

Robust ZnO/HNTs-Based Superhydrophobic Cotton Fabrics With UV Shielding, Self-Cleaning, Photocatalysis, and Oil/Water Separation

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Abstract

In this work, robust superhydrophobic cotton fabrics with UV shielding, self-cleaning, photocatalysis, and oil/water separation were successfully prepared based on micro/nano hierarchical ZnO/HNTs (halloysite nanotubes) hybrid particles and silicone elastomer polydimethylsiloxane (PDMS). ZnO/HNTs hybrid particles were prepared by in-situ growth of ZnO nanoparticles on the surface of halloysite nanotubes (HNTs). ZnO/HNTs hybrid particles and PDMS were used to successively coat cotton fabric by dip-coating approach. The coated cotton fabric displayed excellent superhydrophobicity with a water contact angle of $162.5 \pm 1^\circ$ and photocatalytic degradation of methylene blue solution under UV irradiation owing to the roughness and photocatalytic performance provided by micro/nano hierarchical ZnO/HNTs hybrid particles and low surface energy achieved by PDMS. The as-prepared fabric also displayed outstanding self-cleaning and antifouling properties. In addition, due to its both superhydrophobic and superoleophilic characteristics, the as-prepared cotton fabric can be used to separate several oil/water mixtures and showed good recoverability. The superhydrophobic cotton fabric also exhibited excellent UV shielding performance with a large UV protection factor of 1643.28 due to strong ultraviolet-absorption, light scattering and frequent light reflection of ZnO nanoparticles in ZnO/HNTs composites coated on cotton fabric. Importantly, the as-prepared fabric retained superhydrophobic performance after 2000 cycles rubbing, 90h UV illumination, and immersing in acidic and alkali solutions with different pH values ranging from 1 to 14 for 1 h. These characteristics make multifunctional cotton fabrics a satisfactory candidate in various promising fields.

1. Introduction

Cotton fabrics, one of the most common natural cellulosic fabrics, are used in costume, household textiles, and outdoor protection because of their softness, low cost, air permeability and environmental friendliness. Unfortunately, the cotton fabric can be easily wetted and contaminated by liquids such as water and cola owing to the great number of surface hydroxyl groups on the cellulose fibers of cotton fabric (Zhou et al. 2018). It has been demonstrated that introduction of superhydrophilicity is a simple and effective strategy to overcome the above-mentioned disadvantages (Xu et al. 2020; Yang et al. 2019; Yang et al. 2018).

Inspired by lotus leaf, many researches confirmed that preparation of superhydrophobic surfaces required the coordination of hierarchical micro/nano structures and ultralow surface free energy (Zhang et al. 2019; Shishodiaa et al. 2019; Tu et al. 2017). A large number of methods have been developed to prepare artificial superhydrophobic surfaces, such as layer-by-layer self-assembly technique (Lin et al. 2018, Jiang et al. 2017), deposition method (Rezaei et al. 2014; Gang et al. 2017), sol-gel method (Zhang et al. 2017; Banerjee et al. 2015), and spray method (Gao et al. 2017). However, to construct superhydrophobic surfaces, the fluoro compounds with ultralow surface energy are widely used, and they display excellent repellence to a wide range of liquids (such as water, glycerol, sunflower oil, n-hexadecane) (Kim et al. 2018; Ma et al. 2017; Wang et al. 2019). Unfortunately, the expensive long-chain perfluoroalkyl materials have a potential environmental risk due to difficult biodegradation, long-

distance migration, and high bioaccumulation (Zuo et al. 2018; Martin et al. 2003; Cao et al. 2016). Recently, polydimethylsiloxane (PDMS) is an ideal candidate for the fabrication of superhydrophobic surface owing to its low surface energy, environmental friendliness, strong adhesion, and excellent chemical, thermal stability. Cao et al. have reported an environmentally friendly strategy to prepare robust superhydrophobic fabric by dipping in silica aerogel (ormosil) solution and PDMS solution respectively, which possessed self-cleaning and oil-water separation property (Cao et al. 2016). Zheng et al. studied a self-assembly approach to prepare conductive superhydrophobic cotton fabric, which employed carboxylated and aminated multiwalled carbon nanotubes to create hierarchical roughness with modification with PDMS (Zheng et al. 2019).

Moreover, for preparation of superhydrophobic surfaces, the construction of these micro/nano hierarchical structures often depends on synthetic nanoparticles (Lin et al. 2017; Jin et al. 2018), etching (Wen et al. 2017; Kim et al. 2007), and template (Jin et al. 2005). These building blocks applied for superhydrophobic coatings are often costly, complicated in process, and can easily cause environmental pollution problems, restricting broader applications. Superhydrophobic surface based on naturally occurring nanomaterials are strongly advocated, but so far, only a very few superhydrophobic coatings with natural nanomaterials have been developed. Zhang et al. obtained waterborne nonfluorinated superhydrophobic coatings based on natural nanorods, palygorskite (PAL), followed by methyl polysiloxane modification with polyurethane (PU) as the adhesive layer (Zhang et al. 2017). Qu et al. fabricated superamphiphobic materials employing kaolin particles and silanes (Qu et al, 2018). HNTs (halloysite nanotubes) is a kind of natural aluminosilicate clay mineral with a unique needlelike microstructure. The one-dimensional structure, large surface area, low cost, and tunable surface chemistry of HNTs could benefit for their application in the construction of organic-inorganic nanohybrid materials (Ma et al. 2018). The re-entrant structure could be formed when nanoparticles were introduced on surfaces of HNTs, resulting in rod-dot hybrid particles. Hierarchical micro/nano structures could be generated when a great number of rod-dot hybrid particles aggregated and/or stacked, and the vacancies or pores may be filled with air, showing the potential for water repellency. Liu et al. have reported a facile surface coating technique to fabricate superamphiphobic protein-based films materials based on fluorinated HNTs/SiO₂ particles (Liu et al. 2019). The micro/nano hierarchical HNTs/SiO₂ particles were prepared via situ growth of SiO₂ on the surface of HNTs through sol-gel method.

ZnO nanoparticles is characterized by eco-friendly, low cost, ultraviolet-proof, biocompatibility and photocatalysis activity, which could be used to prepare superhydrophobic surface and has potential applications in the field of multifunctional textiles (Yang et al. 2019). Yang et al. obtained multifunctional cotton textiles based on PDMS/ZnO composite solution via one-pot dip-coating method (Yang et al. 2019). Moreover, some studies reported that ZnO nanoparticle assembled on HNTs can improve photocatalytic activity and absorptivity. Cheng et al. reported an impregnation method to successfully synthesize N-doped ZnO nanoparticle assembled into HNTs, which exhibited remarkable photocatalytic activity compared to pure ZnO nanoparticles (Cheng et al. 2015). So far there is rare report on the facile

fabrication of superhydrophobic cotton fabrics with self-cleaning, UV shielding, photocatalysis, and oil/water separation using hierarchical ZnO/HNTs hybrid particles.

In this paper, HNTs was used as the initial building block to prepare robust, superhydrophobic cotton fabrics with self-cleaning, UV shielding, photocatalysis, and oil/water separation after in-situ growth of ZnO nanoparticles. The surface morphologies, chemical composition, wettability, mechanical durability, UV stability, and anti-corrosion, self-cleaning, photocatalysis, and oil/water separation performances of all samples were characterized. These results demonstrated that the obtained multifunctional cotton fabric showed wide application even in harsh environment.

2. Experimental

2.1 Materials

Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), methylene blue (MB), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 30%) were offered by Sinopharm Chemical Reagent Co. (China). Polydimethylsiloxane (PDMS) with the curing agent was purchased from Dow Corning Co. (USA). The halloysite nanotubes (HNTs, purity > 97%) were purchased from Ishu International.

2.2 Preparation of ZnO/HNTs nanocomposites

ZnO/HNTs nanocomposites were synthesized via situ growth of ZnO on the surface of HNTs by sol-gel method. Firstly, 2g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.5g HNTs were added into 100 mL of deionized water and were stirred vigorously to form a homogenous solution at room temperature. Then pH of solution was adjusted to 9-10 with $\text{NH}_3 \cdot \text{H}_2\text{O}$. The mixed solution was further reacted at 60 °C for 2 h to obtain the ZnO/HNTs sol. After centrifugal washing and drying, a white powder was obtained. Finally, it was calcined in a muffle furnace at 450°C for 2 h to obtain a ZnO/HNTs hybrid particles.

