Superhydrophobic and photocatalytic self-cleaning on cotton fabric using fluorine-free flower-like-TiO2/PDMS coatings

Esfandiar Pakdel
Deakin University
Hai Zhao
Wuhan Textile University - Yangguang Campus: Wuhan Textile University
Jinfeng Wang (jinfeng.wang@deakin.edu.au)
Deakin University https://orcid.org/0000-0002-2568-2170
Bin Tang
Deakin University
Russell Varley
Deakin University
Xungai Wang
Deakin University

Research Article

Keywords: Self-cleaning surfaces, photocatalytic activity, superhydrophobic fabrics, cotton fabric

Posted Date: May 10th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-404885/v1

Version of Record: A version of this preprint was published at Cellulose on July 20th, 2021. See the published version at https://doi.org/10.1007/s10570-021-04075-3.

Abstract

This research presents the development of novel self-cleaning cotton fabric with dual functionalities of superhydrophobicity and photocatalytic activity. Fluorine-free coating formulations composed of either flower-like TiO_2 or nitrogen-doped TiO_2 particles, with a hierarchical surface morphology, and polydimethyl siloxane (PDMS) polymer were applied to cotton fabrics using a facile dip-coating method. The self-cleaning performance of fabrics was assessed based on their superhydrophobicity and effective removal of oil-based food stains. Additionally, the impact of nitrogen doping on photocatalytic activity of flower-like TiO_2 particles was investigated. The obtained results demonstrated that the presence of both PDMS and hierarchical particles generated excellent superhydrophobicity on the cotton fabric with a water contact angle of 156.7 ± 1.9°. In addition, the coated fabric exhibited highly efficient photocatalytic activity, decomposing stains under simulated sunlight. Nitrogen doping process significantly boosted the photocatalytic activity of TiO_2 particles in degrading stains and dye solution. The developed superhydrophobic fabric showed high robustness against both chemical and physical durability tests. This research contributes significantly to the continued advancement of highly efficient self-cleaning textiles via the development of dual functions of superhydrophobicity and photocatalytic activity.

1. Introduction

Fabrication of self-cleaning surfaces particularly for textiles has attracted considerable attention in recent years. The term of self-cleaning denotes two types of surfaces comprising either superhydrophobic or photocatalytic, each of which functions on different mechanisms. On a superhydrophobic surface, water droplets form a spherical shape with a water contact angle (WCA) more than 150° and a sliding angle (SA) less than 10° (Geyer et al., 2020; Nguyen-Tri et al., 2019). This condition prevents any dirt adsorption onto the surface prompting water droplets to roll off the surface, and collecting impurities and cleaning it at the same time (Ghasemlou et al., 2019). To achieve the desired superhydrophobicity on a fabric, it is necessary to increase surface roughness by introducing hierarchical micro/nanostructures, and to decrease surface tension using low surface energy chemicals such as fluorinated compounds (Pakdel et al., 2020). Several strategies such as dip-coating, hydrothermal treatment, electrostatic layer by layer assembly, surface etching, UV-induced grafting, and cross-linking, to name but a few, have been used to obtain superhydrophobic coatings on textiles (Dalawai et al., 2020; Ghasemlou et al., 2019). One of the widely reported strategies is treating fabrics surface with different types of nanomaterials to acquire the roughness, followed by applying low surface energy fluoroalkyl silanes (FAS) (Yang et al., 2018; H. Zhou et al., 2012). However, the resultant superhydrophobic effects suffer from main drawbacks such as the necessity of using fluorinated chemicals and poor durability (Dalawai et al., 2020). In addition, the oxidation by-products of fluorinated compounds are potentially harmful to the environment and human health due to their low bio-elimination rate and potential accumulation in living organisms causing illnesses such as cancer, immune disorder, and hormonal disturbance (Ju et al., 2017; Schellenberger et al., 2019; Zahid et al., 2019). The use of fluorine-free chemicals such as polydimethyl siloxane (PDMS) as a low surface energy polymeric binder is a promising approach to displace the banned FAS additives. The combination of PDMS with different types of nanomaterials has been reported to be effective at creating highly superhydrophobic surfaces (Zahid et al., 2019).

Another category of self-cleaning textiles refers to functionalised products with photocatalytic activity (Pakdel et al., 2014; Pakdel et al., 2020; Panwar et al., 2018). The main function of these coatings is based on the elimination of stains or pollutions from fabrics using the photocatalytic activity of incorporated nanomaterials such as TiO_2 and ZnO under a suitable light source (Long et al., 2016; Nozari et al., 2021; Solovyeva et al., 2020). However, low efficiency of the developed coatings and the necessity of using UV light to activate the self-cleaning function are limitations of this approach (Lu et al., 2020). To address these issues, different methods such as enhancing the photocatalytic activity of coatings with the addition of silica and metal oxides (Pakdel & Daoud, 2013), narrowing the band gap of the photocatalysts through doping with noble metals (gold, silver, etc) (Luna et al., 2019; Pakdel et al., 2015) or nitrogen (Sun et al., 2020), and dye-sensitisation (S. Afzal et al., 2012) have been employed. These strategies can boost the photocatalytic activity of coatings and enable the use of visible light to activate the self-cleaning function of coatings. Other types of photoactive particles including zirconium oxide (ZrO_2) (Parvinzadeh Gashti & Almasian, 2013) and two dimensional nanosheets such as graphitic carbon nitride (g-C_3N_4) (Fan et al., 2018) and bismuth oxyiodide (P. Zhou et al., 2019) have also been used to develop self-cleaning fabrics.

Using particles with hierarchical surface morphologies referred to as flower-like particles in combination with low surface free energy materials is a promising approach to the development of robust superhydrophobic surfaces (Li et al., 2015; Pakdel et al., 2020; Xu et al., 2018). These particles can generate the required roughness due to having numerous nanosheets and nanopores in their hierarchical surface. The developed coatings usually display a low sliding angle enabling water droplets to roll across the created surface protrusions. A variety of flower-like particles have been used to coat textile surfaces to achieve superhydrophobic effect. For instance, Huang et al (Huang et al., 2015) developed a superhydrophobic cotton through applying flower-like TiO_2 particles using a hydrothermal method followed by surface modification with fluoroalkyl silanes and reported a WCA of 160°. However, their adopted method would be challenging to scale up to practical applications considering the use of hydrothermal method and fluorinated compounds. They also used amorphous TiO_2 in their work which did not result in any photocatalytic self-cleaning effect on coated fabrics. Zhang et al (Zhang et al., 2017) applied flower-like ZnO particles to different substrates including cotton fabric and used an epoxy resin to improve the coating durability. The coated fabrics showed superhydrophobicity with a WCA of 150° and SA of 2°, but no further information on the photocatalytic self-cleaning was reported. Xu et al (Xu et al., 2018) reported a superhydrophobic coating on cotton with WCA of 157° and SA of 7.2° based on the combination of copper sulfide (CuS) and PDMS. Similarly, Cao et al (Cao et al., 2020) developed a superhydrophobic cotton through depositing cupric oxide (CuO) nanostructures on the fabric via a solution immersion process. The coated fabric showed a WCA of 151° and was employed as a superhydrophobic-superoleophilic filter for oil/water separation. However, the applied CuO coating changed the colour of cotton fabrics and despite having a visible-light-induced photocatalytic activity, no information was provided regarding the capability of the developed coatings on cleaning the stained fabrics.

