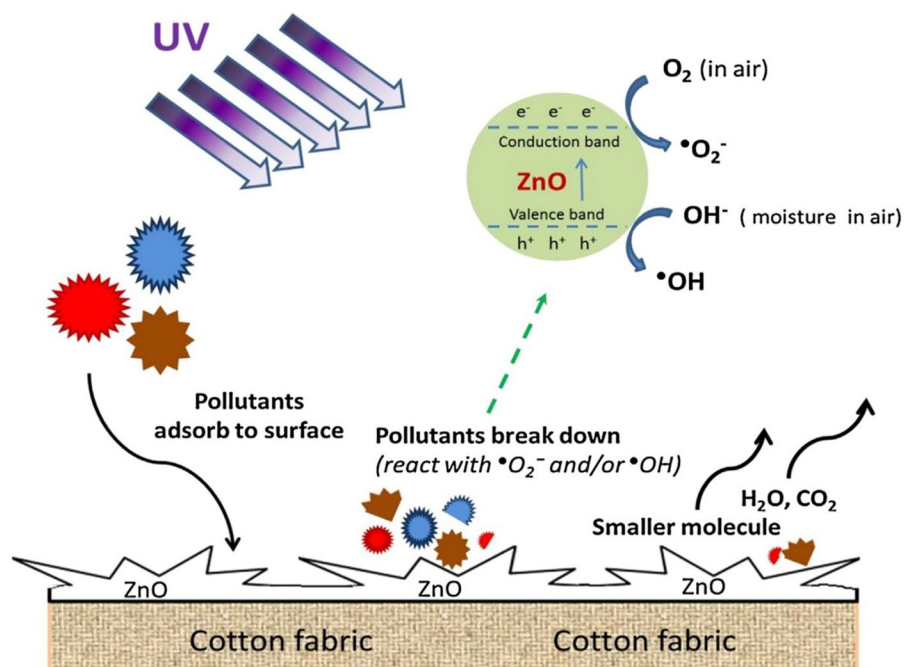
AgNPs can be applied to textile materials for creating the super-hydrophobic surface by creating the surface roughness which follows the properties of lotus effect (Fig. 15). Due to this surface structure, the inorganic dust and dirt particles can be removed along with the rolling bead of water droplets (Xue et al. 2012; Shen et al. 2012). Though the chemical binding capability of AgNPs with textiles fibers like cellulosic polymer chain is very difficult resulting unsatisfactory durability of the nanoparticles. Previously, chemical binders were used to fix AgNPs with textiles, but they produce unusual effects to the human body. This problem can be overcome by introducing plasma treatment through oxidation and engraving techniques, which can generate polar oxygen bearing components, ultimately improving binding (Karahan and Özdoğan 2008; Wang et al. 2017).

### Photocatalytic self-cleaning textiles

#### Mechanism of photocatalytic self-cleaning activity

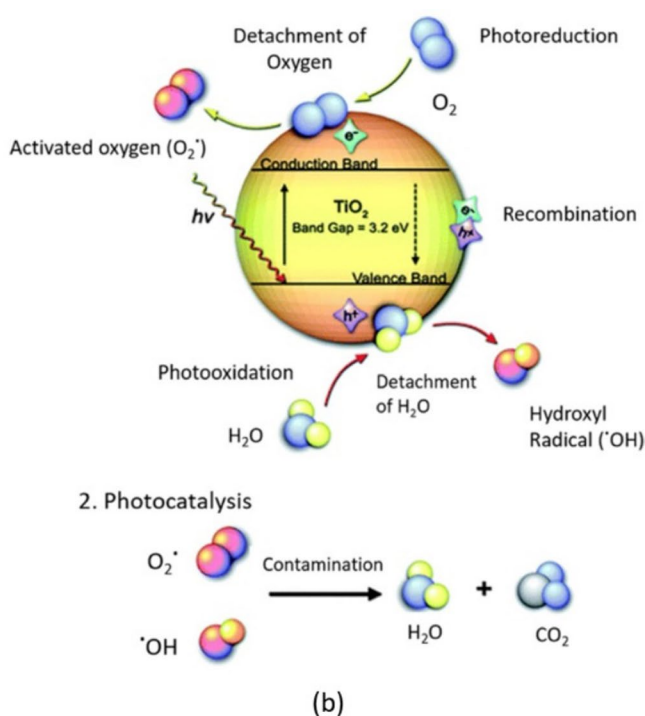
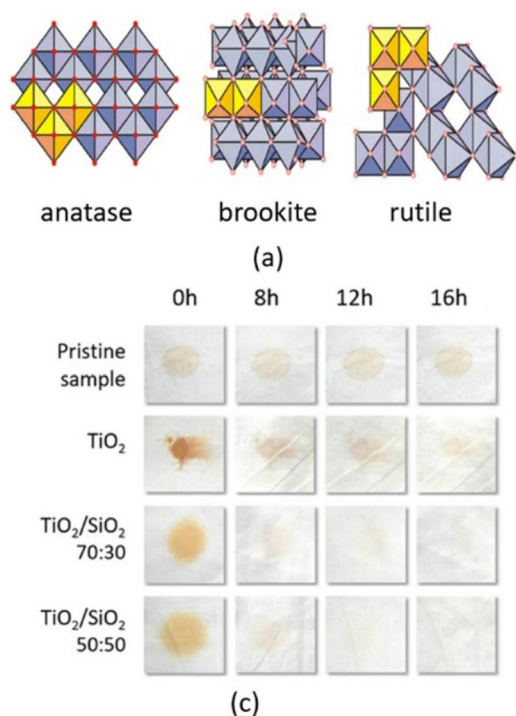
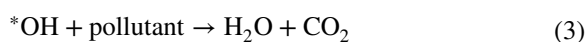
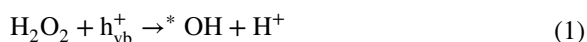
Modern approach of introducing self-cleaning functionality to the hydrophilic surface is by applying photocatalysts on the surface of the materials. Photocatalysts are some kinds of photoactive agent that produce catalytic purifications on substrates (Zhang et al. 2012). The mechanism of photocatalysis is a collation of photochemistry with catalysis process. Catalysis is a process in which the substance, known as the catalyst, can alter the rate of the chemical reaction by decreasing the activation energy. However, the catalysts do not take part directly in the chemical reaction and remain unchanged at the end. Thus, photocatalysis is a catalytic process that requires light energy to catalyze the reaction (Serpone 2000). Semiconductor nanoparticles provide this type of finishing to textile materials that produce a self-cleaning surface that can be cleaned by itself. The process follows an advance oxidation process which generates reactive oxygen species (ROS), that accelerate the photoreaction in the presence of a catalyst and thus, resulting the separation of charge (Aarthi et al. 2007). When the photocatalyst coated surface is exposed to light energy, the photon energy excites the electrons

**Fig. 16** Mechanism of photocatalysis (ZnO) on cotton fabric when exposed to UV radiation. Reproduced with permission (Tran Thi and Lee 2017) Copyright © 2017, Elsevier



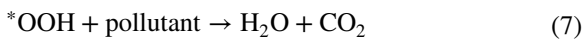
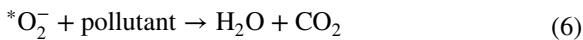
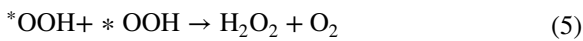
of the valence band. Due to this excitation, there is a transfer of electron from valence band to conduction band of the photocatalyst creating a hole in the valence band. Photocatalysis is achieved as a result of the generation of this electron–hole combination. The energy of the radiation should be equal to or greater than the band gap energy of the catalyst to excite the electrons (Fujishima and Zhang 2006). In presence of air and moisture in the air, the activated photocatalysts generate reactive oxygen species including super oxide anion ( $O_2^-$ ), hydrogen peroxide ( $H_2O_2$ ), singlet oxygen ( $^1O_2$ ), hydroxyl radicals ( $\cdot OH$ ) and other chemical species (Huang et al. 2012). The holes remaining in the valence band can generate hydroxyl radicals by reacting with absorbed water molecules. Hydroxyl radicals are strong oxidizing agents that can outbreak organic materials like contaminants and microorganisms and decompose them into carbon dioxide and water. The electron on the conduction band can react with the dissolved oxygen species and form super oxide anions. The super oxide ions are responsible for degrading the organic stains

(Daoud et al. 2005; Kiwi and Pulgarin 2010; Banerjee et al. 2014). Generally, these electron–hole pairs perform successive oxidation and reduction reaction with organic materials like microorganism or stains (Fig. 16). The oxidation occurs when the redox level of organic materials is greater than the valence band and reduction occurs when the redox level is lower than the conduction band (Saravanan et al. 2017b; Ameta et al. 2018). Following Reactions (1–7) represents the chemistry behind the photocatalytic degradation process of organic stains and pollutants which produce  $CO_2$  and  $H_2O$  (Pakdel et al. 2021).