2.3 Fabrication of ZnO/HNTs/PDMS@Cotton, HNTs/PDMS@Cotton, and PDMS@Cotton

Firstly, appropriate ZnO/HNTs hybrid particles were dispersed in water to formed homogeneous solution A. Besides, a certain amount of PDMS and curing agent (PDMS: 10:1 curing agent by mass ratio) were added to tetrahydrofuran to form solution B. The clean cotton fabric sample was immersed in the solution A and then dried at 80 °C. The obtained cotton fabric was called as ZnO/HNTs@Cotton. Then the as-prepared ZnO/HNTs@Cotton was dipped in the solution B and then cured at 130 °C for 0.5 h in an oven. The resultant cotton fabrics were named as ZnO/HNTs/PDMS@Cotton. The cotton fabric sample PDMS@Cotton coated by only PDMS was also prepared by the same method.

2.4 Sample characterization

The surface morphologies of samples were observed by using scanning electron microscope (SEM, Hitachi S-4800). The element distribution of cotton surface was examined by an energy dispersive spectrometer (EDS, Escalab250Xi). Chemical groups of samples were identified by Fourier

transformer infrared spectrometer (Nicolet IS 10, Thermo, USA). Thermogravimetric analysis (TGA) was tested using a thermogravimetric analyzer (Q500, TA, USA). The UV-blocking property of the samples was measured by a Labsphere UV-2000 ultraviolet transmittance analyzer.

Wettability test

The static water contact angles (WCA) of cotton fabric surface were tested by Krüss DSA 30 (Krüss, Germany). The water shedding angle (WSA) was tested according to reported literature (Wu et al. 2013; Zhang et al. 2013). The average of five values from same sample was defined as the final WCA and WSA of the cotton fabric surface.

Durability test

The abrasion resistance was measured by a fabric abrasion tester according to previous literature (Xu et al. 2020). The superhydrophobic cotton fabric was illuminated under a UV lamp of 150 W for 90 h continuously. The contact angles of the ZnO/HNTs/PDMS@Cotton were recorded to evaluate the UV resistance. The chemical stability of the modified cotton fabric was investigated by testing contact angles of modified cotton fabric after immersing into corrosive liquids with different pH levels ranging from 1 to 14 for 1 h.

Oil/water separation test and oil absorption test

The oil/water separation experiment of coated cotton fabric was carried out by using a simple and facile laboratory-made setup. The coated cotton fabric was placed between cylindrical filter funnel and conical flask as filter membrane, and the 100 ml yellow oil and 100 ml blue water mixed solution were poured into the funnel. The separation efficiency (η) was calculated according to $\eta = \frac{M_{\text{After}}}{M_{\text{Before}}}$, where M_{After} and M_{Before} is the quality of the oil/water mixed solution before and after separation process.

The flux was obtained according to $J = \frac{V}{S \cdot t}$, where V is the volume of oil permeated coated fabric, S is valid area of the film, and t is the time for collect of V ml of oil.

Photocatalytic activity

The photocatalytic activity of the superhydrophobic cotton fabric with the size of 3 cm × 5 cm and other samples were investigated by degrading 10 mg/L methylene blue (MB) solution. To avoid adsorption effects, the samples were magnetically stirred thoroughly in the dark environment until reaching the adsorption–desorption equilibrium of MB with photocatalyst before 150W high-pressure Hg lamp. Every 30 minutes, 2ml of the reaction solution was extracted and centrifuged to remove photocatalyst particles. Then the corresponding absorbance of the characteristic peak at 665 nm was measured by UV-visible absorption spectrum to record the concentration change of MB.

3. Results And Discussion

3.1 Preparation of ZnO/HNTs and ZnO/HNTs/PDMS@Cotton

The preparation process of the ZnO/HNTs and ZnO/HNTs/PDMS@Cotton was schematically shown in Fig. 1. First, the Zn^{2+} ionized by $Zn(NO_3)_2 \cdot 6H_2O$ in the aqueous solution attracts water molecules to form the solvent unit $Zn(H_2O)_2$. The solvent unit releases H^+ in an alkaline environment to maintain the coordination number to generate the precursor $Zn(OH)_2$. $Zn(OH)_2$ combined with Al-OH and Si-OH groups on the inner and outer walls of HNTs nanotubes by hydrogen bonding. The active sites on the inner and outer surfaces of the HNTs nanotubes can play a role in dispersing the precursors and prevent the precursors from agglomerating. Subsequently, the precursor-loaded HNTs nanotubes were calcined at a high temperature of $450^\circ C$ to obtain ZnO/HNTs nanocomposites. Then, the pristine cotton fabric was dipped into micro/nano hierarchical ZnO/HNTs hybrid particles dispersion to obtain ZnO/HNTs@Cotton. The ZnO/HNTs hybrid particles dispersion can endow fibers desirable roughness, which could generate micro/nano hierarchical structure combined with the natural morphology of the cellulose fiber. Finally, the ZnO/HNTs@Cotton was modified by PDMS to obtain superhydrophobic cotton fabric, which can lower the surface tension of ZnO/HNTs@Cotton.

3.2 Characterization of ZnO/HNTs and superhydrophobic cotton fabrics

The surface morphology of HNTs, ZnO/HNTs, PDMS@Cotton and ZnO/HNTs/PDMS@Cotton were observed by SEM. As illustrated in Fig. 2A, HNTs showed a homogeneously nanorod-like structure with a length and a diameter range of 0.7-1.5 μm and 30-50 nm, respectively. Compared to nanorod-like structures of the HNTs, the ZnO/HNTs hybrid particles exhibited unique rod-dot micro/nano hierarchical structures when the ZnO nanoparticles were introduced on surfaces of HNTs (Fig. 2C, D). PDMS@Cotton fabric with relative smooth surface, but there were still special folds and grooves in the longitudinal direction (Fig. 2E, F). In contrast, the ZnO/HNTs/PDMS@Cotton became much rougher, with particulate protrusions compacted on the cotton fabric surface (Fig. 2G). Moreover, the higher magnification SEM image of ZnO/HNTs/PDMS@Cotton shown in Fig. 2H revealed that ZnO/HNTs coating was covered with a thin layer of PDMS coating.

For further investigation of coated cotton fabric, the chemical components of the untreated cotton fabric, PDMS@Cotton, and ZnO/HNTs/PDMS@Cotton were characterized by EDS and FTIR. As shown in Fig. 2J, the C, O, Si and Zn elements were distributed on the surface of the coated fabric, suggesting the successful coating of ZnO/HNTs and PDMS on coated fabric surface and ZnO/HNTs/PDMS@Cotton was successfully prepared. In addition, the uniform distribution of C, O, Zn and Si elements indicated that ZnO/HNTs hybrid particles and PDMS were evenly covered on cotton surface (Fig. 2I).

As shown in Fig. 3A, in FT-IR spectrum of pristine cotton fabric, it could be clearly observed from the infrared spectrum that a strong and broad absorption peak appeared at 3332 cm^{-1} , which was the characteristic peak of the stretching vibration of the hydroxyl group in the cellulose macromolecule of the

pristine cotton fabric. Two characteristic absorption peaks can be observed at 2893 cm^{-1} and 1310 cm^{-1} , namely $-\text{CH}_3$ stretching vibration and bending vibration absorption. The strongest absorption peak at 1027 cm^{-1} originated from the flexural vibration of the hydroxyl group ($-\text{OH}$) in the cotton cellulose macromolecule and the C-O-C stretching vibration absorption. When the cotton fabric was coated with PDMS, new peaks at 2967 cm^{-1} , 1258 cm^{-1} , and 783 cm^{-1} occurred, which were assigned to $-\text{CH}_3$ stretching vibration, Si-C bend vibration and Si-O-Si symmetrical stretching vibration, respectively, which were due to a lot of $-\text{CH}_3$ groups and Si-O-Si groups of PDMS. The appearance of these characteristic peaks indicated that PDMS had been successfully grafted onto cotton fabrics. Compared with PDMS@Cotton, there were no obvious new bands from FT-IR spectra of ZnO/HNTs/PDMS@Cotton.

