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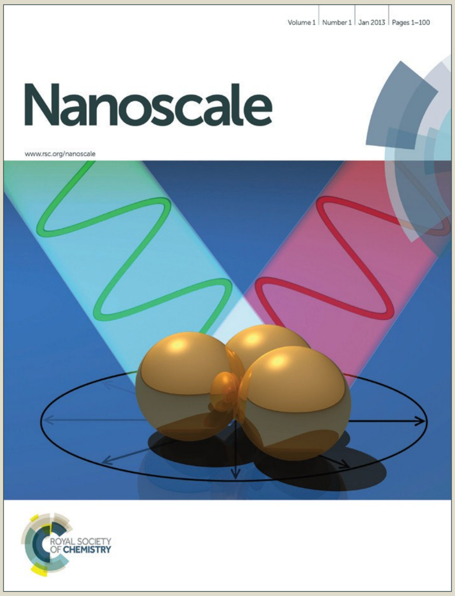

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Self-cleaning Polybenzoxazine/TiO_2 Surface with Superhydrophobicity and Superoleophilicity for Oil/water Separation

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Two important properties—the low surface free energy of polybenzoxazine (PBZ) and the photocatalysis-induced self-cleaning property of titanium dioxide (TiO_2) nanoparticles—are combined to develop a promising approach for oil/water separation. They are integrated into a multifunctional superhydrophobic and superoleophilic material, PBZ/TiO_2 modified polyester non-woven fabrics (PBZT), through a simple dip coating and subsequent thermal curing method. The resulting PBZT reveals excellent mechanical durability and strong resistance to ultraviolet (UV) irradiation as well as acid and alkali. This durably superhydrophobic and superoleophilic fabric is efficient for separating oil/water mixtures by gravity with high separation efficiency, and it can also purify wastewater that contain soluble dyes, which makes it more effective and promising in treating water pollution. Importantly, the PBZT demonstrates an integrated self-cleaning performance on the removal of both oil and particle contaminations. It is expected that this simple process can be readily adopted for design of multifunctional PBZ/TiO_2 based materials for oil/water separation.

Introduction

Oil contamination is a main source of water pollution, which has long been a major concern in daily life and industrial production especially in that oil spills generated from oil exploration, transportation, storage, usage as well as oily sewage emissions are catastrophic for marine and aquatic ecosystems.[1] Conventionally, skimming, centrifugation and coagulation-flocculation are the three basic approaches to remove oils from water, while those are short for low separation efficiency, high operation costs and the generation of secondary pollutants.[2]

Inspired by nature, superhydrophobic and superoleophilic filtration materials, such as fabric[3,4], mesh[5-9] and membrane[2,10,11], have been fabricated through rational control of surface morphology and chemical compositions to selectively filter insoluble oil from oil/water mixtures.[12-14] Generally, sophisticated processes such as etching[15], templating[16] and nanoimprint lithography[17] are involved in constructing a rough surface, and fluorine-containing low surface free energy materials such as perfluorocarbon and fluoroalkylsilane are used to realize desired surface wettability.[18] In practical applications, however, a cost-efficient and straightforward process is much preferable. As a new type of low surface free energy material, polybenzoxazine (PBZ) is promising for a stable superhydrophobic and superoleophilic surface due to its low cost, high thermal stability and good resistance to acid and alkali.[19-21] Yu et al have constructed fluorine-containing superhydrophobic and superoleophilic nanofibrous membranes from PBZ/SiO_2 by electrostatic spinning process for gravity-driven oil/water separation.[22,[illegible]] Although the authors have demonstrated that PBZ/SiO_2 membrane possesses large oil flux (above 3000 L m^{-2} h^{-1}), they have failed to address the membrane fouling caused by either oil or particles, which is a common problem in practice and can lead to severe flux decline, affect the quality of recycled water and shorten the life span of filtration materials.[24,25]

Self-cleaning is a desired property that can make the dream of a contamination-free surface come true and maintain high oil/water separation efficiency as well as its reusability in practice. Recently, a self-cleaning superhydrophobic octadecylphosphonic acid-modified coating has been applied on mesh for oil/water separation,[8] and a superhydrophobic and superoleophilic polyurethane foam modified by fluoroalkylsilane has also been demonstrated self-cleaning property and excellent performance on oil/water separation.[illegible] But the self-cleaning performance of the above two materials is limited to the removal of particles from the surface. In terms of the removal of liquid oils, titanium dioxide (TiO_2) nanoparticles has received great attention owing to its important applications in photodegradation of organics and

