Superhydrophobic Surfaces with pH-Induced Switchable Wettability for Oil−Water Separation

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ABSTRACT: The oily wastewater generated in the industrial field is adversely affecting the environment, while the current methods for oil−water separation are complex and costly. Therefore, it is significant to use low cost and environmentally friendly materials to prepare a smart responsive superhydrophobic coating for the effective separation of oil−water mixtures. In this paper, a fluorine-free copolymer with pH responsiveness was fabricated by a solution impregnation method, and it was compounded by silica nanoparticles/polydimethylsiloxane to prepare a superhydrophobic coating on the paper and cotton fabric. The prepared superhydrophobic coating remained in the superhydrophobic state after the alkali treatment, while it would be converted into the hydrophilic state after the acid treatment. Therefore, the pH-responsive superhydrophobic coating will be applied in controlled selective oil−water separation.

1. INTRODUCTION

A lot of oily wastewater is produced in the fields of printing, textile, food processing, leather, and petrochemical industries. The separation of oil−water mixtures has become an urgent problem to be solved in industrial production, so it is very important to design materials for effective separation of oil−water mixtures.1−4 The current methods for oil−water separation are complex, time-consuming, costly, and prone to secondary pollution. In addition, there is no switchable wettability in these materials, which limits their practical and commercial applications to some extent. Therefore, it is significant to design smart materials with switchable surface wettability.5−8

Smart response materials refer to the materials whose surface energy and surface microstructure will be changed under the stimulation of pH, temperature, light, electric potential, and so on, resulting in transition in surface wettability.9−18 These materials can be used in the separation of oil−water mixtures via single-phase selective absorption or filtration. Therefore, the development of smart response materials has become a hotspot of present research. Liu et al. prepared a ZnO nanorod/epoxy composite membrane which achieved reversible transition of wettability by the UV-induced photocatalytic effect.19 Geissler et al. developed superhydrophobic paper with temperature response characteristics using cellulose stearoyl ester solutions and nanoparticles.20 Zheng et al. fabricated a nanostructured polyaniline that can induce oil−water separation by electrical selective penetration.21 However, most of these smart response surfaces require high cost and complicated processes, which limit their applications. The pH responsiveness is more favored because of easy operation, fast response, and there is no need for additional equipment. There are protonatable groups including carboxyl groups, pyridines, and amines in usual pH-responsive materials. Xu et al. fabricated a superamphiphobic coating using coordination chemistry, showing a special capability to control oil−water separation and remove water from bulk oil selectively.22 Wang et al. successfully prepared pH-responsive fabrics by in situ-growing Ag nanocrystals on the fabric and modifying them with a mixture of methyl-terminated thiol and carboxyl-terminated thiol.23 However, most of these coatings are prepared using precious materials such as Ag or fluorine-containing substances which are considered to be harmful to the environment. Therefore, it is an inevitable trend to use environmental friendly materials with low cost to prepare smart responsive superhydrophobic coatings.

In our work, a random copolymer is synthesized by solution-processable free radical polymerization using inexpensive fluorine-free monomers. Silica nanoparticles/polydimethylsiloxanes (SiO2 NPs/PDMS) are compounded to build a high-roughness surface because of the strong interaction between SiO2 NPs/PDMS and the covalent linkage of the triblock copolymer. The paper and cotton fabric are then selected as the substrate for the superhydrophobic coating because of their low cost, environmental friendliness, and permeability, and they are coated with the prepared pH responsive copolymer to obtain a smart response superhydrophobic capability. The test of surface...
wettability proves that the coating is superhydrophobic in both neutral and alkali environments. In an acidic environment, the coating will change from a superhydrophobic state to a hydrophilic state, which can be used for efficient selective oil—

**Figure 1.** Different magnifications of SEM images of (a–c) original cotton fabric, (d–f) the copolymer-coated cotton fabric, and (g–i) copolymer–SiO$_2$ NPs/PDMS-coated cotton fabric.

**Figure 2.** Different magnifications of SEM images of (a–c) original paper, (d–f) the copolymer-coated paper, and (g–i) copolymer–SiO$_2$ NPs/PDMS-coated paper.

**Figure 3.** Different magnifications of SEM images of modified cotton fabric treated by (a–c) acid and (d–f) alkali.
water separation to meet the demand in different environments. The superhydrophobic coating prepared by the method in this paper is considered to have a good application prospect.