The thermal stability of the ZnO, ZnO/HNTs, pristine cotton fabric, PDMS@Cotton and ZnO/HNTs/PDMS@Cotton were investigated by thermo gravimetric analysis. As shown in Fig. 3B, there was 11% weight loss at temperatures below 350°C in the case of the pristine cotton fabric, and the weight loss was 13% for PDMS@Cotton and 10% for ZnO/HNTs/PDMS@Cotton, respectively. The weight loss of the samples from room temperature to 350°C was small, mainly due to the water volatilization and impurities decomposition which absorbed on cotton fabric surface. From 350°C to 420°C , the weight loss of pristine cotton fabric was 78.5% because of the decomposition of cellulose. Untreated cotton fabric showed residual weight rate of about 0.01% after being heated to 700°C because of the residual groups (such as $-\text{CH}_2-$, etc.) decomposition. It was indicated that there was little pristine fabric left. In contrast, the remaining weight percentage of PDMS@Cotton was 2.3%, which was higher than 0.3% of pristine cotton fabric. This was mainly caused by the incomplete decomposition of PDMS at high temperature. However, for ZnO/HNTs/PDMS@Cotton, the residual weight percentage reached to 9.1%, showed the improved thermal stability. As mentioned above, ZnO/HNTs hybrid particles had excellent thermal stability. Thereby, TG result of ZnO/HNTs/PDMS@Cotton revealed the successful incorporation of ZnO/HNTs hybrid particles and PDMS on the cotton fabric surface.

3.3 Wettability of superhydrophobic cotton fabrics

Surface roughness and chemical composition are two key factors for preparation of superhydrophobic surface. Therefore, the controlled variable method was adopted to study the wettability of coated cotton fabric by changing the content of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and PDMS. As displayed in Fig. 4A, the HNTs/PDMS@Cotton exhibited hydrophobicity with a water contact angle of $143.9 \pm 1.2^\circ$. This result indicating that the only HNTs and PDMS were unable to endow pristine cotton fabric superhydrophobicity. With the mass fraction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ increased to 2 wt. %, the ZnO/HNTs/PDMS@Cotton displayed the superhydrophobicity with a WCA of $162.5 \pm 1^\circ$. This result can be explained that the cotton fabric surface was composed of hierarchical micro/nano structures with higher roughness after modified by ZnO/HNTs hybrid particles. However, the superhydrophobicity of ZnO/HNTs@Cotton was negatively affected by the further increase of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ mass fraction (6 wt. %), the WCA was $150.2 \pm 0.7^\circ$. This may be caused by the slight disappearance of the micro/nano hierarchical structure of ZnO/HNTs/PDMS@Cotton due to excessive $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, resulting in a

decrease in roughness. Therefore, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with mass fraction of 2 wt. % was the optimal choice for subsequent experiments.

Similarly, in Fig. 4B, for only the ZnO/HNTs hybrid particles were employed to the pristine cotton fabric, the ZnO/HNTs@Cotton was easily wetted due to the inherent hydrophilic properties of the ZnO/HNTs hybrid particles and cellulose. The WCA of ZnO/HNTs@Cotton increased dramatically from 0° to $148.1 \pm 1^\circ$ even if only 5% of PDMS was introduced. This was because the introduction of PDMS lowered the surface tension of ZnO/HNTs@Cotton. As the PDMS mass fraction was up to 15%, the WCA of ZnO/HNTs@Cotton increased to $162.5 \pm 1^\circ$ and the rolling angle dropped to 4° . However, the WCA of ZnO/HNTs@Cotton decreased to $152.4 \pm 0.8^\circ$ when the mass fraction of PDMS reached 25%. This was because excessive PDMS completely cover ZnO/HNTs hybrid particles hierarchical micro/nano structure, which made the surface of ZnO/HNTs/PDMS@Cotton too smooth to construct roughness.

To further evaluate superhydrophobic property of the coated cotton fabric, the Cassie-Baxter model was used to explain the influence of hierarchical rough surface on wettability. According to Cassie-Baxter's equation, the apparent contact angle on the surface (θ^*) is calculated as

$$\cos\theta^* = r\cos\theta - f + 1 \quad (1)$$

where θ presents the Young's contact angle that is obtained on the slippy surface with the same composition, r is the actual wetted area divided by the projected wetted area of the surface, f is the fraction of the projected area of the solid surface contacting the liquid.

In Equation (1), r is greater than 1, f is less than 1, and both are positive. The $\theta < 90^\circ$ is due to the natural hydrophilic properties of cotton fabric. Therefore, if f is small enough, θ^* can be greater than 150° according to equation (1). One strategy to minimize the f value is to increase the surface roughness of the material, such as flower-like structure, and micro/nano re-entrant structure. As shown in Fig. 5A, after HNTs and PDMS coating, HNTs/PDMS@Cotton showed hydrophobicity with a WCA of 143.9° . Compared with the microrod-like HNTs stacked coating, the roughness factor of ZnO nanoparticles has increased, showing a certain degree of superhydrophobicity with a water contact angle of 152.4° (Fig. 5B). In this paper, a micro-/nano hierarchical re-entrant structure was constructed by depositing ZnO nanoparticles onto the rod-like HNTs surfaces. As displayed in Fig. 5C, the deposition of ZnO nanoparticles further increases the surface roughness of ZnO/HNTs hybrid particles, resulting in a significant reduction in the liquid/solid contact area. The coated cotton fabric displayed excellent superhydrophobicity with a water contact angle of 162.5° due to could trap the more air layer.

The surface wettability of superhydrophobic cotton fabrics were analyzed by evaluating their static/dynamic wettability performances and antifouling ability. As shown in Fig. 6A, different liquid droplets including blue colored water, juice, and cola were dropped on pristine cotton fabric and ZnO/HNTs/PDMS@Cotton. These aqueous droplets collapsed on the untreated cotton fabric due to its hydrophilic nature. In contrast, the ZnO/HNTs/PDMS@Cotton could hold on all liquid droplets in a spherical shape without any penetration. When pristine cotton fabric and ZnO/HNTs/PDMS@Cotton were

immersed in water, photographs of cotton fabrics were shown in Fig. 6B. The untreated cotton fabric promptly sank to the bottom of water. However, ZnO/HNTs/PDMS@Cotton can float on water without any wetting. As illustrated in Fig. 6C, when the fixed ZnO/HNTs/PDMS@Cotton was immersed in water, a silver mirror surface was observed due to the existence of an air cushion surrounded by the coating. Additionally, a jet of red water could easily bounce off from the coated cotton fabric surface without leaving a trace. In contrast, a jet of red colored water easily wet on pristine cotton fabric (Fig. 6D, E).

3.4 Durability evaluation of the superhydrophobic cotton fabrics

In practical applications, most of superhydrophobic coatings easily lose their superhydrophobicity under harsh conditions, such as mechanical abrasion and UV irradiation. As illustrated in Fig. 7A, after 2000 abrasion cycles, the WCA of ZnO/HNTs/PDMS@Cotton showed only slight change, still higher than 150° . This result indicated that ZnO/HNTs hybrid particles with silicone elastomer PDMS coating still maintained excellent superhydrophobicity after mechanical abrasion although ZnO/HNTs hybrid particles of the fiber surface was partially destroyed (Fig. 7B). This was attributed to PDMS, which not only lowered the surface energy of the coating, but also formed a dense film on the surface of the cotton fabric coating and bonded the ZnO/HNTs hybrid particles tightly on the surface of the cotton fiber to enhance the mechanical durability of superhydrophobic cotton fabric. In addition, as presented in Fig. 7C the WCAs of superhydrophobic cotton fabric remained around 150° after 150W UV irradiation for 90h, showing good UV-durability. From Fig. 7D, typical micro/nano hierarchical structure was retained on the microscale fiber surface of ZnO/HNTs/PDMS@Cotton after UV irradiation for 90h. This was mainly due to the anti-ultraviolet properties of ZnO/HNTs hybrid particles and the strong bond energy of the -Si-O-Si- bond contained in the PDMS layer, which made PDMS resistant to UV decomposition. Moreover, the chemical stability of the coated cotton fabric was also evaluated. The influence of acid and alkali on the wettability of the superhydrophobic cotton fabric was tested by immersing in different pH value solutions ranging from 1 to 14 for 1 h. As displayed in Fig. 7E, the WCA of ZnO/HNTs/PDMS@Cotton after dipping in solution with pH value varying from 1 to 14 still kept higher than 151° . As shown in Fig. 7F, there were still hierarchical rough morphology on ZnO/HNTs/PDMS@Cotton fiber surface. These results indicated that the prepared cotton fabric showed great potential in arousing consumer interest and large-scale industrial applications.