**Fig. 17** **a** Three major crystalline forms of TiO<sub>2</sub> nanoparticles. Reproduced with permission (Khataee and Kasiri 2010). Copyright © 2010, Elsevier; **b** photocatalytic self-cleaning mechanism of TiO<sub>2</sub> nanoparticles. Reproduced with permis-

sion (Pakdel et al. 2020). Copyright © 2020, Elsevier and **c** Self-cleaning mechanism of cotton fabric surface coated with TiO<sub>2</sub> and TiO<sub>2</sub>/SiO<sub>2</sub> nanoparticles. Reproduced with permission (Pakdel and Daoud 2013). Copyright © 2013, Elsevier



### Assessment of photocatalytic self-cleaning surface

Photocatalytic self-cleaning surfaces follow the photodegradation of organic stains and compounds to clean the surface. Photocatalytic self-cleaning activities of the treated textile materials are assessed by the decrease in the concentration of the stains. To assess the performance, first the nanoparticles treated textile samples (dried) have to be stained with organic dyes [Methyl Orange (Tan et al. 2013), Methylene Blue (Rehan et al. 2013), Methylene Green (Lam et al. 2021), Malachite Green (Sayilkan et al. 2008), Rhodamine B (Ahmad and Kan 2017) etc.] and/or organic stains [red wine (Mejía et al. 2009), coffee stain (Yuzer et al. 2022), tea stain (Kumbhakar et al. 2018), curry stain (Scacchetti et al. 2017) etc.]. The stained samples were then exposed to solar radiation or UV radiation for certain hours. After certain time the color or stains are started to degrade and some hours later the stains or color will be degraded completely if the efficiency of the nanoparticles is very good (Fig. 17c). To determine and calculate the degradation of stains and colors, Kubelka-Munk theory (Ahmad et al. 2019) is to be used which is based on the reflectance of light of a certain wavelength from colored surface (fabric, paper, plastic, metal etc.). The term  $K/S$  is used for the measurement of the colored surface, and the value is measured using a spectrophotometer. Comparison of the  $K/S$  value between exposed and unexposed samples is recorded, and percentage (%) decrease in the values are calculated using Eq. (8) (Gupta et al. 2007; Jeong and Lee 2019).

$$\% \text{ decrease in } K/S = \frac{(K/S) \text{ of unexposed sample} - (K/S) \text{ of exposed sample}}{(K/S) \text{ of unexposed sample}} \times 100 \quad (8)$$

According to Kubelka-Munk theory, the  $K/S$  is determined by Eq. (9) (Alcaraz de la Osa et al. 2020),

$$K/S = \frac{(1 - R)^2}{2R} \quad (9)$$

where  $K$  is the absorption coefficient,  $S$  is the scattering coefficient,  $R$  is the percentage (%) reflectance of dyed sample at  $\lambda_{\max}$  and  $\lambda_{\max}$  is the wavelength at which the aqueous solution of color shows the maximum absorption. The general concept is that, with increasing color concentration, the  $K/S$  will increase linearly, and with decreasing color concentration, the  $K/S$  decrease. Thus, the theory is used for assessing the photocatalytic self-cleaning performance (Moafi et al. 2011). The evaluation of photocatalytic degradation of stained samples can also be done by calculating the color differences ( $\Delta E$ ) between non-irradiated and irradiated samples through spectrophotometer following Eq. (10).

$$\Delta E = (\Delta L^*{}^2 + \Delta a^*{}^2 + \Delta b^*{}^2)^{1/2} \quad (10)$$

here  $\Delta E$  represents the color differences before and after radiation,  $L^*$  represents lightness,  $a^*$  represents redness-greenness and  $b^*$  represents yellowness-blueness (Abo El-Ola et al. 2021). Another method is the visual assessment which means to assess the degradation of color/stain with open eye or comparing the photographs taken after a certain time interval (Zhu et al. 2017a).

### Nanoparticles used for photocatalytic self-cleaning textiles

#### Titanium dioxide (TiO<sub>2</sub>) nanoparticles

Previous studies showed that among all the photocatalysts, titanium dioxide exhibits better chemical stability, low toxicity, relatively low production cost and better oxidizing capability compared to other photocatalysts. It also does not produce any secondary pollutants after application (Wang et al. 2015). Titanium dioxide is a semiconductor material having large

band gap energy between valence band (low energy state) and conduction band (high energy state) and have polymorphic structure which has basically three

forms according to its crystalline structure: rutile, anatase and brookite (Fig. 17a). First, the rutile form, which is mostly composed of amorphous regions and is the stable form over the other two forms. The second one is the anatase form, which contains most of the crystalline region (Boujday et al. 2004; Paul et al. 2010) and the brookite form also contains a crystalline region which is produced as a by-product when the anatase form is synthesized. Both anatase and brookite forms are metastable and can be converted to rutile form under high heat (Allen et al. 2018). The anatase form is more photoactive than the rutile form (Kaihong Qi et al. 2011). Due to the great effectiveness of the titanium dioxide nanoparticle, it is the most widely used photocatalyst in the field of self-cleaning activity on super-hydrophilic surfaces. Nanoparticles of  $\text{TiO}_2$  exhibit strong photocatalytic reactivity when exposed to UV radiation (wavelength < 390 nm). It is extremely capable of destroying organic substances and organic stains due to its strong oxidative potential and chemical stability (Fig. 17b) (Shahid-ul-Islam et al. 2017; Romagnoli et al. 2020). Several investigations have been conducted to evaluate the self-cleaning functionality of  $\text{TiO}_2$  nanoparticles applied on textile materials. Also there are several studies that have shown the self-cleaning activity of cotton treated with nano  $\text{TiO}_2$  is very capable of destroying organic dyes like methyl orange, methylene blue etc. and organic stains produced from coffee, tea, red wine, curry, fruit juice or ketchup etc. (Kaihong Qi et al. 2011; Palamutcu et al. 2011; Mihailović et al. 2011; Scacchetti et al. 2017; RBSD et al. 2018). Different application methods for developing photocatalytic self-cleaning cotton surfaces are also summarized in Table 2 for degradation of different colorants. Although  $\text{TiO}_2$  nanoparticles are very effective in self-cleaning, excessive use of these nanoparticles can have a harmful effect on human health (Baranowska-Wójcik et al. 2020). Other drawbacks for nano  $\text{TiO}_2$  are its low photo efficiency as the rate of the combination of electron–hole is high and the second one is the large band gap energy (3.2 eV). The electron–hole recombination happened within  $10^{-9}$  s, while the photocatalysis takes place within  $10^{-8}$  to  $10^{-3}$  s. This recombination of electron–hole ultimately reduces the reactivity of the nanoparticles. Therefore, doping with metal ions and nonmetallic elements is introduced to improve

the effectivity of photocatalysis (Bingham and Daoud 2011; Sher Shah et al. 2012; Dumitrescu et al. 2020).

