

Journal of Materials Chemistry A

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Versatile Superhydrophobic and Photocatalytic Films Generated from TiO₂-SiO₂@PDMS and their Applications on Fabrics

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

First published on the web Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

We report a simple and available approach to facilely produce TiO₂-SiO₂@PDMS versatile hybrid films via a sol-gel process, which confer superhydrophobic and photocatalytic properties. The as-prepared films present herein highly thermal stability even up to 400 °C, and then switch to superhydrophilicity at 470 °C by calcination. Also, we successfully employed TiO₂-SiO₂@PDMS hybrid solution to coat onto flexible polyester-cotton fabrics with large scale, allowing them to be superhydrophobic. The superhydrophobic fabrics are wash resisting and resistant to strong acid attack and can be applied to the filter cloth for both oil/water separation and colorful pattern printing. For more practice, we further applied TiO₂-SiO₂@PDMS hybrid solution to treat dye waste water, allowing it to be colorless under UV irradiation. More interestingly, the small balls coated by TiO₂-SiO₂@PDMS hybrid solution can move faster than the control sample owing to its smooth superhydrophobic surface. This finding suggests that this multifunctional TiO₂-SiO₂@PDMS hybrid material can be applied to fabric treatment and water-repellent ship coating.

Introduction

In nature, many luxuriant surfaces of both butterfly wings and lotus leaves possess special self-cleaning property and superhydrophobicity resulting from their hierarchical micro/nanoscale binary structures.¹ Mimicking these morphologies has led to the development of numerous artificial superhydrophobic surfaces,^{2,3,4} opening new possibilities in industrial and biological fields.⁵ “Superhydrophobicity” is typically used to describe surfaces with a water contact angle (WCA) greater than 150° and a sliding angle lower than 10°. To date, various elegant methods have been proposed for imparting surface roughness to substrates, such as sol-gel processing,^{6,7} colloidal self-assembly,⁸ lithography,^{9,10} electrospinning,^{11,12,13} layer-by-layer deposition,^{14,15} template methods^{16,17} and others,^{18,19,20} have been successfully exploited to tailor surface topography and to enhance hydrophobicity via coating a fabricated rough surface with a hydrophobic thin layer and monolayer. However, challenges still remain in developing large scale superhydrophobic surfaces in a technically simple, inexpensive and easy-handling way. In addition, more innovative low-toxic and multifunctional materials are highly needed to fabricate flexible superhydrophobic surfaces to meet the demands of industrial applications.

From the practical point of view, many researchers have chosen silica or titania to fabricate superhydrophobic surfaces

owing to their controllable structure and desired steadiness.^{21,22} Vollmer *et al.* developed a procedure to grow silica particles on a polystyrene core, and obtained a transparent, thermally stable and mechanically robust superhydrophobic surface.²³ Yang *et al.* fabricated a transparent superhydrophobic surface via the coassembly of amine-functionalized silica nanoparticles of two different sizes.²⁴ Parkin *et al.* recently reported a superhydrophobic photocatalytic coating that incorporate polydimethylsiloxane (PDMS) polymer and functionalized titania nanoparticles by aerosol-assisted chemical vapor deposition (AACVD).²⁵ Particularly, growing interests have been concentrated on superhydrophobic fabrics coated with silica or titania for their virtues of low toxicity and promising strength.²⁶ Bellmann *et al.* prepared a water-repellent textile via decorating fibers with Janus silica particles.²⁷ Lin *et al.* reported a superhydrophobic fabric coating that was made of fluorinated alkyl silane functionalised silica nanoparticles.²⁸

In this work, we demonstrated a simple route for the fabrication of thermally stable and photocatalytic TiO₂-SiO₂@PDMS hybrid films with the use of non-fluorinated materials. The resultant coating with excellent adhesion to glass slides showed a water contact angle (WCA) larger than 160° and sliding angle less than 5°. On the other hand, the large scale flexible superhydrophobic polyester-cotton fabrics coated by TiO₂-SiO₂@PDMS hybrid solution were reported here without using any complicated instruments and rigorous experiment conditions. This simple and low cost coating shows excellent durability against repeated washes and strong acid attack, while retaining its superhydrophobicity. Also, the

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as-prepared superhydrophobic and oleophilic fabrics can be applied to colorful pattern printing and functioned as “filter cloth” to separate oil and water effectively. In addition, a superhydrophobic ball can decrease fluid friction drag on the water surface, thereby making it possible to apply in water-repellent ships and even yachts. This available approach to design multi-functional superhydrophobic surfaces, together with their potential commercial utilization in various substrates, may provide a convenient and inexpensive platform for the facile fabrication and extensive applications of the versatile hybrid powder.

