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# Superhydrophobic paper fabricated via nanostructured titanium dioxide-functionalized wood cellulose fibers

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## ABSTRACT

Herein, an eco-friendly and straightforward method was provided for the fabrication of superhydrophobic paper from native wood cellulose fibers via in situ hydrolysis of tetraethyl titanate(IV) without any chemical pretreatment. By simply adjusting the amount of acetic acid (HAc), the surface micro/nanomorphology could be well controlled. After papermaking and hexadecyltrimethoxysilane modification, superhydrophobic paper can be easily achieved with static water contact angle of 152.3° (± 1.3°). The paper also possessed good self-cleaning property against contamination and durability toward mechanical damages of finger wiping over 50 cycles as well as excellent oil/water separation, which expands its utility in various paper-based technologies. The whole procedure possesses the advantages of friendly raw material, mild reaction conditions and with no toxic modifier, which hold potential application in cellulose-based superhydrophobic material in large scale.

## Introduction

Due to environmental pollution and resources shortage, bio-based materials made from cellulose fibers, starch, lignocellulosic, chitosan and their bio-derivatives have attracted great attention. Among these, cellulose, as the most widely distributed and abundant polysaccharide in nature, has many excellent properties, including biodegradability, recyclability, excellent mechanical strength as well as flexibility, portability, lightweight and processability [1, 2]. Hence, cellulose fibers are widely used in the manufacture of paper-based materials for printing, packaging [3], stimuli-responsive chromic paper devices [4], supercapacitors and antibacterial [5–7]. However, the inherent hydrophilicity of cellulose largely limited paper-based products application in moisture circumstances. Therefore, it is important to

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improve the hydrophobic properties of cellulose fiber-based paper for practical applications.

Inspired by lotus leaf, lowing surface energy on rough surfaces or fabricating micro/nanoroughness on low-energy surfaces are two key strategies for constructing superhydrophobic surfaces [8–18]. Methods have been reported for the construction of superhydrophobic cellulose fabrics or superhydrophobic paper [19–22]. Avijit et al. [23] presented an eco-friendly and facile methodology for the fabrication of waterproof paper using fluoroalkyl-functionalized CNFs which were first chemically functionalized with 1H,1H,2H,2H-perfluorooctyltriethoxysilane and 3-(2-aminoethylamino)-propyltrimethoxysilane via a wet chemical process. Satapathy et al. [24] reported a facile strategy to construct superhydrophobic paper via solution casting technique of LLDPE and $SiO_2$ + LLDPE coatings. Liu et al. [25] presented a novel strategy to construct durable superhydrophobic fabrics by pre-applying long alkyl chain silane on the surface of the fabrics and then argon vacuum plasma treatment. However, the complex equipment, complicated synthetic procedures or expensive raw materials greatly limited the application of superhydrophobic materials in large scale. The development of a facile, straightforward and economical method to prepare superhydrophobic paper, especially without changing the original structural properties of cellulose fibers, is in great demand.

Herein, we report a novel and green strategy for the fabrication of superhydrophobic paper from native wood cellulose fibers prepared via in situ hydrolysis of IV without any chemical preprocessing. The surface micro/nanohierarchical rough surface can be well controlled by adjusting the amount of acetic acid (HAc). After papermaking process and subsequent modified with HDTMS, superhydrophobic paper can be well achieved. The structure, chemical composition and surface morphology of the cellulose fibers before and after titanium dioxide functionalization were characterized by FT-IR, XPS, SEM and TGA, respectively. Besides, the wetting stability against abrasion, self-cleaning and oil/water separation properties of the obtained superhydrophobic paper was also studied to evaluate the actual practical performance of the resultant superhydrophobic paper.

## Experimental

### Materials

Bleached hardwood pulp (moisture content 80 wt%, 75 SR°) was kindly provided by Guangzhou Chenhui Paper Co., Ltd., China. Tetraethyl titanate (IV, 98 wt%), acetic acid (HAc, 99%,) and hexadecyltrimethoxysilane (HDTMS, 99%) were purchased from Sigma-Aldrich. Anhydrous ethanol was purchased from Guangzhou Chemical Reagent Co. Deionized water was obtained from a Millipore Milli-Q water purification system. All the chemicals were used as received without any further purification.

### Synthesis of titanium dioxide-functionalized cellulose fibers

The wood cellulose pulp (1.0 g) was suspended in 50 mL ethanol with a mechanical stirrer until it was completely dispersed. Then, IV (500 mg) and a certain amount of HAc were added to the above solution and conducted for 3 h at 50 °C. The titanium dioxide ($TiO_2$)-functionalized cellulose fibers were obtained by centrifugation, ethanol washing and centrifugation repeatedly.