2. RESULTS AND DISCUSSION

2.1. Surface Morphology Analysis. In order to study the effect of the prepared copolymer and SiO₂ NPs on the surface morphology of the samples, the surface morphologies of the original samples, the samples coated with the copolymer, and the samples coated with copolymer and SiO₂ NPs/PDMS are observed and analyzed by scanning electron microscope (SEM) images. For the original samples (Figures 1a−c and 2a−c), it can be intuitively seen that the native striations of the fiber structure are obvious and the surface is flat without an uneven structure. For the samples coated with a pH-responsive copolymer (Figures 1d−f and 2d−f), it can be seen that the surface of the fiber is covered with a thin coating of copolymer with certain roughness, which is conducive to enhancing the hydrophobic properties of the substrate. For the samples modified by the copolymer compounded by the SiO₂ NPs/PDMS (Figures 1g−i and 2g−i), it can be clearly observed that SiO₂ NPs and pH-responsive copolymer coating are deposited on the surface, showing a state of unevenness. Compared with the above two kinds of samples, the surface roughness is greatly promoted after adding SiO₂ nanoparticles into the copolymer.

In addition, the effects of acid and alkali on the surface morphology of fibers are also studied, as shown in Figures 3 and 4. It can be seen from the figures that there is no significant change in the surface structure of modified paper and cotton fabric treated by the acid and alkali. The original rough structure is still maintained. It turns out that different pH solutions have no obvious effect on the surface of modified paper and cotton fabric.

2.2. Structure Characterization. The molecular structure of pH-responsive copolymer was characterized by ¹H nuclear magnetic resonance (¹H NMR) (Figure 5a). The −CH₂ peak of poly(butyl methacrylate) (PBMA) was observed at 1.4 ppm. The −N−(CH₃)₂ and −N−CH₂ peaks of poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) were located at 2.23 and 2.3 ppm. The groups appeared at 3.97 ppm were contributed to −CH₂OH and −CH₂ linked to an ester group of PDMAEMA. The Fourier transform infrared spectroscopy (FT-IR) studies (Figure 5b) were carried out on the copolymer monomers, prepared copolymer, SiO₂ NPs/PDMS, and copolymer compounded by SiO₂ NPs/PDMS to identify the chemical structure of the synthesized products. The band around 3427 cm⁻¹ was contributed to the stretching vibration of −OH in poly(2-hydroxyethyl methacrylate) (PHEMA). The absorption at 2954 cm⁻¹ was ascribed to the C−H stretching of PBMA. The peaks at 1720 and 1166 cm⁻¹ corresponded to the C=O and C−N stretching peaks in PDMAEMA segments, respectively. All the characteristic absorption peaks could be observed in the spectra of the corresponding monomers with the same wave numbers. For SiO₂/PDMS, C−H bond was observed at around 2954 cm⁻¹. The characteristic peak assigned to Si−CH₃ of PDMS was located near 800 cm⁻¹. The Si−O−Si stretching vibration appeared at 1087 cm⁻¹. All of the above characteristic absorption peaks were found in the spectrum of...
pH-responsive copolymer compounded by SiO₂ NPs/PDMS. The ¹H NMR and FT-IR results showed that the copolymer was synthesized successfully and SiO₂ NPs was introduced into the pH-responsive copolymer.²⁹

2.3. XPS Analysis. X-ray photoelectron spectroscopy (XPS) shown in Figure 6 was analyzed to verify the successful loading of the copolymer on the paper and the mechanism of pH responsiveness. For original paper, Figure 6a showed that only C and O elements emerged at 283 and 530 eV, respectively. Compared with the original paper, the N 1s peak at 399.1 eV appeared on the surface of copolymer−SiO₂ NPs/PDMS-coated paper, which was ascribed to the tertiary amine of PDMAEMA. After immersing in a pH 1 solution, a distinctive peak was attributed to Cl 2p. The N 1s peaks at 399.1 and 401.3 eV (Figure 6c) corresponded to the tertiary amine and the quaternary amine, indicating that the PDMAEMA chain was protonated. When treated by using alkali, the Na peak appeared. The N 1s peak was only observed at 399.1 eV (Figure 6d), which was due to the deprotonation of PDMAEMA.³⁰⁻³²

In terms of atomic content, the N atom content of the modified paper without the acid/alkali treatment was 0.11%. After the acid treatment, the N atom content on the surface of the paper increased to 0.55%. This was caused by the quaternary amines produced by the protonation of PDMAEMA. After the alkali treatment, the content of the N atom on the surface of the paper did not substantially change, corresponding to the tertiary amine in the PDMAEMA segment. This result further demonstrated that the wettability of the paper could be altered by the protonation and deprotonation processes of the PDMAEMA segment in different pH solutions.