#### Zinc oxide (ZnO) nanoparticles

ZnO nanoparticles are another effective semiconductor photocatalyst after  $\text{TiO}_2$  nanoparticles, which have gained much attention due to their high photocatalytic activity, chemical stability, less toxicity, electrical and electronic, optical and antibacterial properties. Because of these features, the material is important and widely used in medical and energy sectors. It is also capable of degrading organic pollutants like stains and microorganisms (Fig. 3). The photocatalytic activity of the ZnO nanoparticle is almost similar to the photocatalytic activity of  $\text{TiO}_2$  nanoparticles (Çakır et al. 2012; Karthik et al. 2017; Irfan et al. 2022). Major advantage of using ZnO nanoparticles as compared with  $\text{TiO}_2$  nanoparticles is its higher band gap energy (3.37 eV) which ultimately allows it to absorb a wide spectrum of UV radiation up to 420 nm (Behnajady et al. 2006). Thus, some researchers also describe ZnO nanoparticles to be more effective than others (Diaa and Hassabo 2022). There are various methods for the synthesis of ZnO nanoparticles including sol–gel methods, hydrothermal processes, chemical vapor depositions, etc. among which the sol–gel synthesis method is more effective. Some recent studies by Zayed et al. (2021) as well as other research describe the green synthesis process for ZnO nanoparticles using a biocatalyst extracted from natural sources (Karthik et al. 2017; Saha et al. 2018; Zayed et al. 2021; Irfan et al. 2022). There are several examples of using ZnO nanoparticles for developing photocatalytic self-cleaning cotton through different processes (Table 3).

#### Stannic oxide ( $\text{SnO}_2$ ) nanoparticles

Among metal oxide semiconductors, stannic oxide ( $\text{SnO}_2$ ) or tin oxide reveals a lot of interest because of its strong chemical and physical properties. Studies found that, the stannic oxide is a n-type (oxygen-deficient) semiconductor with a tetragonal crystal structure (Patil et al. 2012). The nanoparticles having particle structure, chemical structure and band gap energy which is comparable with titanium dioxide nanoparticles; the commonly used metal oxide

**Table 3** Photocatalytic self-cleaning functionality of cellulosic materials (specially cotton) with different nanoparticles

Photocatalysts	Dopants	Application method (s)	Materials	Colorant/stain	Wash durability	References
TiO <sub>2</sub> NPs	Nitrogen	Dip coating	Cotton woven fabric	Food stain & Rhodamine B		Pakdel et al. (2021)
	Manganese	Spray coating	Cotton woven fabric (bleached)	Methylene blue	Up to 10 washes	Zahid et al. (2018)
	Copper	Dip coating	Cotton fabric	Methylene blue, Coffee stain		Harya et al. (2018); Yuzer et al. (2022)
	Iron-Nitrogen	Dip coating	Cotton knit fabric	Methylene blue & coffee stain		Stan et al. (2016)
		Dip coating	Cotton woven fabric (bleached + OBA treated)	Commercial tea stain		Palamutcu et al. (2011)
		Pad-dry-cure	Cotton fabric	Orange II	Up to 10 washes	Kale et al. (2016)
		Pad-dry-cure	Cotton fabric	Tea, juice, coffee, cola, milk & soybean oil.		Yang et al. (2019a)
ZnO NPs		Dip-pad-dry-cure	Cotton fabric	Methyl orange		Wu et al. (2009)
		Pad-dry-cure	Cotton fabric	Coffee stain	Up to 10 washes	Butola et al. (2018)
		Dip-pad-dry-cure	Cotton woven fabric	Methylene blue	Up to 10 washes	Zhu et al. (2017a)
SnO <sub>2</sub> / TiO <sub>2</sub> nanomixture		sol-gel	Cotton fiber	Methylene blue		Moafi et al. (2011)
		Pad-dry-cure	Cotton fabric	Coffee stain	Up to 15 washes	Pillai and Sundaramoorthy (2022)
Ag/ TiO <sub>2</sub> nano-composite		Pad-dry-cure	Viscose fabric	Methylthioninium chloride	Up to 10 washes	El-Hamshary et al. (2021)
		Pad-dry-cure	Plain woven cotton fabric	Methylene blue		Hebeish et al. (2013)
Au/TiO <sub>2</sub> nano-composite		Sol-gel	Cotton fiber	Methylene blue		Uddin et al. (2008)
TiO <sub>2</sub> /SiO <sub>2</sub> /Chitosan nanocomposite		Dip-spin-coating	Cotton fabric	Rhodamine B		Rilda et al. (2021)
TiO <sub>2</sub> /poly-acrylate hybrids		Dip-pad-dry	Cotton fabric	Grape syrup		Jiang et al. (2011)

nanoparticles. The band gap energy for SnO<sub>2</sub> is between 3.6 and 4.0 eV (Ramanathan et al. 2012; Patil et al. 2012; Elango and Roopan 2016). There are various crystalline structures of the SnO<sub>2</sub> nanoparticles among which the rutile structure plays important role in application. The nanoparticles have large surface area, higher thermal conductivity and sensitivity while it has no negative health issues as it is absorbed poorly by the human body (Nipa et al. 2022). The

cleaning mechanism of SnO<sub>2</sub> follows the photocatalysis process exhibit by the metal oxide semiconductors. In case of SnO<sub>2</sub> nanoparticles, due to the reduction of band gap energy from the standard value, defects in the crystal structure are created and for this the electron jumps from the valence band creating oxygen vacancies. The defects also produce charge carriers which are responsible for reducing the electron-hole recombination and generate free radicals.



Further photocatalytic reaction is carried out by this generated free radicals (Esmaelzadeh Kandjani et al. 2010; Diallo et al. 2016; Nipa et al. 2022).

Though the nanoparticle is very effective in photocatalysis, due to the random production of  $\text{Sn}^{2+}$  ions or even the formation of SnO, it is difficult to apply in pure form for functional finishing. Rather, it is used as a nanocomposite with other metal oxide semiconductors such as  $\text{TiO}_2$ , ZnO, etc. (Esmaelzadeh Kandjani et al. 2010; Ramanathan and Murali 2022).  $\text{SnO}_2$  nanoparticles have a great ability of doping with many dopants' materials like iron, graphene, antimony, copper, zinc, silicon, etc. When the nanoparticles are doped with suitable dopants, the various properties of the nanoparticles can be improved to a great extent, which include optical, structural, chemical, compositional, electrical, and electrochemical properties. This is due to the presence of a large oxygen deficiency (Sivakumar and Manikandan 2019; Sreekar Reddy et al. 2019; Prabhu et al. 2022). Another research also concludes that, by adding some kind of co-catalyst can increase the efficiency of the nanoparticles. Addition of co-catalyst can support the process of oxidation and reduction effectively and utilize the light energy for effective charge carrier separation (Shalini et al. 2022). In one of the research papers in this field, the photocatalysis of  $\text{SnO}_2$  is experimented using different coloring materials where the photodecomposition of Methyl Orange, Methylene Blue, Rhodamine B and textile dyes were investigated. Due to the higher band gap energy, the nanoparticles can effectively decompose the coloring materials easily. It is also found that, the increase in concentration and particle size can reduce the decomposition time and the percentage of decomposition is also increased (Ramanathan and Murali 2022).