### Fabrication of functionalized fiber-based superhydrophobic paper

The functionalized fiber-based superhydrophobic paper was fabricated through a simple vacuum filtration process [26]. Typically, 15 mL aqueous suspension containing 50 mg $TiO_2$-functionalized cellulose fibers was poured onto the filter paper in a sand core funnel with a diameter of 45 mm. After suction filtration and subsequent immersed into petri dish with 30 mL ethanol solution containing HDTMS (1 wt%) for 15 min, superhydrophobic paper was obtained.

### Characterization

The structure and chemical composition of cellulose fibers before and after $TiO_2$ functionalization were characterized by FT-IR (Spectrum 2000, PerkinElmer) and XPS (Escalab 250, Thermo Electron) with Al Ka radiation (20 eV) as the exciting source. The morphology of the surfaces of cellulose fibers before and after surface modification were carried out by FE-

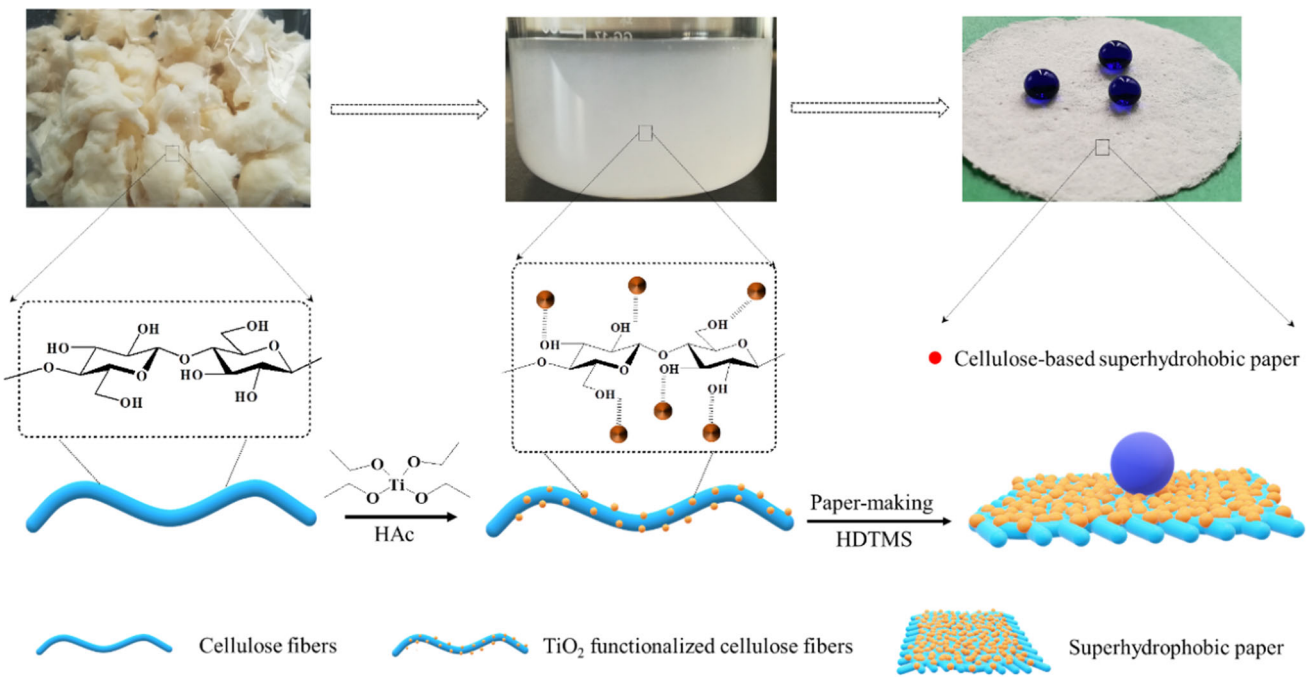
SEM (Quanta 400F, FEI) at 15 kV. Thermogravimetric analysis (TGA) was measured with TA Instruments (Q600). The samples were heated at a heating rate of 20 °C/min from 40 to 600 °C in nitrogen atmosphere. The static water contact angles (WCAs) were measured at least five different positions on a contact angle system (Dataphysics OCA20) with liquid droplets of 5 μL.

## Results and discussion

As is well known, cellulose fibers have a significant number of hydroxyl groups on their surface. Titanate coupling agent that contains four inorganic reactive groups on titanium will bond well to the hydroxyl groups on cellulose fibers. So, the cellulose fibers can act as the template to lead the in situ hydrolysis of IV. This is the basis for modifying cellulose fibers with IV without any chemical pretreatment. Specifically, methoxy groups of the IV can be hydrolyzed under acidic environment to give titanitol groups. The reactive titanitol groups formed can be absorbed rapidly through condensation with the hydroxyl groups present on cellulose fiber surface forming Ti–O–Ti bond linkages. This reaction results in the chemically bonded $TiO_2$ nanoparticles to the cellulose fiber surface, which was beneficial for the construction of micro/nanoroughness structure. The reaction which occurs between cellulose fibers and IV is depicted in Scheme 1.