Experimental

Materials

Sylgard-184 (Silicone elastomer) was purchased from Dow Corning, Zhejiang Runhe Silicone New Material Co., Ltd. Thermoplastic polyurethane (TPU 95A) and Polycaprolactone (PCL) were supplied by Bayer and Suzhou Dong wei Chemical Co., Ltd., respectively, and used without any treatment. 1,1,1,3,3,3-hexamethyl disilazane (HMDS), Tetraethylorthosilicate (TEOS 98%), Titanium isopropoxide were purchased from Sinopharm Chemical Reagent Co., Ltd., ammonia solution (about 28%, AR), acetic acid (98%), absolute ethanol (99.5%) were supplied by Shanghai Lingfeng Chemical Co., Ltd., and used as purchased without further purification. High-purity water (resistivity, $\sim 18 \text{ M}\Omega\cdot\text{cm}^{-1}$) was used throughout these experiments. White commercial polyester/cotton fabric were obtained from a local fabric store, which was rinsed with ethanol and distilled water before using, washed exhaustively with an excess of water.

Preparation of HMDS modified $\text{TiO}_2\text{-SiO}_2$ hybrid gels

First the SiO_2 sol was obtained by hydrolyzing tetraethylorthosilicate (TEOS) in the presence of acetic acid and anhydrous ethanol. A typical composition was $[\text{TEOS}]:[\text{EtOH}]:[\text{CH}_3\text{COOH}]:[\text{H}_2\text{O}] = 1:9.47:0.3:4 \text{ mol/mol}$. Then half of the anhydrous ethanol was mixed with TEOS and acetic acid with stirring for one day at room temperature. Subsequently, a solution of the other half ethanol with a known volume of water and three drops of HCl were added dropwisely to the above solution within 30 min by peristaltic pump. Moreover, TiO_2 sol was prepared with Titanium isopropoxide as the precursor, mixed with absolute ethanol and acetic acid under stirring for 3 h, and the volume ratio was $[\text{Titanium isopropoxide}]:[\text{CH}_3\text{COOH}]:[\text{EtOH}] = 1:1.87:1.87$. The whole silica and titania sol solutions were turned into gels by adding respective certain amounts of NH_4OH solution to adjust the pH close to 9, and kept overnight for aging. To prepare hydrophobic hybrid $\text{TiO}_2\text{-SiO}_2$ gels, certain quantity of HMDS in ethanol with 1:8 in wt/wt ratio (mass ratio of HMDS to hybrid gels was 1.67) was added into the hybrid gels, and the mixture was kept at 70°C for 20 h in a closed container. After that, the obtained hybrid gels were washed with ethanol three times to remove excessive free HMDS and dried at 70°C for 2 h.

Preparation of coating solution

HMDS-modified hybrid $\text{TiO}_2\text{-SiO}_2$ gels (0.12 g) were dispersed in chloroform (4 mL) for about 10 min in an ultrasonic bath. HMDS (0.2 g) and PDMS (Sylgard 184 elastomer base, 0.08 g) were then added into the above solution and subjected to ultrasonication for another 1 h. To the above mixture 0.008 g of the curing agent dissolved in chloroform (4 mL) was added and kept rapidly stirring for 10 min.

Preparation of the superhydrophobic films and fabrics

Prior to coating treatment: glass slides were cleaned by immersion in piranha solution (conc. H_2SO_4 , 33% H_2O_2 and water in a 6:3:2 volume ratio; Warning! Piranha should be handled with caution; it can detonate unexpectedly!) for one day, and then carefully rinsed with Milli-Q water three times. The polyester/cotton fabrics were washed several times with acetone, ethanol, and finally water. Then the obtained homogenized $\text{TiO}_2\text{-SiO}_2\text{@PDMS/CHCl}_3$ solution was spin-coated on the glass slides at a rate of 3000 rpm with 30 s, while the polyester/cotton fabrics were immersed in the solution for 1 h, padded with a pick-up twice, and then cured at 120°C for 30 min.

