Cellulose (2020) 27:9005–9026
https://doi.org/10.1007/s10570-020-03369-2

ORIGINAL RESEARCH

One-pot preparation of robust, ultraviolet-proof superhydrophobic cotton fabrics for self-cleaning and oil/water separation

Lihui Xu · Yadong Liu · Xiaoling Yuan · Jing Wan · Liming Wang · Hong Pan · Yong Shen

Received: 27 March 2020 / Accepted: 25 July 2020 / Published online: 10 August 2020

Abstract Robust superhydrophobic cotton fabrics with ultraviolet (UV)-proof performance were prepared via a simple one-pot method with composite coating of hierarchical CuS microflower nanoparticles and silicone elastomer polydimethylsiloxane (PDMS). The facile preparation of CuS microflower nanoparticles was conducted via relatively low-temperature reaction. The surface morphology, chemical composition, thermal degradation behavior, and crystal structure of the products were evaluated. The simultaneous roughening due to hierarchical rough morphology of CuS microflower nanoparticles and PDMS hydrophobization resulted in the coated fabric with microscale fibers exhibiting superhydrophobic property and its water contact angle was 159.3° ± 0.6°. The superhydrophobic textile also displayed outstanding UV-proof performance with a large ultraviolet protection factor of 535.36 due to ultraviolet-absorption, light scattering and frequent light reflection of hierarchical CuS nanoparticles. The superhydrophobic textile showed excellent stain resistance and self-cleaning property and also was able to separate oil and water with high efficiency and good separation reusability caused by the contrasting wettability of the coated textile for water droplets and oil droplets. The as-prepared superhydrophobic fabric displayed excellent robustness against 2000 cycles rubbing, water jetting and long-time UV illumination and satisfactory chemical stability. This superhydrophobic coating showed no negative impact on the mechanical strength of cotton fabric. The facile approach in favor of large-scale preparation showed promising potential for wide application of flexible superhydrophobic cotton textiles with ultraviolet-blocking performance.

Keywords Superhydrophobic · Ultraviolet-proof · Hierarchical CuS · Self-cleaning · Oil/water separation · Cotton fabric

Introduction

Cotton fabric as one of natural fabrics is renewable and environmentally friendly and it exhibits wide application in clothing, household textiles and industrial textiles due to its softness, air permeability and moisture absorption. Unfortunately, cotton fabrics with excellent hydrophilicity are easily contaminated by a large number of pollutants with the rapid development of various modern industries, seriously affecting their function, appearance and application. However, the

---

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10570-020-03369-2) contains supplementary material, which is available to authorized users.

L. Xu (✉) · Y. Liu · X. Yuan · J. Wan · L. Wang · H. Pan · Y. Shen
School of Textiles and Fashion, Shanghai University of Engineering Science, Shanghai 201620, China
e-mail: xulh0915@163.com

traditional cleaning methods not only consume a large amount of water resources and detergent chemicals, but also seriously threaten the ecological environment. In recent years, superhydrophobic surface has aroused great interest and extensive attention due to its outstanding characteristics like self-cleaning, anti-corrosion, anti-fouling, and extreme waterproofing, etc. (Avramescu et al. 2018; Dalawai et al. 2020; Ghasemlou et al. 2019; Rius-Ayra et al. 2019). Like lotus leaf, the water droplets on the inclined superhydrophobic surface could roll off easily and take away dust particles to keep the surface clean, known as the "lotus effect" (Foorginezhad et al. 2019). Superhydrophobic surfaces also had excellent oleophilic property, that is to say, oil droplets could spread quickly on superhydrophobic surfaces. Therefore, superhydrophobic surface could be also used for oil water separation to purify oily wastewater resulting from a variety of industries, oil spillages or leakage of oil and organic solvents (Rostami et al. 2019; Yuan et al. 2018). Especially, superhydrophobic cotton fabrics own great advantages including flexibility, renewability, breathability, light weight, porous structure, wide applications, and so forth (Li et al. 2018; Yang et al. 2019a, b; Zhang et al. 2019). Furthermore, with deeper understanding of the harmful effects of ultraviolet (UV) radiation, anti-ultraviolet fabrics are also in great demand. Thus, development of superhydrophobic cotton textiles with ultraviolet-blocking property applied to self-cleaning as well as oil/water separating which can be widely used in technology, industry, medicine, military as well as daily life is urgently needed for improving living quality and is very significant to water saving, energy saving and environmental protection (Dong et al. 2019; Khan et al. 2018).

Learning from lotus, many researches verified that construction of superhydrophobic surfaces required the cooperation of micro/nano rough morphology and low surface tension (Ghasemlou et al. 2019; Jeong et al. 2020; Razavi et al. 2019). The fabrication approaches of superhydrophobic textile mainly included pre-roughening and post-hydrophobization method (such as dip-coating method, plasma processing, chemical etching), and one-pot method for simultaneous roughening and hydrophobization (such as chemical coating, electrochemical deposition) (Li et al. 2017). As textiles have their inherent micro-scale fiber structure, up to now superhydrophobic textile surface micro/nano rough morphology had been achieved by introducing some nano materials such as SiO_2 (Lahiri et al. 2019; Yu et al. 2019), TiO_2 (Foorginezhad et al. 2019; Riaz et al. 2019) or ZnO (Jeong et al. 2020; Patil et al. 2019) onto the fiber surface. Low surface energy of textile can be obtained by polysiloxanes or fluorochemicals like perfluorocarbon or fluoroalkylsilane (Tu et al. 2018). TiO_2 or ZnO due to its excellent UV-blocking property is commonly used to fabricate superhydrophobic and UV-proof textiles with the combination of surface hydrophobization. However, superhydrophobic and UV-proof fabrics using TiO_2 or ZnO probably showed poor UV-durability as a result of powerful photodegradation of photocatalyst for fibers as well as low surface tension substances (Chen et al. 2019a, b; Lee et al. 2016).

Huang et al. fabricated amorphous flower-like titanium oxide without photocatalytic activity on cotton fabrics via one-pot hydrothermal method followed by fluoroalkylsilane modification to prepare stable superhydrophobic and UV-resistant cotton fabrics (Huang et al. 2015). But this hydrothermal reaction involved hydrochloric acid solution and the mechanical strength of cotton fabric may be probably damaged under strong acidic condition. Furthermore, it was reported that superhydrophobic and UV-blocking textiles were prepared using materials like metal–organic frameworks (MOFs), bismuth oxyiodide (BiOI) nanosheets, organic UV absorber, CeO_2 sol, nano-Al sol, or carbon nanotubes, et al. Yang et al. prepared superhydrophobic and UV-resistant cotton textiles by in-situ growth of NH_2-MIL-125(Ti) (Ti-MOF) nanoparticles with subsequent polydimethylsiloxane (PDMS) coating (Yang et al. 2019a, b). Zhou et al. obtained multifunctional cotton textiles by immobilization of BiOI nanosheets via successive adsorption and reaction (SILAR) exhibiting superhydrophobic, UV-blocking and self-cleaning properties (Zhou et al. 2019). Xiong et al. fabricated superhydrophobic cotton textiles with UV-resistant property based on organic ultraviolet absorber prepared via grafting of polyethyleneimine using 2,4-dihydroxybenzophenone, SiO_2 sol and hexadecyltrimethoxysilane by successive layer-by-layer assembling and dip-coating method (Xiong et al. 2019). Duan et al. obtained superhydrophobic and ultraviolet protection cotton fabrics based on CeO_2 sol followed by fluoroalkyl silane modification (Duan et al. 2011).

Pan et al. prepared superhydrophobic cotton textile with ultraviolent-resistant property using nano-Al sol via dip-coating method as well as subsequent hydrophobization (Pan et al. 2012). Guo et al. fabricated superhydrophobic, ultraviolet protection and electrical conductive poly(ethylene terephthalate) (PET) fabrics by layer-by-layer assembling carbon nanotubes (Guo et al. 2017). However, the preparation methods usually had some drawbacks, like harsh treatment conditions (Huang et al. 2015), poor durability, expensive materials (such as fluorochemicals, nanotube), and complicated processes (Duan et al. 2011).

Copper sulfide (CuS) as a semiconducting material with excellent physical and chemical characteristics especially for CuS with nanostructure shows potential application in the field of energy, biomedicine and environmental engineering etc. (Chen et al. 2019a, b; Shi et al. 2017). In particular, CuS with flower-like hierarchical structure has attracted more and more attention recently (Zhai et al. 2019; Zhu et al. 2020), which could be also used for the preparation of superhydrophobic surfaces. However, only few researches used CuS to construct superhydrophobic surfaces. Cao et al. prepared superhydrophobic textile by forming copper sulfide nanostructures on textile surface followed by stearic acid modification (Cao et al. 2020). CuS was incorporated on textile surface via sequential immersion of cotton fabric into $Cu(NO_3)_2$ solution, NaOH solution and Na_2S solution. Thereby, this report about incorporation of CuS on textile surface involved complicated processes. Khosravi et al. prepared superhydrophobic and superoleophilic mesh by grafting CuS and Cu_2S microparticles on copper mesh with hydrothermal method and subsequent stearic acid (SA) hydrophobization for oil/water separation (Khosravi et al. 2019). But this research for the preparation of superhydrophobic mesh involved two-step process and hydrothermal method. Our previous study prepared flower-like CuS particles with the diameter of 2–5 µm (Hu et al. 2016). But the flower-like CuS particles were synthesized by solvothermal method, involving harsh reaction conditions like high-temperature reaction and long reaction time (170 °C, 5 h). Additionally, the obtained CuS showed relatively large particle size, not favoring uniform distribution on substrate surface for superhydrophobic coating. In contrast, CuS nanoparticles with hierarchical rough morphology and relatively small particle size via facile low-temperature preparation are more beneficial to uniform superhydrophobic coatings on substrates. However, the reports about preparation of superhydrophobic surfaces using CuS mostly involved complicated processes or harsh conditions. So far there is rare report on the facile one-pot fabrication of superhydrophobic and ultraviolet-proof cotton textiles for self-cleaning and oil/water separation using hierarchical CuS nanoparticles via facile low-temperature preparation.

In this work, a facile one-pot method was reported to prepare robust superhydrophobic coating with ultraviolet-proof property on cotton textiles based on hierarchical CuS microflower nanoparticles for self-cleaning as well as oil/water separation. The hierarchical CuS microflower nanoparticles were prepared via a simple method. The synthetic method was comparably simple and safe with lower reaction temperature and shorter reaction time (65 °C, 50 min). The prepared hierarchical CuS microflower nanoparticles had diameters in the range of 150–250 nm, showing relatively small particle size. The prepared CuS nanoparticles were more beneficial to uniform distribution on substrate surface for superhydrophobic coating. Silicone elastomer polydimethylsiloxane (PDMS) and hierarchical CuS microflower nanoparticles were mixed to obtain PDMS/CuS composite coating. PDMS/CuS was used to coat cotton textiles via dip-pad-dry process. The coated cotton textiles showed outstanding superhydrophobicity with UV-blocking property and were promising for self-cleaning as well as oil/water separating application. The superhydrophobic cotton textile also demonstrated mechanical durability, UV-durability and anti-corrosion. The approach was facile and beneficial to large-scale preparation and the obtained flexible superhydrophobic fabrics with UV-blocking property showed wide application.

Materials and methods

Materials

Copper chloride ($CuCl_2{\cdot}2H_2O$), thioacetamide (TAA), 1-butyl-3-methylimidazolium chloride [BMIm]Cl, isopropanol and methanol were offered by Sinopharm Chemical Reagent Co. (China). Polydimethylsiloxane (PDMS) with curing agent was procured from Dow

Corning Co., USA. After desizing, scouring, bleaching and mercerizing, woven cotton textiles (504 ends/236 picks) were applied as the substrates.

Preparation of CuS microflower nanoparticles

As shown in Fig. 1, Firstly, [BMIm]Cl (0.4 mol) was added into 120 mL of methanol and was stirred vigorously for 10 min at 65 °C. After that, $CuCl_2\cdot 2H_2O$ (0.08 mol) was dropwise added into the mixture solution with agitating for another 10 min. Then, TAA and de-ionized water were added into the mixture solution successively under stirring. After continuing reaction at 65 °C for 50 min, black products were formed. Volume ratio of methanol and de-ionized water was 2:1. Molar ratio of $CuCl_2\cdot 2H_2O$ and TAA was 1:3. After cooling down, washing with deionized water and ethanol and drying, CuS microflower nanoparticles were acquired.