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Shanghai Key Laboratory of Multiphase Materials Chemical Engineering, State Key Laboratory of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, 130 Meilong Road, Xuhui District, Shanghai 200237, People's Republic of China.
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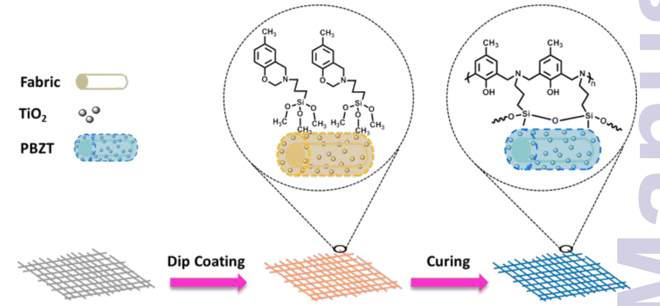
Electronic Supplementary Information (ESI) available: Element distribution on and specific surface area of PBZT10. SEM images of PBZT3, PBZT10 and PBZT20. Water and oil contact angles on prepared samples. FTIR spectra of OA/PBZT10 before and after heating. Images of water droplet on PBZT10 before and during rolling when the base was tilted. Video recordings of cyclohexane droplet on PBZT10, oil/water separation process and self-cleaning process. See DOI: 10.1039/x0xx00000x fabrication of self-cleaning surfaces.[26] Sun et al have used graphene-TiO_2 composite to build a ultralow fouling membrane with self-cleaning performance for the degradation of oils on the as-prepared superhydrophilic surface.[27] Sodium silicate/TiO_2[28] and carbon nanotube/TiO_2[29] based self-cleaning superhydrophilic surface has also been prepared for oil/water separation. Nevertheless, it is tough to build a self-cleaning superhydrophobic surface based on TiO_2 since contaminated surface can transform into a hydrophilic or even a superhydrophilic one due to constantly produced hydrophilic compounds from oil decomposition.[30] Furthermore, incorporation of TiO_2 into a superhydrophobic surface is challenging because TiO_2 will become hydrophilic under UV exposure, causing a superhydrophilic surface.[31] Thus, fabrication of durably superhydrophobic and superoleophilic materials with integrated self-cleaning property for the removal of both oil and dirt particle contaminations that are suitable for solving water pollution still remains a big challenge. To overcome the limitations mentioned above, a new strategy for oil/water separation filtration materials with integrated self-cleaning through a simple, cost-effective and environmentally friendly approach is highly desirable. Herein, we for the first time, to our best knowledge, demonstrate a PBZ/TiO_2 based self-cleaning superhydrophobic and superoleophilic fabric through a simple dip coating and subsequent thermal curing method where no fluorine containing material is required to achieve the special wettability. The introduction of TiO_2 nanoparticles is expected to form nanoscale structure and thus along with the microscale rough surface of polyester non-woven fabric to induce superhydrophobic and superoleophilic surface. Moreover, the resulting PBZT is effective for oil/water separation, and oils and dirt particles on this surface can be photodegraded by TiO_2 and removed by water respectively, endowing the fabric with integrated self-cleaning performance and long-term use in oil/water separation. This simple approach to achieving self-cleaning superhydrophobic and superoleophilic surfaces may provide a convenient and an inexpensive platform for extensive applications of PBZ/TiO_2 based materials.

Results and discussion

Surface preparation, wettability and morphology

Scheme 1 illustrates the fabrication process of polybenzoxazine/titanium dioxide modified polyester non-woven fabric (PBZT). The whole process only involves simple dip coating and further thermal curing treatment. Upon curing at 200 °C, the polymerization of benzoxazine monomers and condensation of siloxane groups lead to the formation of Mannich Bridge and Si-O-Si dual-crosslinking structure.[32] Silane-functionalized PBZ serves as a low surface free energy material to improve the surface hydrophobicity and oleophilicity. Meanwhile, it performs as 'glue' during the curing when the oxazine ring opens and silane groups condense to fix the TiO_2 nanoparticles on fibers, which is expected to maintain the stability and durability of special wettability on the surface.[32] The presence of PBZ and TiO_2 on the fabric surface is also verified by energy dispersive spectrometer (EDS) characterization. As shown in Figure S1, the signals of carbon (C), oxygen (O), silicon (Si) and titanium (Ti) atoms corresponding to PBZT appear clearly in the EDS spectra. It can be seen in Figure S1e-f that Si and Ti atoms are distributed homogeneously on the surface of modified fibers, indicating uniform coverage of PBZ and TiO_2 on the fabric surface.



Scheme 1. Fabrication process of superhydrophobic and superoleophilic PBZT.

The introduction of TiO_2 nanoparticles is expected to form nanoscale structure and thus along with the microscale rough surface of polyester non-woven fabric to induce superhydrophobic and superoleophilic surface. It is found that the content of TiO_2 in the composite plays a key role in PBZT surface morphology and wettability. Figure 1 shows the morphology of PBZT with various TiO_2 content. The pristine fabric surface is composed of microfibers (15 to 20 µm in diameter) exhibiting a flat fiber surface (Figure 1a), while the PBZT rough. When the content of TiO_2 is 3 wt%, the nanoparticles disperse uniformly and form a relatively thin nanoscale structure layer on the fiber as shown in Figure 1b and Figure S2a. This relatively uniform TiO_2 structure on PBZT3 exhibits a number of shallow grooves, while a larger content of TiO_2 on PBZT10 and PBZT20 turn to be aggregated and form a TiO_2 structure with many deep grooves on the fabric as shown in Figure 1c-d and Figure S2b-c. The air-solid interfaces trap air within these deep grooves beneath the water reveals that the water could not totally penetrate into the surface structures, demonstrating a superhydrophobic surface.[33] On the contrary, the water droplet will partially penetrate into the surface structures and the water CA decreases when the grooves are shallow as PBZT3. As a result, the PBZT3 is highly hydrophobic, while PBZT10 and PBZT20 superhydrophobic. The difference in the surface morphology and chemical composition is reflected in PBZT surface wettability. Benefiting from these micro- and nanoscale structures, superhydrophobic and superoleophilic fabrics are obtained when the content of TiO_2 is increased, which are well consistent with surface wettability shown below.