Although there are several publications on using flower-like particles for developing superhydrophobic textiles as mentioned, several aspects of the discussed coatings have not fully been explored yet. The self-cleaning textiles developed so far, have mainly focused on using superhydrophobicity to protect the fabric against dust and water-borne contaminants as the main mechanism. However, repelling all types of stains including high- (water) and low-surface-tension (oils) liquids is challenging as it requires developing omniphobic coatings by creating sophisticated surface topographies and using fluorinated compounds with long perfluoroalkyl chains, which mainly result in low durability (Cai et al., 2019; Wu et al., 2017; H. Zhou et al., 2016). Therefore, new strategies are required to develop novel fluorine-free self-cleaning coatings for all types of impurities and stains. This study intends to address these shortcomings by developing a durable coating on cotton fabric with dual functionalities of superhydrophobicity and photocatalytic activity using hierarchical TiO_2-based particles. The developed self-cleaning fabric can repel water-based stains due to its superhydrophobic behaviour and at the same time photocatalytically decompose oil-based contaminants using visible-light.

2. Experimental

2.1.Materials

A pure cotton woven fabric was used as the substrate in this study. Elemental metal powder of titanium (Ti) with a purity of 99.7% and average particle size of 45 µm (Atlantic Equipment Engineers, USA) was used as the precursor for the flower-like TiO_2 particles. Polydimethylsiloxane (PDMS) pre-polymer (Sylgard 184 Industrial Elastomer Base) and the curing agent (Sylgard 184 Silicone Elastomer Curing Agent) were purchased from Dow Corning (USA).

2.2.Synthesis of flower-like TiO_2 particles

The synthesis of TiO_2 particles was carried out based on the hydrothermal method reported previously (Pakdel et al., 2016). In brief, 60 mg of Ti powder was mixed with 60 ml of sodium hydroxide (NaOH) solution (10 M) for 10 min followed by the addition of 0.5 ml of 30% hydrogen peroxide (H_2O_2) to the mixture and stirring for 3 min. The resultant mixture was transferred into a Teflon-sealed autoclave and heated at 150 °C for 90 min. After cooling down to room temperature, the TiO_2 particles were separated by vacuum-filtering, followed by washing with HCl solution (0.2 M) then washing 5 times with water. The synthesised particles were calcinated at 550 °C for 2 h to obtain the white TiO_2 powder. Nitrogen doping was carried out through exposing the samples to a flow of 2 % NH_3 in N_2 gas for 4 h at 550 °C where greyish powders were obtained.

2.3.Preparation of PDMS/flower-like TiO_2 coatings

The cotton fabrics were scoured in a solution containing 2 g/L of nonionic detergent at 50 °C based on a liquid to good ratio of 50:1 for 20 min to remove any impurities. The prepared cotton fabrics were then coated using a dip-coating method in an ultrasonic bath. PDMS prepolymer (1 g) and curing agent (0.1 g) were added to 50 ml of isopropanol and mixed for 10 min under ultrasonication. The cotton fabrics were treated with pure PDMS, TiO_2/PDMS, and N-doped-TiO_2/PDMS formulations for 30 min in an ultrasonic bath. 0.2g of the synthesised powders were used in each coating formulation containing either TiO_2 or N-doped-TiO_2. The coated samples were dried at room temperature followed by curing at 140 ºC for 1 h.

2.4. Characterisation methods

The superhydrophobicity of coated fabrics was measured using a water contact angle meter (KSV CAM101). The contact angles were measured at five different spots on each fabric and the average values were obtained. The crystalline structure of the synthesised particles was investigated using X-ray diffractometer (X'Pert Powder, PANalytical, Netherlands) with a Cu Kα radiation over 2θ range of 20-80° operating at 40 kV and 30 mA. The Brunauere-Emmette-Teller (BET) specific surface area of powders was measured at 77 K according to the N_2 adsorption using a Quantachrome Autosorb Automated Gas Sorption System (USA). Scanning electron microscopy (SEM) images were taken using Zeiss Supra 55VP (Germany).

The photocatalytic activities of TiO_2 and N-doped TiO_2 powders were assessed based on the degradation of Rhodamine B (RhB) dye solution (6 g/L) under both simulated sunlight (350 W/m^2) without any filter and pure visible light. To this end, 1.0 mg of the synthesised powders was added to 40 ml of the dye solution and exposed to the light sources. At certain time intervals, 5 ml of the dye solution was taken out and the dye concentration was measured at 510 nm using a UV-vis spectrophotometer. The photocatalytic self-cleaning property of coatings was also assessed based on monitoring the discolouration rate of oil stains after exposure to visible light and simulated sunlight.

To assess the durability of coatings, the samples were immersed into the acidic and alkali aqueous solutions with pH levels of 1, 3, 5, 7, 9, 11, and 14 for 24 h at room temperature followed by drying and measuring their WCA. The pH levels were adjusted using hydrochloric acid and sodium hydroxide. The physical durability of coatings was assessed based on measuring WCA of fabrics after 50 cycles of sandpaper abrasion test and adhesive tape peeling. The fabrics were located onto sandpaper under constant pressure of 100 g and pulled for 20 cm horizontally. For tape-peeling test, the sticky tape was located on fabrics under a maximum finger pressure and then was removed. The washing test was conducted through immersing the samples into the water/detergent (5g/L) mixture for 1 h under agitation followed by drying.

3. Results And Discussion

3.1.Characterisation of the synthesised particles

The surface morphology of the synthesised particles was observed using SEM images (Figure 1a) where the obtained particles displayed a three-dimensional hierarchical structure with a size of around 1 μm. The particles consist of self-centred radial nanoflakes creating a porous structure, which is consistent with previously reported results (C. Wang et al., 2010). The XRD patterns indicated the dominant presence of anatase crystalline phase in the structure of the calcinated powders (Figure 1b). The diffraction peaks that appeared at 25.2°, 37.5° and 48° were characteristic of anatase TiO_2 corresponding to the lattice parameters of 3.5 (101), 2.4 (004), 1.9 (200), respectively (Pakdel et al., 2018). The peak at 40.07° is related to the Ti phase left in the core of the synthesised particles (C. Wang et al., 2010). There is a slight shift to lower angles for the nitrogen doped TiO_2 diffraction peak at 25.2°, which is due to the incorporation of nitrogen atoms into the lattice of anatase TiO_2, indicating the distortion and strain in the synthesised crystals after nitrogen doping. This is in good agreement with the findings reported by Boningari et al (Boningari et al., 2018). The BET surface areas of pure TiO_2 and N-TiO_2 powders, calculated based on their N_2-adsorption-desorption isotherms were 70.305 and 76.590 m^2/g, respectively (Figure 1c and d). The pore radiuses for pure and doped TiO_2 were 16.573 and 14.862 Å, respectively, showing a slight decrease after the doping process.