Preparation of superhydrophobic coating on cotton textiles

PDMS (1.5%) with curing agent (0.15%) was added to isopropanol. The PDMS/CuS composite coating solution was obtained via addition of CuS (2%) into the mixture and subsequent ultrasonical dispersion. The fabrics were coated with PDMS/CuS by dip-pad-cure approach, as shown in Fig. 1. The fabrics were immersed into PDMS/CuS and squeezed with a padder. Afterwards, fabrics were dried as well as subsequently cured. The temperature and time for curing was 150 °C and 60 min, respectively. The prepared textile was named as PDMS/CuS@Cotton. The fabric sample PDMS@Cotton coated by only PDMS was also prepared via dip-pad-cure approach.

Sample characterization

The surface morphologies of CuS and cotton fabrics were recorded by scanning electron microscope (SEM, Hitachi S-4800, Japan). The average particle size of CuS was tested by Zetasizer Nano ZS Particle Size Analyzer (Zetasizer Nano ZS, Malvern, Britain).

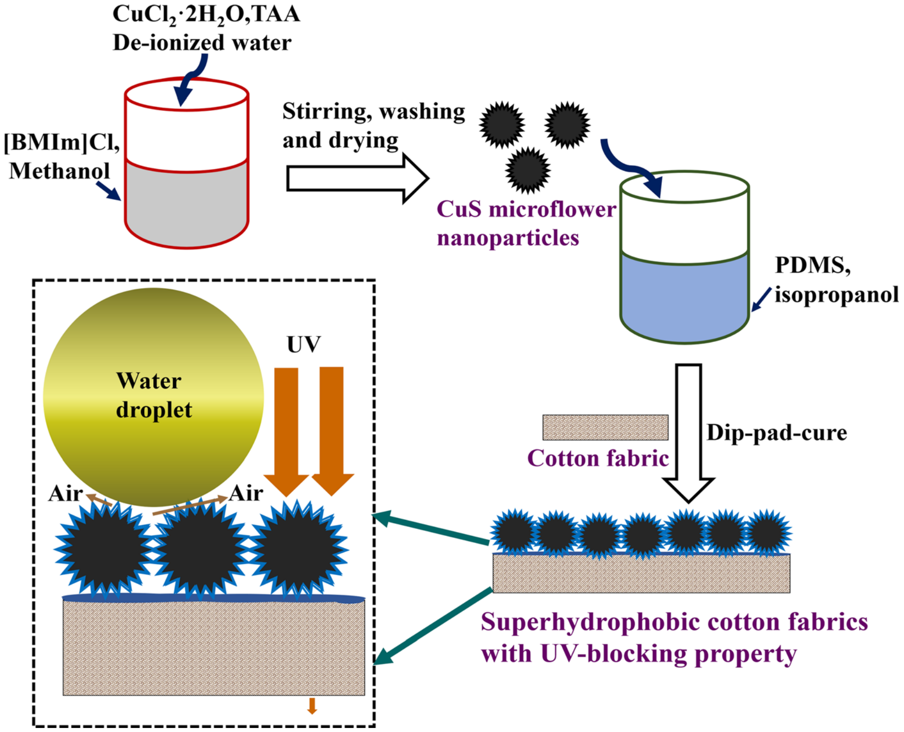

Fig. 1 Schematic of preparation of CuS and superhydrophobic fabrics with UV-proof property

The surface roughness of cotton fabric was measured by atomic force microscope (AFM, NanoManVS, Veeco, USA). Fourier transform infrared (FT-IR) spectra was taken by Fourier-transform infrared spectrometry (Nicolet IS 10, Thermo, USA). Thermogravimetric analysis (TGA) was carried out by thermogravimetric analyzer (Q500, TA, USA). The phase structures of samples were characterized by X-ray diffractometer (XRD, X'Pert PRO MPD, Panalytical, Netherlands). X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XI, Thermo, USA) used to analyze the chemical composition of cotton fabrics. The Brunauer–Emmett–Teller (BET) analysis of the samples was analyzed by automatic specific surface area and porosity analyzer (TriStarII3020, USA). UV–vis absorption spectra of the samples was taken by Hitachi U-3900H spectrophotometer. Breaking tenacity of cotton fabric was measured according to GB/T3923-2103 standard using electronic universal testing machine (H10K-S, USA).

Wettability test

Wettability test was performed via water contact angle (WCA) and water shedding angle (WSA) analysis with Kruss drop shape tester (DSA30, Germany). Contact angles (CA) were tested ten times with 5 µL water droplets at different points on sample surface and averaged. Dynamic contact angle measurements had been performed, including advancing contact angles (θa), receding contact angles (θr) and contact angle hysteresis ($\triangle\theta = \theta a - \theta r$). Water shedding angle (WSA) was the minimum tilt angle at which 15 µL water droplet completely rolled off. The sample was tested at five different points and the average WSA was obtained.

UV-blocking property test

The ultraviolet protection factor (UPF) and UV transmittance were measured by Labsphere UV-2000 Fabric Ultraviolet Transmittance Analyzer to evaluate UV-blocking property of the fabrics. UVA transmittance and UVB transmittance were named as T(UVA) and T(UVB).

Oil/water separation test and oil absorption test

Oil/water separation property was performed using the simple laboratory-made setup composed of cylindrical filter funnel, sand core filter, special clamp and conical flask used for collecting liquid. The coated cotton fabric was placed on sand core filter as filter membrane and the outer ring was sealed with paraffin to prevent liquid leakage. The cylindrical funnel was put on filter membrane. Then they were connected with flask and fixed by special clamp. The oil/water mixture was poured into cylindrical filter funnel and the liquid which can pass through the filter membrane was collected by the conical flask. The separation efficiency (η) was obtained based on the equation below:

$$\eta(\%) = \frac{M_{after}}{M_{before}} \times 100 \qquad (1)$$

where M_{before} is the weight of the initial oil in the oil/water mixture before separation and M_{after} is the weight of the collected oil after separation, respectively.

The oil absorption property of fabric samples was evaluated by testing oil absorption capacity. For a typical absorption process, the fabric was immersed into the oil for 1 h, and then taken out quickly and weighed immediately to avoid oil evaporation. The oil absorption capacity (Q) was calculated by the following equation:

$$Q(\%) = \frac{m_{after} - m_{before}}{m_{before}} \times 100 \qquad (2)$$

where m_{before} is the weight of initial PDMS/CuS@Cotton fabric before oil absorption and m_{after} is the weight of PDMS/CuS@Cotton fabric after oil absorption.

Durability test

The mechanical abrasion durability tests were performed by Martndale abrasion tester. The fabric sample was fixed and abraded with standard rubbing cloth according to Lissajous curve with a pressure of 12 kPa. Water jetting test was carried out by placing fabric samples on a platform with inclination angle of 45°. Water was jetted on the fabric samples. The ultraviolet-durability tests were carried out by placing fabric samples under mercury lamp for continuous artificial UV irradiation. The anti-corrosion property of the fabrics was measured by testing contact angles of fabrics after dipping fabrics into solutions with different pH values for 1 h.

Results and discussion

Characterization of CuS and cotton fabrics

The morphology of obtained CuS, PDMS@Cotton textile, and PDMS/CuS@Cotton textile were characterized by SEM. As shown in Fig. 2a, b, the obtained CuS microflower had spherical nanoparticles with hierarchical nanostructures. The diameters of hierarchical CuS microflower nanoparticles consisting of self-assembled nanosheets were in the range of 150–250 nm with relatively narrow size distribution. The CuS microflower nanoparticles were prepared based on the literature (Liu et al. 2018) with some modifications. In order to further estimate the diameters of hierarchical CuS microflower nanoparticles, the Zetasizer Nano ZS Particle Size Analyzer was used to measure the size distribution by intensity of CuS nanoparticles. From Fig. S1 (Supplementary data), the prepared CuS microflower nanoparticles showed average diameter of 185.4 nm with the corresponding polydispersity index (PDI) of 0.096. The CuS particles size ranged from 150 to 250 nm with relatively narrow size distribution. This result consisted with CuS SEM

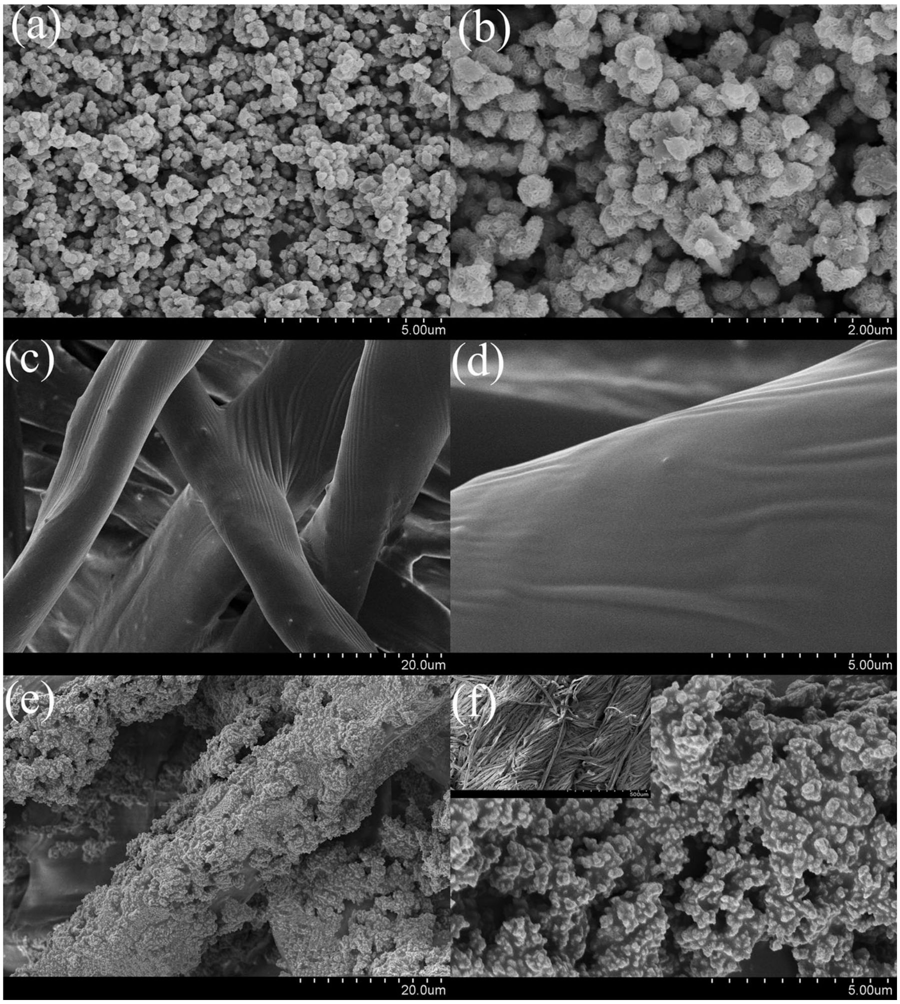

Fig. 2 SEM images of **a**, **b** CuS with different magnifications, **c**, **d** PDMS@Cotton textile with different magnifications, and **e**, **f** PDMS/CuS@Cotton textile with different magnifications (lower magnification SEM image of PDMS/CuS@Cotton textile is in the inset.)

characterization and the literature (Liu et al. 2018). PDMS@Cotton fabric with relative glossy surface still showed the intrinsic fibrils with cannelures of micro-scale fiber surface (Fig. 2c, d). After coating by PDMS/CuS, it was clearly visible that dense hierarchical CuS microflowers and PDMS film were coated on the surface of PDMS/CuS@Cotton fibers (Fig. 2e, f). Moreover, as shown in lower magnification SEM image of PDMS/CuS@Cotton textile (the inset of Fig. 2f), the woven PDMS/CuS@Cotton fabric consisted of micro-level fibers. Silicone elastomer PDMS film as adhesive layer was tightly linked with CuS microflower nanoparticles on microscale fiber surface, making the fiber coated by PDMS/CuS having typical hierarchical rough structure as well as low surface tension, which were beneficial for superhydrophobic property.