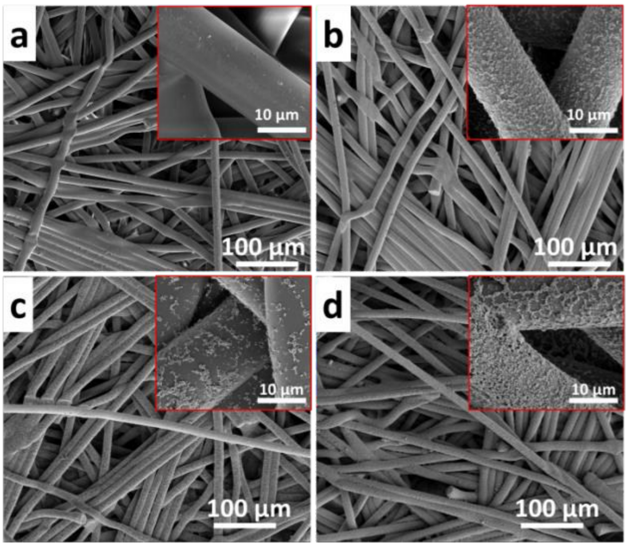


Figure 1. SEM images of (a) pristine fabric, (b) PBZT3, (c) PBZT10, and (d) PBZT20 with low and high magnifications.

The pristine polyester fabric can be easily wetted by water and oil. Figure S3 shows the water CA recordings of a pristine fabric surface in a few seconds demonstrating the intrinsic hydrophilicity of pristine fabric. After being treated by a pure PBZ solution, a hydrophobic and superoleophilic fabric with a water CA of ~128±1^{o} is achieved as shown in Figure 2a and oils can also spread out on this fabric surface. It is well known that both surface rough structure and low surface free energy chemical composition are beneficial for a superhydrophobic surface.[34] These microscale fabric fibers form a rough surface and PBZ works as a low surface free energy agent, thus improving the hydrophobicity of pristine fabric. With the increasing of the TiO_2 content, relatively to the weight of benzoxazine monomer, a superhydrophobic and superoleophilic fabric with micro- and nanoscale surface structures is developed as shown in Figure 2. The water CA of PBZT3, PBZT5, PBZT10 and PBZT20 surface is ~143±1^{o}, ~148±2^{o}, ~155±1^{o} and ~156±1^{o} respectively. The superhydrophobicity can be attributed to the introduction of nanoscale structures to the microscale fibers. Therefore, the cooperation of low surface free energy chemical composition and surface hierarchical structures is important for the superhydrophobic surface. Oils, such as n-hexadecane, dichloromethane (DCM) and cyclohexane (Video S1), can spread out on, be absorbed by and permeate PBZT10 surface as shown in Figure 2b, indicating the superoleophilic property. This simultaneous superhydrophobicity and superoleophilicity is essential for filtration materials in oil/water separation. Since TiO_2 nanoparticles are essentially separated from the surface of fibers and polybenzoxazine is performed as 'glue' to fix them on the surface, less TiO_2 shall be advantageous for the stability of superhydrophobicity. Considering the stability of special wettability and energy-efficiency, PBZT10 modified fabric (PBZT10) is chosen for further investigation.

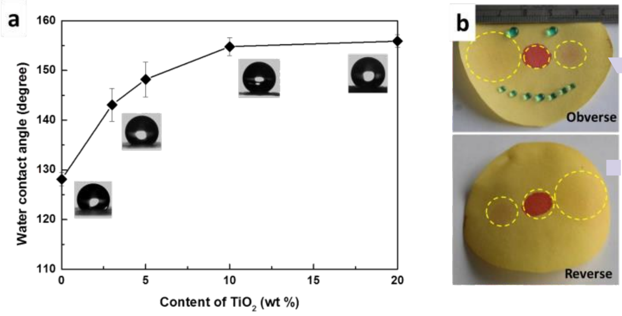


Figure 2. (a) Variations in water CAs of fabrics with different contents of TiO_2 in the composite, and the insets are the corresponding water CA images of each sample. (b) Photograph of PBZT10. Water was dyed with methylene blue (MB) and oil was dyed with oil soluble red dyes which were squeezed out from fine point marker of Zebra, Japan. On the obverse side, oil droplets in the three yellow dashed circles from left to right are n-hexadecane, dichloromethane (DCM) and cyclohexane respectively.