3.5 Self-cleaning antifouling performance

Self-cleaning behavior refers to the phenomenon that various contaminants on solid surfaces can be eliminated under natural circumstance. To investigate self-cleaning of the cotton fabric samples prepared in this study, a layer of methyl orange powder was used as contaminant. When a continuous process of water droplets was dropped onto ZnO/HNTs/PDMS@Cotton surface, they quickly rolled off and picked up the dissolved methyl blue powder without adhering to it (Fig. 8A). Consequently, the preferable superhydrophobic self-cleaning ability of the ZnO/HNTs/PDMS@Cotton was confirmed.

Moreover, to demonstrate the excellent antifouling ability of the superhydrophobic cotton fabric, liquid pollutants experiments were carried out. As presented in Fig. 8B, the ZnO/HNTs/PDMS@Cotton was immersed in red colored aqueous solutions and then taken out. The superhydrophobic cotton fabric still maintained dry without any residue due to the presence of a layer of air between the surface and the liquid, which protects the cotton fabric from wetting.

3.6 Photocatalytic performance

To investigate the photocatalytic degradation of samples, photodegradation experimental toward MB was carried out. Fig. 9A displayed the photodegradation efficiencies of ZnO, ZnO/HNTs, ZnO/HNTs@PDMS, and ZnO/HNTs/PDMS@Cotton toward MB under UV-vis irradiation. Fig. 9B given the UV-vis absorption spectra of MB in ZnO/HNTs/PDMS@Cotton photocatalytic process. As can be seen in Fig. 9A, the ZnO photodegradation efficiencies reached 98% after UV-vis irradiation about 1.5 hours. While the absorption bands of MB solution in the presence of the ZnO/HNTs hybrid particles decreased significantly and 96.7% photodegradation efficiencies was obtained after UV-vis irradiation for 0.5 hours. The excellent photocatalytic performance of the ZnO/HNTs hybrid particles may be ascribed the active sites on the inner and outer surfaces of HNTs hinder the agglomeration of precursors to form smaller-sized ZnO nanoparticles and HNTs support as adsorbent. Compared with ZnO/HNTs photocatalyst, ZnO/HNTs@PDMS and ZnO/HNTs/PDMS@Cotton takes longer time to achieve the similar photocatalytic efficiencies. Interestingly, ZnO/HNTs@PDMS mostly floated on the surface of methyl blue dilution because of its excellent superhydrophobicity. Undoubtedly, this great superhydrophobicity of ZnO/HNTs@PDMS negatively affected its degradation effect in this experiment. When ZnO/HNTs@PDMS was coated on cotton fabric, its photocatalytic efficiencies were reduced. This was because the contact area between ZnO/HNTs/PDMS@Cotton and methylene blue was smaller than that of ZnO/HNTs@PDMS. As can be seen in Fig. 9B, in 0-3 h, the degradation rate of ZnO/HNTs/PDMS@Cotton to MB gradually decreases. This can be attributed to the fact that in the range of 0-3h, as the degradation reaction progresses, the MB concentration in the system gradually decreased, resulting in the gradually decreased of the contact between ZnO/HNTs/PDMS@Cotton and MB. When the degradation reaction progressed to 3h, the degradation rate of ZnO/HNTs/PDMS@Cotton to MB gradually increased. This can be explained by the fact that as the degradation reaction progresses, the hydrophobicity of ZnO/HNTs/PDMS@Cotton was getting worse and the contact surface with MB gradually becomes larger, and this effect was greater than the reduction of MB concentration in the system on the degradation reaction.

3.7 Oil-water separation of the superhydrophobic cotton fabrics

The ZnO/HNTs/PDMS@Cotton possessed both superhydrophobic and superoleophilic characteristics and had a certain attraction for the separation of oil/water mixtures. Herein, dichloromethane was used to measure the oil/water separation ability of the ZnO/HNTs/PDMS@Cotton. Fig. 10A shown the separation processes of dichloromethane by the as-prepared cotton fabric. As expected, while the dichloromethane/water mixture was poured into the filter apparatus, yellow dichloromethane could

permeate through the superhydrophobic cotton fabric filter membrane instantaneously due to gravity, leaving only the water above the filter. After 10 cycles of separation, the superhydrophobic cotton fabric still exhibited high separation efficiency, and the separation efficiency and flux of dichloromethane/water mixture was up to 94.6% and $636 \text{ Lm}^{-2}\text{s}^{-1}$, indicating excellent recyclability (Fig. 10B). As displayed in 10C, with the increase of oil/water separation cycles, WCA of ZnO/HNTs/PDMS@Cotton decreased slightly but remained above 150° . These results above mentioned demonstrated that ZnO/HNTs/PDMS@Cotton showed wide application prospects in the field of oil/ water separation.

3.8 UV-shielding property of the superhydrophobic cotton fabrics

Figure 10 shows the ultraviolet transmittance spectra and UPF values of pristine cotton fabric, PDMS@Cotton, and ZnO/HNTs/PDMS@Cotton. From Fig. 11, pristine cotton fabric and PDMS@Cotton displayed similar transmittances curves and didn't show UV shielding performance. In comparison, pristine cotton fabric and PDMS@Cotton, ZnO/HNTs/PDMS@Cotton exhibited high UV shielding effect and UPF value significantly improved to 1643.28 and T(UVA) and T(UVB) were only 0.3% and 0.05%, respectively. This result was attributed to strong ultraviolet-absorption, light scattering and frequent light reflection of ZnO nanoparticles in ZnO/HNTs hybrid particles coated on cotton fabric (Momen et al. 2012).

4. Conclusion

In summary, a facile approach to prepare robust, ultraviolet-proof superhydrophobic cotton fabric based on PDMS and hierarchical ZnO/HNTs hybrid particles for self-cleaning, photocatalysis, and oil/water separation. When the mass fraction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and PDMS were 2% and 15% respectively, the prepared coated cotton fabric achieved superhydrophobicity with a WCA of $162.5 \pm 1^\circ$. Moreover, the superhydrophobic fabric displayed desirable self-cleaning, antifouling, photocatalysis, and oil/water separating performance. The prepared functional cotton fabric also demonstrated good ultraviolet-proof performance. Importantly, the superhydrophobic cotton fabric was stable enough to withstand mechanical abrasion test, chemical corrosion, and UV irradiation. This work provides a low cost and environmentally friendly approach for development of multifunctional textiles, which can be employed in self-cleaning, degradation of dye waste and UV shielding fields.