Surface roughness is one of key factors for preparation of superhydrophobic surfaces (Ghasemlou et al. 2019). The coated fabrics were evaluated by AFM characterization according to root mean square (RMS) value. AFM photographs of PDMS@Cotton as well as PDMS/CuS@Cotton are shown in Fig. 3. PDMS@Cotton without copper sulfide microflower nanoparticles showed the RMS value of about 9.70 nm (Fig. 3a, c). However, PDMS/CuS@Cotton fabric exhibited obvious surface topography and increased roughness with the RMS value of 71.80 nm as shown in Fig. 3b, d, indicating that micro/nano scale roughness had been constructed onto fiber surface coated with PDMS/CuS. This result was consistent with SEM result. This demonstrated that the cotton fabrics were successfully coated by PDMS/CuS and the coated cotton fibers became roughened due to hierarchical rough structure favoring the superhydrophobic surfaces.

Fourier transform infrared (FT-IR) characterization of untreated textile, PDMS@Cotton, and PDMS/CuS@Cotton was carried out (Fig. 4a). In FT-IR spectrum of untreated textile, it was clear that a wide peak with high strength at 3320 cm^{-1} represented hydroxyl groups stretching vibration absorption stemming from cellulose macromolecule of cotton. Two peaks observed at 2893 cm^{-1} and 1312 cm^{-1} were assigned to -CH_2- stretch vibrations as well as bend vibrations. Strong band at nearly 1019 cm^{-1} corresponded to hydroxyl bend vibration and the C–O–C stretching vibration. By contrast, in FT-IR spectra of

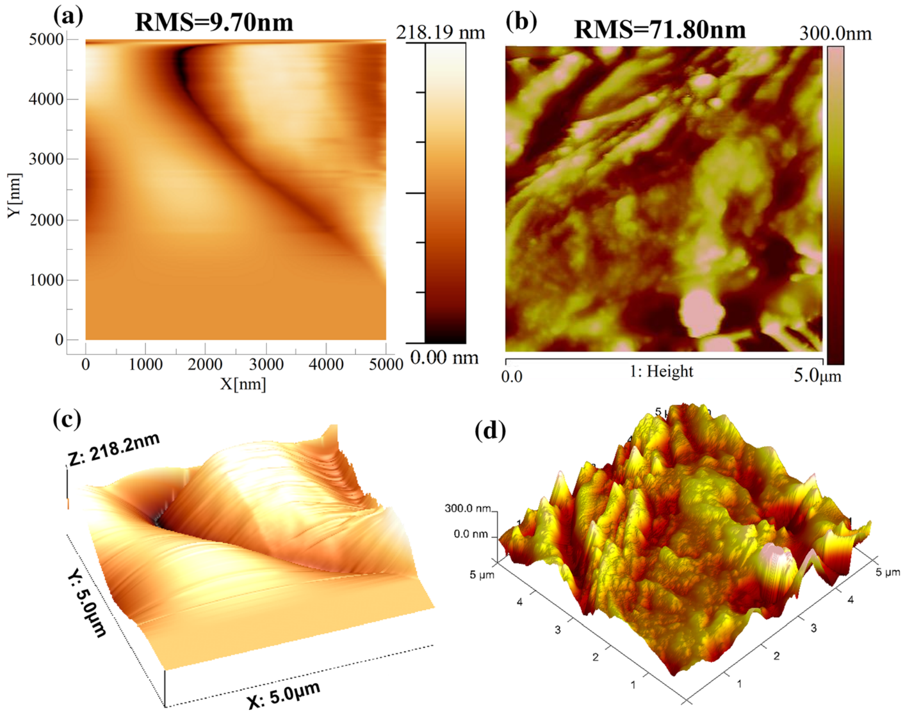

Fig. 3 AFM images: **a** 2-dimensional (2D) AFM of PDMS@Cotton textile, **b** 2D AFM of PDMS/CuS@Cotton textile, **c** 3-dimensional (3D) AFM of PDMS@Cotton textile, and **d** 3D AFM of PDMS/CuS@Cotton textile

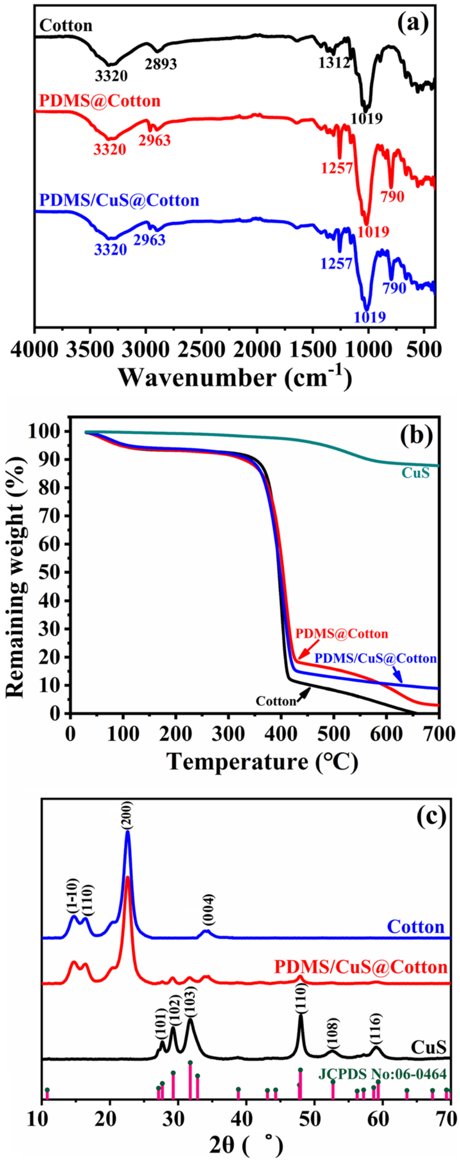

Fig. 4 **a** FTIR spectra of cotton textile, PDMS@Cotton textile and PDMS/CuS@Cotton textile, **b** TGA curves of CuS, PDMS/CuS@Cotton textile, PDMS@Cotton textile and cotton textile, and **c** XRD patterns of CuS, cotton textile and PDMS/CuS@Cotton textile

PDMS@Cotton fabric additional absorption bands appeared at 2963 cm^{-1}, 1257 cm^{-1} and 790 cm^{-1} originating from –CH$_3$ stretching vibration, Si–C bend vibration and Si–O–Si symmetrical stretching vibration, respectively, which were due to a lot of -CH$_3$ groups and Si–O–Si groups of PDMS. Compared with PDMS@Cotton fabric, there were no obvious new bands from FT-IR spectra of PDMS/CuS@Cotton fabric, indicating that CuS had no absorption in the infrared spectra. The results were consistent with the research reported by Hu et al. (Hu et al. 2016). All the above characteristic peaks demonstrated successful incorporation of PDMS/CuS onto cotton fabric.

The thermal stability of the obtained CuS, untreated textile, PDMS@Cotton textile, and PDMS/CuS@Cotton textile was assessed with thermogravimetric analysis (TGA) and their TGA curves are shown in Fig. 4b. For the TGA curve of hierarchical CuS microflower nanoparticles, a very small weight loss occurred from room temperature to 220 °C, mainly caused by the residual solvent volatilization and moisture. The final weight loss of CuS was about 17.29% with heating temperature of 700 °C, probably caused by partial oxidation or decomposition. TGA finding indicated excellent thermal stability of the obtained CuS. TGA curve of pristine cotton fabric showed a three-step weight loss. Weight loss of 7.54% below 300 °C was observed probably caused by moisture evaporation and impurities decomposition which absorbed on fabric surface. From 300 °C to 420 °C, pristine fabric completely lost its weight of 80.58% due to the decomposition of cellulose. Untreated fabric showed residual weight rate of about 0.01% after being heated to 700 °C because of the residual groups (such as-CH$_2$-, etc.) decomposition. It was indicated that there was little pristine fabric left. By contrast, PDMS@Cotton textile and PDMS/CuS@Cotton textile showed similar TGA curves with three-step weight loss and partial overlapping thermal degradation process. The residual weight percentage of PDMS@Cotton fabric reached to 2.93% after being heated to 700 °C. The weight loss was mainly due to the decomposition of the groups such as the –CH$_3$ in the PDMS and cotton decomposition. But there were some residual undecomposed molecular groups. Thus, the residual weight percentage is higher than that of untreated fabric. However, for PDMS/CuS@Cotton textile, the residual weight percentage reached to 7.47%, showing the improved thermal stability. As mentioned above, CuS had excellent thermal stability. Thereby, TGA result of PDMS/CuS@Cotton revealed the successful incorporation of PDMS/CuS on the cotton surface.

X-ray diffractometer (XRD) was used to characterize crystal structure of obtained CuS, untreated fabric as well as PDMS/CuS@Cotton textile. Figure 4c shows the XRD pattern of CuS microflower nanoparticles. The diffraction peaks of the prepared CuS at 28.1°, 29.3°, 32.8°, 48.9°, 53.1° and 59.5° could be attributed to the crystal hexagonal CuS of (101), (102), (103), (110), (108) and (116), respectively (Nemade et al. 2015). The calculated cell parameters were a = b = 3.792 Å, and c = 16.34 Å. This result was indexed to criterion XRD of copper sulfide with hexagonal phase (JCPDS card No. 06-0464). There were no other diffraction peaks, indicating that the prepared CuS showed high purity. From XRD pattern of untreated cotton, some characteristic peaks of the untreated cotton at 2θ = 14.9°, 16.4°, 22.4° and 34.1° can be corresponding to the respective (1–10), (110), (200), and (004) peaks of the cellulose diffraction pattern. (French 2014). XRD pattern of PDMS/CuS@Cotton displayed several additional peaks at 2θ = 28.1°, 29.3°, 32.8°, 48.9° and 59.5°, which were consistent with XRD pattern of CuS. It was confirmed that PDMS/CuS layer was successfully introduced on fabric.

The fabric surface was also evaluated via XPS test. Figure 5 displays XPS spectra of untreated fabric as well as PDMS/CuS@Cotton. XPS spectra of untreated fabric surface only showed strong peaks at 284 eV and 532 eV which were attributable to C and O elements, respectively. However, besides the cotton fabrics signals peaks, the new characteristic peaks attributed to Si2s, Si2p, S2p as well as Cu2p could be clearly detected in XPS spectra of PDMS/CuS@Cotton fabric. In addition, XPS spectrum of PDMS/CuS@Cotton revealed the large increase of characteristic peak intensity of C1s and O1s, due to the introduction of polydimethylsiloxane (PDMS) with methyl groups and Si–O–Si groups on textile surface. Figure 5b–d clearly show XPS spectra of Cu2p, S2p and Si2p of PDMS/CuS@Cotton fabric, respectively. Moreover, the above results verified that CuS nanoparticles and PDMS film were successfully coated on textile.

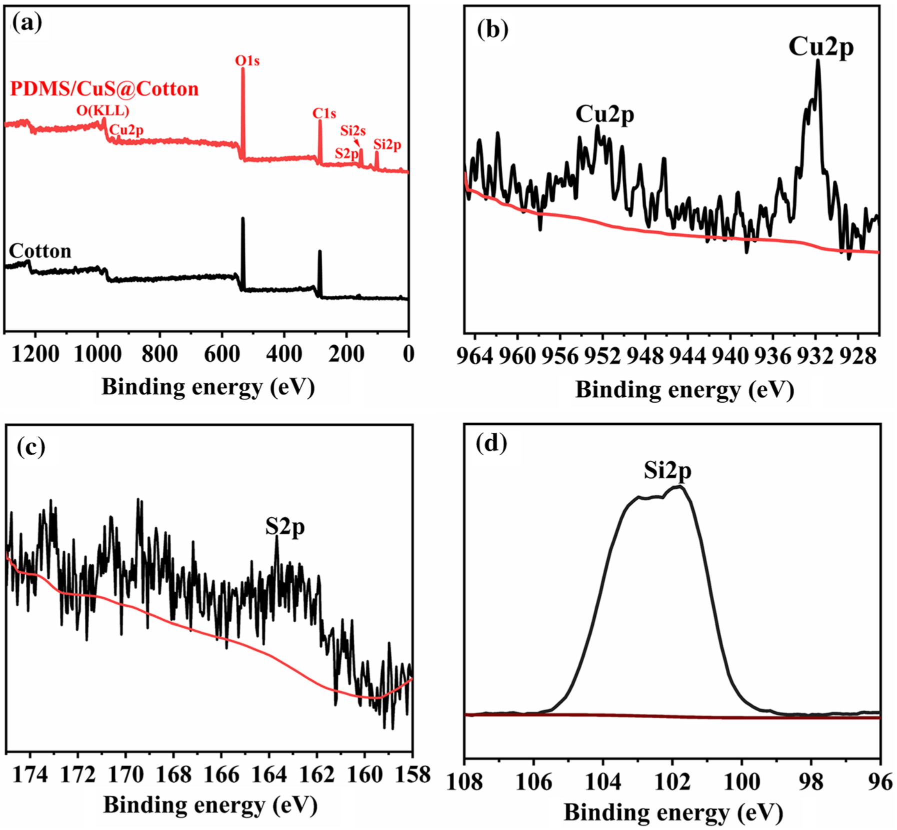

Fig. 5 XPS spectra of **a** untreated cotton and PDMS/CuS@Cotton, **b** Cu2p of PDMS/CuS@Cotton, **c** S2p of PDMS/CuS@Cotton and **d** Si2p of PDMS/CuS@Cotton