Preparation of superhydrophobic ball

Two balls were washed several times with acetone, ethanol, and finally water. Then one of them was dipped into the homogenized $\text{TiO}_2\text{-SiO}_2\text{@PDMS/CHCl}_3$ hybrid solution for 10 min and kept in the air at room temperature to wait for the evaporation of the solvent for several minutes.

Stability Measurements

The abrasion resistance and washing durability of the treated polyester/cotton fabrics were examined by scrubbing the coated fabrics in JTX-II architecture coatings washing durability machine. This wash procedure is equivalent to five cycles of home laundry washing. We used the equivalent number of home laundering for convenience.

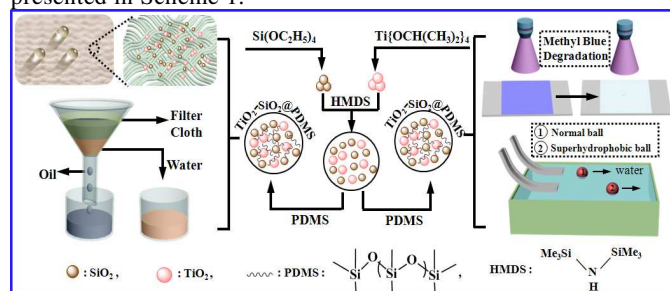
Characterization

The microstructure of the inorganic-organic polymer hybrids on the substrate (*e.g.* glass, polyester/cotton fabric) was observed by scanning electron microscopy (SEM, QUANTA 200) and the Atomic force microscope (AFM) images were taken on a Park Scientific Instrument Auto Probe Research System (Park, America). Fourier-transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 FT-IR spectrometer. The samples were ground with KBr powder to form well-defined slides for FT-IR measurement with 32 scans from 4000 to 500cm^{-1} at a resolution of 4cm^{-1} . Contact angle (CAs) of a $5\ \mu\text{L}$ water droplet and sliding angle (SAs) of a $10\ \mu\text{L}$ water droplet on the surface were measured with a KRUSS DSA100 contact angle system from three different points on the substrate at ambient temperature.

Results and discussion

Facile synthesis of $\text{TiO}_2\text{-SiO}_2\text{@PDMS}$ hybrid materials

A typical procedure of preparing the $\text{TiO}_2\text{-SiO}_2\text{@PDMS}$ hybrid powder is shown in Scheme 1. Initially, we fabricated silica and titania gels by a typical hydrolysis-condensation reaction of tetraethylorthosilicate (TEOS) and titanium isopropoxide at $\text{pH} = 9$, respectively. Then, hexamethyldisilazane (HMDS) was employed to the mixed gels to functionalize the surface of silica and titania with hydrophobic $-\text{CH}_3$ groups, which will be facilitate to the favorable miscibility of silica and titania gels in the organic matrix. Finally, the hydrophobic gels were incorporated into a mixture of PDMS/ CHCl_3 to form a coating solution. The FT-IR spectra of PDMS, HMDS-modified and $\text{TiO}_2\text{-SiO}_2\text{@PDMS}$ hybrid powder are presented in Fig. S1. Moreover, schematic representation for the versatile applications of hybrid powder on fabrics, photocatalytic film and floating balls are also presented in Scheme 1.



Scheme 1 Schematic illustration of the synthesis of $\text{TiO}_2\text{-SiO}_2\text{@PDMS}$ coating solution, and the applications on these aspects: superhydrophobic polyester/cotton fabrics, oil-water separation (left); superhydrophobic photocatalytic film and floating balls (right).

Thermal Stability of the Films

To study the thermal stability of $\text{TiO}_2\text{-SiO}_2\text{@PDMS}$ hybrid superhydrophobic film with respect to the WCA, we sintered the compared samples with various calcination temperatures ranging from 100 to 470 $^\circ\text{C}$ for a 2 h period. Fig. 1a clearly shows the scanning electron microscope (SEM) images of the pristine film. Many micrometer-sized pores are formed to allow more air to be trapped between water and surface, which results in a maximum WCA of 162° . When the film was calcinated at 200 $^\circ\text{C}$, the appropriate micro-sized holes are still preserved on the surface which enhances its roughness and hydrophobicity (Fig. 1b). The WCA decreased to 132° at 300 $^\circ\text{C}$ and gradually became thoroughly hydrophilic at 450 $^\circ\text{C}$ with the WCA of only 40° , indicating that the decomposition of organic groups led to the formation of Si-OH and Ti-OH bonds on the hydrophilic surface (Fig. 1c, d). As expected, the corresponding SEM-EDS mapping reveals the presence of the surface element Si and Ti after annealing at 450 $^\circ\text{C}$ (Fig. 1e). Eventually, the relation between WCA and calcination temperature is clearly presented in Fig. 1f. We observe that the $\text{TiO}_2\text{-SiO}_2\text{@PDMS}$ hybrid film is thermally stable compared with organic coatings. The film preserved hydrophobic even after treated at 400 $^\circ\text{C}$ for 2 h, which may thus serve to prepare superhydrophobic surfaces on high temperature condition.