Declarations

Acknowledgements

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Figures

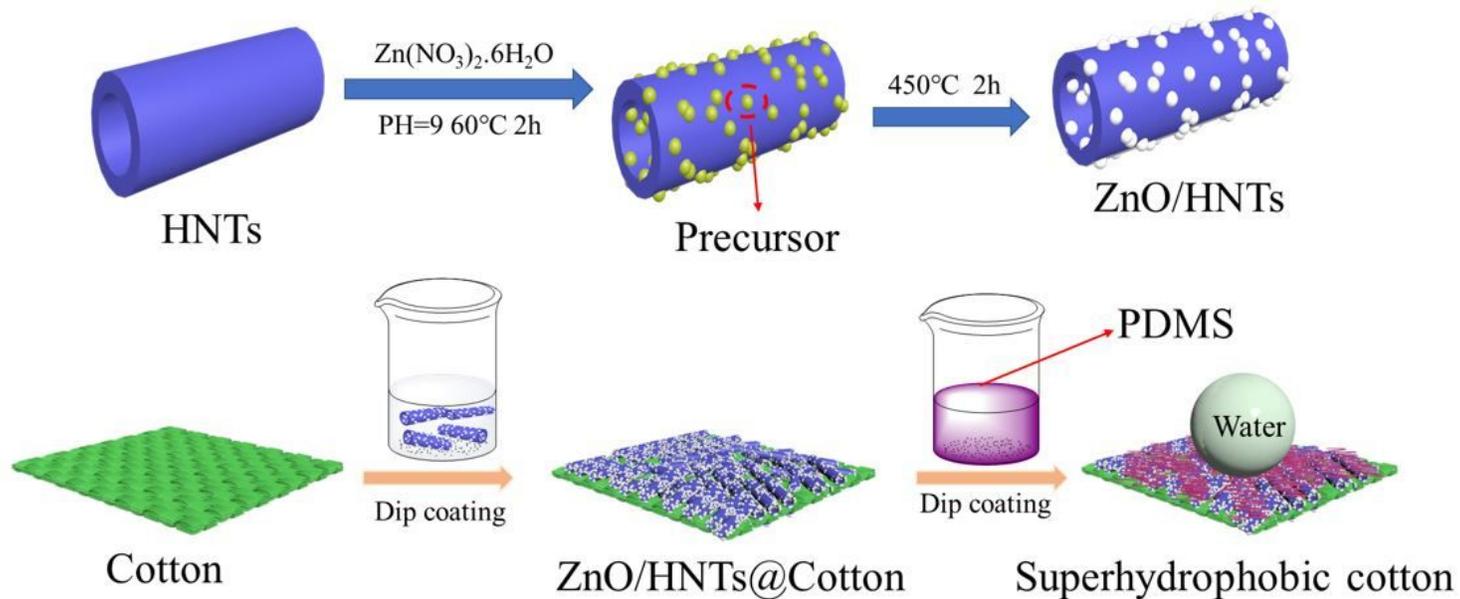


Figure 1

Diagram illustrating the fabrication process of ZnO/HNTs and superhydrophobic fabrics

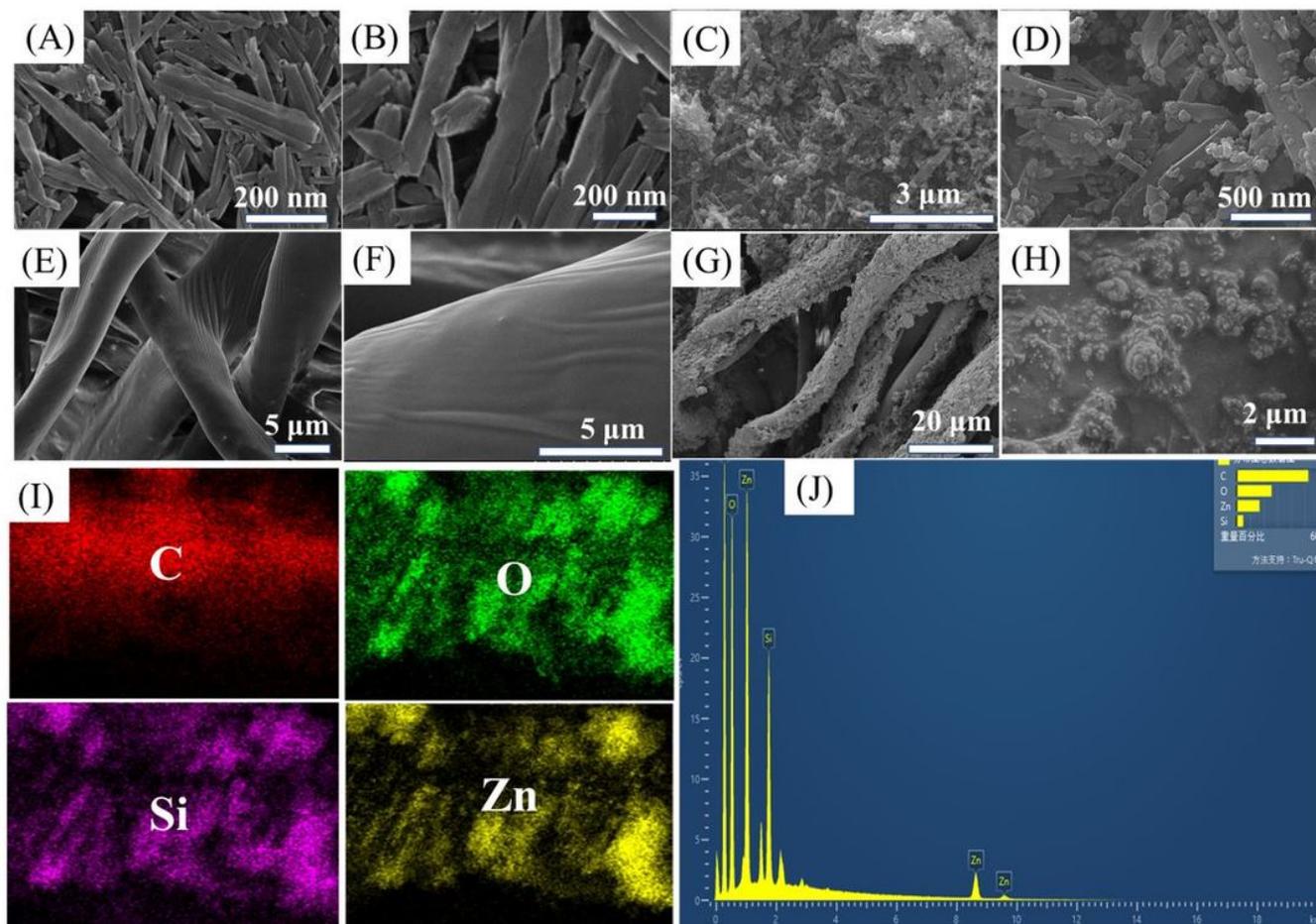


Figure 2

SEM images: A, B HNTs with different magnifications; C, D ZnO/HNTs with different magnifications; E, F PDMS@Cotton with different magnifications; G, H ZnO/HNTs/PDMS@Cotton with different magnifications; EDS I Elemental mapping of C, O, Zn and Si for the ZnO/HNTs/PDMS@Cotton; J spectrum of the ZnO/HNTs/PDMS@Cotton.

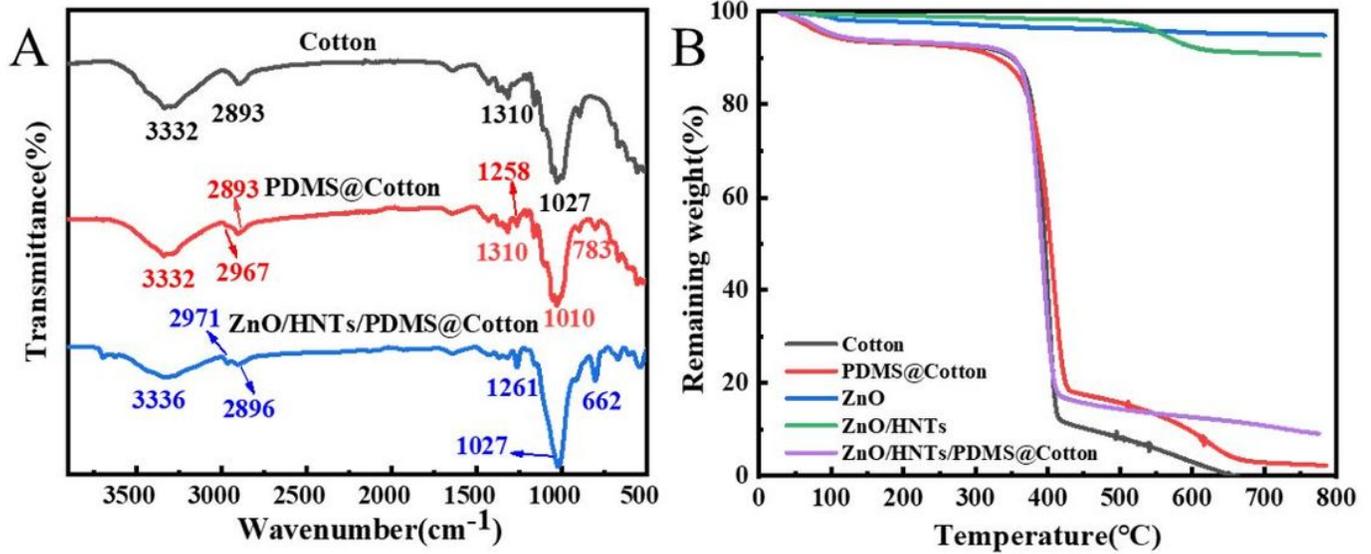


Figure 3

A FTIR spectra of pristine cotton, PDMS@Cotton and ZnO/HNTs/PDMS@Cotton; B TG curves of ZnO, ZnO/HNTs, pristine cotton PDMS@Cotton, and ZnO/HNTs/PDMS@Cotton.