Wettability of cotton textiles

The superhydrophobic textiles were obtained with PDMS/CuS via dip-pad-cure approach. CuS concentration and PDMS concentration were important for PDMS/CuS@Cotton textile hydrophobicity. As shown in Fig. 6a, as CuS concentration increased, water contact angle (WCA) of coated textile was also enhanced and water shedding angle (WSA) was decreased. Similarly, in Fig. 6b, with the increase of PDMS concentration, WCA of treated textile also increased and WSA was decreased. In addition, as CuS concentration was up to 2% and PDMS concentration was above 1.5%, WCA and WSA of treated textile had little change while the standard deviation showed little decrease, favoring uninform distribution of CuS and PDMS on cotton fabric. This result can be explained that the uniform introduction of hierarchical CuS microflower nanoparticles with rough porous structure onto the fabric could increase surface topography and roughness of the coated fabric. Furthermore, incorporation of PDMS can lower surface tension of coated textile. Advancing contact angles (θa), receding contact angles (θr) and contact angle hysteresis ($\triangle\theta = \theta a - \theta r$) of cotton fabrics coated by PDMS/CuS with different CuS concentrations or PDMS concentrations were tested. As displayed in Fig. 6c, d, advancing water contact angles (θa), receding water contact angles (θr) and water contact angle hysteresis ($\triangle\theta$) showed a close relationship to CuS concentrations or PDMS concentrations. The contact angle hysteresis showed slight decrease when the CuS concentrations or PDMS concentrations was increased. Advancing water contact angles (θa), receding water contact angles (θr) and water contact angle hysteresis ($\triangle\theta$) almost kept unchanged when CuS concentration exceeded 2% and PDMS concentration exceeded 1.5%. Thus, cooperation of CuS with concentration of 2% and PDMS with concentration of 1.5% led to superhydrophobic cotton fabric. When CuS concentration was 2% and PDMS concentration was 1.5%, the cotton fabric was coated by PDMS/CuS via dip-pad-cure approach and the final dry add-on percentage of PDMS/CuS@Cotton fabric was calculated as follows.

$$Dry\,add\text{-}on\,(\%) = \frac{W_{after} - W_{before}}{W_{before}} \times 100 \tag{3}$$

Here W_{after} is cotton fabric weight after treatment and W_{before} is cotton fabric weight before treatment, respectively. The final dry add-on percentage of PDMS/CuS@Cotton fabric was calculated as 6.3%.

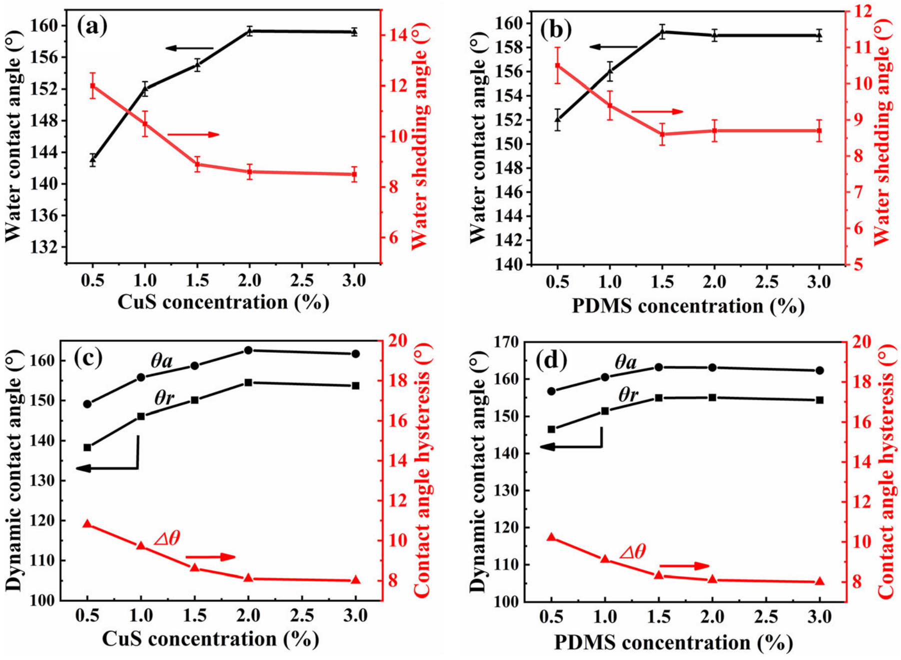

Fig. 6 The effect of CuS concentration and PDMS concentration on the hydrophobicity of PDMS/CuS@Cotton textile

The obtained PDMS/CuS@Cotton fabric showed superhydrophobicity with a WCA of 159.3° ± 0.6° and a WSA of 8.6° ± 0.3°.

The surface wettability of different cotton fabric samples was further analyzed. Water droplets on pristine textile surface can promptly spread caused by abundant hydroxyl groups of untreated textile surface. The PDMS@Cotton fabric showed a water contact angle (WCA) of 132.3° ± 1.2° (Fig. 7a), not achieving superhydrophobicity. It was worth noting that PDMS/CuS@Cotton fabric showed considerable enhancement in its water repellency and demonstrated outstanding superhydrophobic property with water contact angle of 159.3° ± 0.6° (Fig. 7b). However, an oil droplet dropped on PDMS/CuS@Cotton was rapidly absorbed. Therefore, PDMS/CuS@Cotton fabric showed oil contact angle (OCA) of 0° (Fig. 7c). It was indicated that PDMS/CuS@Cotton fabric showed superhydrophobicity and oleophilic property, demonstrating the promising application in oil/water separation. When the fixed PDMS/CuS@Cotton textile was immersed in water, PDMS/CuS@Cotton surface clearly showed air film, producing a silver mirror-like surface and showing the efficient inhibiting of water penetration (Fig. 7d). When untreated textile and PDMS/CuS@Cotton were dropped in water, photographs of textiles were presented in Fig. 7e. The pristine textile easily absorbed water and sank into the bottom of the beaker, due to its intrinsic hydrophilic property. However, PDMS/CuS@Cotton fabric could float in water because of its excellent superhydrophobicity. When it was taken

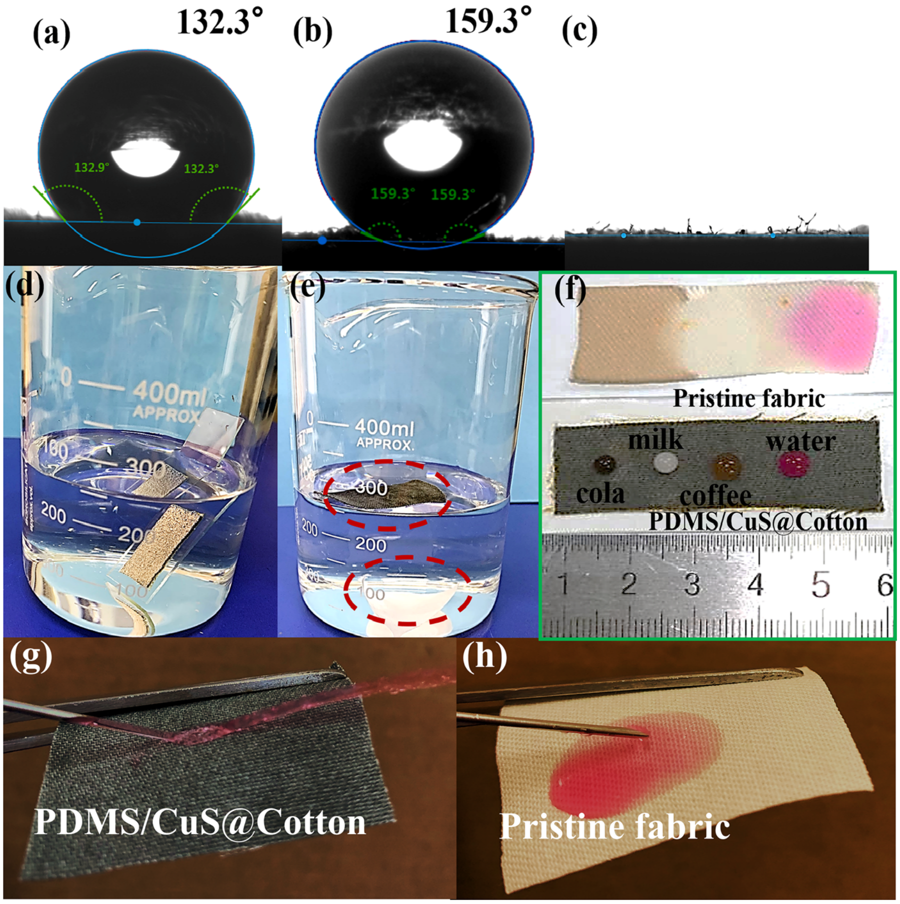

Fig. 7 Images of wettability of cotton textiles: **a** WCA of PDMS@Cotton textile, **b** WCA of PDMS/CuS@Cotton textile, **c** OCA of PDMS/CuS@Cotton textile, **d** immersion of PDMS/CuS@Cotton textile stuck on glass into water, **e** PDMS/CuS@Cotton textile and pristine cotton textile in water, **f** different liquid droplets on the surface of the pristine cotton textile and PDMS/CuS@Cotton textile, **g** a jet of colored water is bouncing off from PDMS/CuS@Cotton textile, and **h** a jet of colored water spread on the pristine cotton textile

out of the water, PDMS/CuS@Cotton fabric kept dry and showed no wetting. PDMS/CuS@Cotton fabric was covered with the hierarchical rough microstructures due to copper sulfide nanoparticles and low surface tension caused by polydimethylsiloxane polymer film. More air trapped between hierarchical rough microstructures produced air layer and liquid–air–solid interface, protecting cotton substrate against water penetration. As illustrated in Fig. 7f, different liquid droplets including cola, milk, coffee and red colored water were dropped on untreated textile and PDMS/CuS@Cotton. These liquid droplets can easily wet on untreated textile. In contrast, these liquid droplets could keep spherical and stay on PDMS/CuS@Cotton surface without any penetration. The bouncing of water droplets on our obtained superhydrophobic textile (PDMS/CuS@Cotton) had been demonstrated. As shown in Fig. 7g, it was clear that a jet of colored water could easily bounce off from the superhydrophobic textile without leaving a trace. The superhydrophobic textile remained completely dry after bouncing of water droplets. However, a jet of colored water quickly spread on the pristine cotton fabric (Fig. 7h).

Researches widely applied the Cassie-Baxter model for explaining roughness influence on wettability of a rough porous surface. The superhydrophobicity of PDMS/CuS@Cotton fabric could be analyzed via Cassie-Baxter equation as follows (Cassie et al. 1944)

$$\cos\theta_{CB} = f_{ls}\cos\theta_s + f_{lv}\cos\theta_v \tag{4}$$

where θ_{CB} presents the observed CA on uneven solid surface, θ_s and θ_v present the intrinsic CA on corresponding slippy solid surface as well as air surface, respectively. f_{ls} is liquid/solid contact area. f_{lv} is liquid/vapor contact area. The liquid/vapor contact angle θ_v was 180°. If it is given that f is the solid fraction ($f_{lv} = 1 - f$) and r_f is the surface roughness factor of the wetted solid area ($r_f \geq 1$, $f_{ls} = r_f\ f$), Eq. (1) can be modified for the local surface as follows.

$$\begin{aligned}\cos\theta_{CB} &= r_f f\cos\theta_s + (1-f)\cos 180^{\circ} \\ &= r_f f\cos\theta_s + f - 1\end{aligned} \tag{5}$$

The cotton fiber had the intrinsic curvature, rendering $r_f > 1$. After only PDMS modification, PDMS@Cotton fabric showed water contact angle of 132.3° ± 1.2° but was not superhydrophobic. By introducing composite coating of hierarchical CuS microflower nanoparticles and silicone elastomer PDMS, PDMS/CuS@Cotton fabric obviously achieved superhydrophobic property with a WCA of 159.3° ± 0.6° as SEM and AFM measurements clearly manifested that indeed r_f was further increased to a higher level. The introduction of hierarchical rough structure of CuS microflower nanoparticles composed of self-assembled nanosheets onto microscale fiber rendered dual-size uneven surface topology on the cotton fabric.

