A method for preparing the pH-responsive superhydrophobic paper with high stability

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Abstract

In this paper, a simple method for preparing high stability superhydrophobic paper with pH-induced wettability transition was proposed. Firstly, the pH-responsive monomer 2-(dimethylamino)ethyl methacrylate (DMAEMA), the silicon-containing crosslinking monomer 3-trimethoxysilyl propyl methacrylate (TSPM) and the fluorine-containing monomer hexafluorobutyl methacrylate (HFMA) were polymerized to prepare the pH-responsive polymer PHFMA-PTSPM-PDMAEMA. Afterwards, the amino-modified SiO₂ was grafted onto the polymer to provide roughness and then coated on the paper to prepare the superhydrophobic paper with pH-responsive properties. Further research found that the modified paper prepared by this method not only has strong stability and transparency, but also can realize the reversible regulation of superhydrophobic & lipophilic and super-oleophobic & hydrophilic properties under different pH-induction, and it has important application value in the field of oil-water separation in industrial applications.

1. Introduction

Generally, the difference in wettability of materials will cause the liquid to show different states on the surface of different materials. Specifically speaking, when the droplet contacts the surface of the material, the difference in wettability of the liquid to the surface of the material will cause the material to show adsorption or repulsion to the droplet, so that the droplet spreads on the surface or remains spherical. In scientific research, the wettability of a material is usually characterized by its surface contact angle. When the contact angle formed by water droplets on a solid surface is less than 90°, such a solid surface is called a superhydrophilic surface; when the contact angle is greater than 90°, the solid surface is called a hydrophobic surface; and when the contact angle is greater than 150°, the solid surface is called a superhydrophobic surface (table 1). This relationship between contact angle and wettability also applies to oil droplets. When the contact angle formed by the oil droplets on the solid surface is less than 90°, the surface is called a lipophilic surface, and when the contact angle is greater than 150°, the solid surface has super-oleophobicity.

In recent years, with the frequent occurrence of crude oil spills in the world and the increasing discharge of industrial wastewater, how to deal with these pollution sources scientifically and effectively has become a very important issue. In this regard, the relevant research and practice have proved that by controlling the wettability of the material surface to water and oil to achieve oil-water separation, thereby separating the organic matter in the pollution source and reducing the emission of harmful substances, these problems can be effectively solved [1]. However, the common oil-water separation films are hydrophobic and oil-friendly materials, and most of these materials have relatively poor surface hydrophobicity. In the process of oil-water separation, water droplets are easy to adhere to the surface of materials, which makes the oil permeability slower, thus reducing the efficiency of oil-water separation. Moreover, the wettability of these materials is difficult to achieve free...
switching under certain application conditions [2]. Therefore, it is of great significance to explore the preparation methods of intelligent materials with switchable surface wettability.

With the continuous development of modern industry and the increasing requirements of packaging materials in daily life, the preparation of intelligent superhydrophobic surface has become an important field of industrial production and academic research [3–5]. In practical applications, some intelligent superhydrophobic surfaces have been developed, which can respond to external environmental stimuli, and these external environmental factors mainly include temperature, pH, light, ultrasound, electron transfer (redox change), etc [6–11]. Among these external environmental factors, pH-responsive wetting materials have many unique advantages, compared with other response conditions, such as fast response speed, relatively simple operation, and extremely strong reversible wettability change without additional modification [12]. However, in most cases, the application value of intelligent response materials in industrial production is largely limited by the demand for specific substrate, high preparation cost and relatively complex preparation process [13–16].

Paper is a non-toxic, low-cost, renewable, and environmentally friendly material, and it is widely used in various fields of daily life [17, 18]. However, the paper is made of a large number of fibers interwoven, which makes it natural with high hydrophilicity, and which also limits its application value in industrial production to a great extent. Therefore, further improving the hydrophobic properties of paper and giving it intelligent response properties can greatly broaden the application fields of paper [19–22]. From the perspective of existing methods to improve the hydrophobicity of the substrate, most of the research explored the methods to improve the surface hydrophobicity of metal, plastic and other steel substrates [23, 24]. However, due to the essential differences between the physical and chemical properties of paper and these materials, these methods are all difficult to apply to paper.