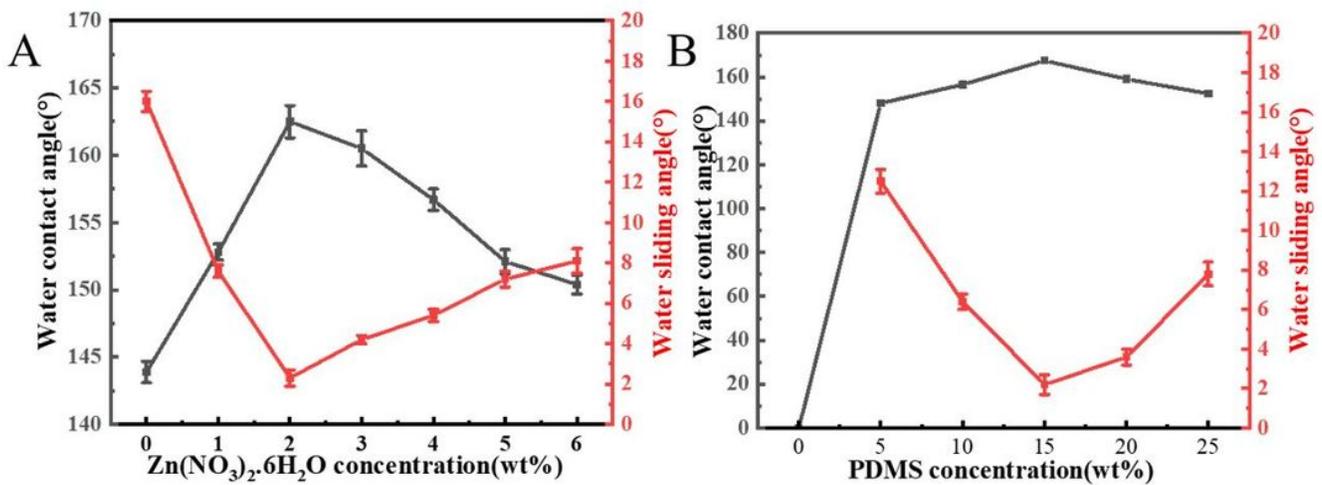


Figure 4

The effect of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ concentration and PDMS concentration on the hydrophobicity of $\text{ZnO}/\text{HNTs}/\text{PDMS}@Cotton$

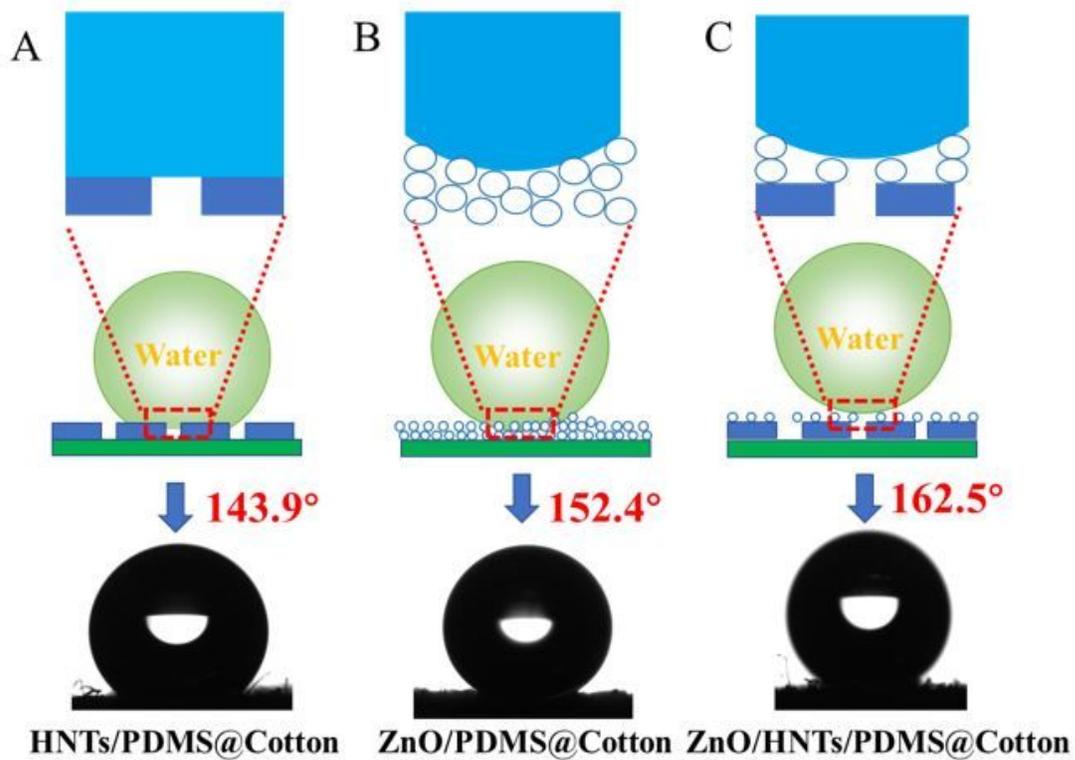


Figure 5

Different structure wetting states (A) Micro HNTs wetting state; (B) Nano ZnO wetting state; (C) Micro/nano ZnO/HNTs wetting state.

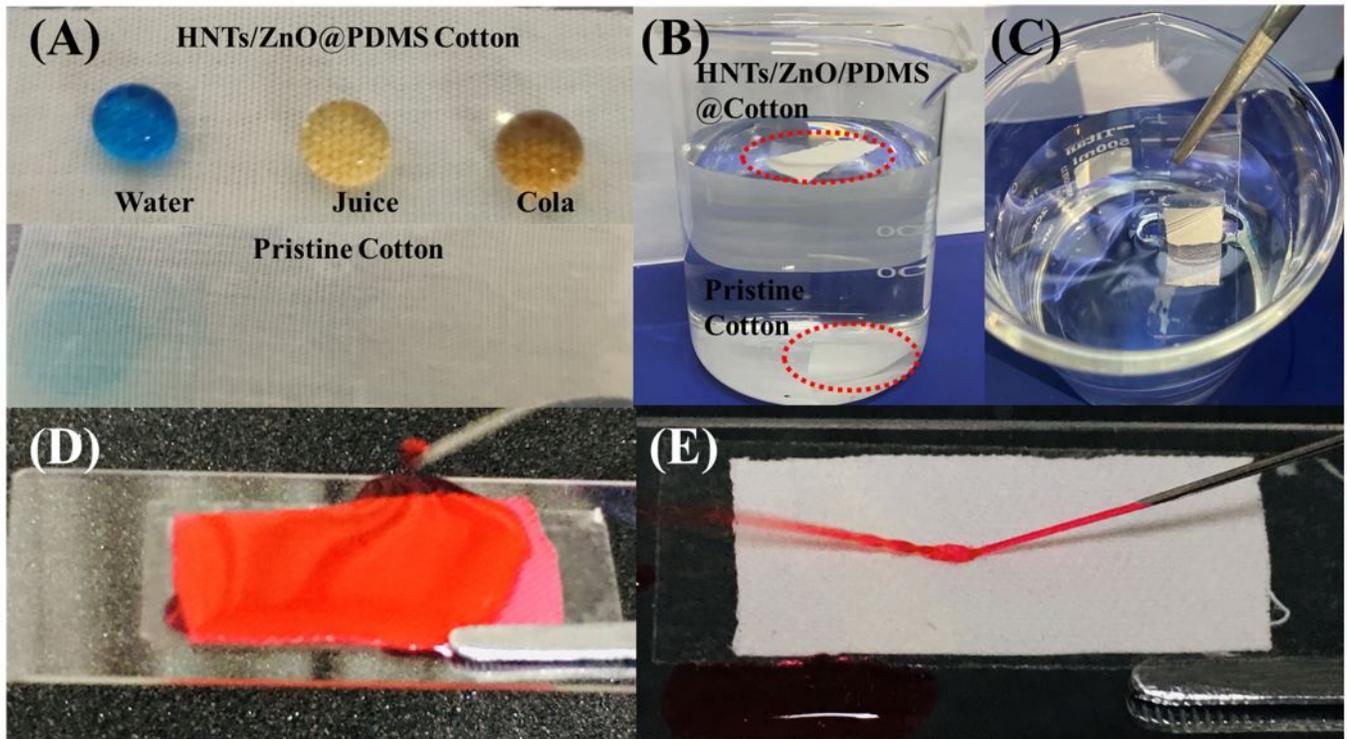


Figure 6

A different liquid droplets on the surface of the pristine cotton fabric and ZnO/HNTs/PDMS@Cotton; B ZnO/HNTs/PDMS@Cotton and pristine cotton fabric in water; C immersion of ZnO/HNTs/PDMS@Cotton stuck on glass into water; D a jet of colored water spread on the pristine cotton fabric; E a jet of colored water was bouncing off from ZnO/HNTs/PDMS@Cotton