The presence of the $TiO_2$ nanoparticles on the surface of cellulose fibers was confirmed by FT-IR spectra. Figure 1 shows the FT-IR spectra of pristine cellulose fibers and $TiO_2$-functionalized cellulose fibers. Comparing with the spectra of pristine cellulose fibers in Fig. 1a, the wide absorption band at 400–750 $cm^{-1}$ was the typical absorption peak of Ti–O stretching and Ti–O–Ti bridging stretching modes in $TiO_2$. Besides, the peak in 2854 $cm^{-1}$ ($\nu$ $CH_2$) of the as-synthesized $TiO_2$-functionalized fibers can be attributed to the characteristic frequencies of $Ti(OH)_x(OC_2H_5)_{4-x}$ due to the surface in situ hydrolysis of IV on cellulose fibers [27]. These results proved that $TiO_2$ nanoparticles were successfully grafted onto the surface of the cellulose fibers.

To further prove the above results, XPS were used to measure the surface chemical composition of pristine cellulose fibers and titanium dioxide-functionalized cellulose fibers. As depicted in Fig. 2a, the spectra of pristine cellulose fibers revealed only carbon (284.6 eV) and oxygen (532.6 eV) in cellulose fibers, which was similar to other literature reports [28, 29]. For the titanium dioxide-functionalized cellulose fibers, new peaks with binding energies of 456.36 eV (Ti 2p) and 462.48 eV (Ti 2p1) were




**Scheme 1** Schematic of $TiO_2$ functionalized cellulose fiber-based superhydrophobic paper.

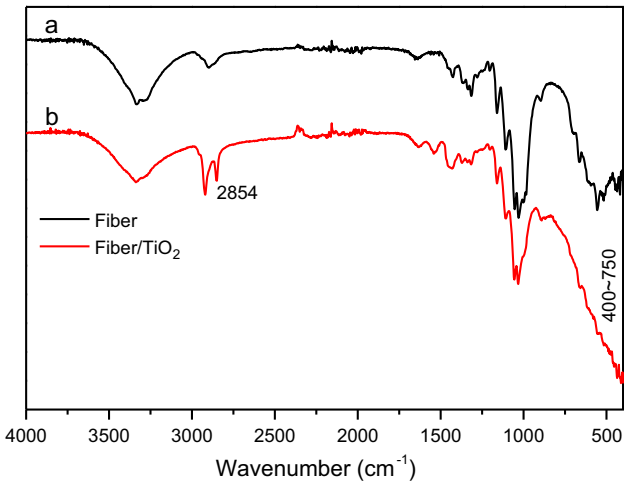



**Figure 1** FT-IR spectra of pristine cellulose fibers (a) and $TiO_2$ functionalized fibers (b).

appeared in high resolution of Ti 2p region in Fig. 2b, and the relative atomic concentration of carbon increased from 54.12 to 67.08%, and the relative atomic concentration of oxygen decreased from 45.88 to 23.88%, which strongly confirmed that the titanium dioxide particles were covered on the surface of cellulose fibers [30, 31].

High-resolution C1*s* and O1*s* XPS spectra for pristine cellulose fiber and $TiO_2$-functionalized cellulose fibers were also performed. As shown in Fig. 2c, the C1*s* peak can be deconvoluted into three peaks located at 284.8 eV, 286.8 eV and 288.1 eV, which are typical signals of carbon atoms of C–C, C–O and –C=O, respectively [29]. After surface in situ hydrolysis of IV, the C1*s* peak of fiber@$TiO_2$ composites has been deconvoluted into three peaks located at 284.4 eV, 285.9 eV and 288.2 eV as shown in Fig. 2d. The signal of carbon atoms of C–C at 284.4 eV obviously increased from 5.3 to 19.01 due to the hydrolysis of IV to form the $Ti(OH)_x(OC_2H_5)_{4-x}$ on the surface of cellulose fibers, where $x$ was related to the amount of acetic acid added to the reaction solution [32, 33]. Figure 2e depicts the spectra of O1s region, taken on pristine cellulose fibers. The O1s region can be resolved into three peaks: 531.9 eV (C=O), 533.0 eV (OH) and 534.0 eV (C–O). After modification with $TiO_2$ (Fig. 2f), the high-resolution XPS spectra of O1s region can be divided into five small