Durability and Stability of superhydrophobic and superoleophilic PBZT surface

In practical applications, the enhancement of durability and stability in complex environments, such as mechanical scratch, acid and alkali conditions, is important. Furthermore, good resistance of TiO_2 based self-cleaning surface to UV irradiation is also significant for sustainable applications. The as-prepared superhydrophobic and superoleophilic PBZT10 has been conducted for durability and stability tests in detail. The mechanical durability is important for superhydrophobic surface and a sandpaper scratch test has been carried out to measure the durability of PBZT10 surface. Figure 3a shows that PBZT10 surface keeps its superhydrophobicity and superoleophilicty with water CA of ~150±2^{o} and oil CA of ~0^{o} after 14 cycles of sandpaper scratch test, demonstrating an excellent resistance of PBZT10 surface to mechanical scratch. Moreover, Figure 3b illustrates the variations in water CA of PBZT10 surface with UV irradiation time. It can be seen that PBZT10 maintains superhydrophobicity/hydrophobicity even under an 8-hour strong UV light irradiation (250 W) despite the presence of photo-induced superhydrophilic TiO_2. On one hand, the silane-functionalized PBZ used in this work barely affects the stability of superhydrophobicity under UV light irradiation because the pure PBZ film without TiO_2 keeps its hydrophobicity with a stable CA under UV light irradiation which was reported in our previous work in detail.[32] On the other hand, in term of a PBZ/TiO_2 composite film in the previous results, the reversible hydrophobic-hydrophilic transitions of PBZ/TiO_2 film can be observed, which was proved to be associated with the content of Ti-OH on the film surface. The ability of recovery to its initial hydrophobicity of PBZ/TiO_2 film also verifies that PBZ barely changes or affects the special wettability of PBZ/TiO_2 under UV irradiation. Furthermore, it has been suggested that the sufficient roughness offered by microscale fibers and nanoscale particles dominates the surface wettability rather than the chemical composition of resulting fabric surface.[35] It is noteworthy that this UV resistance of TiO_2 based surface will make the dream of self-cleaning PBZT surface with stable superhydrophobicity come true. To measure the surface wettability of PBZT10 w contacted with acid and alkali, solutions with various pH values are prepared from HCl and NaOH. Figure 3c demonstrates that the surface superhydrophobicity and superoleophilicity of the modified fabric is stable on a wide pH range from 3 to 11. The sharp drop of water CA when the pH is 13 is probably due to the non-resistance of PET fabric to strong alkali. The PBZT10 is mechanically durable and shows good resistance to strong UV exposure and acid or alkali substances, which are advantageous in industrial applications.

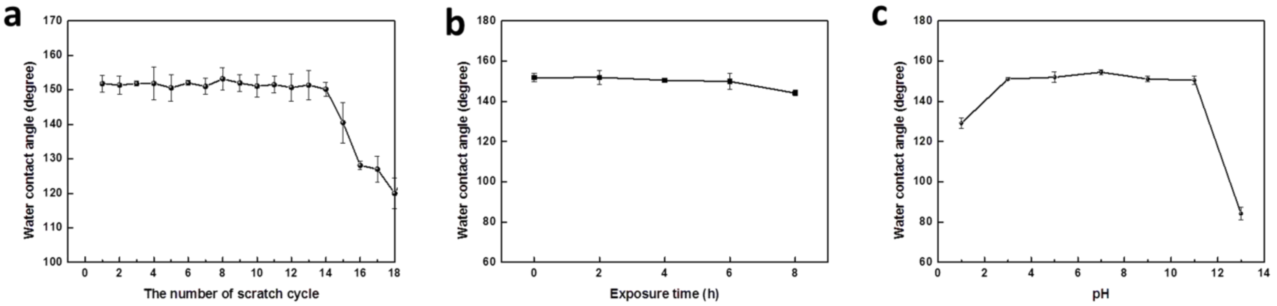


Figure 3. (a) Variations in water CA of PBZT10 after sandpaper scratch test, (b) under UV irradiation with various time, and (c) relationship between pH value and the corresponding water CA on PBZT10 surface. Oil droplet on each specimen surface spreads out immediately.

Gravity driven oil/water separation and water purification

As a proof of concept, the gravity driven oil/water separation experiment of PBZT10 has been performed in a simple setup. Prior to the practical separation, specific surface area and pore structure of PBZT10 has been studied. Its average pore size is 18.9 µm, while Figure S4 demonstrates various types of adsorption including monolayer adsorption, multilayer adsorption and capillary condensation, and the hysteresis loop reveals that the pores are open. Furthermore, the Brunauer-Emmett-Teller (BET) specific surface area is 26.30m^3/g indicating a large surface area of PBZT10. The large opening pore structure and remarkable surface area are advantageous parameter in oil/water separation. Figure 4a shows the setup for separating heavy oil/water mixture, *e.g.* DCM/water mixture (Video S2). Due to the superhydrophobicity and superoleophilicity of PBZT10, water is retained above, while oil phase will permeate and pass through the fabric quickly by gravity. The reusability performance of resulting PBZT10 for heavy oil/water separation has been assessed in our experiment. The oil flux is calculated by Equation 1.

$$F = V/At \qquad (1)$$

Where F is the oil flux (L m^{-2} h^{-1}), V is the oil volume measured in 25 s (t) in each cycle, and A (12.56 cm^2) is the valid test area of the modified fabric. As seen in Figure 4b, the flux shows slight fluctuation and keeps ~3000 L m^{-2} h^{-1} even after ten cycles of oil/water separation. Additionally, the water CA of the PBZT10 surface after ten times is ~153±3^{o}. Both results indicate reusability and antifouling performance of PBZT10 surface, which are important traits for oil/water separation in industrial application.