In another effort, we tried to give a deep insight into the relationship between the concentration of polymer PDMS and the hydrophobicity of the film with respect to certain amount of $\text{TiO}_2\text{-SiO}_2$ hybrid gels. Accordingly, the mass ratio of

$\text{TiO}_2/\text{SiO}_2 = 1:2$ (wt/wt) and the concentration of PDMS = 0.65 wt % were investigated as the optimal conditions during our experiments (Fig. S2).

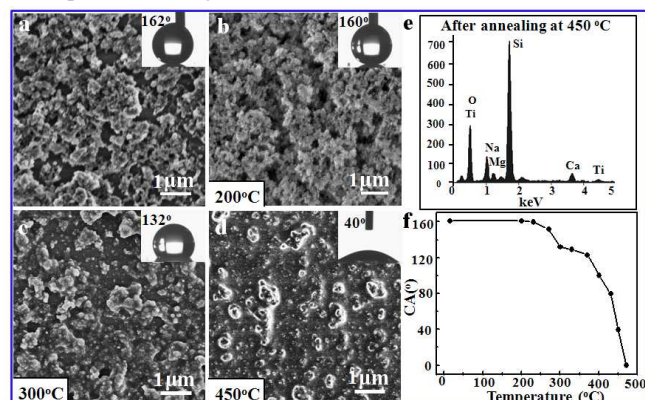


Fig. 1 SEM images of the films: (a) $\text{TiO}_2\text{-SiO}_2\text{@PDMS}$, (b, c, d) calcinated for 2 h at 200 $^\circ\text{C}$, 300 $^\circ\text{C}$ and 450 $^\circ\text{C}$, respectively. Insets: water drop profile in WCA measurement (5 μL droplet size) on the corresponding surfaces. (e) SEM-EDS spectrum of the film on the glass after annealing at 450 $^\circ\text{C}$. (f) Dependence of contact angle on calcination temperature, for 2 h duration at each temperature.

Photocatalytic property of TiO_2

The photocatalytic activity of $\text{TiO}_2\text{-SiO}_2\text{@PDMS}$ hybrid powder was tested against the breakdown of methylene blue molecule, which was loaded on both dyed film and dyed water solution respectively under UV-irradiation (365 nm). In the first run, the prepared blue superhydrophobic film dramatically discolored within 30 min (Fig. 2a, b), giving a minor decrease of WCA from 157° to 151° (Fig. 2c, d). Clearly, the changes in WCA and SA values are shown in Fig. 2e, and the irradiated film still remains superhydrophobic. We attribute the small reduction of WCA and increase of SA to the decomposition of dye molecules into small hydrophilic molecules existing on the surface of the hybrid film. In addition, the hydrophobic PDMS polymer matrix exposed on the surface either supports these particles or resists photocatalytic breakdown caused by the embedded hybrid powder²⁶. In the second run, the as-prepared suspension was exchanged for a 4:1 (wt/wt) methanol: water mixture to ensure the absolute wetting of the superhydrophobic surface, and the concentration of $\text{TiO}_2\text{-SiO}_2$ hybrid powder was 5 wt %. Photographs of the dye degradation process are shown in Fig. 2f-i. Following irradiation with UV light, the colored solution completely decolorized within 30 min. (Fig. 2j). The reason is that titania gels possess high surface area and imperfect anatase phase, which produce abundant electron-hole pairs under UV irradiation for the redox reaction.²⁹ Thus, we believe that this hybrid powder may offer valuable opportunities of applications in functional paint industry and wastewater treatment.