### Silver (Ag) nanoparticles

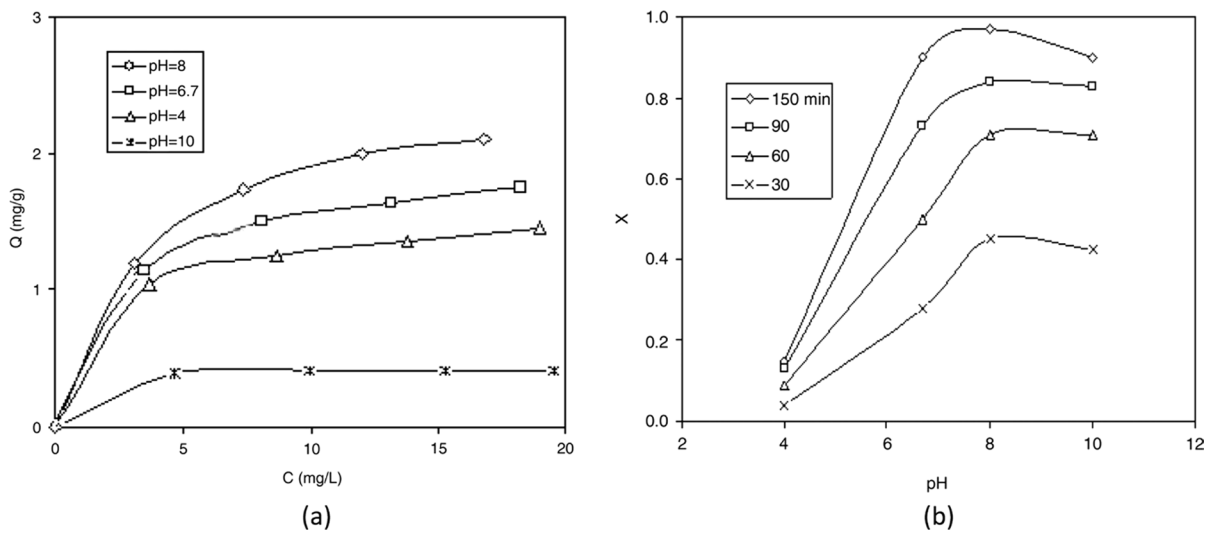
Silver nanoparticles (AgNPs) are well known for their strong antimicrobial properties. The nanoparticles can easily destroy the pathogenic microorganisms through attacking the outer membrane of the lipopolysaccharides, which damage the DNA of the organism releasing the  $\text{Ag}^+$  ion (Hillyer et al. 2020; El-Naggar et al. 2021). Apart from various functional properties of AgNPs like antimicrobial, electrical conductivity, UV-blocking, coloration properties, the nanoparticles also exhibit photocatalysis which is

responsible for developing self-cleaning surface (Gao et al. 2021). Due to its high surface area-to-volume ratio, the nanoparticles are very effective in degradation of dyes and stains. Researchers conducted studies on the photocatalytic degradation of Methylene Blue dyes using AgNPs applied on plasma-treated cotton. These AgNPs loaded textiles showed strong photocatalytic degradation properties. The photocatalytic properties of AgNPs were improved due to the change in optical response to the radiation (Wang et al. 2017; Atta and Abomelka 2021). Other studies also revealed that the nanoparticles are very efficient in photocatalytic decomposition of many organic dyes like Congo red, methyl orange etc. Photocatalytic activity has also been described to increase with increased concentration of nanoparticles and the duration of exposure time (Saravanan et al. 2017a; Chand et al. 2021). It is reported that, the mechanism of photocatalytic activity of AgNPs are not so similar to that of the metal oxide semiconductors like  $\text{TiO}_2$ , ZnO etc. Rather, its photocatalytic activity is produced due to which is called plasmon resonance (Zhou et al. 2012). Noble metal nanoparticles when get excited because of the exposure in certain range of wavelength, the freed electrons can produce plasmon oscillation. When the frequency of the exposed light is equal to the oscillation, the light absorption capability of metal enhances that is known as surface plasmon resonance. This plasmon energy is responsible for the photocatalytic activity of metal nanoparticles and thus the organic dyes can be easily degraded. Plasmonic photocatalysts are also used to enhance the photocatalytic activity of other metal oxide nanoparticles as a dopant (Awazu et al. 2008; Xu et al. 2011b, 2013; Zhou et al. 2012).

### Nanocomposites and nano-hybrids

Above all these nanoparticles, recently researchers are also working on nanocomposites and nano-hybrid structures to obtain better and more durable self-cleaning surfaces. Nanoparticles doped with another nanoparticles ( $\text{TiO}_2/\text{ZnO}$ ,  $\text{ZnO}/\text{SiO}_2$ ,  $\text{TiO}_2/\text{SiO}_2$ ) or metals ions or even with the grafting of non-metals (Carbon, Nitrogen, Sulphur) are some examples. Pakdel et al. (2022) studied the self-cleaning functionality of  $\text{TiO}_2$  on wool fabric doped with noble metals ( $\text{TiO}_2/\text{Pt}$ ,  $\text{TiO}_2/\text{Au}$ ,  $\text{TiO}_2/\text{Ag}$ ) under different light sources and found that incorporating the noble metals





**Fig. 18** Effects of pH of the solution on **a** adsorption isotherm of m-cresol and **b** degradation of m-cresol purple on ZnO treated surface (Khezrianjoo and Revanasiddappa 2016)

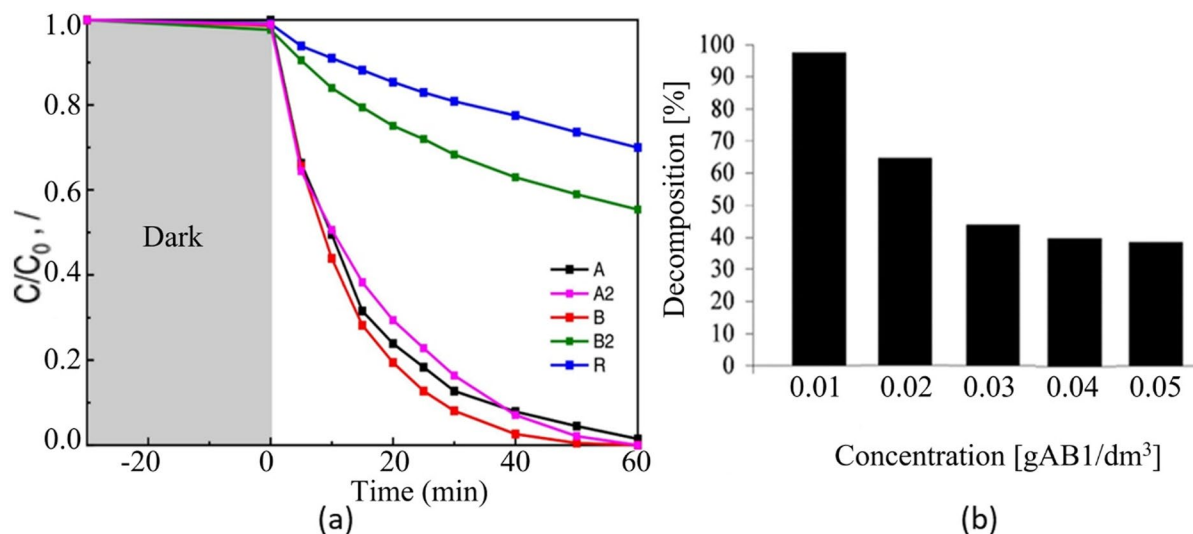
into the coating improves the stain removal efficiency (Pakdel et al. 2022). Arshad et al. (2019) investigated the photocatalytic activity of TiO<sub>2</sub>-ZnO nanocomposites to degrade the methylene blue dye and obtained satisfactory results at 1:1 weight ratio (Umair Arshad et al. 2019). Various studies are conducted on textile materials with nano-TiO<sub>2</sub> and multi-wall carbon nanotubes following the application of different cross-linking agents. The treated fabric exhibits better photocatalytic degradation compared to pure TiO<sub>2</sub> nanoparticles (Lee et al. 2014; Karimi et al. 2015). Table 3 showed several nanocomposites and nano-hybrids used for cotton fabric for photocatalytic self-cleaning properties.

### Parameters influencing on photocatalytic self-cleaning activity

Self-cleaning properties of substrates are not only influenced by a single parameter, but the efficiency is also dependent on several parameters simultaneously. There are various parameters that can influence the self-cleaning functionality of treated substrates. When certain parameters remain constant, change of a single parameter can affect the photodegradability of the photocatalysts.