Figure 4c displays the separation process for those light oil/water mixtures, *e.g.* toluene/water mixture (Video S3). To make light-density oil able to contact and permeate the fabric by gravity, the separation device is titled for 45^{o}. Because of the titled separation device, it will be inaccurate to calculate the oil flux. Therefore, the separation efficiency for each oil/water mixture is compared in Figure 4d. It is calculated by Equation 2.

$$R(\%) = (V_p + V_c)/V_o \times 100\% \qquad (2)$$

Where V_o and V_c are the oil volume of the original oil/water mixture and the collected oil after separation respectively. It is calculated by dividing the oil density with the increased weight of fabric after each separation. It can be concluded that the as-prepared PBZT10 is effective to separate different types of oil/water mixture, including toluene, isooctane xylene, hexadecane, petroleum ether, dichloromethane and cyclohexane. They all prove high separation efficiency, which is above 98 %, demonstrating it to be a good candidate for oil polluted water treatment.

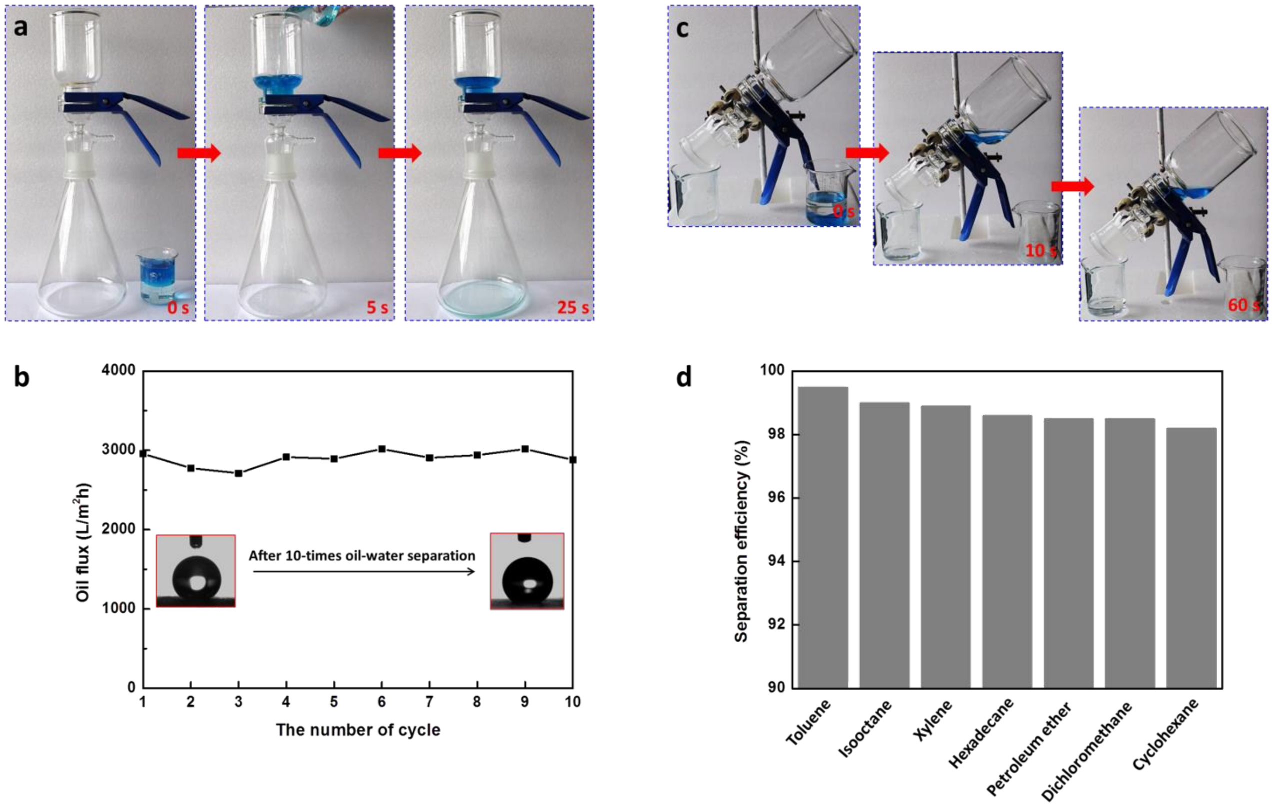


Figure 4. (a) Gravity-driven DCM/water separation setup. (b) Changes in DCM flux with the number of cycles during the separation of DCM/water mixture and the insets show the water CA images of PBZT10 surface before DCM/water separation and after 10-times separation. (c) Gravity-driven light oil/water separation setup. (d) Variations in oil separation efficiency of different types of oil/water mixture.