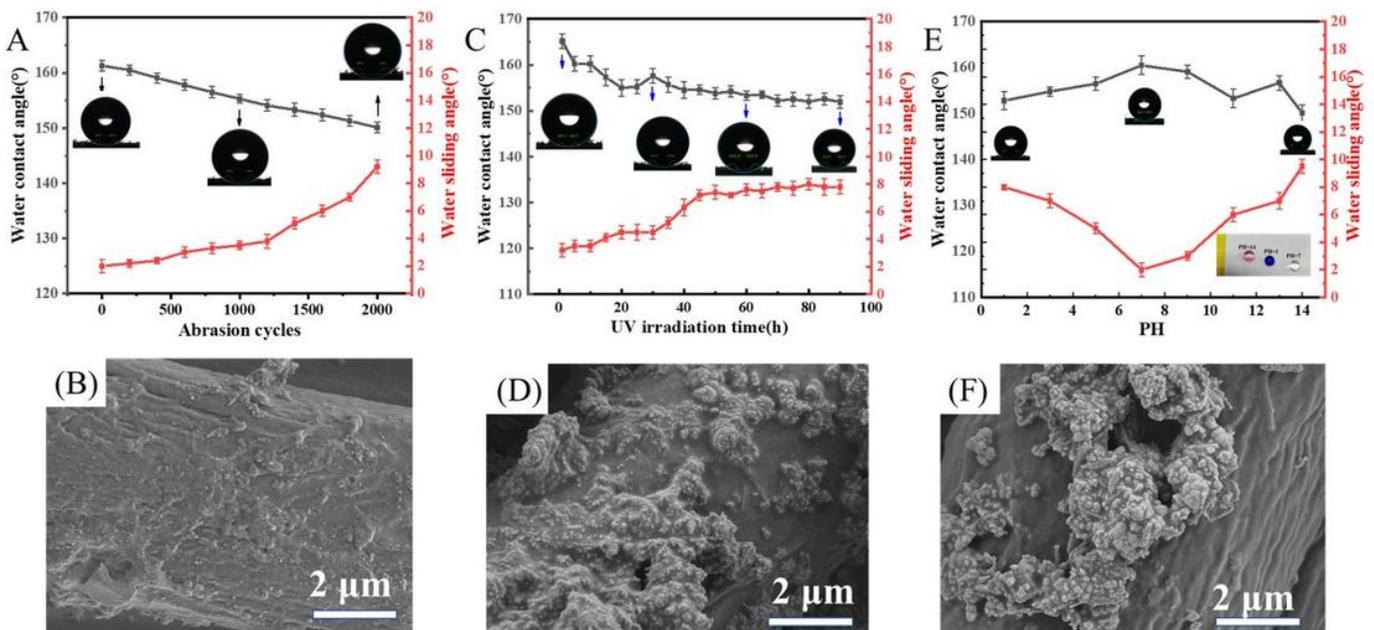


Figure 7

A WCA of ZnO/HNTs/PDMS@Cotton after different abrasion cycles test; B SEM image of ZnO/HNTs/PDMS@Cotton after abrasion for 2000 cycles; C WCA of ZnO/HNTs/PDMS@Cotton after different UV irradiation time; D SEM image of ZnO/HNTs/PDMS@Cotton after UV irradiation for 90 h; E WCA of ZnO/HNTs/PDMS@Cotton after immersion in solution with different pH values; F SEM image of ZnO/HNTs/PDMS@Cotton after immersion in solution with PH value of 14

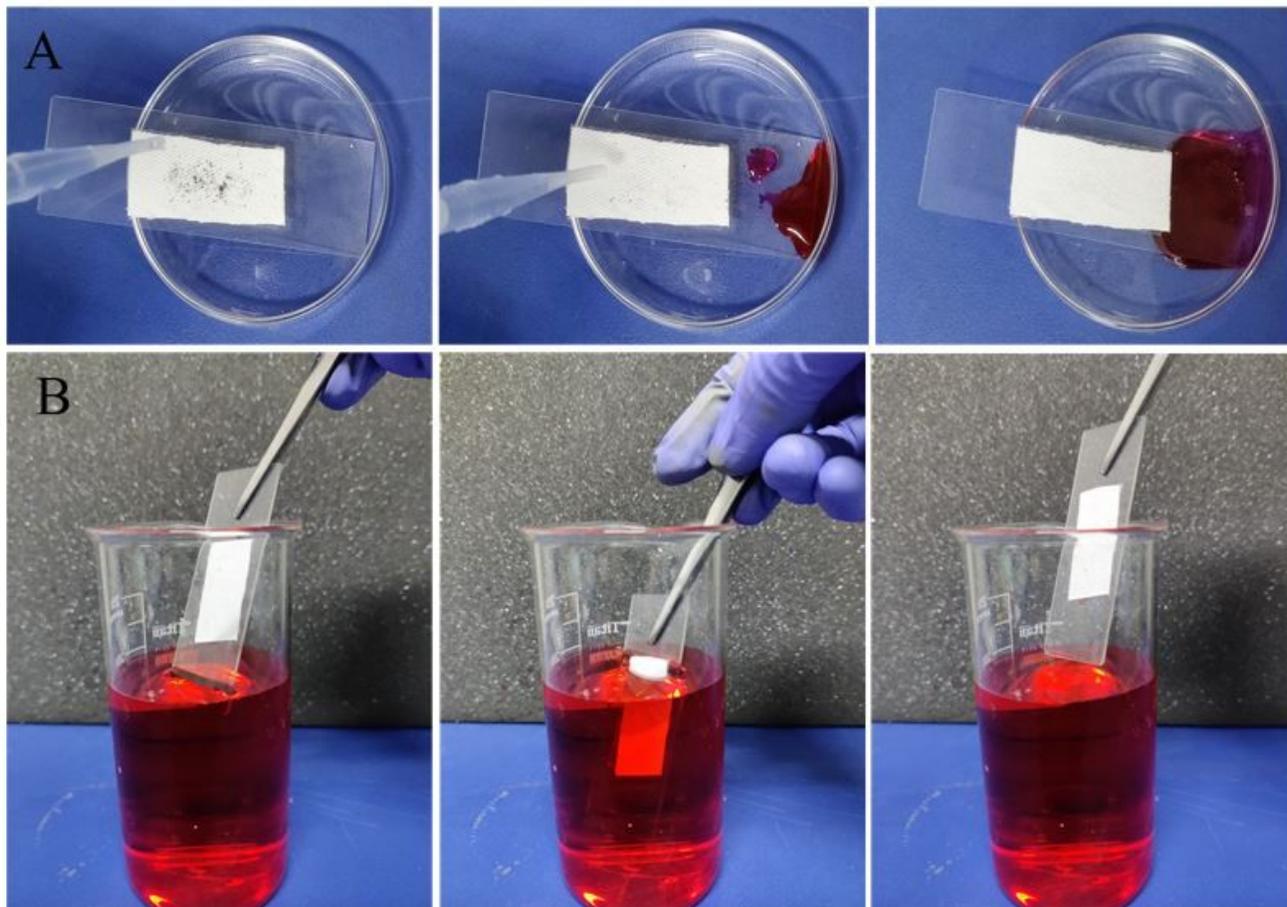


Figure 8

A Self-cleaning property test of ZnO/HNTs/PDMS@Cotton and B antifouling property test of ZnO/HNTs/PDMS@Cotton