There are ionizable tertiary amine groups in PDMAEMA, which can be protonated and deprotonated, leading to changes in the wettability of pH-responsive coatings as shown in Figure 7. When in an acidic environment, the tertiary amine groups in PDMAEMA will be protonated to form positively charged ammonium groups. Molecular hydrogen bonds between the groups bind to surrounding water molecules, turning the coating into a hydrophilic state. When in a neutral or alkaline condition, tertiary amine groups will be deprotonated and Cl⁻ in the quaternary ammonium will be removed, which will keep the coating in a superhydrophobic state.

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2.4. TG Analysis. It could be seen from Figure 8 that the original paper lost approximately 90% weight within the temperature range. The weight loss of the copolymer-coated paper and copolymer–SiO$_2$ NPs/PDMS-coated paper was about 80 and 76%, respectively, indicating that the paper was modified successfully. The amount of the copolymer and SiO$_2$ NPs/PDMS was about 10 and 4 wt %, respectively. This phenomenon demonstrated that the copolymer interacted with the micro–nanostructure to create a superhydrophobic surface.\textsuperscript{31,33,34}

2.5. Surface Wettability and pH-Responsiveness. The water contact angle (WCA) of the coating was measured by selecting several points of the same sample randomly at ambient temperature. To observe the superhydrophobic stability and pH response of the coating, methylene blue-dyed deionized water was randomly dropped on the surface of the modified paper, acid-treated paper, and alkali-treated paper. As shown in Figure 9, the paper treated differently was initially in a superhydrophobic state. The surface of the acid-treated paper was gradually infiltrated by the droplets, indicating that the paper was converted to a hydrophilic state. However, for the modified paper and alkali-treated paper, the shape of droplets remained unchanged after 30 min.

As shown in Figure 10, the WCA of the modified paper and alkali-treated paper reached above 150° and remained substantially constant. The WCA of the acid-treated paper was initially larger than 150°, but it began to decrease until it became 0° after 30 min. The modified paper was affected by amine protonation and deprotonation, resulting in the change of surface wettability. In addition, a graph describing the change of WCA with time was also drawn in Figure 11. The coated paper still remained superhydrophobic after 3 h. The result further illustrated the stability and pH responsiveness of the prepared superhydrophobic coating.\textsuperscript{35–37}

2.6. Mechanical Durability Test. The mechanical durability was characterized by the abrasion test. The super-
hydrophobic paper was placed face-down to the sandpaper with a weight of 200 g and pulled 20 cm back and forth along the horizontal line as a cycle, which was shown in Figure 12a. The paper was dragged at different cycles to determine the change in the contact angle. Figure 12b demonstrated that the WCA of the superhydrophobic surface changed with the increase of the pulling cycles. It could be seen that the contact angle ranged from 165° to 151° and it still was more than 150° after 30 cycles. The result indicated that there was a strong bonding force between the superhydrophobic coating and the substrate.

2.7. Oil–Water Separation. The oil–water separation experiment was carried out on a device as shown in Figure 13 to verify the function of superhydrophobic paper. The copolymer–SiO2 NPs/PDMS-coated paper was treated by using alkali, 1,2-dichloroethane as an example, because of the hydrophobic and lipophilic nature of the modified paper, the bottom heavy oil 1,2-dichloroethane passed through the paper driven by gravity while water was retained. Therefore, the selective oil–water separation was achieved by altering the wettability of the pH-responsive coating.

3. CONCLUSIONS

In this paper, a pH responsive random copolymer is prepared by a simple solution impregnation method, and it is compounded by SiO2 NPs/PDMS to prepare a fluorine-free superhydrophobic coating. The results of characterizations such as SEM and FT-IR show that the prepared copolymer compounded by SiO2 NPs/PDMS is successfully coated on the substrate. The tests of WCA and oil–water separation show that the prepared coating successfully obtains pH-responsive superhydrophobic capability. The WCA of pH-responsive coating reaches more than 150° in both neutral and alkali environments. After the acidic treatment, the coating transitions to a superhydrophilic state because of the protonation of the responsive monomer DMAEMA. The pH-responsive superhydrophobic coating prepared in this paper can be applied well to both paper and cotton fabric. Therefore, it has a good application prospect in effective oil–water separation in industries.