Furthermore, for Cassie-Baxter model, air is embedded in boundary layer of water and solid, forming solid/liquid/air interface. For PDMS/CuS@Cotton fabric, in order to investigate the air film trapped by hierarchical porous rough structures, the BET of CuS microflower nanoparticles was analyzed as shown in Fig. S2 (Supplementary data). The nitrogen adsorption–desorption isotherms of CuS microflower nanoparticles showed type IV isotherm curves. The curves had representative hysteresis loop primarily due to porous structures and slit pores formed by the accumulation of self-assembly nanosheets. The pore size distribution of CuS microflower nanoparticles estimated by the Barrett-Joyner-Halenda (BJH) process ranged from 2 to 20 nm, showing average pore size of 16.92 nm.

It was indicated that CuS microflower nanoparticles showed porous structures and BET surface area of 10.76 m^2/g. With the simultaneous incorporation of hierarchical CuS microflower nanoparticles and PDMS, when water droplets were dropped on PDMS/CuS@Cotton, vapor film was trapped by hierarchical rough structures caused by mesopores among copper sulfide nanosheets, making vapor fraction significantly improved. Therefore, liquid/solid contact area was reduced significantly, showing effective resistance to water contact with PDMS/CuS@Cotton fabric surface. Additionally, the low surface energy PDMS coating covered on the surface of CuS microflower nanoparticles and PDMS/CuS@Cotton fiber prevented the direct water contact with cotton fiber. The water droplet only contacted the top of hierarchical rough structures and rolled off easily. Thereby, the synergistic effect of the hierarchical rough porous structure caused by CuS microflower nanoparticles as well as low surface tension polydimethylsiloxane layer lead to superhydrophobicity of PDMS/CuS@Cotton fabric.

Durability of superhydrophobic cotton fabric

The mechanical stability of superhydrophobic property of PDMS/CuS@Cotton fabric was comprehensively examined by the abrasion test and water jetting test. The abrasion test was conducted by abrading fabric samples using Martndale abrasion tester with the abrasion test cycles of 2000. As shown in Fig. 8a, after 100 abrasion cycles, the WCA of PDMS/CuS@Cotton textile was improved slightly, which was ascribed to the increase of the surface roughness of the fabric resulting from appearance of additional fine fibers on textile surface after friction. As rubbing cycles increased from 100 to 2000, water contact angle of PDMS/CuS@Cotton fabric showed only slight change, still higher than 150°. This result indicated that the obtained PDMS/CuS@Cotton fabric demonstrated excellent abrasion durability in superhydrophobicity. It should be noteworthy that silicone elastomer PDMS not only lower surface tension of PDMS/CuS@Cotton textile to give fabric superhydrophobicity, but also act as adhesive layer to enhance the mechanical durability of superhydrophobic textile. When PDMS/CuS was coated on textile by dip-pad-dry approach, PDMS could be cured and melted to form a dense crosslinked rubber on surface of CuS microflower nanoparticles and onto the cotton fibers. PDMS with elastomeric property showed high recoverability under severe mechanical abrading and firm interaction between CuS microflower nanoparticles and the coated cotton fibers, resulting in the durable resistance to mechanical abrasion of the obtained superhydrophobic cotton fabric (Xue et al. 2014). In order to further investigate mechanical stability of the as-prepared superhydrophobic fabric (PDMS/CuS@Cotton fabric), the impact of water jetting on our obtained superhydrophobic textile was evaluated by subjecting treated fabrics to water jetting test. With different water jetting time hydrophobicity test of PDMS/CuS@Cotton fabric was performed. Figure 8c showed the WCA and OCA changes of PDMS/CuS@Cotton fabric with different water jetting time. With prolonging water jetting time, the WCA decreased slightly. But WCA still maintained above 150° and the OCA remained 0° after water jetting for 60 min, demonstrating that the obtained superhydrophobic textile possessed good mechanical stability. The surface micromorphology of fabric coated by PDMS/CuS after durability tests had been investigated. From Fig. 8b, hierarchical rough morphology was retained on the microscale fiber surface of PDMS/CuS@Cotton textile after abrasion for 2000 cycles, which was responsible for maintenance of superhydrophobicity. As shown in Fig. 8d, the surface morphology on the fiber surface of PDMS/CuS@Cotton textile after water jetting was still rough although nano scale structure of the surface was partially destroyed. As PDMS had good adhesiveness with CuS nanoparticles and fiber surface, PDMS/CuS@Cotton textile could withstand abrasion and water jetting, demonstrating good mechanical stability.

When the cotton fabric sample is applied outdoor, the durability against UV irradiation of the superhydrophobic fabric is important. The influence of UV irradiation on the wettability of the superhydrophobic fabric with exposure to UV irradiation ranging from 12 to 264 h was evaluated. As presented in Fig. 8e, the treated cotton fabric (PDMS/CuS@Cotton) still retained highly hydrophobicity with WCA about 150° after UV exposure for 264 h, showing good UV-durability. On one hand, CuS microflower nanoparticles showed excellent ultraviolet shielding property probably resulting from outstanding absorption, scattering as well as continual reflection in many micropores caused by its special hierarchical microstructure composed of self-assembled nanosheets. The refractive index value of the obtained copper sulfide in our study was tested using Abbe Refractometer method. The results showed that refractive index value of the obtained copper sulfide was 1.45. UV–vis absorption spectra of CuS microflower nanoparticles from 200 to 800 nm was characterized to investigate their optical performance, as shown in Fig. S3 (Supplementary data). CuS microflower nanoparticles exhibited strong absorption in both ultraviolet and visible region with the maximum absorption peaks occurring at 320 nm and 693 nm, respectively. It might be caused by quantum confinement effect of open-pore crossed nanosheets and its efficient separation of electron and hole pairs. On the other hand, low surface tension polymer PDMS with lots of Si–O groups was highly chemically stable under UV irradiation (Lee et al. 2016). Because Si–O groups have chemical bonding energy of 460 kJ/mol, higher than UV irradiation energy (314–419 kJ/mol).

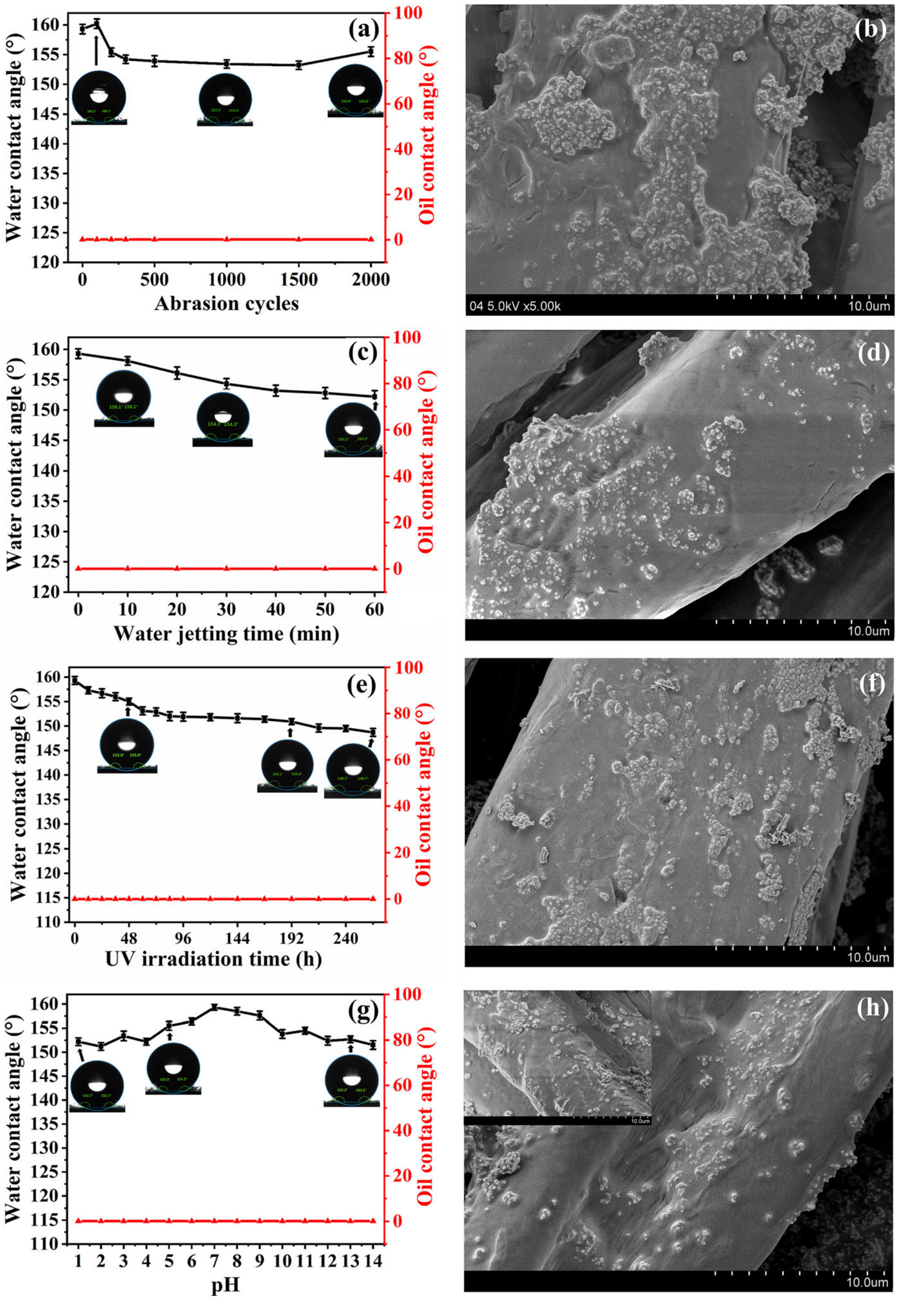

Fig. 8 Durability of PDMS/CuS@Cotton textile: **a** contact angles of PDMS/CuS@Cotton textile after mechanical abrasion, **b** SEM image of PDMS/CuS@Cotton textile after abrasion for 2000 cycles, **c** contact angles of PDMS/CuS@Cotton textile after water jetting, **d** SEM image of PDMS/CuS@Cotton textile after water jetting for 60 min, **e** contact angles of PDMS/CuS@Cotton textile after UV irradiation, **f** SEM image of PDMS/CuS@Cotton textile after UV irradiation for 264 h, **g** contact angles of PDMS/CuS@Cotton textile after immersion in different pH value solution, and **h** SEM image of PDMS/CuS@Cotton textile after immersion in solution with pH value of 1 (SEM image of PDMS/CuS@Cotton textile after immersion in solution with pH value of 14 is in the inset)

Therefore, for PDMS/CuS@Cotton fabric, low surface energy polymer PDMS and hierarchical CuS microflower particles was sustained under long-term UV illumination. UV irradiation caused slight effect on PDMS/CuS coating. Therefore, the obtained superhydrophobic PDMS/CuS@Cotton fabric had excellent resistance to UV irradiation. Surface morphology of PDMS/CuS@Cotton textile after UV irradiation was presented in Fig. 8f, hierarchical rough microstructure of the PDMS/CuS coating still remained on PDMS/CuS@Cotton fiber surface except for partially removed, leading to the maintenance of highly hydrophobicity.