Related research has also proposed some preparation methods for superhydrophobic surfaces with pH-responsive properties, but most of these preparation methods are only suitable for rigid substrates such as metals and not suitable for paper surfaces, and the preparation process or the prepared superhydrophobic surface still have certain limitations. Firstly, by using self-assembly technology to immobilize DNA on the gold surface, the special structure of DNA enables the pH responsiveness to transform the molecular configuration, thereby realizing the reversible conversion of superhydrophobic and superhydrophilic on the material surface. However, this method not only has harsh experimental conditions and complex preparation processes, but also has relatively expensive raw materials, poor substrate flexibility, and difficult processing, recycling and degradation, which limits its application value to a certain extent [25]. Secondly, by using copper (0)-mediated reversible-deactivation radical polymerization to synthesize poly(methyl methacrylate)-block-poly(4vinylpyridine) (PMMA-b-P4VP), then the electrosprinning method was used to deposit on the stainless steel mesh to prepare the copolymer with pH-responsive properties, and the prepared surface could be switched between a neutral environment of pH = 7 and an acidic environment of pH = 3 to realize the reversible conversion between superhydrophobicity and superhydrophilicity. However, the transparency of the coating prepared by this method was not ideal, which affects the color and light transmittance of the substrate [26]. Thirdly, by using decanoic acid to react with butyl phthalate, and then using nanoparticles for roughness modification, and immersing the fiber substrate in the modified solution multiple times, a smart superhydrophobic surface with pH-control can be obtained. However, the adhesion between the polymer and nanoparticles on the surface of the fiber prepared by this method was insufficient, which makes the polymer or nano-microspheres easy to fall off, and the stability of the superhydrophobic surface was low [27].

In this study, the pH-responsive monomer 2-(dimethylamino) ethyl methacrylate (DMAEMA) was introduced to prepare the pH-responsive polymer PHFMA-PTSPM-PDMAEMA by one-step method, and the SiO2 modified by APTES was grafted onto the polymer to improve the surface roughness of the substrate and enhance the stability of the superhydrophobic properties, so as to construct the pH-responsive superhydrophobic paper. It was found that the prepared superhydrophobic paper could be used for high efficiency selective oil-water separation. In practice, the optimal ratio of SiO2 and polymer could be determined based on the influence of SiO2 dosage on the surface superhydrophobicity and oil-water separation efficiency of paper. In addition, the superhydrophobic paper prepared by this method can not only realize reversible switching between superhydrophobic & lipophilic and super-oleophobic & hydrophilic properties under pH-induction, but also has high stability and good transparency, which has great potential application value.

| Contact Angle       | Hydrophilic/Hydrophobicity | Exhibited Regularity                        |
|--------------------|-----------------------------|---------------------------------------------|
| 0° < θ < 90°       | Hydrophilic                 | The smaller of θ the better of hydrophilicity|
| 90° < θ < 150°     | Hydrophobic                 | The larger of θ the better of hydrophilicity |
| 150° < θ < 180°    | Superhydrophobic            | The larger of θ the better of superhydrophobic|
2. Experimental section

2.1. Materials
The main chemicals used in this study are as follows, all of which have not been further purified before use:

- 3-trimethoxysilyl propyl methacrylate (TSPM) (98%) (Union Silicon)
- 3-aminopropyltriethoxysilane (APTES) (98%) (Union Silicon)
- Hexafluorobutyl methacrylate (HFMA) (96%) (Xuejia fluorosilicone)
- 2-(Dimethylamino) ethyl methacrylate (DMAEMA) (99%) (Aladdin)
- Sodium bisulphite (NaHSO₃) (99.9%) (Aladdin)
- Tetrahydrofuran (99.5%) (Aladdin)
- Aluminum oxide (99.3%) (Aladdin)
- Potassium bromide (99.5%) (Aladdin)
- 1,2-Dichloroethane (99%) (Aladdin)
- Bromobenzene (99.5%) (Aladdin)
- Chloroform (99%) (Aladdin)
- Toluene (99.5%) (Aladdin)
- N-hexane (99%) (Aladdin)
- Ethyl acetate (99.9%) (Aladdin)
- Nano silica (70 nm) (Aladdin)
- Azobisisobutyronitrile (AIBN) (99.9%) (Four Hevi)
- Anhydrous ethanol (99%) (Miura)
- Triethylamine (99.5%) (Tianli)

2.2. Experimental steps
Preparation of pH-responsive superhydrophobic polymers. First of all, filter the TSPM with an alumina chromatography column to remove the polymerization inhibitor. Then, TSPM (5 g), HFMA (5 g) and DMAEMA (3.5 g) were dissolved in 150 g of tetrahydrofuran, and after they were evenly mixed, AIBN (0.5 g) and NaHSO₃ (0.3 g) were added (AIBN and NaHSO₃ were used as catalysts and initiators for the polymerization reaction respectively). Next, the solution was poured into a three neck round bottom flask, and nitrogen was introduced into the flask to provide an oxygen-free environment for the polymer preparation. Finally, the flask was sealed and placed in a water bath at 70 °C, heated and stirred magnetically for 4 h. After the reaction, the solution was allowed to stand at room temperature until the tetrahydrofuran solvent was slowly volatilized to obtain a superhydrophobic polymer with pH-responsive properties (the synthetic route is shown in figure 1).

Preparation of amino modified nano-SiO₂. In the first instance, add 200 ml of ethanol and 5 g of SiO₂ to the beaker for ultrasonic dispersion to obtain the silica ethanol dispersion. Afterwards, triethylamine was added dropwise 6 ml to the beaker to reach an alkaline environment, and after the coupling agent APTES (5 g) was added, it was heated in a water bath and magnetically stirred for 12 h to obtain a dispersion of amino-modified SiO₂. Eventually, the obtained dispersion was centrifuged at 3000 rpm for 30 min, dried and ground in an oven at 80 °C for 8 h to obtain powdery amino-modified nano-SiO₂.

Preparation of superhydrophobic paper with pH-responsive properties. In the first place, dissolve the pH-responsive superhydrophobic polymer in tetrahydrofuran, and add amino-modified silica and stir magnetically for 1 h at room temperature to form a uniform and stable pH-responsive hydrophobic coating (PHFMA-PTSPM-NIPAAm-SiO₂). Then, the modified solution was sprayed on a 5 cm × 5 cm paper substrate (the paper is German Duni brand wood pulp paper, the size of the original paper is 40 cm × 40 cm, and the weight of a single sheet was about 9.5 g, the gram weight is 60 g, the thickness is 0.48 mm, the surface smoothness is about 87 s. In this experiment, each 5 cm × 5 cm paper was uniformly sprayed with 1 ml of pH modification solution, the spray height was 15 cm, and the spray pressure was 0.15 Mpa), and dried at 85 °C to obtain superhydrophobic paper (the reaction process is shown in figure 2).