The photocatalytic activities of pure TiO_2 and N-doped TiO_2 powders for degradation of RhB dye under both simulated sunlight and pure visible light sources were evaluated and shown in Figure 2. The results confirmed the positive role of nitrogen doping on enhancing the photocatalytic activity of TiO_2 particles. For instance, the pure TiO_2 particles degraded the dye solution within 4.5 h under simulated sunlight, while N-doped TiO_2 showed much faster pace where they successfully decomposed the RhB molecules after 2 h of irradiation under simulated sunlight. The same trend was also observed for samples tested under pure visible light but at a much slower pace. This is related to the lower energy and intensity of the incident visible light for activation of the photocatalytic activity of the particles. According to related studies, higher photocatalytic activity of the N-doped TiO_2 is attributed to embedding the nitrogen atoms into the lattice of TiO_2 (Liu et al., 2017). This narrows the band-gap of TiO_2 particles through introducing nitrogen 2p states into the bandgap of anatase nanocrystals above the valence band, shifting the photocatalytic activation threshold to the visible-region and thus enhancing photocatalytic activity (Liu et al., 2017). The results obtained here confirmed that N-doped TiO_2 particles were more active under the incident lights. This demonstrates that the modified TiO_2 particles were more responsive to a larger portion of the incident simulated sunlight due to their narrowed bandgap, hence a higher photocatalytic activity (Boningari et al., 2018). Photocatalytic activity of the TiO_2-based photocatalysts is activated through absorbing the incident light energy by the electrons existing in the valence band of TiO_2 and promoting them to the conduction band. This phenomenon produces electrons and positive holes on TiO_2 surface where they can react with oxygen and water molecules in their surroundings producing active species such as hydroxyl radicals ($^{\bullet}OH$) and superoxide anions ($^{\bullet}O_2^-$) (Boningari et al., 2018). These species can actively react with organic molecules, breaking them down into harmless products such as water and carbon dioxide (Boningari et al., 2018; Zhao et al., 2017).

$TiO_2 + hv \rightarrow h_{VB}^+ + e_{CB}^-$

$e_{CB}^- + h_{VB}^+ \rightarrow$ energy

$H_2O + h_{VB}+ \rightarrow \bullet OH + H^+$

$O_2 + e_{CB}^- \rightarrow O_2\bullet^-$

$\bullet OH$ + pollutant $\rightarrow\rightarrow\rightarrow H_2O + CO_2$

$O_2\bullet^- + H^+ \rightarrow \bullet OOH$

$\bullet OOH + \bullet OOH \rightarrow H_2O_2 + O_2$

$O_2\bullet-$ + pollutant $\rightarrow\rightarrow\rightarrow CO_2 + H_2O$

$\bullet OOH$ + pollutant $\rightarrow CO_2 + H_2O$

3.2. Self-cleaning coating on cotton fabric

The synthesised particles combined with PDMS were applied to the surface of cotton fabrics. SEM images showed that both PDMS and the flower-like particles were coated evenly on the fibres surface (Figure 3). The pure PDMS coating did not lead to any surface roughness; however, the presence of well-dispersed flower-like TiO_2 particles, significantly increased surface roughness contributing to the superhydrophobicity of the fabrics. Fibres coated with N-doped TiO_2 particles showed a similar morphology to pure TiO_2. EDX analysis confirmed the presence of Ti and Si elements on fibres surface (Figure 3e and f). The ATR-FTIR spectra of the cotton fabrics before and after the coating process showed characteristic peaks related to cotton and PDMS (Figure 4). The broad peaks at 3100-3600 cm^{-1} were assigned to -OH groups located at the outer surface of fabrics (Abidi & Manike, 2018). Pristine fabric showed the peaks at 2900 cm^{-1}, 1311 cm^{-1}, and 1053 cm^{-1}, related to the stretching vibration of C-H, symmetric bending of CH_2 and stretching vibrations of C-O present in the cellulose structure, respectively (Abidi & Manike, 2018). In addition, the small peak at 890 cm^{-1} was associated with β-linkages between monosaccharides (Abidi & Manike, 2018). Applying pure PDMS to cotton fabric resulted in some peaks located at 2960 cm^{-1} and 1260 cm^{-1} which were ascribed to stretching and bending modes of $-CH_3$ existing in the structure of PDMS (Zahid et al., 2017). The sharp peaks at 1020 cm^{-1} and 800 cm^{-1} were attributed to the asymmetrical stretching vibration of Si—O (Hu et al., 2019; Y. Wang et al., 2019). For samples coated with PDMS/TiO_2 formulations, the sharp peaks located at 800 cm^{-1} and 1010 cm^{-1} were related to Ti-O, and Si-O-Si bonds, respectively (Foorginezhad & Zerafat, 2019; Tavares et al., 2014).

The presence of flower-like particles on the surface of cotton fabrics has resulted in self-cleaning functionality based on two mechanisms of photocatalytic stain removal and superhydrophobicity. Both TiO_2 and N-doped TiO_2 particles were stabilised on cotton fabrics using the PDMS binder which was crucial, as a fluorine free polymer, to provide low surface free tension on coated cotton. The thickness of PDMS layer on top of the applied particles on fabrics surface can determine the resultant features. The coated fabrics showed suitable photocatalytic activity in decomposition of stains, implying the adequate contact between stains and photocatalysts' surface. Figure 5 shows that the pristine cotton does not have any photocatalytic self-cleaning in the absence of TiO_2 particles. Comparing the performances of TiO_2 and N-doped TiO_2, the latter one provided higher photocatalytic activity over the same period of irradiation. As mentioned earlier, this is related to the modification of the bandgap of TiO_2 particles after nitrogen doping and the resultant higher activation potential under the light source. Under this condition, an increased number of negative electrons are excited to the conduction band from the valence band, leading to producing higher contents of active species of hydroxyl radicals and superoxide anions. This promoted more intense reactions with the stains on the fabrics surface, breaking them down into colourless compounds. This explains the reason of having a better self-cleaning performance on cotton fabrics coated with N-doped TiO_2 particles. It seems that the presence of a thin PDMS layer on flower-like particles did not inhibit the photocatalytic activity after exposure to the light source. Moreover, testing the re-useability of coated samples with modified N-doped TiO_2 showed that it can maintain its high performance even after 5 cycles of consecutive photocatalytic self-cleaning test.

In addition to the photocatalytic self-cleaning mechanism, the developed coating of PDMS/N-doped TiO_2 showed excellent performance for superhydrophobic self-cleaning effect. The presence of three-dimensional particles with a hierarchical surface morphology created the required roughness on fabrics surface which in combination with PDMS produced a superhydrophobic surface. Indeed, Figure 6a shows that the surface of the pristine cotton fabric was hydrophilic in nature as a water droplet was able to spread rapidly on the surface. After applying the PDMS coating, the WCA increased to around 131°, indicative of the hydrophobic nature of the resultant surface. It is known however, that a pure PDMS coating using conventional coating methods will not lead to a superhydrophobic surface (Pakdel et al., 2020), complementing our observations. Introducing the flower-like particles to the coating formulation, significantly boosted the WCA to around 157°, indicating the superhydrophobicity of the coated surface. There were no significant differences between the superhydrophobic performance of coatings developed from pure TiO_2 and N-doped TiO_2 particles. Figure 6b displays the self-cleaning property on coated fabric in removing the dust and soil impurities from the fabric surface using a stream of water. Also, the superhydrophobic performance of the coated fabric was tested for different types of droplets including water in different pH levels, water (dyed with methylene blue), red wine, coffee, milk, and black tea. These droplets were spread rapidly on the surface of pristine cotton while maintaining their spherical shape on the superhydrophobic fabric. Both samples showed superoleophilicity, resulting in a rapid spreading of oil-base droplets (coloured with Red Oil O dye for better visualisation).