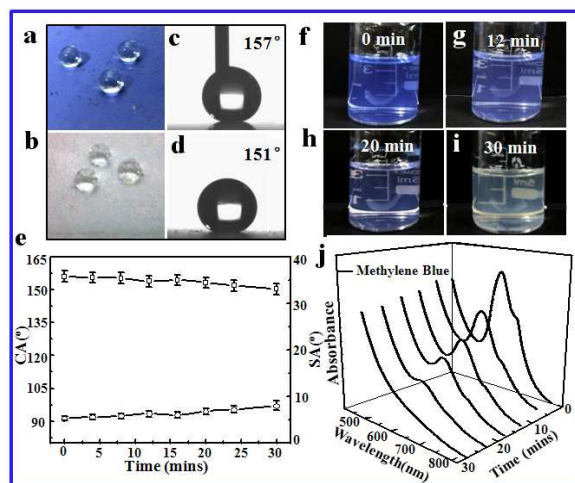


Fig. 2 (a) (b) Photos of 10 μL water droplets on the blue superhydrophobic film and the discolored one, respectively. (c), (d) Profiles of water contact angles (5 μL) on the blue superhydrophobic film and the discolored one, respectively. (e) Water contact angle (WCA, - \square -) and sliding angle (SA, - \circ -) change with irradiation time under UV light (365 nm). (f-i) Photographs of the degradation of methylene blue dispersed in dyed water solution. (j) UV-vis spectra of photocatalytic degradation of the prepared aqueous solutions.

Preparation of superhydrophobic fabrics

We further applied the $\text{TiO}_2\text{-SiO}_2\text{@PDMS}$ suspension on the polyester-cotton fabric to obtain a low-toxic, flexible and large scale superhydrophobic coating. The WCA on the coated fabric is 158° ($> 150^\circ$), and the sliding angle (SA) is 4° ($< 5^\circ$), indicating a very good superhydrophobicity. SEM images of the fabrics before and after coating treatment are shown in Fig. 3a and Fig. 3b, respectively. A tightly woven and fibrous smooth structure is clearly observed on the original fabric (Fig. 3a insert), while the aggregated clusters can be found on the fiber surface or in the gap between numerous fibers (Fig. 3a insert, Fig. S3). We suppose that the superhydrophobicity of the fabric is derived from the combination of the nanoscale roughness of the aggregated clusters and the micro-scale roughness of the inherent textile fabric.³⁰

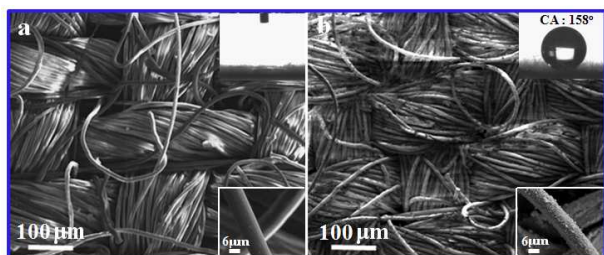


Fig. 3 SEM images of the polyester/cotton fabrics. (a) The pristine fabrics, scale bar: 100 μm . (b) Treated fabrics, scale bar: 100 μm . Insert 1: high magnification images of single pristine and treated fabrics, respectively. Scale bar: 6 μm . Insert 2: Water droplet profile in CA measurement (5 μL droplet size) on the corresponding surfaces.

Durability of the as-prepared superhydrophobic fabrics

The abrasion resistance and washing durability of the coated fabrics were examined by JTX-II architecture coatings washing durability machine, which is more convincing and

convenient than home laundry washing. Fig. 4a shows the change of WCA and SA values with machine washing cycles. The resulting fabric still shows satisfactory durability with WCA of $> 148^\circ$ after being washed for 400 cycles. The aggregated clusters still remain on the surface to support its morphology (Fig. 4b and 4c), and the water droplet on the fabric can still form round ball without obvious hysteresis (Fig. 4d). Moreover, the SEM-EDS mapping further confirms the presence of Si, Ti and O in addition to the bulk C (Fig. 4e). It should be noted that PDMS itself has satisfactory stability and good adhesive force to the substrate because of the strong covalent bonding between the polymer and the fabric, which is consistent with the general inertness of silicones contributing to high stability.³¹