2.3. Characterization
The Fourier Transform Infrared Spectroscopy (FT-IR) test was carried out by Bruker VECTOR-22 infrared spectrometer. The contact angle and rolling angle were measured with the contact angle measuring instrument DS100, and each sample was measured at 5 different points and then the average value was taken. In the test of the wettability of the modified paper surface, we soaked the modified paper in acid solution (HCl, pH = 1),...
alkaline solution (NaOH, pH = 14), salt solution (NaCl, pH = 7) respectively for 0.5 h, then took it out and put it in the oven drying, and randomly selected points on the surface of the paper to measure the change in contact angle. XPS test adopted (Axis Ultpa) x-ray photoelectron spectrometer to measure, using Al/Kα (1486.71 eV) as the ray, and running under the condition of current 10 mA and voltage 10 KV. Scanning electron microscope (SEM) images were measured using JSM-6701F field emission scanning electron microscope, and the sample was sprayed with gold before observing the microscopic morphology. The thermogravimetric analysis (TG) test of the sample was measured by the STA449CTG thermogravimetric analyzer, which was selected to be carried out in an air atmosphere, and the heating rate was 10 °C min⁻¹. In the abrasion resistance test, after sticking sandpaper on the bottom of a 500 g weight, rubbing back and forth in the horizontal direction at a speed of 2 cm s⁻¹ with a friction length period of 20 cm. At different rubbing times, 5 different points were randomly selected to measure the contact angle of the paper, and the average value of the contact angle was recorded. In the ultrasonic experiment, the modified paper was soaked in 100 ml deionized water, then the paper was taken out at different time of treatment with ultrasonic scrubber and dried in the oven at 80 °C, and 5 different points were randomly selected to measure the contact angle of the paper, and the average value of the contact angle was recorded.

3. Results and discussion

3.1. FTIR analysis

Figure 3 shows the infrared spectra of DMAEMA, pH-responsive polymer PHFMA-PTSPM-PDMAEMA, amino-modified SiO₂ and pH-responsive superhydrophobic coating PHFMA-PTSPM-PDMAEMA/SiO₂-NH₂.

Curve 3(a) is the infrared spectrum of DMAEMA. It can be seen from the figure that 2935 cm⁻¹ is the stretching vibration absorption peak of methyl, at 2876 cm⁻¹ is the characteristic absorption peak of methylene stretching vibration, at 1155 cm⁻¹ is the stretching vibration peak of C–N, at 1716 cm⁻¹ is the C=O stretching vibration absorption peak in the ester group, and at 1638 cm⁻¹ is the C=C stretching vibration peak.

Curve 3(b) is the infrared spectrum of the polymer PHFMA-PTSPM-DMAEMA. In addition to the characteristic peaks of curve 3(a), curve 3(b) has a CF stretching vibration absorption peak at 1193 cm⁻¹, and a Si-C symmetrical stretching vibration peak at 801 cm⁻¹. Furthermore, the stretching vibration peak of Si–O–C appeared near 1071 cm⁻¹, and the C–C stretching vibration peak disappeared at about 1650 cm⁻¹. The change of the infrared spectrum indicates the successful synthesis of the polymer PHFMA-PTSPM-PDMAEMA.
Curve 3(c) is the infrared spectrum of amino-modified SiO2. It can be seen from the figure that the anti-symmetric stretching vibration peak of Si–O–Si is at 1051 cm\(^{-1}\), and the characteristic absorption peaks of stretching vibration of methyl and methylene appear at 2973 cm\(^{-1}\) and 2880 cm\(^{-1}\) respectively, the bending vibration peak of NH appears at 1549 cm\(^{-1}\), and the broad peak near 3300 cm\(^{-1}\) is caused by the stretching vibration of N-H. The existence of the above peaks proves the successful modification of SiO2.

Curve 3(d) is the infrared spectrum of the pH-responsive superhydrophobic polymer PHFMA-PTSPM-PDMAEMA/SiO2-NH2. At 1078 cm\(^{-1}\) is the stretching vibration peak of Si-OC in the polymer, around 1190 cm\(^{-1}\) is the stretching vibration peak of C-F in the polymer, and at 1155 cm\(^{-1}\) is the stretching vibration peak of C-N in the polymer. Besides, at 1051 cm\(^{-1}\) is the antisymmetric stretching vibration peak of Si-O-Si in amino-modified SiO2, and near 1550 cm\(^{-1}\) and 3290 cm\(^{-1}\) are the bending vibration peak and stretching vibration peak of N-H respectively. It can be seen from the figure that the characteristic peaks of curves 3(b) and 3(c) can basically be observed in the infrared spectrum of the polymer PHFMA-PTSPM-PDMAEMA/SiO2-NH2. This result indicates the successful synthesis of the polymer and the introduction of amino-modified SiO2 [28, 29].