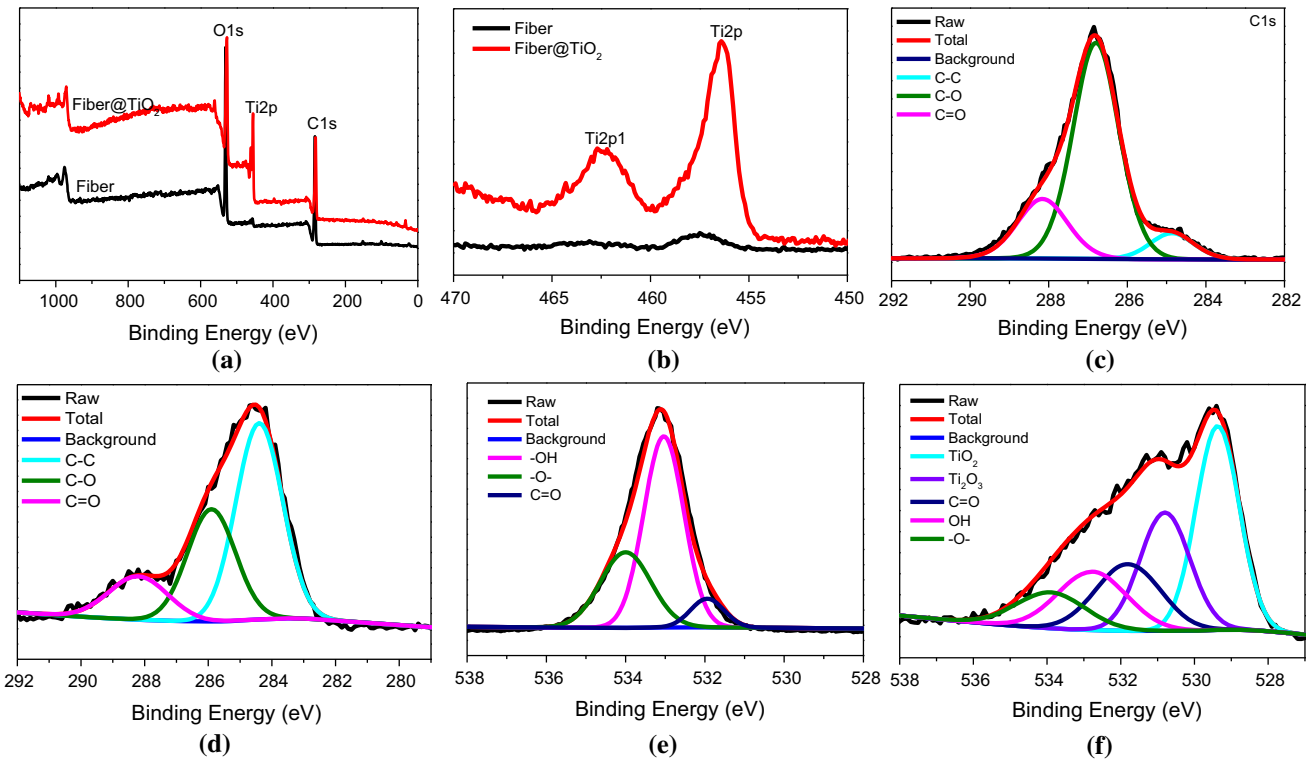



**Figure 2** XPS survey spectra of pristine cellulose fibers and $TiO_2$ functionalized cellulose fibers **(a)**, high-resolution XPS spectra of Ti 2p **(b)**, C 1 s of pristine cellulose fibers and $TiO_2$ functionalized cellulose fibers **(c, d)**, O1s of pristine cellulose fibers and $TiO_2$ functionalized cellulose fibers **(e, f)**.