3.3.Self-cleaning mechanisms

The mechanism of superhydrophobic self-cleaning can be explained based on two models of Wenzel and Cassie-Baxter which are basically determined by the morphology and topography of the surface structure (Figure 7a) (Darmanin & Guittard, 2015). In the Wenzel state, the water droplet penetrates the created micro/nanostructures and is in contact with the substrate. Under this condition, the surface shows superhydrophobic property, high water adhesion force and resultantly a high sliding angle. This mechanism has been found on different natural surfaces such as rose petal with WCA of 152.4° (Zhu et al., 2014). However, the Cassie-Baxter defines the superhydrophobic surface with a low adhesive force for water. In this case, water droplets are suspended on top of the created protrusions on the coated surface. This mechanism is observed on the Lotus leaf surface where water droplets showed WCA of 160° and SA<3° (Zhu et al., 2014). Therefore, it is plausible to claim that the existing superhydrophobic coating on cotton fabric consisting of flower-like particles and PDMS behaves similarly to the Cassie-Baxter model due to the low water adhesion (Abid et al., 2017). Therefore, the dirt and impurities were cleaned easily from the fabrics surface with a stream of water. In addition, the developed coating possessed photocatalytic self-cleaning functionality as well where oily stains were eliminated after exposure to a light source. Due to the presence of PDMS, a superoleophilic behaviour was also observed on the coated fabric surface enabling oil droplets to rapidly spread on the fabric surface and remain in close contact with the photocatalytic TiO_2 particles surfaces. Since the applied PDMS coating was thin and transparent, it did not block the penetration of light through the polymer coating for activation of photocatalytic behaviour of TiO_2 particles. Therefore, food stains on the surface of coated fabrics efficiently broke down into colourless compounds. Figures 7b and c illustrate the proposed mechanisms for the self-cleaning mechanisms of the applied coatings.

3.4.Durability of coatings

The chemical stability of the applied coatings was assessed after immersing the fabrics into different water containers with different pH levels (Figure 8a). It was observed that the strong acidic situations (pH=1 and 3) slightly damaged the superhydrophobicity of the coated fabrics. However, the tested samples maintained a WCA of just below 150°. The fabrics immersed into water with 5≤pH≤11 did not show any tangible sign of reduction in their superhydrophobicity, implying the suitable durability of the applied coatings. Figure 8b compares the WCA of fabrics after washing, sandpaper abrasion resistance, and tape peeling tests. The results demonstrated suitable durability of coatings applied to fabrics where the tested samples maintained a WCA of around 150°.

4. Conclusions

This research has successfully developed fluorine-free self-cleaning coatings on cotton fabrics, by incorporating either flower-like TiO_2 or N-doped TiO_2 particles into a PDMS binder. The nitrogen doping process enhanced the photocatalytic activity of TiO_2 particles under both visible light and simulated sunlight and the developed coating showed more efficient self-cleaning capability in decomposing the absorbed oily stains. The developed coatings on cotton fabrics showed both superhydrophobicity and photocatalytic activity as dual mechanisms of self-cleaning effect. The cotton fabrics prevented the attachment of water-based stains and at the same time decomposed oily absorbed stains under light irradiation. Applying pure PDMS coating to cotton fabric led to a hydrophobic surface with water contact angle around 131° while incorporating flower-like particles generated a superhydrophobic surface with water contact angle of 156.7±1.9°. The resultant superhydrophobicity was maintained after washing test with detergent, 50 cycles of abrasion test with sandpaper, and adhesive tape peeling. In addition, samples showed high chemical stability against different pH of water, implying suitable applicability of the developed coatings.

Declarations

Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest.

Ethical approval: This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent: Informed consent was obtained from all individual participants included in the study.

Code availability: There is no code availability for software application or custom code.

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Figures

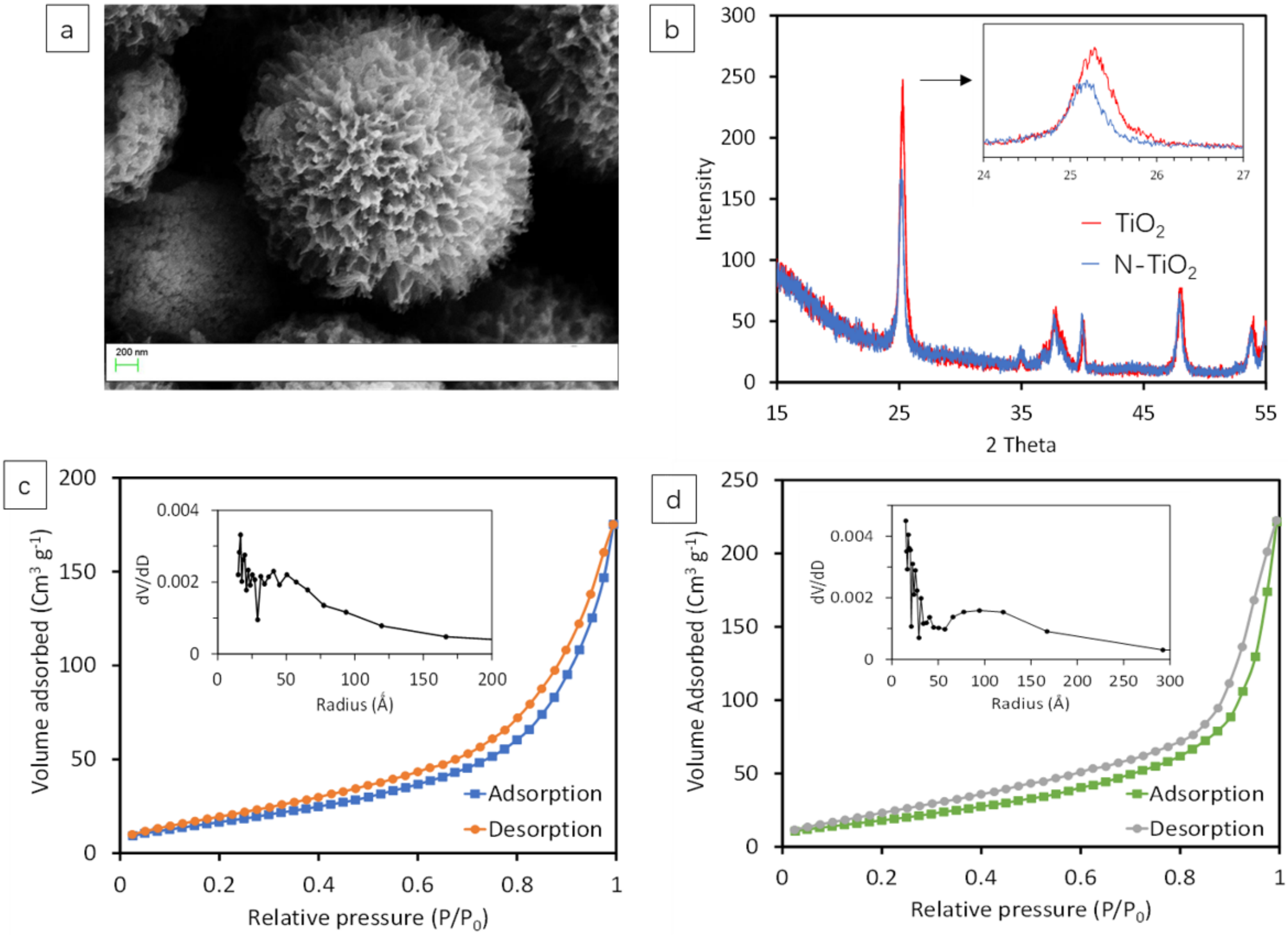

Figure 1

SEM image of the synthesised flower-like TiO2 particles, b) XRD patterns of TiO2 and N-doped TiO2 particles; BET surface area and pore size distribution (inset) of c) TiO2 and d) N-doped-TiO2