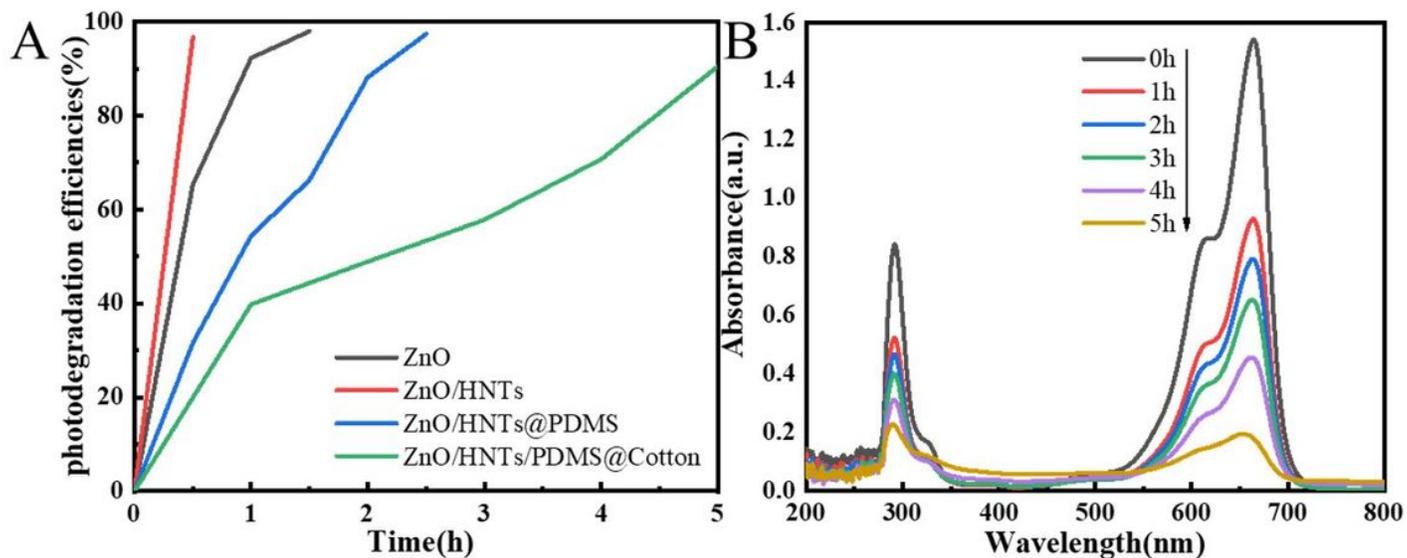


Figure 9

A Photodegradation efficiencies of ZnO/HNTs/PDMS@Cotton and other comparative samples on MB; B UV-vis spectra of MB solutions after different irradiation time with the ZnO/HNTs/PDMS@Cotton

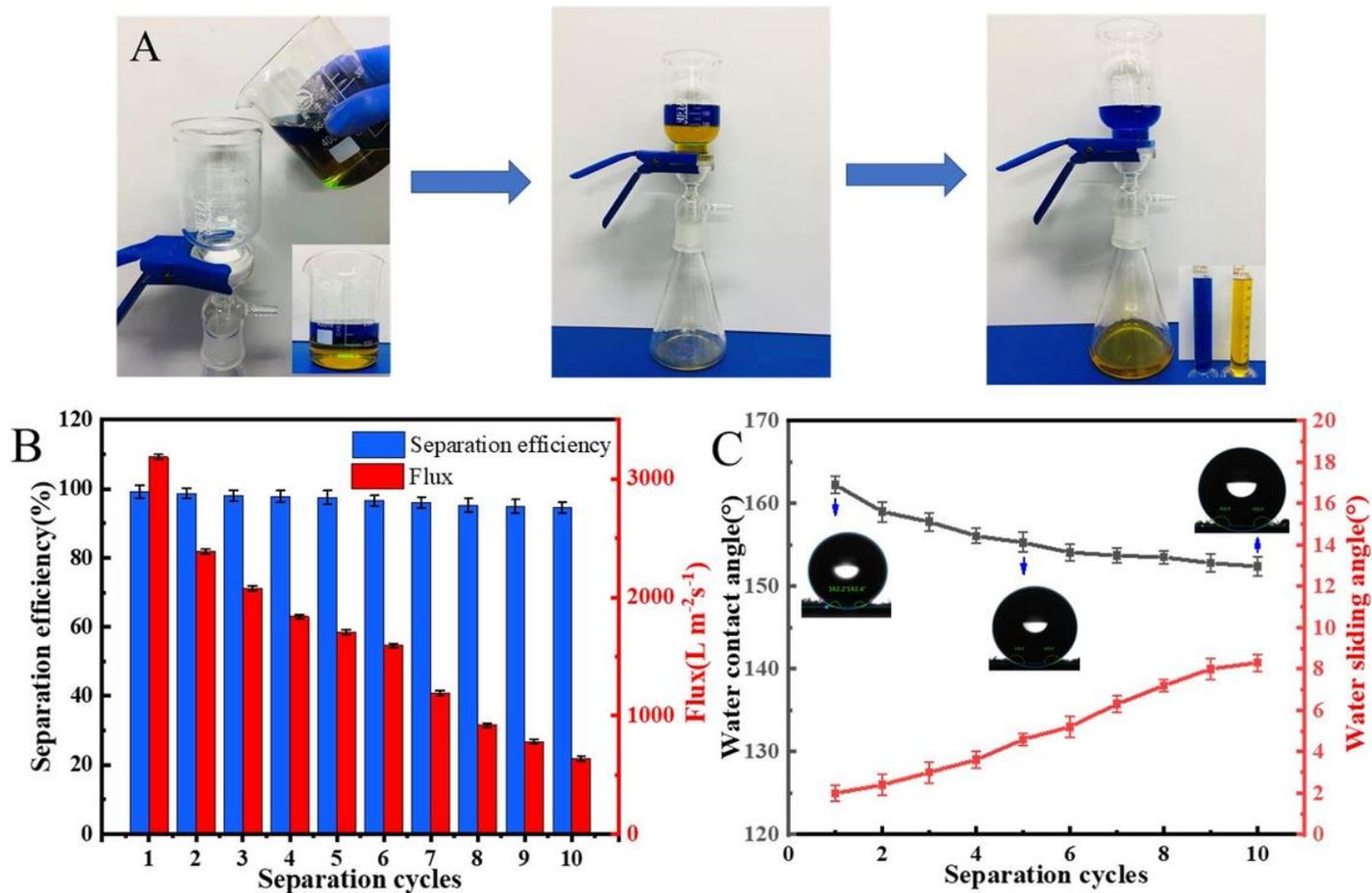


Figure 10

ZnO/HNTs/PDMS@Cotton: A oil/water separation process; B separation efficiency and separation flux after different separation cycles; C WCA after different separation cycles.

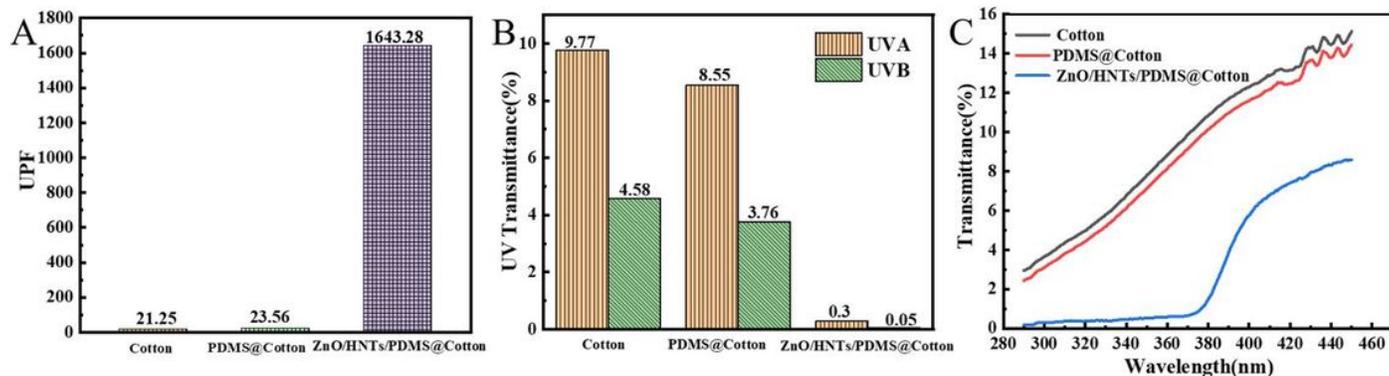


Figure 11

Pristine cotton fabric, PDMS@Cotton and ZnO/HNTs/PDMS@Cotton: A UV transmittance curves, B UPF values, and C UV transmittance