In addition to oil induced water pollution, the contamination caused by soluble pollutant is another sever issue at present. Traditional filtration is generally limited in separating soluble pollutants from water. Then the emergence of oxidation degradation paves a way for water purification and TiO_2 is typical of the materials that possesses photocatalysis property leading to the total mineralization of most organic pollutants.[36] The capability of degrading organic pollutant of PBZT10 has been examined by immersing modified fabric into MB solution and measuring its light absorption after UV exposure for different times. As shown in Figure 5, the absorption intensity corresponding to MB decreases dramatically due to the decomposition by TiO_2 and almost clean water is achieved after UV treatment for 6 h. The additional water purification performance makes PBZ/TiO_2 modified superhydrophobic and superoleophilic materials more effective and promising in treating water pollution.

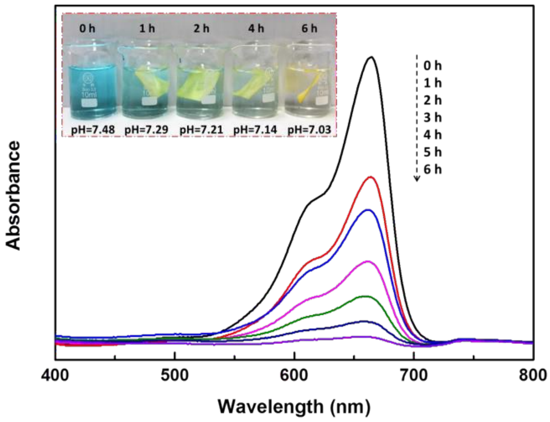


Figure 5. UV-vis absorbance curves of MB aqueous solutions after different exposure times. The original MB aqueous solution has a concentration of 1 ppm. The inset pictures show the corresponding MB solutions and the pH value of each solution after photodegradation for various times.

Self-cleaning performance

As mentioned in the introduction section, surface contamination can greatly affect the superhydrophobicity and the performance of materials used in oil/water separation, which calls for self-cleaning property. It is well known that lotus leaf which possesses high water contact angle and low sliding angle exhibits self-cleaning where dirt particles can be removed readily by water.[37] However, lotus leaf-like self-cleaning has no effect on oil polluted superoleophilic surface. Therefore, the incorporation of TiO$_2$ which degrades organics and induces a self-cleaning surface will tackle the challenge. As shown in Figure 6a, PBZT10 surface lost its superhydrophobicity and becomes hydrophobic with a water CA of ~96±2° when contaminated by model organic contaminants oleic acid. Interestingly, oleic acid contaminated PBZT10 (OA/PBZT10) reveals photo-induced superhydrophilicity. After 4-hour UV irradiation, the fabric becomes superhydrophilic and the water droplet spread out immediately. It is primarily due to the formation of more hydrophilic compounds that decomposed from oleic acid by TiO$_2$.[30] Those more hydrophilic compounds exist on PBZT10 surface, influencing surface chemical composition and leading to the superhydrophilicity. Furthermore, it is found that a subsequent heat treatment can turn the superhydrophilic OA/PBZT10 back into its originally superhydrophobic state. Specifically, the exposed OA/PBZT10 turns to be superhydrophobic with a water CA of ~154±1° when heated at 140 °C for 1h as shown in Figure 6b, indicating the self-cleaning property of PBZT10 surface. Additionally, Figure S5 shows the oil CAs of OA/PBZT10, exposed OA/PBZT10 before and after heat treatment. The surfaces are all superoleophilic with oil CA of ~0°.

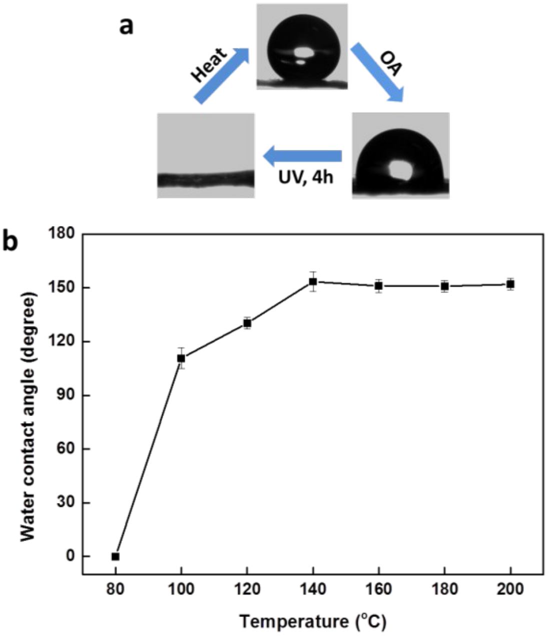


Figure 6. (a) Water CA images to illustrate a self-cleaning process of PBZT10 surface. (b) Variations in water CAs of exposed OA/PBZT10 with the heat treatment at different temperature for 1h.