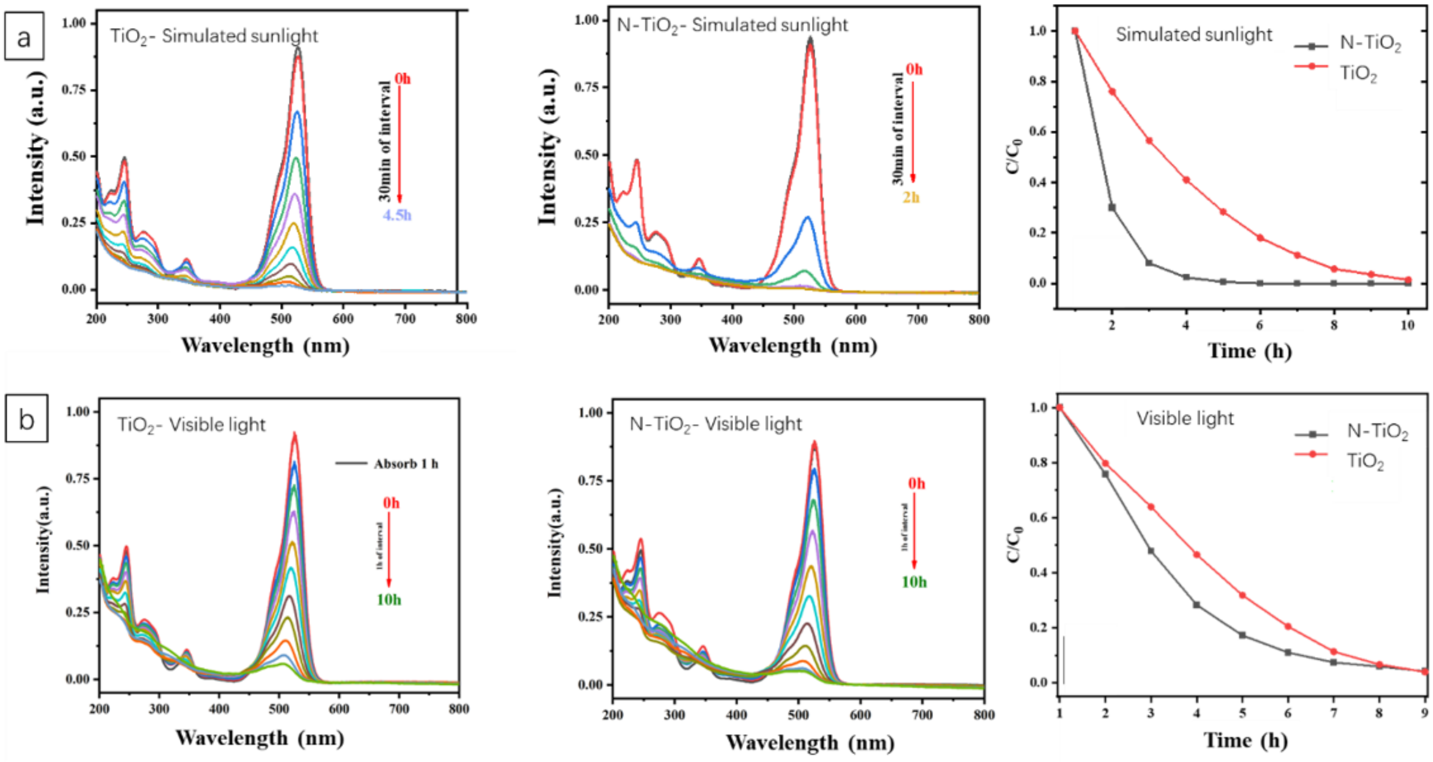

Figure 2

Photocatalytic degradation of RhB dye in the presence of TiO2 and N-doped TiO2 under a) simulated sunlight, and b) visible light irradiation.