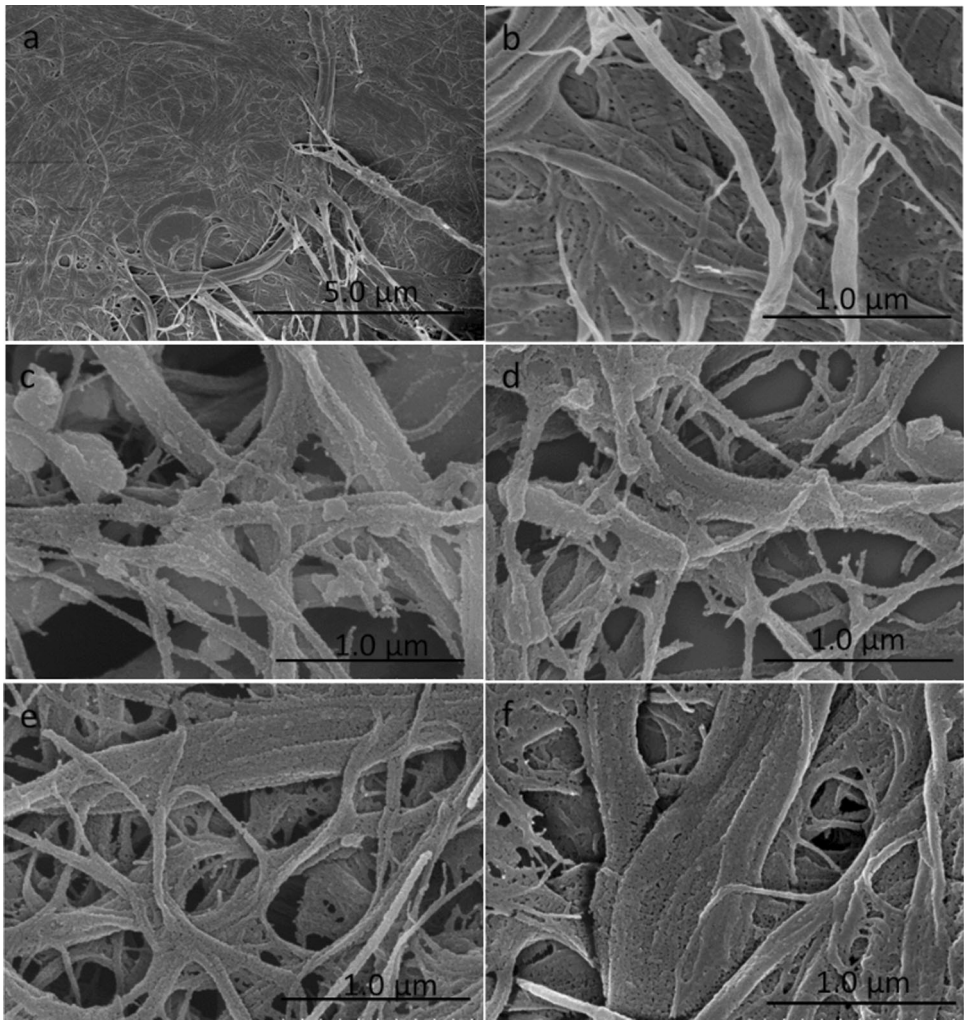



**Figure 3** Scanning electron microscopy images of pristine cellulose fibers **(a, b)** and $TiO_2$ functionalized cellulose fibers with different amounts of HAc **(c)** 50 mg, **(d)** 100 mg, **(e)** 250 mg and **(f)** 500 mg.

peaks. The main contribution is attributed to Ti–O bond of $TiO_2$ (529.37 eV) and Ti–O bond of $Ti_2O_3$ (530.7 eV) [34]. The other three peaks can be counted by the –OH groups (532.8 eV), the C–O bonds (533.9 eV) and C=O bonds (531.8 eV), respectively. The above analyses strongly proved $TiO_2$ particles were successfully attached on the surface of cellulose fibers.

Since the bleached hardwood pulp used in this study has a moisture content of up to 80 wt%, IV with a relatively low electronegativity can rapidly react with polar solvents, especially water, making the resulting titanium dioxide agglomerate [35–37]. So, in order to effectively adjust the hydrolysis of IV, different amounts of HAc were added into the reaction suspension. Surface morphologies of pristine cellulose fibers and $TiO_2$-functionalized cellulose fibers with different amounts of HAc (50 mg, 100 mg, 250 mg and 500 mg) were studied with SEM, as depicted in Fig. 3.

It can be seen that the pristine cellulose pulp was composed of cross-linked micro-nanofibers (Fig. 3a). Higher magnification showed that the surface of pristine cellulose fibers was smooth with natural grooves and veins in Fig. 3b [38]. Figures 3c and 4f show SEM images of $TiO_2$-functionalized cellulose fibers obtained under varied HAc concentrations. When the HAc amount was 50 mg, the cellulose fibers were densely and uniformly covered by $TiO_2$ nanoparticles, which roughen the fibers surface. Besides, heterogeneous $TiO_2$ accumulations were also observed in the region among adjacent fibers which was due to the fast hydrolysis rate of IV (Fig. 3c). When the HAc amount increased to 100 mg (Fig. 3d), the irregularly shaped $TiO_2$ accumulations in the region among adjacent fibers reduced greatly. With the content of HAc increased from 250 to 500 mg, the