### Effect of pH of the solution

The effect of pH on photocatalytic self-cleaning properties has been studied by many researchers. There is no certain correlation between the optimum pH and photocatalytic degradation of dyes and organic pollutants. Previously, there have been different reports that suggest the trend of adsorption and photocatalysis to be similar. However, the adsorption and photodegradation at various pH are not related (Fig. 18) as the adsorption does not change with pH variation (Bhatkhande et al. 2002). Thus, research has been done on the construction of the relationship between pH and photodecomposition of dyes and organic pollutants and to determine the optimal pH for better photocatalysis (Sivalingam et al. 2003). There are different phenomena that explain the effect of pH of the solution on the photocatalysis. Photocatalysis is a type of redox reaction and the reaction is sensitive to the change in potential of the photocatalytic surfaces. With the increase in the pH of the solution, there is an increase in hydroxyl radicals which are responsible for the degradation efficiency of organic pollutants (Koe et al. 2020). Thus, in case of higher pH, that is, in alkaline solution, the degradation of organic matter is remarkable due to the abundance of hydroxyl radicals (Khezrianjoo and Revanasiddappa 2016). Other studies explain that the effect of pH on photocatalysis depends on the nature of dyes, in fact. The process is



**Fig. 19 a** Photocatalytic degradation of bisphenol A in the presence of different crystalline structures of TiO<sub>2</sub> nanoparticles [anatase (A and A2), brookite (B and B2) and rutile (R)] under UV exposure. Reproduced with permission (Žerjav et al.

2022). Copyright © 2022, Elsevier and **b** Effects of initial concentration of dye on photodecomposition of Acid Black 1 over modified TiO<sub>2</sub> in water. Reproduced with permission (Grzechulska and Morawski 2002). Copyright © 2002, Elsevier

a little complex as for example, in the case of TiO<sub>2</sub> nanoparticles, it is positively charged or protonated when there is a pH less than the neutral point and it is negatively charged or deprotonated at a higher pH. As a result of this shifting in surface charge with the variation of pH, the adsorption of dyes on the photocatalytic surface changed, resulting in the change in the reaction rate. Several studies report that, when the photocatalytic surface is positively charged, it can adsorb the anionic dyes very effectively; on the other hand, cationic dyes can be adsorbed when the surface charge is negative (Kumar et al. 2015; Kumar and Pandey 2017). The pH of the solutions controls the potential of the photocatalytic surface. At the isoelectric pH or the point of zero charge of a certain photocatalyst, the adsorption of dye is minimum where the value of zero charge of the point varies for different photocatalysis (Zawawi et al. 2017).

#### Effect of morphological structure of NPs

Morphological structure of nanoparticles includes particle size and agglomerate size which have a remarkable effect on the efficiency of the photocatalytic events. There exists a straight relationship between the degradation of organic pollutants and

the surface structure of nanoparticles (Kormann et al. 1988). Researchers suggest that nanomaterials with relatively smaller particle size show higher efficiency in photocatalysis compared to bulk materials. These results are due to the fact that nanomaterials with smaller particle size possess relatively large surface area and a huge number of atoms gathered on the surface. Smaller particle size also contributes to increase the quantity of active sites on the material surface. Both the large surface area and the increased quantity of active sites effectively enhance the photocatalysis of organic pollutants (Cernuto et al. 2011; Nica et al. 2016). Morphology like crystalline structure can also make some differences in the photocatalytic degradation of pollutants. In the case of TiO<sub>2</sub> nanoparticles, there exist three different crystalline structures, namely rutile, anatase, and brookite. However, the studies showed that the anatase form is more efficient and notable in photocatalysis among the three phases (Fig. 19a). These capabilities of the anatase form are contributed by the stability of the phase, higher degree of hydroxylation, and adsorption power (Gnanasekaran et al. 2015; Allen et al. 2018). On the other hand, for ZnO nanoparticles, there exist different crystalline structures such as spindle-shaped, rod-shaped, flower-shaped, spherical-shaped structures,

among which the spherical-shaped structure is more efficient in photodegradation (Saravanan et al. 2013).

#### Effect of concentration and type of the dyes

Photocatalytic degradation or discoloration of organic stains and dyes strongly depends on the nature and concentration, as well as on other existing compounds of the stains and dyes. For a certain type of photocatalyst, under similar operating conditions (light, irradiation time, temperature etc.), the rate of photodegradation varied with the variation of the initial concentration of stains or dyes and thus also resulting variation in the degradation time (Chen and Mao 2007; Malato et al. 2009). Reports showed that, for photocatalytic degradation, at a certain initial concentration of the stains and dyes, the rate of photocatalysis is at maximum (Fig. 19b). But after that, the rate of degradation decreases with increasing concentration (Grzechulska and Morawski 2002; Reza et al. 2017). This is due to the fact that, after the optimal conditions, the high concentration of contaminants saturates the photocatalytic surface, thus reducing the photonic performances and ultimately resulting in the deactivation of the photocatalyst (Sobczyński and Dobosz 2001). Nature of the contaminations is defined as their chemical structure, which also influences the degradation behavior. The photocatalytic decomposition of dyes and natural stains which are basically pigments, is different due to their chemical structure. Dyes are generally sensitive to light irradiation and follow the reduction mechanism for discoloration. On the other hand, organic stains degrade due to the reaction with the reactive oxygen species generated on the photocatalytic surface (Tian et al. 2009; Nica et al. 2016). There is also another criterion for colorants, which is the adherence properties of the colorants with the photocatalytic surfaces. The colorants that adhere to the photocatalytic surface more effectively, the degradation reaction will be more efficient.

#### Effects of wavelength and intensity of light

As the word ‘photocatalysis’ is defined as the photo induced catalytic process, thus, there is strong effect

of light energy on the reaction. The reaction fully depends on both the wavelength and intensity of the light source (Pakdel et al. 2022). There have been several studies that have described that the photocatalytic efficiency of the photocatalysts directly depends on the wavelength and intensity of incident light. Studies have shown that in the case of photocatalysis, light radiation with a shorter wavelength is considerably more efficient in enhancing photodegradation of stains than light radiation with a longer wavelength, also with a minimum amount of photocatalyst concentration. The phenomenon is explained as the fact that the shorter wavelength is related to the higher photon energy responsible for photocatalysis (Štengl et al. 2009). At shorter wavelengths, the photons with higher energy excite the electrons efficiently from the valence band to the conduction band. This generates a high amount of hydroxyl radicals and superoxide ions that are responsible for stimulating photodegradation (Chen et al. 2019). There has also been work that described the relation between the intensity of light and the degradation rate. The reaction rate is directly proportional to the light intensity or related to the square root of the intensity. However, there is a critical value of the light intensity where the photodegradation is optimal (Kanakaraju 2013). With the variation of light intensity, the electron–hole recombination is also varied and as a result, the speed of the reaction also fluctuates. In case of insufficient intensity of light, the electrons are not capable of extinguishing the conduction band (Saravanan et al. 2017b; Kumar 2017).

#### Effect of contact time

Contact time may also be known as the reaction time or irradiation time as the reaction continues as long as there is contact between the pollutants and photocatalytic surface and irradiation presents. The significance of contact time for photocatalytic degradation is such that when all parameters remain constant, the rate of degradation or decomposition increases with increasing of contact time, until saturation is reached (Vadiraj and Shivaraju 2022). After staining the nanoparticles coated textiles with organic stain or dyes, the materials are

exposed to irradiation with different periods of time. The  $K/S$  values are recorded after a certain time interval and the photocatalytic degradation is measured. Though, Initially the rate of degradation is very high but gradually the rate decreases with time because of the saturation of the photocatalysis. If there are enough nanoparticles, the stains degrade completely within the saturation periods (Montazer and Pakdel 2011; Pillai and Sundaramoorthy 2022).