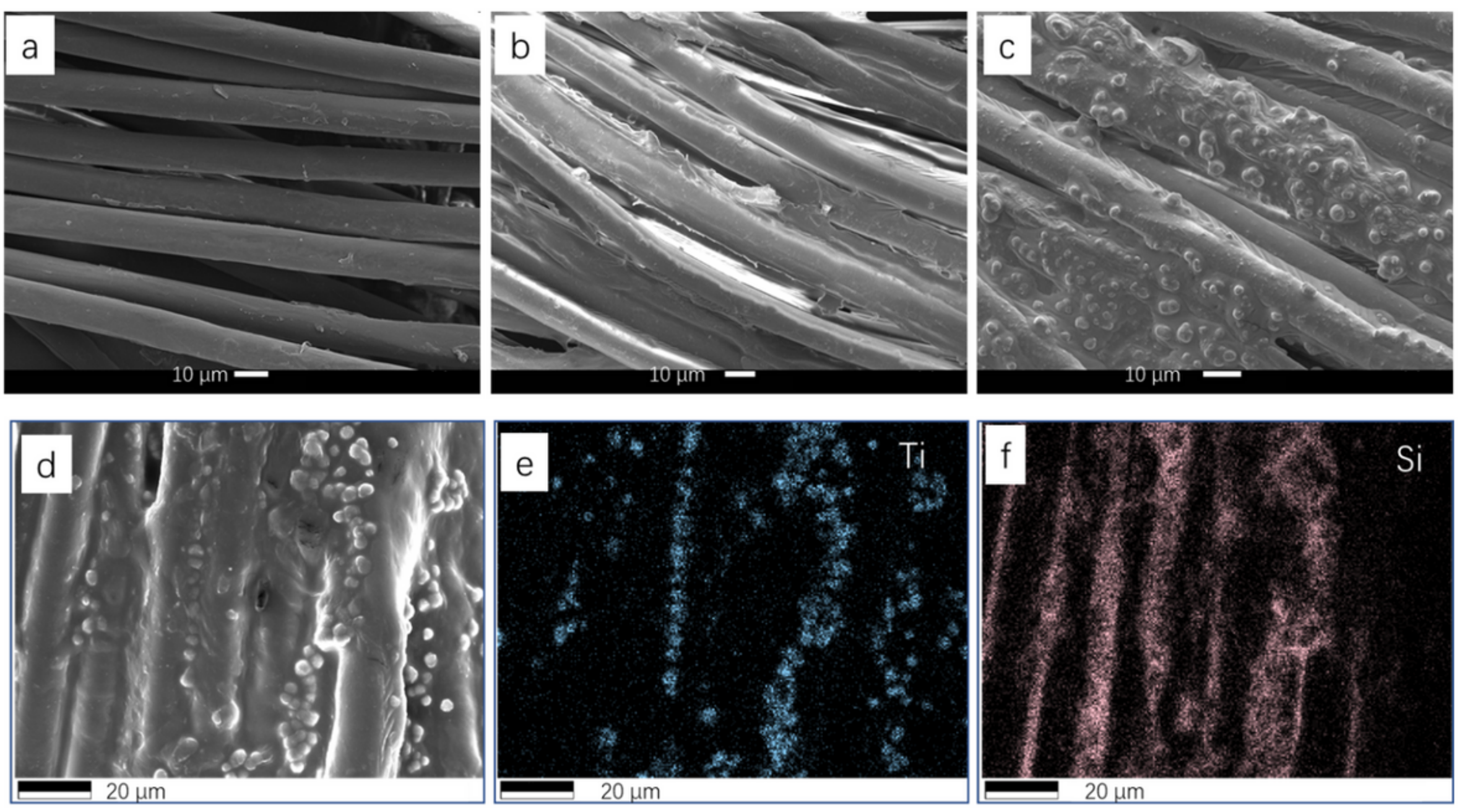

Figure 3

SEM images of a) pristine cotton; cotton coated with b) PDMS, c) TiO2/PDMS, d-f) SEM and EDX mapping of cotton coated with N-doped TiO2/PDMS

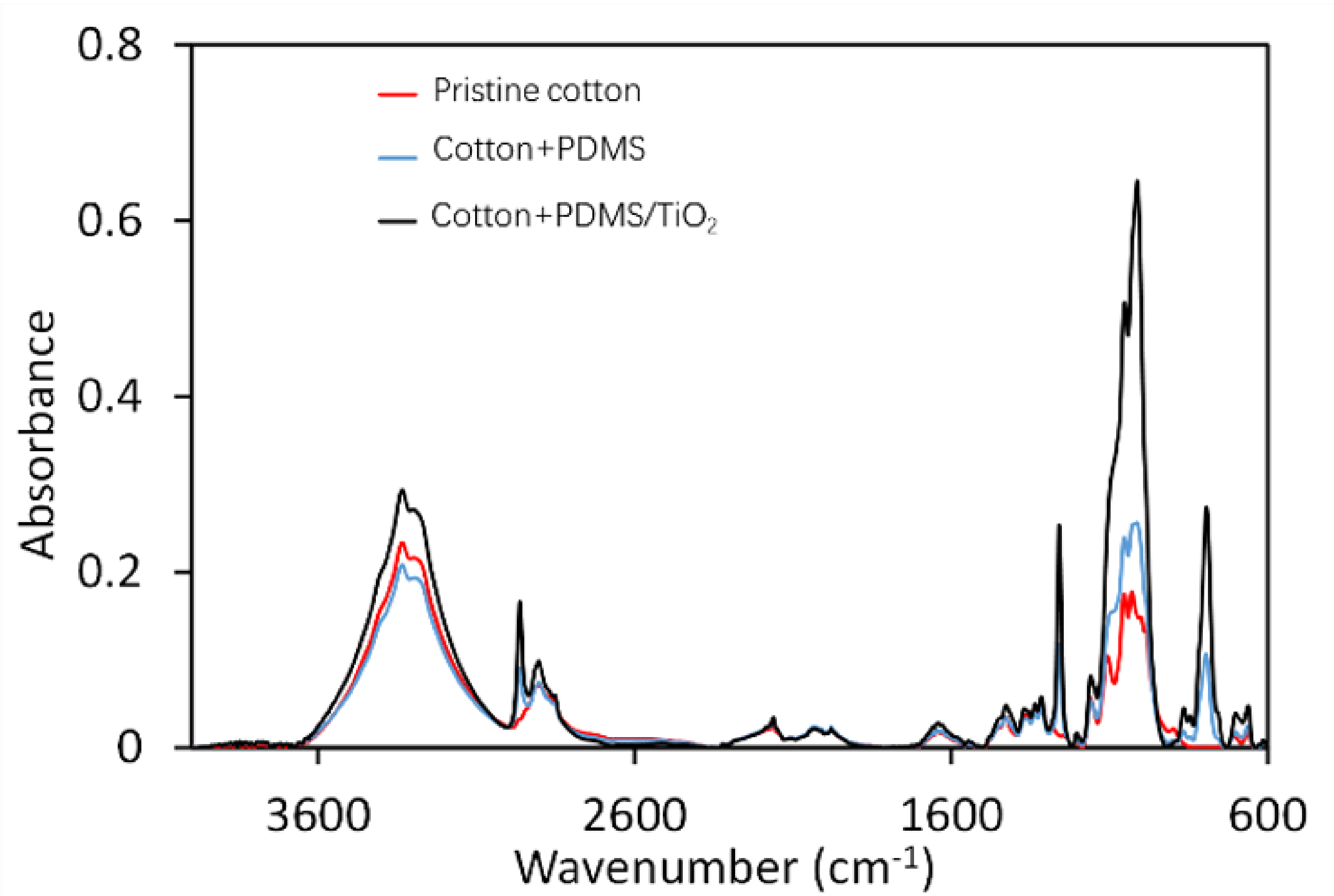

Figure 4

ATR-FTIR spectra of pristine and coated cotton fabrics.