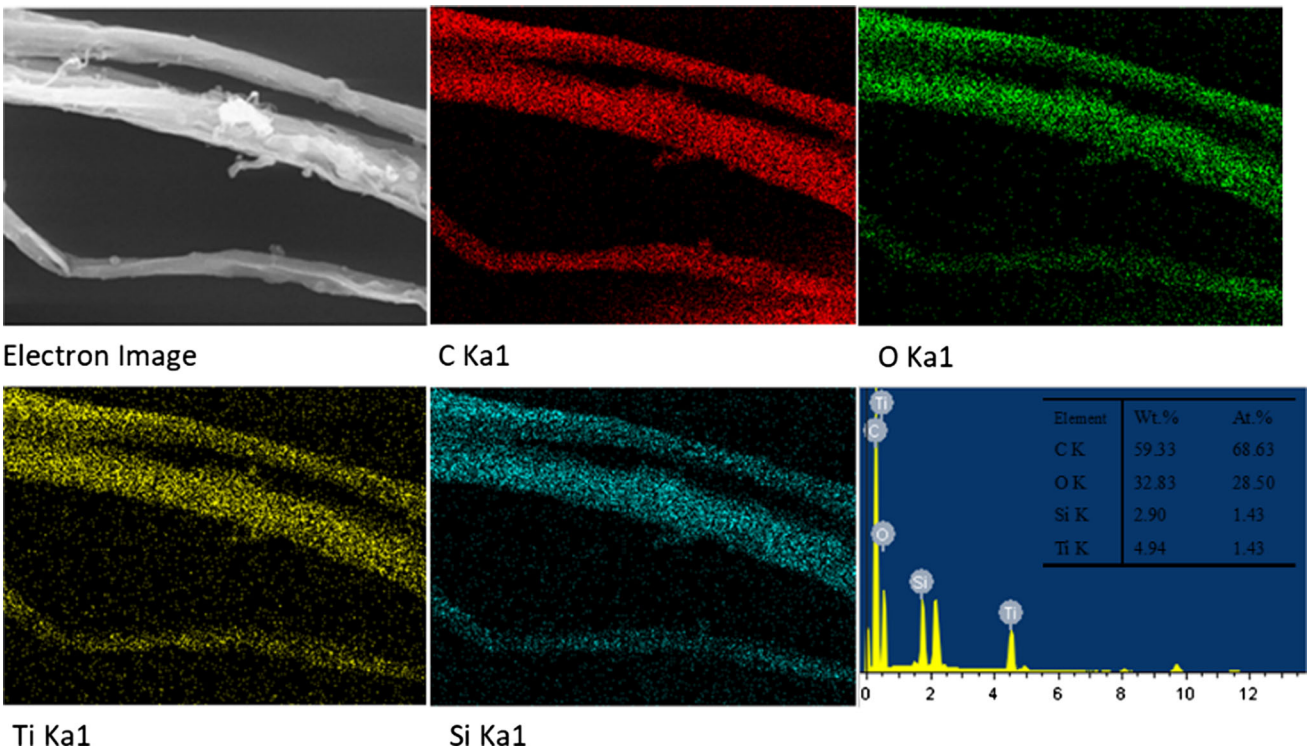



**Figure 4** EDS elemental mapping images of the $TiO_2$ functionalized cellulose fibers.

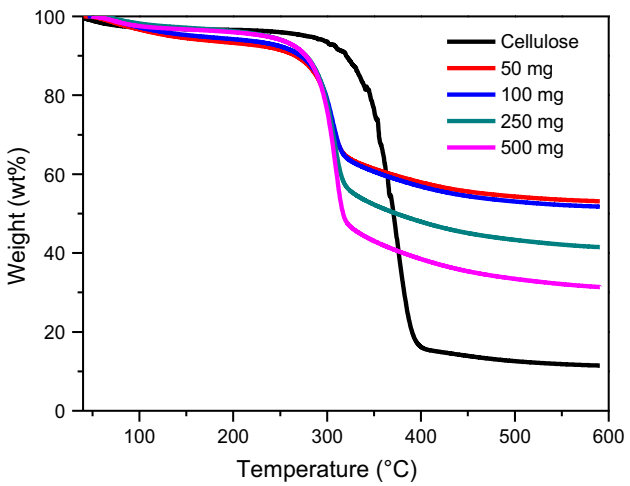



**Figure 5** TGA curves of pristine cellulose fibers and $TiO_2$-functionalized cellulose fibers with different HAc (50 mg, 100 mg, 250 mg and 500 mg).

SEM images (Fig. 3e, f) showed that a homogeneous and complete coverage of $TiO_2$ nanoparticles (20–30 nm) on the fiber surface was presented, forming micro/nanohierarchical rough surface structure. These results indicated that the surface morphology of cellulose fibers functionalized with $TiO_2$ nanoparticles can be well controlled by adjusting the content of HAc, which was crucial to generating a superhydrophobic surface [39, 40].

Moreover, surface elemental mapping analysis was based on X-ray energy-dispersive spectroscopy (EDS) of the $TiO_2$-functionalized cellulose fibers after HDTMS hydrophobic treatment. As shown in Fig. 4, each kind of elements was very complete and uniformly attached on the cellulose fibers, which also certified that cellulose fibers were successfully coated with $TiO_2$ nanoparticles and subsequent HDTMS modification.

Thermogravimetric analysis (TGA) was used to quantitate the thermal properties and the amount of titanium dioxide nanoparticles deposited on cellulose fiber surfaces. Figure 5 shows the TGA results of pristine cellulose fibers and $TiO_2$-functionalized cellulose fibers catalyzed with different HAc (50 mg, 100 mg, 250 mg and 500 mg). It is clearly seen that the residue of raw cellulose fibers was 8.08 wt% due to the present of inorganic ash content [41]. After in situ hydrolysis of IV with 50 mg HAc, the residue content grows to 53.22 wt%. With increasing the amount of HAc from 100 to 500 mg, the final residue weight ratio of the fibers decreased from 52.05 wt%, 41.23 wt% to 31.29 wt%, which was in accordance with SEM analyses. So, 100 mg ~ 250 mg of HAc