3.2. The effect of SiO2 dosage on superhydrophobicity and oil-water separation efficiency

As we all know, oil-water separation is an important application field of intelligent responsive superhydrophobic surface. In this study, different types of oil-water mixtures were prepared to test the oil-water separation performance of the modified paper. The oil-water mixture of 1,2-dichloroethane, bromobenzene, chloroform (heavy oil) and water were respectively configured under the condition that the paper was superhydrophobic and lipophilic (pH > 7), and the oil-water mixture of ethyl acetate, toluene and n-hexane (light oil) and water were respectively configured when the paper was super-oleophobic and hydrophilic (pH < 7). In order to better distinguish the oil phase and the water phase, the oil-water mixture in the experiment was configured by mixing 45 ml of oil red O dyed organics and 45 ml of methylene blue dyed deionized water. Figure 4(a) shows the oil-water separation process of heavy oil by paper under superhydrophobic and lipophilic conditions. In the experiment, the modified paper was fixed between two glassware, and the oil-water mixture was poured into the upper part of the container. Due to the hydrophobic and lipophilic properties of the paper, organic matter would quickly penetrate the paper and flowed into the vessel below, while the deionized water would remain on the paper, completing a separation of the oil-water mixture. Similarly, figure 4(b) shows the oil-water separation process of light oil under super-oleophobic and hydrophilic conditions. In order to explore the relationship between oil-water separation performance and SiO2 content of paper under superhydrophobic and lipophilic conditions, this study takes chloroform as an example, and the oil-water separation efficiency was calculated by the following formula:
Figure 4. (a) The oil-water separation process of heavy oil (pH ≥ 7); (b) the oil-water separation process of light oil (pH < 7); (c) the influence of SiO$_2$ content on contact angle and oil-water separation efficiency; (d) the separation efficiency of oil-water mixtures of different heavy oils under the condition of pH ≥ 7; (e) the change of separation efficiency of heavy oil with separation times when pH ≥ 7; (f) the separation efficiency of oil-water mixtures of different light oils under the condition of pH < 7; (g) the change of separation efficiency of light oil with separation times when pH < 7.
The content of SiO$_2$ not only affects the hydrophobicity by affecting the surface roughness of the substrate, but also affects the efficiency of oil-water separation. Figure 4(c) shows the contact angle and oil-water separation efficiency of modified paper under different SiO$_2$ and polymer content ratios. Theoretically, as the concentration of SiO$_2$ increases, the surface of the paper will become rougher and the contact angle will increase, but the increase in SiO$_2$ content will also block the gaps between the fibers, which will result in a decrease in the efficiency of oil-water separation. As shown in figure 4(c), when the mass ratio of SiO$_2$ to polymer reached 0.2, the contact angle of the paper was 157° ± 2.2°, and the superhydrophobic property was obtained. At this time, the oil-water separation efficiency was 97.4% ± 1.1% and when the mass ratio of SiO$_2$ content to polymer increased to 0.25, the contact angle reached 157.3° ± 1.8°, and the oil-water separation efficiency decreased to 94.6% ± 1.2%. From the above analysis, it can be seen that the contact angle does not change significantly under different SiO$_2$ content, indicating that the superhydrophobic properties of paper change little, but the reduction of oil-water separation efficiency indicates that SiO$_2$ content will have a significant impact on the oil-water separation efficiency of paper. Based on the above analysis, the optimal mass ratio of amino modified SiO$_2$ to polymer should be 0.2 (In this study, all the experiments on superhydrophobic paper with pH-responsive properties, the superhydrophobic paper used was prepared under the condition that the mass ratio of amino-modified SiO$_2$ to polymer was 0.2).