Because of complex environments of actual superhydrophobic fabric application, anti-corrosion property of the as-obtained superhydrophobic fabric was evaluated. To explore the chemical durability of superhydrophobic fabric, the contact angles of water droplets were measured on PDMS/CuS@Cotton fabric after immersion in different pH value solution varying from 1 to 14, as displayed in Fig. 8g. The water contact angles of PDMS/CuS@Cotton fabric after treatment in solution with pH value in the range of 1–14 still remained above 151°. The PDMS/CuS@Cotton fabric showed good superhydrophobicity even under strong acid and alkali harsh conditions, indicating satisfactory anti-corrosion property. It was reported that silicone elastomer polydimethylsiloxane (PDMS) was more durable than most polymers and showed intrinsic excellent anti-acid and anti-alkali property mainly because of chemically stable Si–O groups of PDMS (Zhu et al. 2017). As a result, PDMS/CuS@Cotton fabric exhibited chemical stability and strong resistance to acid and alkali conditions. As displayed in Fig. 8h, there were still typical hierarchical rough structures on PDMS/CuS@Cotton fiber surface. Some bumps were still obviously discernible on PDMS/CuS@Cotton fiber, which was essential for the superhydrophobicity.

In addition, from Fig. 8a, c, e, g, with increasing mechanical abrasion cycles, increasing water jetting time, increasing UV irradiation time, or treatment in solution with different pH values, oil contact angle of PDMS/CuS@Cotton fabric was not changed and was still 0°. It was indicated that PDMS/CuS@Cotton fabric showed stable oleophilic property and oil absorption under harsh conditions.

UV-proof property

The ultraviolet-proof performance of cotton textiles was evaluated according to UV transmittance as well as UPF. Figure 9 displayed ultraviolet transmittance curves and UPF values of untreated textile, PDMS@Cotton, and PDMS/CuS@Cotton. It was noteworthy that untreated textile and PDMS@Cotton showed similar transmittances curves and with the increase of wavelength their transmittances increased gradually. From Fig. 9, compared with untreated textile, the UV transmittance of PDMS@Cotton showed slight decrease and UPF value showed slight increase. It seemed that untreated textile and PDMS@Cotton didn't show ultraviolet-shielding performance.

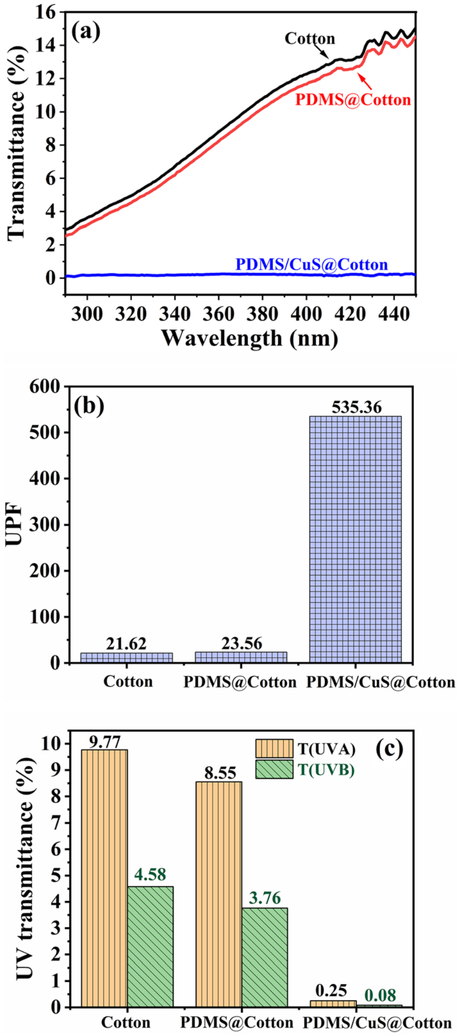

Fig. 9 UV-proof property of untreated cotton textile, PDMS@Cotton textile and PDMS/CuS@Cotton textile: **a** UV transmittance curves, **b** UPF values, and **c** UV transmittance

In comparison with untreated textile and PDMS@Cotton, PDMS/CuS@Cotton exhibited low and almost constant UV transmittance with the increase of wavelength. From Fig. 9, UPF value of PDMS/CuS@Cotton fabric was dramatically improved to 535.36 and T(UVA) and T(UVB) were only 0.25% and 0.08%, respectively. Based on standard AATCC Test Method 183, the material with UPF value higher than 40 and T(UVA) lower than 5% can be referred to as a ‘‘UV protection product’’. This result demonstrated that the PDMS/CuS@Cotton fabric exhibited excellent UV-blocking property. As mentioned above, as for PDMS/CuS@Cotton fabric, the improvement of UV blocking property was probably due to strong ultraviolet-absorption, light scattering and frequent light reflection of CuS nanoparticles with hierarchical microstructure.

Self-cleaning performance

The above obtained PDMS/CuS@Cotton textile showed outstanding superhydrophobic property. Its self-cleaning performance was evaluated. As depicted in Fig. 10a, a sparse layer of methyl orange powder as a model contaminant was distributed on the surface of PDMS/CuS@Cotton textile fixed on glass sheet with a small tilt angle. When water droplets were dropped onto PDMS/CuS@Cotton fabric surface, they rolled off immediately and picked up the dissolved methyl orange powder without any residue (as shown in supplementary data Video S1). Besides, the PDMS/CuS@Cotton fabric surface showed no wetting and no water droplets. It was confirmed that PDMS/CuS@Cotton fabric demonstrated excellent self-cleaning property, achieving the “lotus effect”. By incorporation of PDMS/CuS, the treated fabric surface showed hierarchical porous uneven microstructure and low surface tension. The surface tension of the coated cotton fabric was lower than that of water. More air could be trapped between hierarchical rough porous structures. Water droplets dropped onto coated cotton fabric surface could not spread and easily roll off the surface, simultaneously carrying away the dirt due to the weak adhesion of dirt to coated textile surface.

Antifouling application of as-obtained PDMS/CuS@Cotton fabric was also investigated. As shown in Fig. 10b, the PDMS/CuS@Cotton textile and untreated textile were dipped in red colored water and then taken out, respectively. It was shown that pristine cotton fabric was wetted thoroughly and stained red wholly, while the PDMS/CuS@Cotton fabric kept dry without any residue, showing excellent stain resistance (as shown in supplementary data Video S2). This result further demonstrated that PDMS/CuS@Cotton fabric showed great potential antifouling application.

Oil/water separation property and oil absorption property

The special wettability of PDMS/CuS@Cotton fabric for different liquids including oil and water was further examined. Colored oil was used for better visualization of the oil in water removal test, as displayed in Fig. 11a, b. Figure 11a showed the

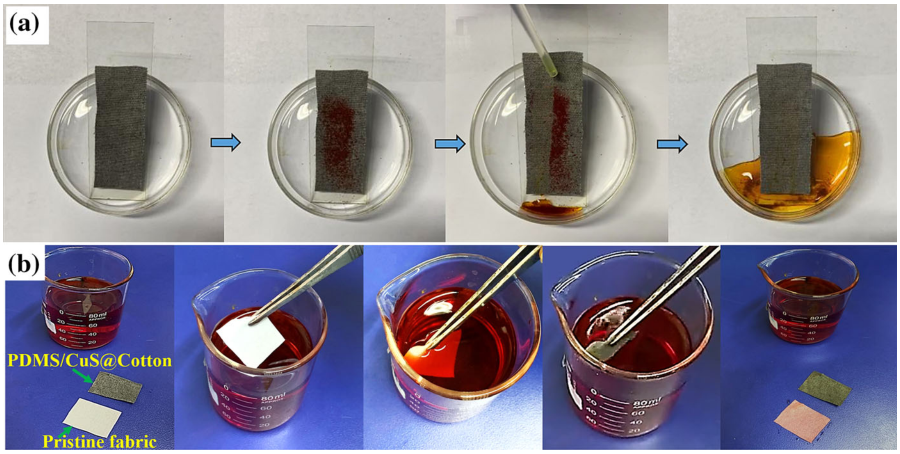

Fig. 10 **a** Self-cleaning property and **b** antifouling property of PDMS/CuS@Cotton textile

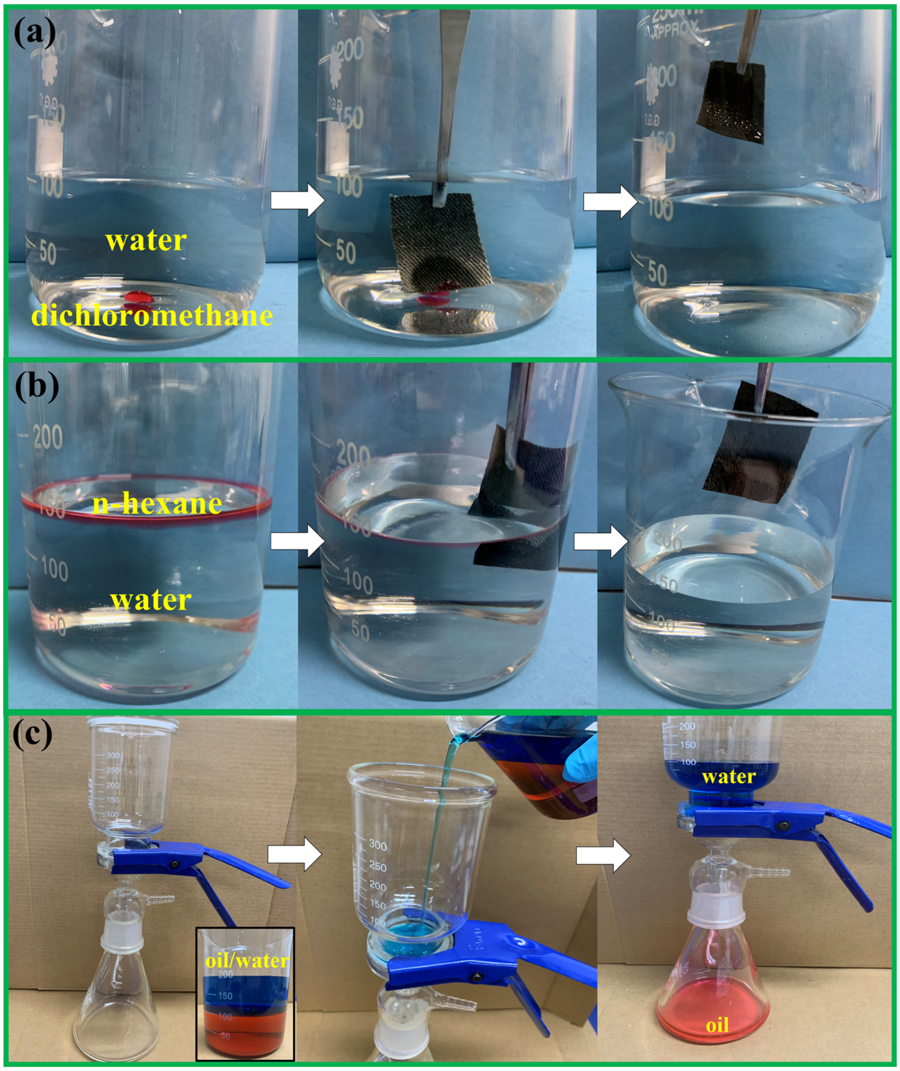

Fig. 11 **a**, **b** Oleophilic and hydrophobic property test, and **c** oil/water separation test of the PDMS/CuS@Cotton textile

mixture of red colored heavy oil (dichloromethane) and water. As the density of dichloromethane is higher than that of water, the oil/water lamination system is composed of water (upper layer) and red colored dichloromethane (lower layer). The PDMS/CuS@Cotton fabric was immersed in the mixture of red colored dichloromethane and water. When the PDMS/CuS@Cotton fabric contacted with lower layer red colored dichloromethane, red colored dichloromethane could be adsorbed quickly, leaving only water. Similarly, Fig. 11b showed the mixture of upper layer red colored light oil (n-hexane) having a lower density than water and water. After immersion, the PDMS/CuS@Cotton fabric could adsorb red colored n-hexane rapidly, leaving only water. The results above mentioned confirmed that the PDMS/CuS@Cotton fabric had excellent oleophilic and hydrophobic effect.

The oil/water separation property of PDMS/CuS@Cotton fabric due to its special wettability was investigated. Oil/water separation test was carried out using a simple laboratory-made setup as shown in Fig. 11c. The blue colored water and red colored oil were mixed and poured into the oil/water separation device with PDMS/CuS@Cotton fabric as filter membrane. In the experiment process, only red colored oil penetrated quickly through the coated cotton fabric filter membrane and fell into the bottom of conical flask as a result of gravity force, while the blue colored water in the mixture totally remained in the upper filter cup, achieving the successful oil/water separation. The heavy oils (dichloromethane and chloroform) and commercially available light oils (n-hexane, kerosene, dimethylsilicone oil, and soybean oil) had been used for the demonstration of oil/water separation. The separation efficiencies of PDMS/CuS@Cotton fabric for different types of oils were investigated as shown in Fig. 12a. A series of oil/water mixtures including dichloromethane/water, chloroform/water, n-hexane/water, kerosene/water, dimethylsilicone oil/water, and soybean oil/water were successfully separated by the obtained PDMS/CuS@Cotton fabric due to its good superhydrophobicity and oleophilicity property. The separation efficiencies for all the chosen oil/water mixtures were above 96.0%, indicating outstanding oil/water separation property of PDMS/CuS@Cotton fabric.