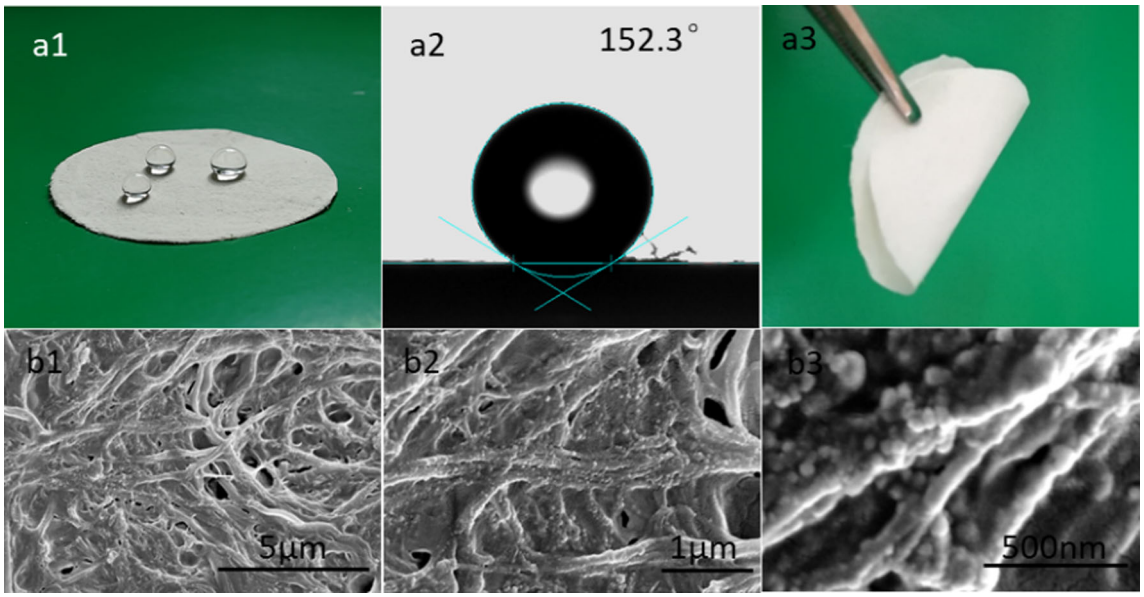



**Figure 6** Optical picture showing static contact angle of water on superhydrophobic paper surface **(a1)**; shapes of water droplet (5 μL) on as-prepared paper surface prepared with 100 mg HAc **(a2)**; physical appearance and flexibility of superhydrophobic paper after refolding tests **(a3)**; SEM image of the as-prepared superhydrophobic paper with different magnification times **(b1–b3)**.

should be appropriate, since the modified cellulose fibers showed controllable surface roughness.

As is well known, regular pure paper is inherent hydrophilic, and water can completely wet on the paper surface. After surface modification with $TiO_2$ constructing micro/nanohierarchical structure and subsequent modified with HDTMS, superhydrophobic paper (catalyzed with 100 mg HAc) can be easily obtained. Water droplets can stand on the paper surface and maintain their spherical shapes with water contact angle of 152.3° ± 1.3° (Fig. 6a1, a2). Besides, the obtained superhydrophobic paper still maintained excellent mechanical flexibility after repeated folding experiments (Fig. 6a3), which is of vital importance in practice. Figure 6b1–b4 shows the SEM images of the as-prepared superhydrophobic paper. As can be seen, a favorable wrinkling surface morphology that formed over the original cellulose fiber could be gained for the obtained paper sample. It was found to contribute to the promotion of surface roughness for the paper and, thus, an elevated WCA (as high as 152°) because of the high surface roughness of the $TiO_2$-functionalized fiber even after strong sorption vacuum filtration steps.

Resistance to staining by water-based fluids is an important feature of superhydrophobic paper. Figure 7a presents raw paper and superhydrophobic paper being immersed in methylene blue dyed water. Figure 7a2 shows raw paper was wetted and stained by the dyed water. Figure 7a4 shows the superhydrophobic paper after immersion in the dyed water showing no wetting or staining. The self-cleaning and antifouling performances are of vital importance for the applications of the final superhydrophobic paper. Hence, to observe self-cleaning properties of the superhydrophobic paper, a layer of carbon black was acted as contaminants spread on the surface, which was more difficult to be washed away than common contamination [42, 43]. As shown in Fig. 7b1–b4 and Movie S1, the carbon powders were easily got washed away with rolling water droplets leaving a thoroughly clean paper surface. This demonstrated that the obtained paper also possessed excellent self-cleaning and antifouling performances.