#### Effect of loading of nanoparticles

According to several studies, the efficiency of the self-cleaning property of the surface is dependent on the concentration of the nanoparticles. Studies showed that, increased amount of photocatalysts is important for enhancing the photodegradation of pollutants. With an increase in the concentration of nanoparticles, there is also an increase in the total surface area which indicates that there are more active sites that ultimately increases the photocatalytic self-cleaning properties (Saad et al. 2016a; Abdel-Khalek et al. 2018). A higher concentration of the photocatalyst has a higher degradation rate although, after a certain concentration, the photocatalysis decreases strongly. This can be explained by two phenomena; firstly, the higher number of nanoparticles on the surface decreases the number of surface-active sites and secondly, the high concentration of nanoparticles, which can aggregate, resulting in a decrease in the transparency of the coating (Daneshvar et al. 2004; Haji et al. 2015). This prevents the light from passing through the nanoparticle layer, blocking the functionality. So, as a result, if there is an excess amount of photocatalysts, the degradation reaction may slow down accordingly. Therefore, an optimum concentration is important to get the best effect (Muruganandha and Swaminathan 2006; Sohrabi and Ghavami 2008).

#### Effects of dopants on photocatalytic self-cleaning

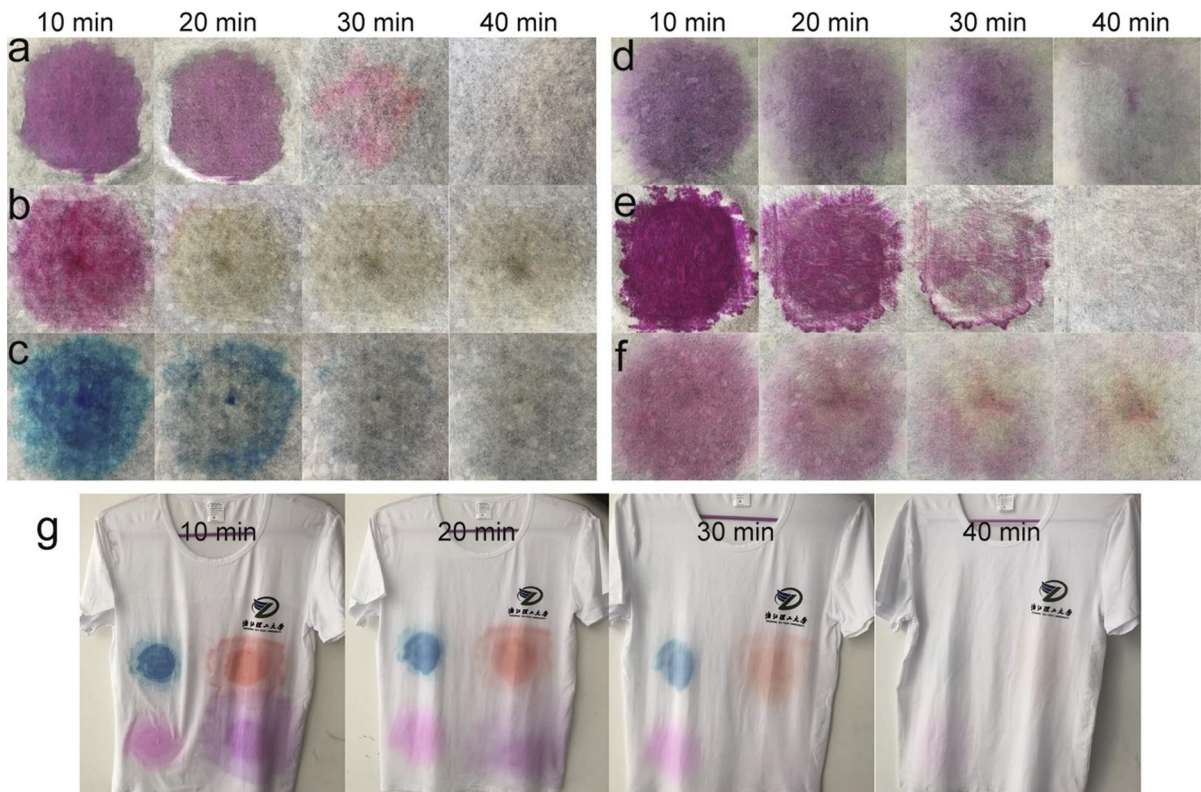
For effective photocatalytic self-cleaning activity, many researchers investigated the influence of dopants or pollutants with pure nanoparticles. Various investigations have found that with the addition of a small amount of dopants, the photocatalytic activity of the nanoparticles may increase. According to

the method used to deposit coating, there exist single phase dopants. Different types of dopants may behave differently depending upon its form (Parkin and Palgrave 2005). One of the major problems of photocatalysts like  $\text{TiO}_2$  nanoparticles is the rapid recombination of photoinduced electrons and holes, resulting in a low photo-quantum efficiency. Furthermore,  $\text{TiO}_2$  is not active under exposure to sunlight as it contains small amount of UV portion, thus effective use of sunlight cannot be done. By doping the photocatalysts with various metal and non-metal dopants can overcome the limitations (Rajeshwar et al. 2008). The primary function of doping is to overcome the limitations through a bathochromic shift. This phenomenon results in the absorption of visible light with the reduction in the band gap or introducing the intra-band gap states. Researchers have studied the doping of photocatalysis with different materials. The doping system can be either the incorporation of 3d transitional metal ions (Cu, Co, Mn, Fe etc.), lanthanides and noble metals or non-metal doping with N, C and S has shown enhanced photocatalysis in the visible light region. Also there are reports suggesting the metal–non-metal co-doping which has gained much attention in this fields (Banerjee et al. 2015). It is found that when the dopants exist as a mixed form of oxide, they may show different oxidation states namely lower oxidation states and higher oxidation states. Lower oxidation states which are lower than +4 ( $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  etc.) decrease the effect of photocatalytic activity, whereas higher oxidation states ( $\text{Mo}^{5+}$ ,  $\text{Nb}^{6+}$ ,  $\text{W}^{6+}$  etc.) may improve the photocatalytic activity (Karakitsou and Verykios 1993; Park et al. 2004; Zhang et al. 2012). Sometimes phase separated dopant can also be used which is a mixed form of two pure materials (Tada et al. 2004).

#### Effect of reaction temperature

For photocatalysis, the rate of degradation of stains or dyes can also be affected by the reaction temperature. It is observed that, the rate constant of the photocatalysis increases with the increasing reaction temperature up to a certain limit (Hashimoto et al. 2005; Mozia et al. 2009). Studies showed that when the reaction temperature decreases, it enhances the adsorption of the reactants and favors the adsorption of the final reaction products, which is very necessary to continue the photocatalysis. Lowering the





**Fig. 20** Photocatalytic self-cleaning performance of CNNS modified cellulose fibers under sunlight for 40 min: **a** RhB, **b** neutral red, **c** methyl blue, **d** reactive violet, **e** juice of red

pitaya, **f** juice of waxberry; **g** self-cleaning performance of a commercial T-shirt. Reproduced with permission (Yao et al. 2019). Copyright © 2019, Elsevier

temperature increases the activation energy. But, if the temperature increases near boiling points of water, the reaction tends to inhibit due to the limited adsorption capability (Mehrotra et al. 2005; Soares et al. 2007). This is because at higher temperature, reduced absorptivity associated with the organics and dissolved oxygen decreases the rate of degradation. The optimum temperature range for effective photocatalytic degradation is found to be in the range of 20–80 °C (Mamba et al. 2014).

### Applications of self-cleaning textiles

#### Daily apparel products and Household appliances

One of the main problems for our daily used clothing is that they have to undergo frequent washing cycles. Textile fibers or cloths made from these fibers attract dust, dirt, soil, and other particles and get

dirty. Again, the apparels can produce unpleasant odor resulted from perspiration, microorganisms or smoke from vehicles or cigarette. Stains from organic materials like tea, coffee, wine, curry and others also produce permanent or semi-permanent mark on the cloths. To remove these impurities or stains, washing is a must process to clean the fabric one or several times (Yılmaz and Bahtiyari 2022). But frequent washing cycles of these items can damage it ultimately by physical or chemical means and also the organic stains cannot be removed fully from the cloths. So, self-cleaning textile materials can be a great solution for these daily wearable items (Fig. 20). Super-hydrophobic self-cleaning fabrics repel the dust, dirt and other impurities, while the photocatalytic self-cleaning fabrics can degrade the odor and organic compounds when exposed to proper irradiation. Due to this self-cleaning functionality, the necessity of washing cycles will decrease to a great extent. Chemical



washing is also not very eco-friendly as the process requires consumption of a lot of water and the synthetic detergent ultimately pollutes the environment. Furthermore, some specialty fabrics like chiffon and satin may be distorted easily and get dimensional damage due to washing. These fabrics require less washing to maintain dimensional stability. The use of both super-hydrophobic and super-hydrophilic self-cleaning mechanisms in our daily apparels thus make them very useful and extended their lifetime (Tung and Daoud 2011b). Household products like curtains, kitchen cloths, bath towels and other furnishing fabrics also get dirty very easily. Traditional agents are used for their cleaning. But these products are very difficult to clean due to their comparatively larger size and physical structure. With the application of super-hydrophobic self-cleaning mechanism, the items can be made dustproof and with super-hydrophilic self-cleaning mechanism, the items can clean the stains (Fujishima and Zhang 2006).