Under the condition of the best mass ratio of amino-modified SiO$_2$ to polymer, the separation efficiency of different oil-water mixtures was calculated, and it can be seen that the separation efficiency of modified paper for a variety of oil-water mixtures including 1,2-dichloroethane, bromobenzene and chloroform can reach more than 97% ± 1.3% when the pH is ≥7 (figure 4(d)). In the research, we also tested the recycling performance of paper by calculating the changes in oil-water separation efficiency after different times of oil-water separation cycles. The study found that after 40 cycles, the paper could still maintain an oil-water separation efficiency of more than 95.5% ± 1.1% (figure 4(e)).

Take out three beakers and add deionized water to them, then add ethyl acetate, toluene, and n-hexane separately to make three oil-water mixtures. Afterwards, drop an acidic solution into three beakers to make them all reach the acidic condition of pH < 7, and carry out the oil-water separation experiment of light oil under the acidic condition (the process is shown in figure 4(b)). Due to the modified paper has super-oleophobicity and hydrophilicity when the pH < 7, the water would penetrate the paper and flow into the glassware below under
the action of gravity, while the organic matter would still remain in the glassware above. At this time, the separation performance and separation efficiency of the paper for the oil-water mixture are shown in figures 4(f) and (g). It can be seen from figure 4(f) that the separation efficiency of modified paper for a variety of oil-water mixtures can reach more than 96% ± 0.9%, and the paper can still maintain an oil-water separation efficiency of more than 94.5% ± 1.4% after 40 oil-water separation cycles (figure 4(g)).

From the above experiments and analysis, it can be seen that the prepared superhydrophobic paper not only has good oil-water separation performance, but also can effectively separate the oil-water mixture of heavy oil and light oil under different pH conditions.

3.3. The wettability test of modified paper surface
The pH-responsive properties of the prepared superhydrophobic paper was tested by measuring the change of contact angle, to verify whether it successfully possesses pH responsiveness, and to investigate the wettability of the modified paper to water and oil under pH-induction (the change of contact angle is shown in figure 5).

Figure 5(a) shows the wettability of paper to water and oil after being treated with an acid solution (pH = 1). It can be seen from the figure that the water droplet penetrates the paper surface rapidly within 30 s until it disappears completely, while the oil droplet can basically maintain the original contact angle after 5 h (the contact angle is maintained at about 158° ± 2.3°, almost unchanged). It shows that paper has super-oleophobic and hydrophilic properties under acidic conditions. Figures 5(b) and (c) respectively show that after the paper was treated with a neutral solution (pH = 7) and an alkaline solution (pH = 14), the water droplets remained superhydrophobic after 5 h on the paper surface, and the contact angle was maintained at approximately 158.3° ± 1.7°, while the oil droplets completely penetrated the surface of the paper within 30 s, and the contact angle becomes 0°, which indicates that the paper has superhydrophobic and lipophilic properties under neutral and alkaline conditions, and the wettability transition of modified paper to water and oil is completely reversible within 5 cycles (as shown in figures 5(d) and (e)).