We also evaluated the chemical durability of the superhydrophobic coatings by measuring the changes of WCA and SA values with different pH values in aqueous solutions (Fig. 4f). No obvious fluctuation except a little decrease of WCA value is observed after being treated for 100 h under strong acidic (pH = 2) and weak acidic (pH = 5) condition, respectively. Accordingly, the WCA value decreases to 126° after being soaked in strong base solution (pH = 12) for 100 hours. SEM images confirm that there is no obvious morphological change developed on the coated fiber surface after being attacked by strong acid (Fig. 4g). On the other hand, most parts of the strong base treated fibers are smooth with small number of aggregated clusters on it (Fig. 4h), which denotes a damage to the superhydrophobic surface. As a consequence, water droplet can still form a round ball on strong acid treated fabric (Fig. 4i), while a nearly hemisphere-like water droplet with high hysteresis on the base treated fabric (Fig. 4j). Significantly, physical and chemical durability are both important properties of superhydrophobic fabrics and they also play an important role on accessing the applicability of the functional fabric surfaces.³²

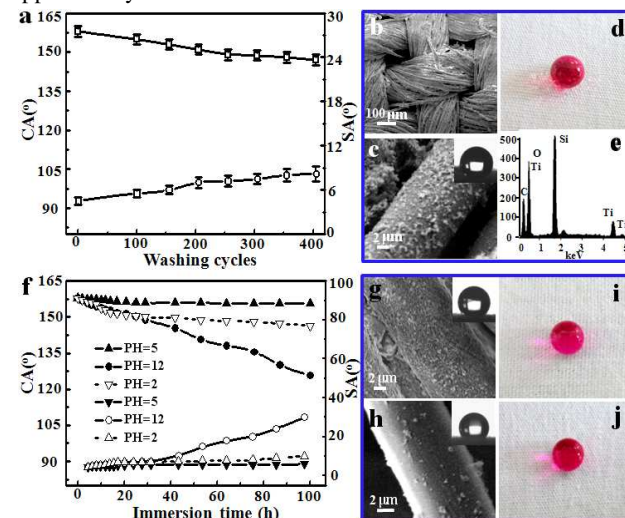


Fig. 4 (a) Water contact angle (WCA, - \square -) and sliding angle (SA, - \circ -) change with washing cycles. (b) Low and (c) High magnification SEM images of coated fabric after 400 machine washing cycles. (d) Pictures of water droplet (10 μL) on coated fabric after 400 machine cycles. (e) SEM-EDS spectrum of the washed fabrics. (f) Water contact angle (WCA, - \square -) and sliding angle (SA, - \circ -) change with immersion time at different PH values on superhydrophobic fabric.

(g) and (i) SEM images of coated fabrics after immersing in H_2SO_4 (pH = 2) solution and NaOH (pH=12) for 100 hours, respectively.

Silk-screen printing on superhydrophobic fabric

In a further experiment, we investigated the oleophilicity of the superhydrophobic fabric. As shown in Fig. 5a, three nearly sphere-like water droplets (dyed with methyl blue) could form on the superhydrophobic fabric (the left cloth strip in Fig. 5a), while coal oil (dyed with Rhodamine B) completely wetted the fabric (the right cloth strip in Fig. 5a). This is consistent with the difference in surface tension between oil ($<30 \text{ mN m}^{-1}$) and water ($<70 \text{ mN m}^{-1}$). Moreover, an easily-handled method, silk-screen printing was further used to confirm this property intuitively (Fig. 5b). Chloroform aqueous solution was magnetically blended with hydrophobic polymer polycaprolactone (PCL), and the mixture was screened through woven meshes by extrusion using a scraper blade onto the coated and uncoated fabrics, respectively. Fig. 5 (c, e) and (d, f) show the photographs of “Tai Chi” patterns printed on the superhydrophobic and pristine fabrics, respectively. The superhydrophobic fabric displays deeper and clearer pink “Tai Chi” pattern under daylight, and also shows brighter red-orange emission “Tai Chi” pattern under UV light (365 nm). In this case, the functional superhydrophobic fabric will provide a potential possibility for colorful pattern printing, and the fabric could be a better candidate for oil/water separation due to its flexibility, softness and stability in organic solvents.^{33,34,35}