Additionally, the oil/water separation reusability of PDMS/CuS@Cotton textile was evaluated by taking dichloromethane as an example. After each cycle of oil/water separation, PDMS/CuS@Cotton textile was cleaned thoroughly and dried and then could be reused. The separation efficiency and WCAs and WSAs of PDMS/CuS@Cotton textile after different oil/water separation cycles for dichloromethane were measured, respectively. In Fig. 12b, with separation cycles arranging from 1 to 10, oil/water separation efficiencies of PDMS/CuS@Cotton textile for dichloromethane decreased slightly, but they were all above 96.0%. In Fig. 12c, with increase of oil/water separation cycles, WCAs and WSAs of PDMS/CuS@Cotton textile showed little change. WCA was still above 154° and WSA maintained still below 9.4° after 10 separation cycles. As a result, PDMS/CuS@Cotton textile had high-efficiency oil/water separation effect and good separation reusability, showing wide application prospect.

The oil absorption property of PDMS/CuS@Cotton fabric was evaluated by testing oil absorption capacity. The oil-absorbing capacities of the as-prepared PDMS/CuS@Cotton fabric for a variety of model oils like dichloromethane, chloroform, n-hexane,

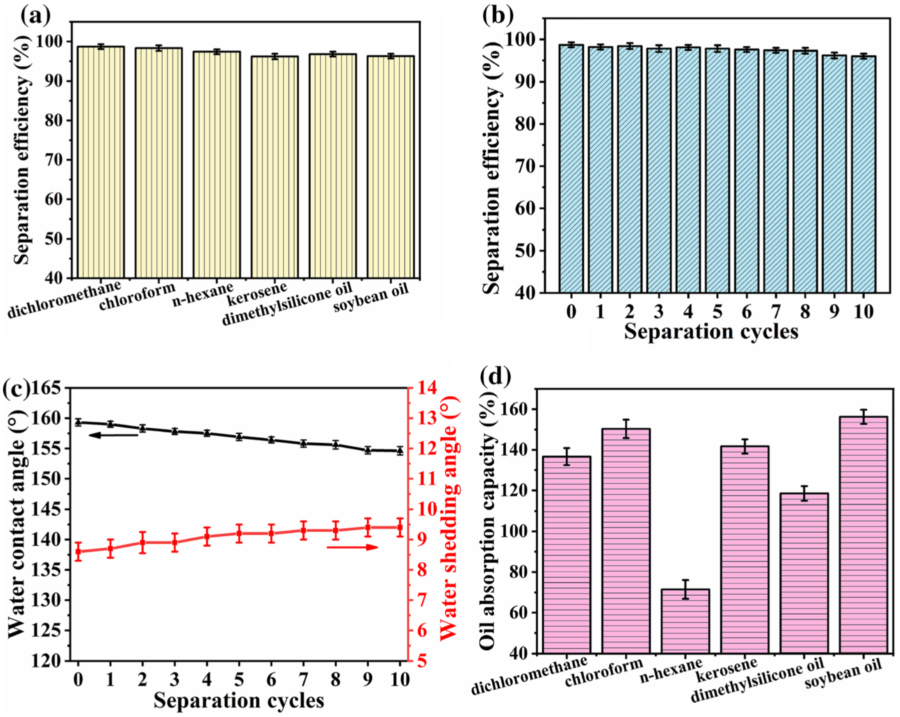

Fig. 12 **a** Oil/water separation efficiency of PDMS/CuS@Cotton textile for various oil/water mixtures, **b** separation efficiency after different separation cycles for dichloromethane/water mixture, **c** WCAs and WSAs of PDMS/CuS@Cotton textile after different separation cycles for dichloromethane/water mixture, and **d** oil absorption capacity of PDMS/CuS@Cotton textile for various oils

kerosene, dimethylsilicone oil, and soybean oil were investigated. The results were presented in Fig. 12d. The oil absorption capacities of PDMS/CuS@Cotton fabric were above 70% and ranged from 71.43 to 156.24% for the different types of chosen oils. It was founded that oil absorption capacity of PDMS/CuS@Cotton fabric for oils with relatively high densities like dichloromethane and chloroform was higher than those with relatively low densities like n-hexane. It was also indicated that PDMS/CuS@Cotton fabric exhibited relatively high oil absorption capacity for oils with high viscosity like kerosene, dimethylsilicone oil, and soybean oil. These oils with high viscosity were prone to form a thick layer on fabric, leading to high oil absorption capacity (Zhou et al. 2017).

The oil absorption capacity of the as-prepared PDMS/CuS@Cotton fabric in this study had been compared with the literature values. As displayed in Table 1, the oil absorption capacities of these hydrophobic and oleophilic materials varied greatly. Especially for porous or loose materials like 3D porous EcoFlex sponge and PDMS-coated cotton wool, oil absorption capacities for the chosen oils were high (above 2000%). The main reasons for large differences in the oil absorption capacities were as follows. First of all, these reported hydrophobic and oleophilic materials had different oil absorption capacity testing methods for oil absorption capacity, such as the different immersion time of the hydrophobic and oleophilic materials in various oils. Furthermore, two dominant factors have large influences on oil absorption, including microstructures and properties of hydrophobic and oleophilic materials and density and viscosity properties of the oils (Zhou et al. 2017). In comparison, oil absorption capacity of PDMS/CuS@Cotton fabric in this study was higher than that of most of reported hydrophobic and oleophilic materials except 3D porous EcoFlex sponge and PDMS-coated cotton wool. Therefore, PDMS/CuS@Cotton fabric closely correlated with its excellent superhydrophobicity and oleophilicity exhibited good oil absorption property, showing the potential for collecting oil spills in water.

Mechanical strength of cotton fabric

The effect of PDMS/CuS coating on mechanical strength of the cotton fabrics was investigated by testing breaking tenacity including warp strength and

Table 1 Comparison of oil absorption capacities from this study and the reported literatures

Hydrophobic and oleophilic materials	Type of oil	Absorption capacity (%)	References
Phytic acid (PA)-Fe^{III}@PDMS-coated cotton fabric	Chloroform	~ 146	Zhou et al. (2017)
	n-hexane	~ 65	
Multifunctional carbon aerogel	Crude oil	~ 160	Yang et al. (2018)
	Chloroform	~ 108	
PDMS-coated polyethylene terephthalate (PET) non-woven fabric	Silicone oil	~ 19	Kim et al. (2018)
MoS_2-roughened kapok fiber	Soybean oil	~ 130	Zhou et al. (2020)
	Kerosene	~ 80	
Highly oriented sponge	Chloroform	~ 43	Yuan et al. (2019)
	Peanut oil	~ 32	
3D porous EcoFlex sponge	Chloroform	~ 3400	Lu et al. (2019)
	n-hexane	~ 2000	
PDMS-coated cotton wool	Chloroform	~7080	Jin et al. (2015)
	Silicone oil	~ 6100	
PDMS/CuS@Cotton fabric	Chloroform	~ 150	This study
	n-hexane	~ 71	
	Kerosene	~ 141	
	Soybean oil	~ 156	

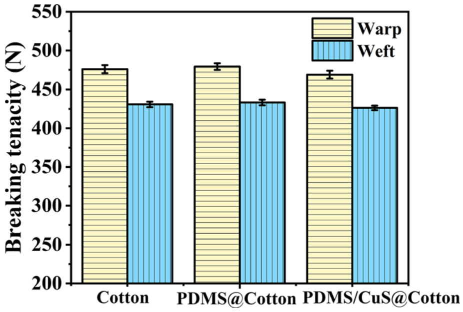

Fig. 13 Breaking tenacity of untreated cotton fabric sample, PDMS@Cotton fabric and PDMS/CuS@Cotton fabric

weft strength. As shown in Fig. 13, compared with untreated cotton fabric sample, the warp breaking tenacity and weft breaking tenacity of PDMS@Cotton fabric and PDMS/CuS@Cotton fabric showed slight variation. Although the coated cotton textiles were obtained with PDMS/CuS via dip-pad-dry process, even after curing at 150 °C for 60 min PDMS/CuS@Cotton fabric demonstrated such little change in mechanical strength. Two reasons may be as follows. On the one hand, PDMS with highly stable chemical structure had elastomeric property. On the other hand, for PDMS/CuS@Cotton fabric, PDMS as adhesive layer could firmly adhere on the cotton fiber surface and CuS nanoparticles. This PDMS dense film resulted in good bonding of the coating with the cotton fiber substrate and protecting cotton fibers from curing treatment, contributing to maintenance of mechanical strength of coated fabric. Hereby, it was revealed that PDMS/CuS coating showed no negative effect on mechanical strength of the cotton fabrics. Therefore, this composite coating with hierarchical CuS nanoparticles and silicone elastomer PDMS has potential in preparation of superhydrophobic textile with UV-proof property.

Conclusion

In summary, robust superhydrophobic cotton fabrics with UV-proof performance for self-cleaning as well as oil/water separation were fabricated using PDMS/CuS composite coating via simple one-pot method. The micro-nano hierarchical rough morphology was obtained due to incorporation of hierarchical CuS microflower nanoparticles on microscale cotton fibers. Low surface energy of coated cotton fibers was achieved because of silicone elastomer PDMS adhesive layer. The cotton fabric treated with PDMS/CuS showed outstanding superhydrophobic property with a water contact angle of 159.3° ± 0.6°. The coated cotton textile showed completely nonwettablity for water-soluble liquid droplets including water, cola, milk, and coffee, but showed contrasting wetting characteristics for oil droplets. Thereby, the prepared coated cotton textile also demonstrated effective self-cleaning, oil/water separating with high-efficiency and good separation reusability, and good oil absorption property. The prepared functional cotton fabric further indicated good ultraviolent-proof performance. Its UPF was 535.36 and T(UVA) was 0.25%. Furthermore, it was revealed that the superhydrophobic cotton fabric was resistant to mechanical rubbing, water jetting, UV irradiation and chemical corrosion, displaying excellent durability due to crosslinking elastomer PDMS coating and hierarchical CuS nanaoparticles with UV blocking property. This coating treatment caused slight change of breaking tenacity of PDMS/CuS@Cotton fabric. The facile approach could contribute to large-scale preparation and the presented flexible superhydrophobic cotton fabrics with UV-proof performance in this work were highly beneficial for potential wide application.

Supporting information

Supplementary data associated with this article can be found in “Supplementary file”.

Acknowledgments The financial support by National Natural Science Foundation of China (51703123), Talent Program of Shanghai University of Engineering Science, and Shanghai Engineering Research Center for Clean Production of Textile Chemistry (19DZ2253200) were acknowledged.