3.4. Paper surface element and pH-responsive mechanism analysis
XPS was used to characterize the paper before and after the modification (figure 6). Although XPS could not fully explain the chemical composition of the paper sample due to the rough surface, it did provide qualitative information about the chemical changes before and after the modification. As shown in figure 6(a), the original paper is composed of 283 eV C elements and 532 eV O elements. And four more peaks appeared on the surface of modified paper at 101 eV, 152 eV, 396 eV and 690 eV, corresponding to the appearance of Si2p, Si2s, N1s, F1s signals, which indicates that the coating PHFMA-PTSPM-PDMAEMA/SiO2-NH2 was successfully modified to the paper surface. In addition, figure 6(a) also shows the changes in surface elements of the modified paper after acid (HCL, pH = 1) and alkali (NaOH, pH = 14) treatments, which provides a basis for the analysis of the pH-responsive mechanism. The N atom content of the modified paper surface without acid-base treatment is about 3.34% (figure 6(b)), after it was treated with acid (HCL), a Cl2p peak appears at 195 eV. At the same time, due to the protonation of PDMAEMA, a new quaternary amine group appeared, and the N element content on the paper surface has increased to 4.83% (it can be seen from the data in figure 6(c)). At this time, the molecular hydrogen bonds between the groups will combine with the surrounding water molecules to form a layer of water molecules on the surface, increasing the surface energy of the material, making the material exhibit hydrophilic properties, and because this layer of water molecules can block the entry of oil, it exhibits oleophobic properties [30]. However, after the paper is treated with alkali (NaOH), the N1s peak appears at 1070 eV, and the N1s peak can only be observed at 396 eV (figure 6(d)). In addition, the N atom content on the surface of the paper has little change compared with figure 6(b), and it is still the tertiary amine group corresponding to PDMAEMA. This is because the hydroxyl group in the alkaline solution releases a proton while attacking the nitrogen atom of N—H, which removes the chloride ion in the quaternary ammonium salt, and the ionizing group is deprotonated. At this time, the surface wettability of the tertiary amine group is dominated by the hydrophobic group, which makes the grafted polymer possess superhydrophobic properties [31]. This indicates that the wettability of the modified paper surface will change due to the protonation and deprotonation of PDMAEMA chain segment after being treated with acid-base solutions with different pH values (the process is shown in figure 6(e)).

3.5. Surface morphology of modified paper
Figure 7 shows the microscopic morphology of the paper samples before and after modification under the scanning electron microscope observation. As shown in figures 7(a) and (b), the original paper fibers present a smooth fiber structure, the fibers are tightly interwoven and the gaps between the fibers are clearly visible, which reflects the excellent properties of the paper, such as good air permeability. And as shown in figures 7(c) and (d), after superhydrophobic treatment, a large number of bumps appear on the surface of paper fiber, which is
endowed with nano scale surface roughness. By comparison, it can be found that the adhesion of the superhydrophobic coating on the fiber surface is relatively uniform, the fiber edge is still clearly identifiable, and the fiber shape does not change much before and after the modification. This not only shows that the

![Figure 5.](image)

Figure 5. The contact angle of water and oil drops on the surface of paper treated with different pH solutions changes with time: (a) pH = 1; (b) pH = 7; (c) pH = 14; (d)–(e) the reversible conversion of the wettability of the modified paper surface to water and oil at pH = 1, 7 and 14.
superhydrophobic coating has successfully adhered to the paper, but also proves that the surface morphology of the paper before and after the modification changes little.

3.6. Thermogravimetric analysis of paper
Figure 8 shows the TGA curves of samples A0, A1, and A2. Sample A0 is the original paper sample, A1 is the sample coated with amino modified SiO2, and A2 is the sample coated with polymer HFMA-TSPM-DMAEMA/SiO2-NH2. After all samples were heated to 700°C in air temperature, the weight loss rate of unmodified original paper was 100%; The paper sample coated with amino-modified SiO2 had a weight loss rate of 90.2% and a remaining weight of 9.8% due to the residue of SiO2; The paper sample coated with the
superhydrophobic coating PHFMA-R-PTSPM-SiO₂ had a weight loss rate of 93.05% and a remaining weight of 6.95%. This indicates that the coating of SiO₂ on the paper surface and the composite of HFMA-TSPM-DMAEMA on the surface of the modified SiO₂ particles affect the thermal stability of the material [32].
3.7. The effect of pH-responsive superhydrophobic coating on paper color

In general, the superhydrophobic modification of paper will not only change the wettability of the paper, but also affect the color. Therefore, in practical applications, the effect of paper modification on color and light transmittance is an important factor that must be considered. In figure 9, curves a and b represent the reflective recording curves of original paper and modified paper respectively, while testing the reflectance spectra of the two papers with the spectrophotometer, the L, a, b values were also tested (L represents brightness, a represents red-green, b represents yellow-blue), the L’, a’, and b’ values, quantitatively characterizing the color of the samples, were reported in table S1. It can be seen from the figure that the paper before and after treatment has similar spectral reflectance in the range of 400–600 nm, and there is a slight deviation in the red spectral region of 600–700 nm, the measured color difference \( \Delta E = 0.85 \) (\( \Delta E < 1 \)), this shows that the effect of superhydrophobic coating on paper color is within the acceptable range for human eye recognition [33].