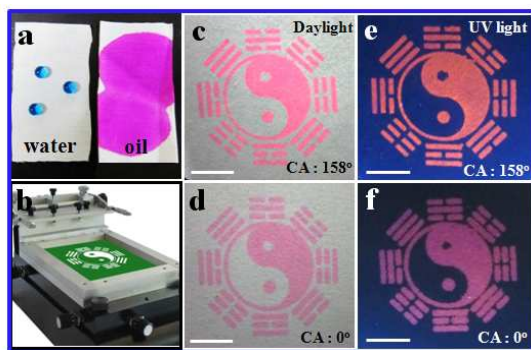


Fig. 5 (a) Photos of 10 μL water droplets on the coated fabric and coal oil droplet on the uncoated fabric, respectively. (b) Scheme of silk-screen printing. Photographs of Tai Chi patterns by silk-screen printing from mixtures of PCL-RhB/ CHCl_3 : (c), (d) on the coated and uncoated fabrics under day light, respectively. (e), (f) on the coated and uncoated fabrics under UV light, respectively. Scale bar = 1 cm.

Oil-water separation

Herein, the process of oil-water separation experiment was performed as shown in Fig. 6. When the mixture of water (dyed with alizarine red) and coal oil was poured onto the “filter cloth” (Fig. 6b), the coal oil spread out rapidly and then penetrated through the filter cloth and dropped into the beaker below, while the dyed water would remain in the superhydrophobic cloth container (Fig. 6c), showing excellent ability of oil-water separation. Moreover, the “filter cloth” still possesses considerable separation efficiency with WCA of 151° and SA of 8° after being repeatedly used for ten times (Fig. 6d and 6e). To the best of our knowledge, few successes of superhydrophobic fabrics for oil-water separation have

been reported because of the stability of superhydrophobic fabrics in nonpolar solvent.³⁶ It is the simple operations studied here, in comparison with other complicated processes that make it possible for practical functional applications in our daily life.

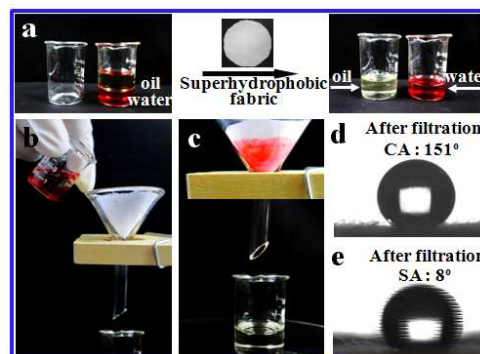


Fig. 6 (a-c) Process of the superhydrophobic fabric for the separation of water (dyed with alizarine red) and coal oil. (d) (e) Profile of water contact angle ($5 \mu\text{L}$) and sliding angle ($10 \mu\text{L}$) on the coated fabrics surface after being used for ten times, respectively.

Movement of normal and superhydrophobic balls on water surface

Interestingly, we also investigated the effects of fluid fraction drag on the hydrophobic surface. We first rendered a normal ball with a superhydrophobic surface via dip-coating the corresponding hybrid solution, and then comparative experiments of a normal and a superhydrophobic ball moving on water surface were carried out (Fig. 7a). The two balls separately rolled down along a steel L-shaped channel and then floated horizontally on the water surface. Notably, the same gravitational potential energy of the two balls could be transferred to the same amount of kinetic energy. The positions measured for two balls versus time are shown in Fig. 7b. Photographs clearly show that the two balls move to different positions at a specific time (Fig. 7c). We calculate the average velocity of movement of the two balls as 27.0 cm min^{-1} for the superhydrophobic ball and 12.5 cm min^{-1} for the normal ball through dividing the total moving distance by the total moving time. The difference in speed between the superhydrophobic ball and the normal ball could be attributed to the different fluidic friction drag exerted by water, since the balls have the same driving force derived from their original parameters, which is corresponding to the reported article.³⁷ Therefore, these results confirm that a superhydrophobic surface can reduce the fluid fraction drag by introducing a thin layer of air surrounding the surface, thereby making it possible to apply in water-repellent ships and yachts.