4. EXPERIMENTAL SECTION

4.1. Materials. Butyl methacrylate (BMA), 2-hydroxyethyl methacrylate (HEMA), and 2-(dimethylamino)ethyl methacrylate (DMAEMA) were all purchased from Ivkeyan Chemical Reagent Co., Ltd., Shanghai, China. PDMS was purchased from Sigma-Aldrich. All the above regents were used as received. 2,2-Azobisobutyronitrile (AIBN) obtained from Damao Chemical Reagent Factory, Tianjin, China was recrystallized from ethanol for further use. The paper and cotton fabric used for modification were purchased from a local store.

4.2. Synthesis of pH-Responsive Copolymer. As shown in Scheme 1, the copolymer was prepared by polymerization process.
under anhydrous and oxygen-free conditions. BMA (5.68 g, 0.04 mol), HEMA (0.52 g, 0.004 mol), and DMAEMA (6.28 g, 0.04 mol) were dissolved in anhydrous toluene (30 g) and then AIBN (0.1 g) was added as the initiator. The mixture was placed in a three-necked round-bottom flask. Nitrogen gas was introduced into the flask for 40 min to get rid of the oxygen to facilitate the polymerization. The sealed reaction flask was placed in a 70 °C constant temperature oil bath with stirring for 6 h. Then, the obtained solution was cooled to room temperature and purified by rotary evaporation to remove the solvent. The resultant copolymer was dissolved in acetone and precipitated in hexane several times and dried under vacuum at 50 °C.

4.3. Preparation of pH-Responsive Coating Solution. Silica nanoparticles (SiO2 NPs) were first dissolved in 20 g of anhydrous toluene with subsequent addition of PDMS and the mixture was ultrasonicated for 30 min. Then, the prepared pH-responsive copolymer was added and the solution was dispersed under ultrasonic conditions for 30 min to form a uniform and stable solution.

4.4. Fabrication of pH-Responsive Paper. The preparation of the pH-responsive paper is illustrated in Scheme 2. The paper and cotton fabric to be used were cut into a size of 3 cm × 3 cm and washed with acetone, absolute ethanol, and distilled water, respectively, to remove impurities. The clean paper and cotton fabric were separately immersed in the prepared copolymer solution and the pH-responsive solution containing SiO2 NPs/PDMS for 30 min. After the completion of soaking, the paper and cotton fabric were dried in an oven at 100 °C for 1 h to complete the cross-linking reaction.

4.5. Selective Oil–Water Separation Experiments. Different oil–water mixtures were prepared to test the selective oil–water separation function of the pH-responsive coating. The separation performances of the superhydrophobic paper were characterized by the separation efficiency, separation flux, and cycle usage. The separation efficiency is calculated by formula 1 as follows

\[ \eta = \frac{V_1}{V_0} \times 100\% \]  

(1)

where \( V_1 \) is the volume of oil collected in the oil–water separation experiment and \( V_0 \) is the volume of oil before the separation experiment. Separation flux can be obtained from formula 2

\[ F = \frac{V}{St} \]  

(2)

where \( V \) is the volume of oil passing the superhydrophobic paper in time \( t \) and \( S \) is the effective contact area between the oil–water mixture and the superhydrophobic paper.

4.6. Characterization. The surface morphologies of all the coated paper and cotton fabric were examined by a SEM (SU-8010, Hitachi, Japan). FT-IR was recorded using an infrared spectrometer (8400S, Shimadzu, Japan) at room temperature.
The structure of the copolymer dissolved in CDCl₃ was analyzed by ¹H NMR (AVANCE III HD 600 MHz, Bruker, Germany) and all chemical shifts were recorded in ppm. XPS (Axis Ultpa, Kratos analytical, UK) with an Al Kα X-ray source at 10 kV and 10 mA was conducted to determine the surface element of samples. Thermogravimetric analysis (TGA, Q600SDT, TA Instruments, USA) was performed on the original sample, copolymer-coated sample, and copolymer–SiO₂ NPs/PDMS-coated sample under nitrogen gas with a heating rate of 10 °C/min and scanned temperature ranging from ambient temperature to 700 °C. The surface wettability and pH responsiveness of the coating were characterized by WCA measured on goniometer (SDC-200, Sindin, China). The bonding force between the coating and substrate was tested by measuring the change of the contact angle after the abrasion test on the surface of superhydrophobic paper.

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