#### Medical and biological protection

There is a huge risk of getting infected by microorganisms, especially the virus and bacteria, in hospitals and biological laboratories. The environment of these places should be sterile and free of contaminations. But it is not so easy to make the environment risk-free as the microorganisms or germs may get adhered with the textile products used in these places very easily including surgical gowns, caps, masks, gloves etc. Thus, the microorganisms can spread around very quickly and attack very easily. In these places, the photocatalytic self-cleaning textiles can play a very important role (Gamage and Zhang 2010; Zahid et al. 2018). As the photocatalysis degrades the organic compounds, the microorganisms are destroyed by the photocatalysis on the photocatalytic surfaces of the fabrics which reduce the chance of infection by the microorganisms. The traditional approach using drugs for antimicrobial treatment has some drawbacks, as the microorganisms gradually make them resist to the drug. However, using a photocatalyst as the agent can overcome the resistance because, the photocatalyst generates radicals which degrade any organic compound when in touch (Yadav et al. 2016; Abualnaja et al. 2021).

#### Sports and athletic wears

Self-cleaning functionality using nanotechnology has a great impact on sports and athletic products. For designing sports items, some factors are important to be considered such as breathability, anti-odor, moisture absorption, repellency, anti-soiling properties, etc. Nanotechnology can impart such kind of multifunctionalities to the sportswear (Nazari et al. 2009). The various applications of self-cleaning approach in sports and athletic wears includes the anti-odor socks with water-proof shoes, water-proof diving suit or swimming suits, antibacterial and UV protective clothing. The safety and physical comfort of athletes are increased by wearing these products. Not only sportswear, but also sports equipment, venues, and fields are also getting advantages from nanotechnology enhanced self-cleaning applications. Anti-staining stadium floor coverings are now gaining much popularity (Kai 2013; Harifi and Montazer 2017).

#### UV protective clothing

As a result of the growing awareness of the increasing radiation, scientists are now projecting their concepts to develop UV-resistant wearable items, which are UV-protective textile materials. The photocatalyst coated fabrics are very effective and capable of blocking the UV radiation and protect the wearer. For protecting the wearer from harmful UV irradiation, there are mainly two types of blockers; organic and inorganic UV blocker. But inorganic UV blockers are more effective as they are non-toxic to the wearer as well as they are chemically stable. Inorganic UV blockers include semiconductor oxides such as ZnO, TiO<sub>2</sub>, SnO<sub>2</sub>, etc. Because of their larger surface area and absorption in the UV region, they effectively block the UV radiation protecting the wearer (Tsu-zuki and Wang 2010; Mondal 2022).

#### Wastewater treatment

Wastewater treatment is one of the major issues for both the industries and the environment. Various organic pollutants and heavy metals disposed from the industries get mixed with the water resulting a serious environmental impact and threatening the aquatic lives. There are several methods for

treatment of the wastewater, of which the membrane technology is very attractive and ecofriendly (Mozia 2010). But the major drawback of using a membrane is the fouling of the membrane in practical usage for a prolonged period of application. This problem can be solved by transforming the hydrophobicity of the membranes to hydrophilic. The membranes treated with photocatalyst can reduce the hydrophobicity making the membrane hydrophilic. This can add self-cleaning properties as well as anti-fouling properties of the membranes (Riaz and Park 2020; Sun et al. 2020).

Apart from these, there are several other applications of self-cleaning textiles including, the air purifications, military uniforms, aerospace, spacesuits, smart textiles etc.

### Challenges, limitations and future trends

#### Challenges and limitations

Self-cleaning textiles have drawn significant attention of researchers and have gained much more importance in different technical fields of textiles as well as other fields. Is there a chance that the self-cleaning approach can obsolete the traditional chemical washing or dry washing? Though the self-cleaning approach is now accepted in practical and economical usage, there are still some challenges and limitations, due to which the practice is still in progress for commercialization. One of the challenges is the exposure of radiation for the photocatalytic self-cleaning textiles. The photocatalytic surface under exposure to radiation stimulates the reaction, and thus cleaning performance is obtained. Photocatalysts like  $\text{TiO}_2$  can work in the range of UV radiation, but not under the visible sunlight. So, if we have to achieve the self-cleaning properties of  $\text{TiO}_2$  coated fabric, we have to expose it under UV radiation. This is a huge drawback, because it will be very difficult to produce UV radiation frequently. Scientists have tried to overcome this problem by doping the photocatalysts with metal or non-metal dopants. By doping or other treatments, the photocatalytic activity can be obtained in the visible region and as a result, the textiles can be cleaned under direct sunlight. However, sunlight is still needed for photocatalysis and if there is no sunlight due to clouds or shades, the approach will not work.

So, there is still the problem of radiation exposure. Secondly, the exposure time is also crucial for effective self-cleaning. But the fact is that, under exposure of radiation, it takes a long time to clean the textile surfaces. The exposure time may take a day for self-cleaning depending on the nature and strength of the stains or organic compounds. Another challenge for both super-hydrophobic and super-hydrophilic surfaces is the durability of the applied nanoparticles. The durability defines both the chemical and physical durability. The proper adhesion of the nanoparticles with the textile materials is still under research, as there is a limitation in bonding between the nanoparticles and the textile materials. In addition, mechanical attachments, such as rubbing, can sometimes cause removal of nanoparticles from the surfaces. A minor limitation includes the change of the color of the textiles which is when nanoparticles applied to colored textile surface, the color can be changed according to the characteristics of the nanoparticles.

Although the nanoparticles treated self-cleaning textile substrates are gaining much popularity day by day, there is still some questions raised concerning the potential risks of these nanoparticles on the environment and human health. Apart from their beneficial outcomes in different fields, the researchers are now investigating the adverse effects of the nanoparticles. Yet, there is little we know about the risks of these nanoparticles. Mass production and application of nanoparticles created problems when the nanoparticles are exposed to the environment. After washing the treated substrates or after the treatment of wastewater, the nanoparticles are gradually separated from the substrates, ultimately getting aggregated in water or soil. It is found that nanoparticles like  $\text{TiO}_2$  can destroy the earthworm which is important for the food chain. The adverse effects of these nanoparticles are measured in terms of lethal dose ( $\text{LD}_{50}$ ), which is measured by the quantity of a given substance, given at the same time, that causes the death of 50% of a group of test animals. The inhalation of the nanoparticles can sometimes cause allergic reactions or inflammation to the human body. Therefore, there are questions about the risks of these nanoparticles, and we know a little about that.

## Future trends

Photocatalytic self-cleaning is strongly dependent on the UV radiation. It is known that the UV radiation is necessary to initiate the photocatalytic reaction. So, there is the limitation of using the day light for the photocatalysis. Researchers are investigating how to utilize the sunlight for photocatalysis. Again, the substrates when used as indoor products, the cleaning mechanisms will be hampered due to the absence of radiation as the indoor light contains 0.1% of the UV radiation. Remote photocatalytic effects are introduced by a research work which suggests that, the photogenerated reactive oxygen species which are the hydroxyl radicals, superoxide ions, per hydroxyl ions etc. can decontaminate a surface located a very short distance from the photocatalytic surface. Although other researchers suggest it as a contradiction because the hydroxyl radicals cannot move from the photocatalytic surface. The primary criteria for photocatalysis are that the contaminants should be absorbed by the surface. The development is also required in case of the synthesis and fabrication process of the nanoparticles. Durability is a major concern for effective photocatalysis and proper binding is very necessary for the nanoparticles with the substrates.