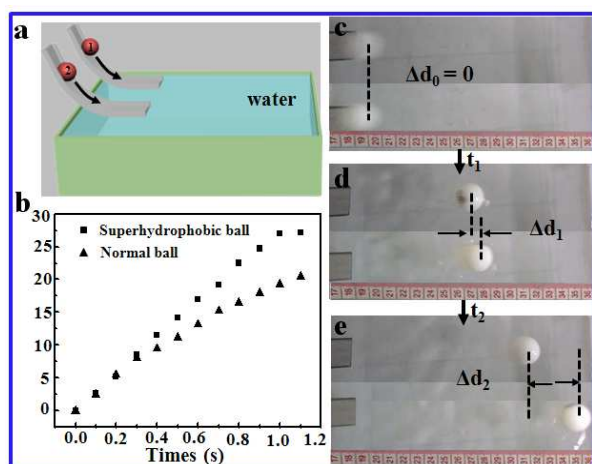


Fig. 7 (a) Schematic illustration of the movement of superhydrophobic and normal balls. (b) The position of the superhydrophobic and normal balls versus time. Photographs of the two balls moving on water surface after rolling down along the channel from the same height at (c) $t = 0$ s (The two balls move horizontally as the position difference is $\Delta d_0 = 0$), (d) $t_1 = 0.61$ s, (e) $t_2 = 1.11$ s.

Finally, we demonstrated that superhydrophobic surfaces can be obtained from other substrates, such as silicon wafers, filter papers, and PMMA slides. The aggregated clusters were deposited on the substrate to generate dual-scale roughness which contributes to the hydrophobicity of the surface. The CA and SA values of the non-treated and treated substrates were listed in Table 1. All the coated surfaces showed superhydrophobicity with CA $>150^\circ$ and SA $<7^\circ$. It should be noted that such hydrophobicity was independent of the physical and chemical properties of the native substrates.

| Substrate | Static contact angles ($^\circ$) | | Sliding angles ($^\circ$) |
|------------------|------------------------------------|-------------|-----------------------------|
| | Before | After | |
| Glass | 11 | 162 ± 2 | 2 ± 1 |
| Silicon wafer | 72 | 162 ± 2 | 3 ± 1 |
| Filter paper | 0 | 152 ± 2 | 6 ± 1 |
| Cotton fabric | 0 | 155 ± 2 | 5.5 ± 1 |
| Polyester fabric | 0 | 158 ± 2 | 4.5 ± 1 |
| PMMA | 58 | 154 ± 2 | 5 ± 1 |

Table 1 Water contact angle data on different substrates

Conclusions

In summary, we have facilely fabricated large scale thermally stable and photocatalytic superhydrophobic films based on the non-fluorinated $\text{TiO}_2\text{-SiO}_2\text{@PDMS}$ hybrid powder. The hydrophobicity of the film could be resistant to 400°C and finally the WCA gradually switched to superhydrophilic region ($<5^\circ$) at 470°C , which may thus serve to produce superhydrophobic films under high temperature condition. Taking advantage of the photocatalytic property of TiO_2 , we successfully develop superhydrophobic photocatalytic films and to carry out dye waste water treatment. On the other hand,

we fabricate large scale flexible superhydrophobic polyester-cotton fabrics, and they remain hydrophobicity when scrubbed for 400 cycles by mechanical washing or immersed in strong acid or strong alkali for 100 hours, which is superior to the similar reports.³² Moreover, the ductility of oil spreading on the superhydrophobic fabrics make them adaptable for colorful pattern printing and oil/water separation, which will promote the utilization of fabrics in textile industry. More interestingly, a faster movement of superhydrophobic small ball on the water surface will be significant for developing coatings for drag-reducing materials. This investigation suggests that this $\text{TiO}_2\text{-SiO}_2\text{@PDMS}$ multifunctional hybrid can produce versatile coating and would have promising commercial applications.

Acknowledgements

This work was supported by the National High Technology Research and Development Program of China (863 Program) (2012AA030313), National Natural Science Foundation of China (21076103), Specialized Research Fund for the Doctoral Program of Higher Education of China (20103221110001), Industrial Project in the Science and Technology Pillar Program of Jiangsu Province (BE2012181) and Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

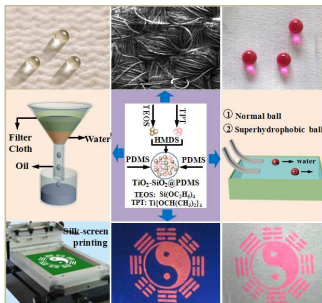
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Versatile Superhydrophobic and Photocatalytic Films Generated from $\text{TiO}_2\text{-SiO}_2\text{@PDMS}$ and their Applications on Fabrics

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We report a facile and available approach to fabricate versatile superhydrophobic and photocatalytic films generated from $\text{TiO}_2\text{-SiO}_2\text{@PDMS}$ hybrids. The as-prepared hybrids can be applied to functional superhydrophobic textile, treatment of dye waste water and water-repellent coating.