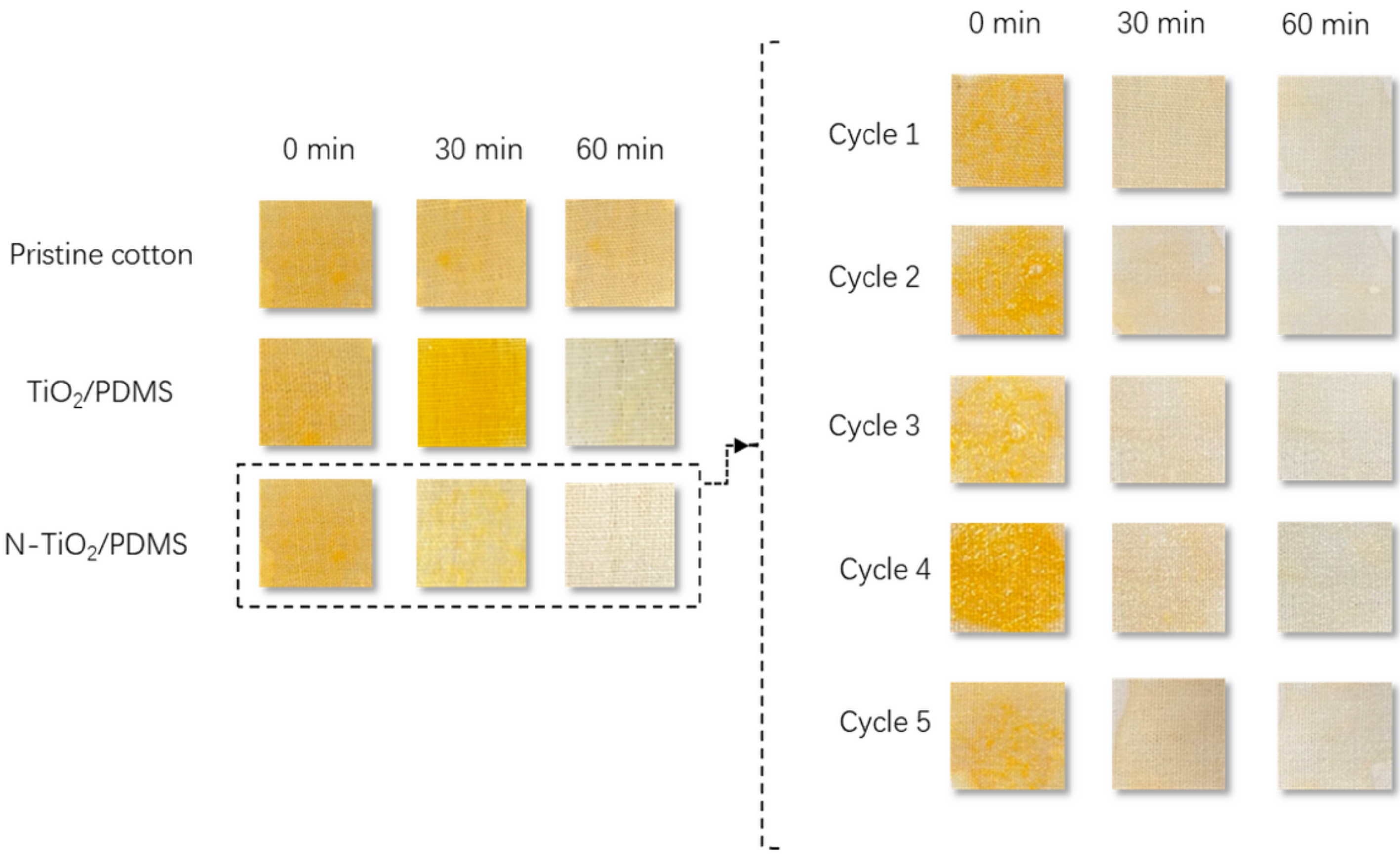

Figure 5

The photocatalytic self-cleaning performance of cotton fabrics in removing oil-base stains under simulated sunlight irradiation (left); repeating the self-cleaning performance on fabrics coated with N-doped TiO2/PDMS (right).

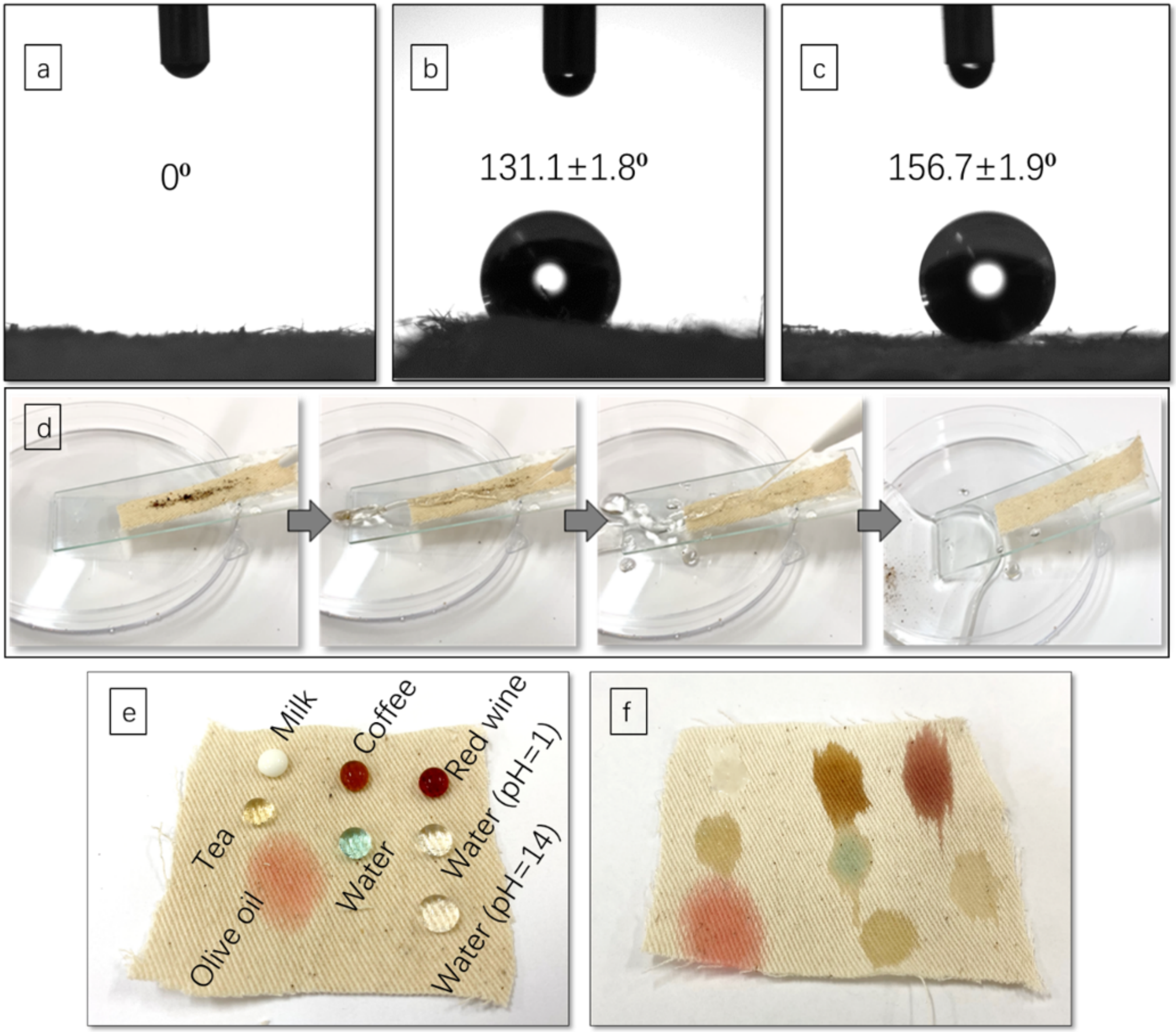

Figure 6

WCA of a) pristine cotton, b) cotton coated with PDMS, c) cotton coated with PDMS/TiO2, and d) self-cleaning effect on cotton fabric coated with N-doped TiO2/PDMS, e) superhydrophobic cotton fabric, f) absorption of droplets on pristine cotton