## Nanoparticle toxicity and environmental issues

The toxicity and environmental issues of nanoparticles are important topics of concern in the field of nanotechnology and its applications. The potential adverse effects of nanoparticles on human health and the environment have raised significant concerns. However, it is crucial to assess the potential toxicity and environmental issues associated with the use of such nanoparticle-treated textiles.

The toxicity of nanoparticle impregnated textiles used for self-cleaning purposes primarily depends on the nanoparticle material, size, shape, surface characteristics, and the level of exposure (Zhang et al. 2022; Abbasi et al. 2023). Several nanoparticles, such as titanium dioxide, zinc oxide, and various fluorinated compounds, have been commonly employed for imparting self-cleaning properties to textiles (Lin et al. 2009). Titanium dioxide nanoparticles are frequently used in self-cleaning textiles due to their photocatalytic properties, enabling them to break down

organic contaminants under UV light. However, there are concerns about the potential toxicity of titanium dioxide nanoparticles, particularly when they are in the nanoscale range. Studies have suggested that titanium dioxide nanoparticles may induce cytotoxicity, oxidative stress, and inflammation in cells, which could be of concern if the nanoparticles are released from the fabric and come into contact with the skin or are inhaled (Tung and Daoud 2011b; Fadeel et al. 2018; Remzova et al. 2019; Leroux et al. 2020).

Zinc oxide nanoparticles are another common choice for self-cleaning textiles. While zinc oxide is generally considered safe for topical use in larger particle sizes, the potential toxicity of its nanoparticles warrants attention. Some studies have indicated that zinc oxide nanoparticles can induce cytotoxicity and cause DNA damage in certain cell types (Remzova et al. 2019; Freire et al. 2021). Inhalation exposure to zinc oxide nanoparticles may also lead to respiratory inflammation and oxidative stress. To mitigate the potential toxicity of nanoparticle impregnated textiles, it is crucial to consider the controlled release and retention of nanoparticles within the fabric. Research efforts are focused on developing methods to immobilize nanoparticles on the fabric surface, ensuring minimal leaching and exposure. Surface modifications, encapsulation techniques, or the use of composite structures can help enhance nanoparticle retention and reduce potential risks (Vigneshwaran 2009; Harish et al. 2022). Regulatory bodies and industry organizations are also working to establish guidelines and standards for the responsible use of nanoparticle-treated textiles. These initiatives aim to assess the potential risks associated with the use of such textiles, ensure appropriate labelling, and promote the use of safer alternatives when possible.

Nanoparticle impregnated textiles produced for self-cleaning purposes can pose environmental issues due to the potential release of nanoparticles into the environment during their production, use, and disposal. These environmental concerns are associated with the nanoparticle materials used, their behavior in the environment, and their potential impacts on ecosystems.

One of the key environmental issues related to nanoparticle impregnated textiles is the release of nanoparticles during manufacturing processes. When nanoparticles are incorporated into textiles, there is a possibility of their shedding or leaching from

the fabric surface. This can occur through abrasion, washing, or exposure to environmental conditions. Once released, nanoparticles can enter water bodies, soil, and air, where they can interact with living organisms and ecosystems (Busi et al. 2016; Saleem and Zaidi 2020; Martínez et al. 2021).

In aquatic environments, the release of nanoparticles from textiles can have adverse effects on aquatic organisms. Nanoparticles may accumulate in water bodies and be taken up by organisms, leading to potential toxicity and bioaccumulation in aquatic organisms such as fish, invertebrates, and algae. These nanoparticles can disrupt biological processes, affect growth and reproduction, and alter the structure and function of aquatic ecosystems (Krysanov et al. 2010). Furthermore, the potential for nanoparticle impregnated textiles to release nanoparticles into the soil is also a concern. Nanoparticles released from textiles can contaminate soil through various pathways, such as during land application of sewage sludge or through disposal in landfills. Soil microorganisms and plants, crucial components of soil ecosystems, may be exposed to these nanoparticles, potentially affecting nutrient cycling, plant growth, and soil fertility (Tourinho et al. 2012; Reidy et al. 2013).

The air can also be impacted by the release of nanoparticles from textiles. When nanoparticles become airborne, they can disperse over a wide area and potentially pose risks to human health and ecosystems. Inhalation exposure to airborne nanoparticles may lead to respiratory issues, inflammation, and oxidative stress. Additionally, nanoparticles can deposit on vegetation, affecting plant health and ecosystem dynamics (Prata 2018; Yin et al. 2022).

Addressing the environmental issues associated with nanoparticle impregnated textiles requires a proactive approach. Researchers are studying the fate, transport, and behavior of nanoparticles in different environmental compartments to better understand their potential impacts. This knowledge can aid in the development of guidelines and regulations to minimize the release of nanoparticles from textiles and ensure responsible manufacturing and disposal practices. Additionally, exploring alternative materials and fabrication techniques can help reduce the environmental impact of nanoparticle impregnated textiles. Researchers are investigating the use of biodegradable or environmentally friendly nanoparticles,

as well as exploring the potential of surface coatings or encapsulation techniques to minimize nanoparticle release while maintaining the self-cleaning functionality.

## Conclusions

The concept of self-cleaning surfaces is now having a great impact on various fields like the automobile, medical, protective clothing and even in our daily wearable items. Practically this is directly or indirectly taking part in the sustainability of environment by saving energy and reducing the consumption of huge amount of water. These ultimately result the reduction of processing costs and it also reduce further use of the chemical required for washing and laundering of the textiles. Nanotechnology plays a very important role in case of introducing the self-cleaning functionality to textile substrates. Some of the nanoparticles produce hierarchical surface roughness which makes the substrate super-hydrophobic and exhibit physical self-cleaning mechanism whereas nanoparticles of photocatalysts applied on textiles materials exhibits chemical self-cleaning mechanism. The self-cleaning surfaces produced from nanoparticles can exhibit other functional properties like antimicrobial, self-healing, anti-fouling properties etc. These multifunctional properties of self-cleaning textile materials are now gaining popularity in our daily used apparels as well as bio-hazardous and protective fields. There are numerous methods of applying the nanoparticles to the textiles surface which includes physical and chemical routes. Each method has separate potential for application of a certain kind of nanoparticles to the substrates. Though there are some challenges in synthesis and fabrication of nanoparticles to textile substrates among which durability of nanoparticles is one of the major limitations. Another limitation includes the difficulty in utilizing the solar radiation or sunlight as most of the photocatalysts nanoparticles work under the exposure of UV radiation. But recent developments are focusing on utilizing the visible light energy for photocatalytic degradation. The efficiency of self-cleaning properties can be affected by different operational parameters. Besides, the doping of the nanoparticles with different metal and non-metal dopants, the performance may increase. Apart from the various functional properties, researchers

are now also investigating the risks of using nanoparticles in self-cleaning textiles. There is very little evidence of the potential risks of these nanoparticles. However, overall, self-cleaning textile materials are now gaining much popularity due to their extraordinary functional properties.

**Acknowledgments** Technical supports from the “ZR Research Institute for Advanced Materials”, Sherpur-2100, Bangladesh are gratefully acknowledged.

**Author contributions** SM has contributed to data collection and original draft preparation. MdRR has contributed to conceptualization, methodology, validation, original draft preparation and visualization. AH has contributed to validation and editing and reviewing. MAJ, TI and MMK have contributed to editing and reviewing. MdRR has supervised all stages of preparing the manuscript and contributed to approval of contents. All authors have read and agreed to the published final version of this review.

**Funding** The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

**Data availability** Not applicable.

#### Declarations

**Conflict of interest** The authors have no relevant financial or non-financial interests to disclose.

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