3.8. Stability test

In actual production applications, the external environmental factors, especially friction, will have a great impact on the surface of the paper. And in certain application areas such as oil-water separation, the paper will sometimes be damaged by ultrasound or the erosion of different acid and alkaline solutions, resulting in a decrease in hydrophobicity. Therefore, the stability of superhydrophobic paper under friction, ultrasonic environment, different acid and alkaline solutions are issues that we must consider.

Figure 10(a) shows the change of the contact angle of the paper surface before and after the wear resistance test of the superhydrophobic paper under the condition of pH = 7. In the experiment, sticking sandpaper to the bottom of the weight and rubbing back and forth on the paper, and pushing the weight to the forefront and then pulling it back to the original position is defined as a cycle. It can be seen from the figure that the contact angle of the paper surface does not decrease much after 100 rubbing cycles, and the paper can still maintain good hydrophobic properties, which shows that the modified paper has good abrasion resistance.

Figure 10(b) shows the change of the paper surface contact angle with the extension of ultrasonic time under the condition of pH = 7. It can be seen from the figure that with the extension of the ultrasonic time of the modified paper, the contact angle gradually decreases. This is because ultrasonic vibration will cause part of the polymer and modified nano-SiO\(_2\) to fall off the surface of the modified paper fiber, thereby reducing the roughness of the paper surface and the hydrophobic properties of the paper. However, after 150 min of ultrasonic destruction, the surface of the paper can still maintain a contact angle of about 154.6\(^\circ\)±1.3\(^\circ\) and still has good hydrophobic properties. Therefore, the superhydrophobic paper prepared by this method has strong stability.
Figure 10 (c) shows the change of contact angle of superhydrophobic paper under different immersion time in acid solution, alkaline solution, and salt solution. The experiments found that when paper was immersed in an acidic solution of hydrogen chloride (HCL, pH = 1), the property of the paper surface changes from superhydrophobicity to hydrophilicity, which was consistent with the previous experimental results. In addition, with the prolongation of the immersion time of sodium hydroxide solution (NaOH, pH = 14) and sodium sulfate solution (Na₂SO₄, pH = 7), although the contact angle of the paper surface has decreased to
varying degrees, it can still maintain a good hydrophobicity. After being soaked for 180 min, the contact angle of the paper surface after soaking in the two solutions was still greater than 150° (It is greater than the critical value of the contact angle for obtaining superhydrophobic properties on the surface of the material, and still has good superhydrophobic properties). This indicates that the prepared superhydrophobic paper has good corrosion resistance to the alkaline and salt solutions.

The analysis of the above experimental results shows that the superhydrophobic paper prepared by the method of this research has relatively strong stability.

4. Conclusion

In this study, the one-step method was used to prepare pH-responsive polymer PHFMA-PTSPM-PDMAEMA by using pH-responsive monomer DMAEMA, silicon-containing cross-linking monomer TSPM and fluorine-containing monomer HFMA. Afterwards, after the amino-modified SiO₂ was grafted onto the polymer to build the roughness, the polymer was then coated on the paper to prepare the superhydrophobic paper with pH-responsive properties. In the study, the contact angle and oil-water separation efficiency were tested, and the final determined optimal mass ratio of amino-modified SiO₂ to polymer was 0.2. On the whole, the preparation of superhydrophobic paper by the method of this research not only requires lower experimental synthesis conditions, the preparation method is relatively simple and easy to implement, and the reproducibility is strong, but the prepared paper also has good transparency and stability, and it can realize the free conversion between superhydrophobic & lipophilic and super-oleophobic & hydrophilic properties under the induction of different pH conditions. All these advantages make the method of this study have a very broad application prospect in the fields of intelligent packaging and oil-water separation in modern industrial production.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

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