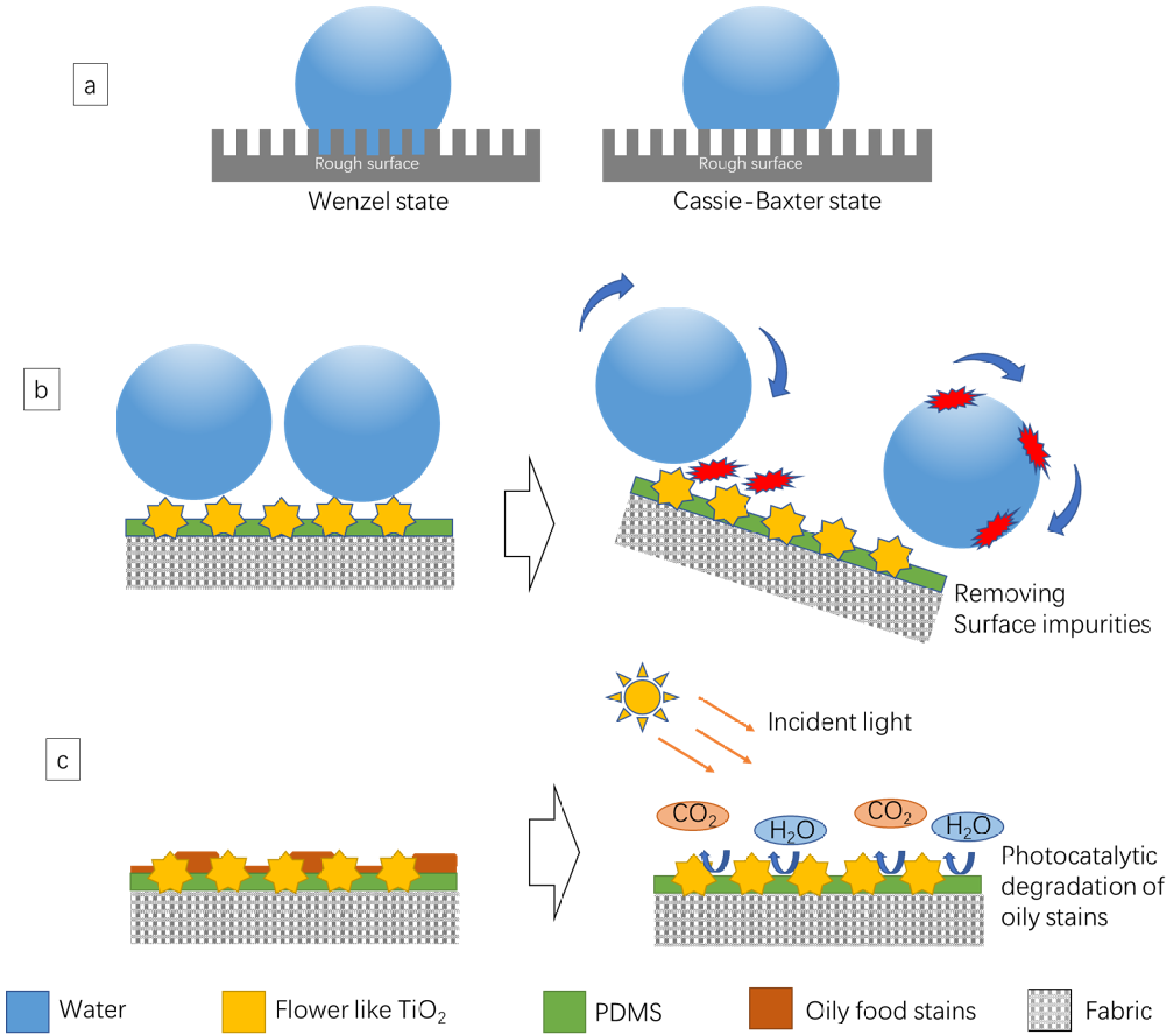

Figure 7

superhydrophobic surfaces based on the Wenzel and Cassie-Baxter states, b) superhydrophobic self-cleaning, and c) photocatalytic self-cleaning mechanism of coated fabrics

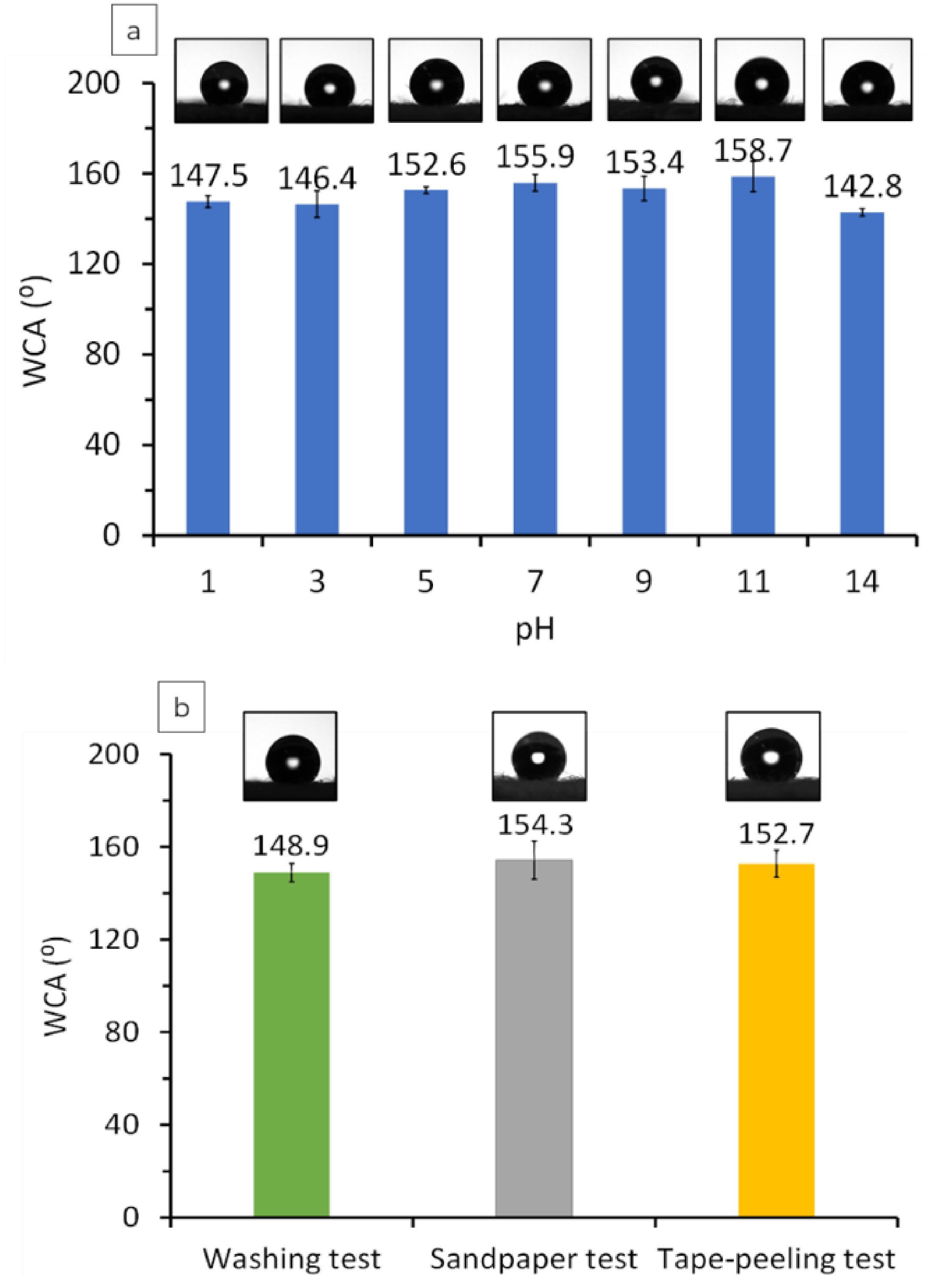

Figure 8

WCA on fabrics coated with flower-like TiO2/PDMS after a) chemical stability test in water with different pH, b) washing fastness and 50 cycles of physical durability tests.