Compliance with ethical standards

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

References

Avramescu RE, Ghica MV, Dinu-Pirvu C, Prisada R, Popa L (2018) Superhydrophobic natural and artificial surfaces—a structural approach. Materials 11:866. https://doi.org/10.3390/ma11050866

Cao C, Wang F, Lu M (2020) Preparation of superhydrophobic CuS cotton fabric with photocatalytic and antibacterial activity for oil/water separation. Mater Lett 260:126956. https://doi.org/10.1016/j.matlet.2019.126956

Cassie ABD, Baxter S (1944) Wettability of porous surfaces. Trans Faraday Soc 40:546–550. https://doi.org/10.1039/tf9444000546

Chen J, Chao F, Ma X, Zhu Q, Jiang J, Ren J, Lou Y (2019a) Synthesis of flower-like CuS/UiO-66 composites with enhanced visible-light photocatalytic performance. Inorg Chem Commun 104:223–228. https://doi.org/10.1016/j.inoche.2019.04.022

Chen L, Hong J, Butt H-J, Wooh S (2019b) Liquid-repellent metal oxide photocatalysts. Chem-Eur J 25:4535–4542. https://doi.org/10.1002/chem.201804411

Dalawai SP, Aly MAS, Latthe SS, Xing R, Sutar RS, Nagappan S, Liu S (2020) Recent advances in durability of superhydrophobic self-cleaning technology: a critical review. Prog Org Coat 138:105381. https://doi.org/10.1016/j.porgcoat.2019.105381

Dong X, Gao S, Huang J, Li S, Zhu T, Cheng Y, Lai Y (2019) A self-roughened and biodegradable superhydrophobic coating with UV shielding, solar-induced self-healing and versatile oil-water separation ability. J Mater Chem A 7:2122–2128. https://doi.org/10.1039/c8ta10869b

Duan W, Xie A, Shen Y, Wang X, Wang F, Zhang Y, Li J (2011) Fabrication of superhydrophobic cotton fabrics with UV protection based on CeO_2 particles. Ind Eng Chem Res 50:4441–4445. https://doi.org/10.1021/ie101924v

Foorginezhad S, Zerafat MM (2019) Fabrication of stable fluorine-free superhydrophobic fabrics for anti-adhesion and self-cleaning properties. Appl Surf Sci 464:458–471. https://doi.org/10.1016/j.apsusc.2018.09.058

French AD (2014) Idealized powder diffraction patterns for cellulose polymorphs. Cellulose 21:885–896. https://doi.org/10.1007/s10570-013-0030-4

Ghasemlou M, Daver F, Ivanova EP, Adhikari B (2019) Bio-inspired sustainable and durable superhydrophobic materials: from nature to market. J Mater Chem A 7:16643–16670. https://doi.org/10.1039/c9ta05185f

Guo XJ, Xue CH, Li M, Li X, Ma JZ (2017) Fabrication of robust, superhydrophobic, electrically conductive and UV-blocking fabrics via layer-by-layer assembly of carbon nanotubes. RSC Adv 7:25560–25565. https://doi.org/10.1039/c7ra02111a

Hu XS, Shen Y, Xu LH, Wang LM, Lu LS, Zhang YT (2016) Preparation of flower-like CuS by solvothermal method for photocatalytic, UV protection and EMI shielding applications. Appl Surf Sci 385:162–170. https://doi.org/10.1016/j.apsusc.2016.05.089

Huang JY, Li SH, Ge MZ, Wang LN, Xing TL, Chen GQ, Lai YK (2015) Robust superhydrophobic TiO_2@fabrics for UV shielding, self-cleaning and oil-water separation. J Mater Chem A 3:2825–2832. https://doi.org/10.1039/c4ta05332j

Jeong SW, Bolortuya S, Eadi SB, Kim S (2020) Fabrication of superhydrophobic surfaces based on PDMS coated hydrothermal grown ZnO on PET fabrics. J Adhes Sci Technol 34:102–113. https://doi.org/10.1080/01694243.2019.1661609

Jin Y, Jiang P, Ke Q, Cheng F, Zhu Y, Zhang Y (2015) Superhydrophobic and superoleophilic polydimethylsiloxane-coated cotton for oil-water separation process: an evidence of the relationship between its loading capacity and oil absorption ability. J Hazard Mater 300:175–181. https://doi.org/10.1016/j.jhazmat.2015.07.002

Khan MZ, Baheti V, Militky J, Ali A, Vikova M (2018) Superhydrophobicity, UV protection and oil/water separation properties of fly ash/trimethoxy(octadecyl)silane coated cotton fabrics. Carbohydr Polym 202:571–580. https://doi.org/10.1016/j.carbpol.2018.08.145

Khosravi M, Azizian S, Boukherroub R (2019) Efficient oil/water separation by superhydrophobic CuxS coated on copper mesh. Sep Purif Technol 215:573–581. https://doi.org/10.1016/j.seppur.2019.01.039

Kim HJ, Han SW, Kim JH, Seo HO, Kim YD (2018) Oil absorption capacity of bare and PDMS-coated PET non-woven fabric; dependency of fiber strand thickness and oil viscosity. Curr Appl Phys 18:369–376. https://doi.org/10.1016/j.cap.2018.01.017

Lahiri SK, Zhang P, Zhang C, Liu L (2019) Robust fluorine-free and self-healing superhydrophobic coatings by H_3BO_3 incorporation with SiO_2-alkyl-silane@PDMS on cotton fabric. ACS Appl Mater Interfaces 11:10262–10275. https://doi.org/10.1021/acsami.8b20651

Lee JH, Park EJ, Kim DH, Jeong MG, Kim YD (2016) Superhydrophobic surfaces with photocatalytic activity under UV and visible light irradiation. Catal Today 260:32–38. https://doi.org/10.1016/j.cattod.2015.05.020

Li D, Guo Z (2018) Metal-organic framework superhydrophobic coating on Kevlar fabric with efficient drag reduction and wear resistance. Appl Surf Sci 443:548–557. https://doi.org/10.1016/j.apsusc.2018.03.030

Li S, Huang J, Chen Z, Chen G, Lai Y (2017) A review on special wettability textiles: theoretical models, fabrication technologies and multifunctional applications. J Mater Chem A 5:31–55. https://doi.org/10.1039/c6ta07984a

Liu Y, Zhou Z, Zhang S, Luo W, Zhang G (2018) Controllable synthesis of CuS hollow microflowers hierarchical structures for asymmetric supercapacitors. Appl Surf Sci 442:711–719. https://doi.org/10.1016/j.apsusc.2018.02.220

Lu Z, Song J, Pan K, Meng J, Xin Z, Liu Y, Zhao Z, Gong R, Li J (2019) Ecoflex sponge with ultrahigh oil absorption capacity. ACS Appl Mater Interfaces 11:20037–20044. https://doi.org/10.1021/acsami.9b04446

Nemade KR, Waghuley SA (2015) Band gap engineering of CuS nanoparticles for artificial photosynthesis. Mater Sci Semicond Process 39:781–785. https://doi.org/10.1016/j.mssp.2015.05.045

Pan C, Shen L, Shang S, Xing Y (2012) Preparation of superhydrophobic and UV blocking cotton fabric via sol-gel method and self-assembly. Appl Surf Sci 259:110–117. https://doi.org/10.1016/j.apsusc.2012.07.001

Patil GD, Patil AH, Jadhav SA, Patil CR, Patil PS (2019) A new method to prepare superhydrophobic cotton fabrics by post-coating surface modification of ZnO nanoparticles. Mater Lett 255:126562. https://doi.org/10.1016/j.matlet.2019.126562

Razavi SMR, Oh J, Haasch RT, Kim K, Masoomi M, Bagheri R, Miljkovic N (2019) Environment-friendly antibiofouling superhydrophobic coatings. ACS Sustain Chem Eng 7:14509–14520. https://doi.org/10.1021/acssuschemeng.9b02025

Riaz S, Ashraf M, Hussain T, Hussain MT, Younus A (2019) Fabrication of robust multifaceted textiles by application of functionalized TiO_2 nanoparticles. Colloid Surf A-Physicochem Eng Asp 581:123799. https://doi.org/10.1016/j.colsurfa.2019.123799

Rius-Ayra O, Castellote-Alvarez R, Escobar AM, Llorca-Isern N (2019) Robust and superhydrophobic coating highly resistant to wear and efficient in water/oil separation. Surf Coat Technol 364:330–340. https://doi.org/10.1016/j.surfcoat.2019.01.077

Rostami A, Pirsaheb M, Moradi G, Derakhshan AA (2019) Fabrication of durable superhydrophobic nanofibrous filters for oil-water separation using three novel modified nanoparticles (ZnO-NSPO, AlOO-NSPO, and TiO_2-NSPO). Polym Adv Technol. https://doi.org/10.1002/pat.4828

Shi B, Liu W, Zhu K, Xie J (2017) Synthesis of flower-like copper sulfides microspheres as electrode materials for sodium secondary batteries. Chem Phys Lett 677:70–74. https://doi.org/10.1016/j.cplett.2017.03.051

Tu KK, Wang XQ, Kong LZ, Guan H (2018) Facile preparation of mechanically durable, self-healing and multifunctional superhydrophobic surfaces on solid wood. Mater Des 140:30–36. https://doi.org/10.1016/j.matdes.2017.11.029

Xiong M, Ren Z, Liu W (2019) Fabrication of UV-resistant and superhydrophobic surface on cotton fabric by functionalized polyethyleneimine/SiO_2 via layer-by-layer assembly and dip-coating. Cellulose 26:8951–8962. https://doi.org/10.1007/s10570-019-02705-5

Xue CH, Li YR, Zhang P, Ma JZ, Jia ST (2014) Washable and wear-resistant superhydrophobic surfaces with self-cleaning property by chemical etching of fibers and hydrophobization. ACS Appl Mater Interfaces 6:10153–10161. https://doi.org/10.1021/am501371b

Yang J, Xu P, Xia Y, Chen B (2018) Multifunctional carbon aerogels from typha orientalis for oil/water separation and simultaneous removal of oil-soluble pollutants. Cellulose 25:5863–5875. https://doi.org/10.1007/s10570-018-1994-x

Yang M, Liu W, Jiang C, Liu C, He S, Xie Y, Wang Z (2019a) Facile preparation of robust superhydrophobic cotton textile for self-cleaning and oil-water separation. Ind Eng Chem Res 58:187–194. https://doi.org/10.1021/acs.iecr.8b04433

Yang Y, Huang W, Guo Z, Zhang S, Wu F, Huang J, Gu S (2019b) Robust fluorine-free colorful superhydrophobic PDMS/NH_2-MIL-125(Ti)@cotton fabrics for improved ultraviolet resistance and efficient oil-water separation. Cellulose 26:9335–9348. https://doi.org/10.1007/s10570-019-02707-3

Yu X, Liu X, Shi X, Zhang Z, Wang H, Feng L (2019) SiO_2 nanoparticle-based superhydrophobic spray and multifunctional surfaces by a facile and scalable method. Ceram Int 45:15741–15744. https://doi.org/10.1016/j.ceramint.2019.05.014

Yuan SJ, Zhang JJ, Fan HX, Dai XH (2018) Facile and sustainable shear mixing/carbonization approach for upcycling of carton into superhydrophobic coating for efficient oil-water separation. J Clean Prod 196:644–652. https://doi.org/10.1016/j.jclepro.2018.06.105

Yuan J, Zhang M, Xia M, Cao W, Du M, Dou J, Zhao D (2019) Novel high-capacity and reusable carbonaceous sponges for efficient absorption and recovery of oil from water. Appl Surf Sci 487:398–408. https://doi.org/10.1016/j.apsusc.2019.05.036

Zhai S, Jin K, Zhou M, Fan Z, Zhao H, Zhao Y, Cai Z (2019) In-situ growth of flower-like CuS microsphere on carbonized cotton for high-performance flexible supercapacitor. Colloid Surf A-Physicochem Eng Asp 575:75–83. https://doi.org/10.1016/j.colsurfa.2019.05.010

Zhang D, Zheng G, Zheng C, Wu Y, Long Z (2019) Preparation and characterization of wear-resistant superhydrophobic cotton fabrics. Prog Org Coat 134:226–233. https://doi.org/10.1016/j.porgcoat.2019.04.070

Zhou C, Chen Z, Yang H, Hou K, Zeng X, Zheng Y, Cheng J (2017) Nature-inspired strategy toward superhydrophobic fabrics for versatile oil/water separation. ACS Appl Mater Interfaces 9:9184–9194. https://doi.org/10.1021/acsami.7b00412

Zhou L, Fu C, Xiao W, Niu B, Sun C, Yu M, Zheng Y (2020) MoS_2-roughened hollow-lumen plant fibers with enhanced oil absorption capacity. Cellulose 27:2267–2278. https://doi.org/10.1007/s10570-019-02943-7

Zhou P, Lv J, Xu H, Wang X, Sui X, Zhong Y, Mao Z (2019) Functionalization of cotton fabric with bismuth oxyiodide nanosheets: applications for photodegrading organic pollutants, UV shielding and self-cleaning. Cellulose 26:2873–2884. https://doi.org/10.1007/s10570-019-02281-8

Zhu C, Wang B, Wang W, Meng J, Deng S, Fan X, Zhao C (2020) A facile method for crystallizing flower-like CuS on the surface of PBO fiber. Mater Lett 258:126652. https://doi.org/10.1016/j.matlet.2019.126652

Zhu T, Li S, Huang J, Mihailiasa M, Lai Y (2017) Rational design of multi-layered superhydrophobic coating on cotton fabrics for UV shielding, self-cleaning and oil-water separation. Mater Des 134:342–351. https://doi.org/10.1016/j.matdes.2017.08.071