The photo- and heat-induced self-cleaning process of the modified fabric can be explained by both the photocatalysis of TiO$_2$ and evaporation phenomenon as illustrated in Figure 7. On one hand, oils on PBZT10 surface can be photodegraded by TiO$_2$ under UV exposure due to the photocatalytic property of TiO$_2$.[36] Consequently, more hydrophilic compounds, such as nonanal and 9-oxononanoic,[30] are formed to make the surface hydrophilic. There is another evidence to support this explanation. As shown in Figure S6, the absorption peak at 1501.64 cm^{-1} corresponds to the stretching vibration of tri-substituted benzene ring, of which the structure does not change during the irradiating or heating treatment. Thus, it is used as a reference to analyse the differences of the peaks at 2924.28 cm^{-1} and 1713.76 cm^{-1} which are the stretching vibration band of C-H and carboxyl group in oleic acid respectively. It can be seen that these two peaks decrease apparently after heating, which confirm the decrease of oleic acid on the surface and demonstrates a self-cleaning performance. It should be mentioned that the absorption peak at 1713.76 cm^{-1} does not totally disappear because of carboxyl groups existing in the PET non-woven fabric. Combined with the rough structure of fabric surface, a superhydrophilic fabric will be obtained. On the other hand, those hydrophilic compounds are usually small volatile molecules and thus can easily evaporate at 140 °C. As a result, oils are removed completely and the exposed OA/PBZT10 turns to superhydrophobic fabric again after the heat treatment.

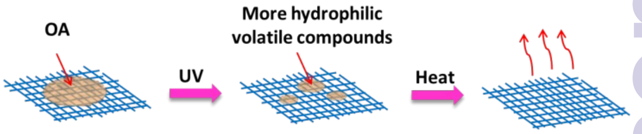


Figure 7. Illustration of photo- and heat-induced self-cleaning property of PBZT10.

Generally, the filtration material fouling is also a process where particles deposit onto the surface.[8,25] To study the self-cleaning effect on the removal of particles, PBZT10 surface has been contaminated with graphite powders scraped from pencil lead. PBZT10 enjoys water sliding angle of ~25° (Figure S7), which means that water droplet will roll down when the base is tilted, demonstrating a self-cleaning performance. Figure 8 and Video S4 shows that the water droplet adsorbs the particles on the surface as it moved over the surface showing a self-cleaning property of PBZT10 surface for the removal of particles. Different from conventional superhydrophobic surface that can realize self-cleaning merely in the elimination of dirt particles, the as-prepared PBZT10 surface possesses an integrated self-cleaning performance in the removal of both oils and particles, which allows long-term use in efficient treatment of water pollution and maintains the oil/water separation efficiency.

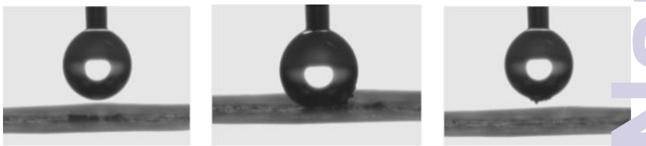


Figure 8. Self-cleaning performance of PBZT10 for the removal of particles deposited on the surface (water droplet, 2 μL).

Experimental

Materials

4-Methylphenol and 3-Aminopropyltrimethoxysilane were purchased from Sinopharm Chemical Reagent Corp. and Shanghai Haiqu Reagent Corp. respectively. Paraformaldehyde, chloroform and calcium hydride were obtained from Shanghai Lingfeng Chemical Corp. Tetrahydrofuran (THF) was purchased from Shanghai Tianlian Fine Chemical Corp. All chemicals were of analytical grade and used as received without further purification except chloroform purified by distillation over calcium hydride. Spherical TiO_2 (P25) nanoparticles were kindly provided by the Evonik Degussa Specialty Chemicals Company. Its mean diameter is ~21 nm and BET surface area is 52.80 m^2/g. Polyester (PET) non-woven fabric (TA3631) was kindly provided by Shanghai Tianlue Textile Corp.

Preparation of PBZ/TiO_2 modified polyester non-woven fabrics

Benzoxazine monomer, 3-(Trimethoxysilyl)-*n*-propyl-3,4-dihydro-6-methyl-2*H*-1,3-benzoxazine was synthesized according to literature at first.[38] Polybenzoxazine/TiO_2 modified fabric (PBZT) was prepared by using a simple dip coating process according to Chinese patent.[39] Prior to dip coating, PET fabric were cleaned ultrasonically in water, ethanol and acetone for 15 min respectively. These fabrics were blown dry with nitrogen gas to ensure a dust-free surface after removing the spare acetone through ultrasonication in water again for 5 min. Subsequently, benzoxazine monomer with a concentration of 10 wt% was dissolved in THF and a certain amount of TiO_2, relative to the weight of benzoxazine monomer, was added to the benzoxazine solution. The mixture was held in an ultrasound bath for 2 h to form a uniform dispersion. The clean fabric was dip-coated into the mixture for twice with a withdraw speed at 80 mm min^{-1} for 1 min each time. Finally, specimens were dried in a vacuum oven at 60 ^{o}C for 1 h and cured at 200 ^{o}C for 1 h. The modified fabric were denoted as PBZTx, where x is the relative weight percentage of TiO_2 (x %) to the weight of benzoxazine monomer. e.g. PBZT10.

Durability and stability measurement

A sandpaper scratch test was carried out to measure mechanical durability of as-prepared superhydrophobic fabric according to the literature.[40] In detail, the sample weighing 200 g was placed face-down to sandpaper (grit no. 240) and moved for 10 cm along the ruler. Then the sample was rotated by 90^{o} (face to the sandpaper) and then moved for 10 cm along the ruler. This process is defined as one scratch cycle. The surface wettability was measure by contact angle measurement after each scratch cycle. The anti-UV property of PBZT surface was conducted under UV exposure. In detail, the UV light source was obtained from a 250 W Hg lamp at 25±1.5 ^{o}C with a relative humidity of 60±2%. The surface wettability of exposed PBZT was measured. Additionally, solutions with various pH values were made from HCl and NaOH to investigate the acid- and alkali-resistant property of PBZT surface. PBZT (2×2 cm^2) was totally immersed into a solution (10 ml) with a certain pH for 1 h. Then the fabric was dried at room temperature and the surface wettability was measure by contact angle measurement.

Oil/water separation and water purification

To conduct an oil/water separation, the PBZ/TiO_2 modified fabric was fixed between a transparent glass feeder and a suction flask by a clip, and the joints were sealed by vacuum grease. The oil/water (*V*:*V*=1:1) mixture was poured onto the fabric and separated by gravity. Seven types of oil/water mixture, toluene/water, isooctane/water, xylene/water, hexadecane/water, petroleum ether/water, dichloromethane/water and cyclohexane/water, were separated by PBZT10 respectively. The separation efficiency for each mixture was calculated. For a recycling test, a certain mixture of 50 ml deionized water and 50 ml dichloromethane was separated by PBZT10. After each cycle, the fabric was rinsed by deionized water for 10 s and dried at 50 ^{o}C for 30 min. The separation and rinsing procedure was repeated for ten times and the oil flux was calculated.

A methylene blue (MB) aqueous solution with a concentration of 1 ppm was utilized for investigating the water purification performance of PBZT10. A piece of PBZT10 (2×2 cm^2) was totally immersed into MB solution (8 ml) and exposed under UV irradiation for various time. The UV light source was obtained from a 250 W Hg lamp at 25±1.5 ^{o}C with a relative humidity of 60±2%. After the exposure, the MB solution was measured by the UV-visible spectrophotometer and pH meter.

Photo- and heat-induced self-cleaning test

For a self-cleaning property test, the PBZT10 was immersed into an acetone solution of 5 wt% oleic acid for 1 min and then placed at room temperature for 30 min. The contaminated PBZT10 was denoted OA/PBZT10. Then it was exposed under UV light for 4 h. The UV light source was obtained from a 250 W Hg lamp at 25±1.5 ^{o}C with a relative humidity of 60±2%. After UV exposure, OA/PBZT10 was treated at various temperatures for 1h. The surface wettability of exposed and heat treated OA/PBZT10 were measured by contact angle measurement.

Characterization

A Data Physics OCA20 optical goniometer interfaced to image-capture software was used to measure water and oil contact angles (CAs) of each sample at room temperature. Deionized water and cyclohexane droplet of 2 μL was injected on the sample surface respectively. Then, sliding angle (SA) measurements were carried out with deionized water droplet of 10 μL by a contact angle OCA20 optical goniometer equipped with a tilting base. Each of the reported CAs and SAs represents the average of six measurements at different areas on two sides of PZBT surface. Surface morphologies of pristine fabric and PBZT were observed with a Nova Nano SEM 50 field emission scanning electron microscope (FE-SEM) at an acceleration voltage of 3 kV. Each specimen was sputtered with gold at 20 mA for 60 s before SEM observation. Chem composition of the film was characterized by energy dispersive spectrometer (EDS) characterization. The specific surface area has been characterized by BK112T-B specific surface area analyzer of Beijing JWGB Science and Technology Corporation, while the pore size has been measured by bubble pressure method of membrane pore size 3H-2000PB analyzer of Beijing Beishide Instrument Corporation. UV-visible absorbance of dye-involved wastewater was measured by UV visible spectrophotometer (Shimadzu, UV1750). Chemical structures of OA/PBZT10 before and after heating were confirmed by fourier transform infrared (FTIR) spectra recorded on a Cary 680 FTIR instrument in ATR mode at a resolution of 4 cm^{-1} accumulating 32 scans.

Conclusions

A simple dip coating and subsequent thermal curing method is utilized to prepare a stable polybenzoxazine/TiO_2 surface onto the commercial polyester non-woven fabric, which has modified the fabric to be superhydrophobic and superoleophilic with self-cleaning performance. The resulting self-cleaning material possesses excellent mechanical durability and good resistance to acid and alkali. It is also stable under strong UV light irradiation for as long as 8 h because of the hierarchical surface structure with both microscale fibers and nanoscale particles. As a superhydrophobic and superoleophilic material, PBZT is effective for separating light- or high-density oil/water mixtures by gravity with separation efficiency above 98% and a high oil flux above 3000 L m^{-2} h^{-1}. Importantly, the as-prepared PBZT surface is reusable for oil/water separation in that the surface enjoys integrated self-cleaning performance for the removal of both oils and particles on its surface. Moreover, the as-prepared PBZT can also purify soluble dyes containing wastewater, which makes PBZ/TiO_2 modified superhydrophobic and superoleophilic materials more effective and promising in treating water pollution.

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