For superhydrophobic interfaces, the superhydrophobicity can be easily destroyed by external friction due to its fragile micro/nanohierarchical surface structure, which was the biggest limitation in practical industrial application. The resistance to mechanical friction of the obtained paper was also investigated, as shown in Fig. 7c, d. Figure 7c1–c4 and Movie S2 demonstrate the finger-wipe test of superhydrophobic paper. It is clearly shown that, after 50 times finger wipes, the water droplets fell off

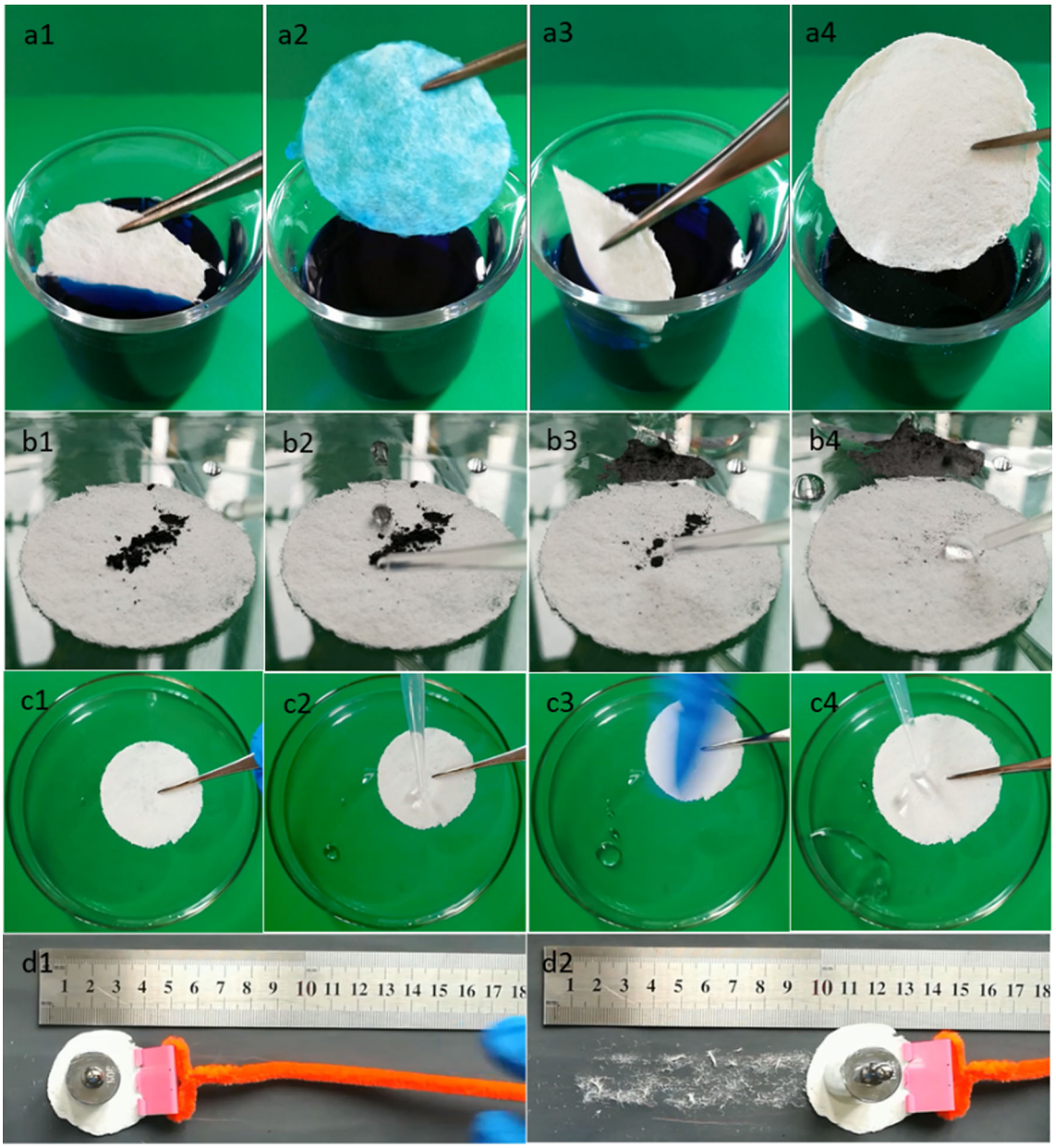



**Figure 7** Images of raw paper **(a1, a2)** and superhydrophobic paper **(a3, a4)** before and after immersion in methylene blue dyed water; self-cleaning property of the superhydrophobic paper **(b1–b4)**; images demonstrating the method of the finger-wipe test of the obtained paper **(c1–c4)**; images demonstrating the sandpaper-abrasion test of the obtained paper **(d1, d2)**.

superhydrophobic paper surface quickly, showing excellent durability against finger wiping. Figure 7d1, d2 shows the sandpaper-abrasion test of superhydrophobic paper under the weight of 50 g. Though after rubbed against sandpaper, the fiber debris on the paper surface was worn away, it still remained good superhydrophobic properties, which can further prove that the obtained paper had excellent friction resistance (Movie S3).

Another application of superhydrophobic surfaces is in the separation of oil and water mixtures. The modified paper was superhydrophobic and superoleophilic, which was suitable for the separation of oil and water mixtures. Figure 8a and Movie S4 show the oil/water separation behavior of the obtained paper. When the oil–water mixture (60 mL, chloroform/water, 1/1, v/v) was poured into the separation column, the chloroform was rapidly permeated through the paper and dropped into the beaker

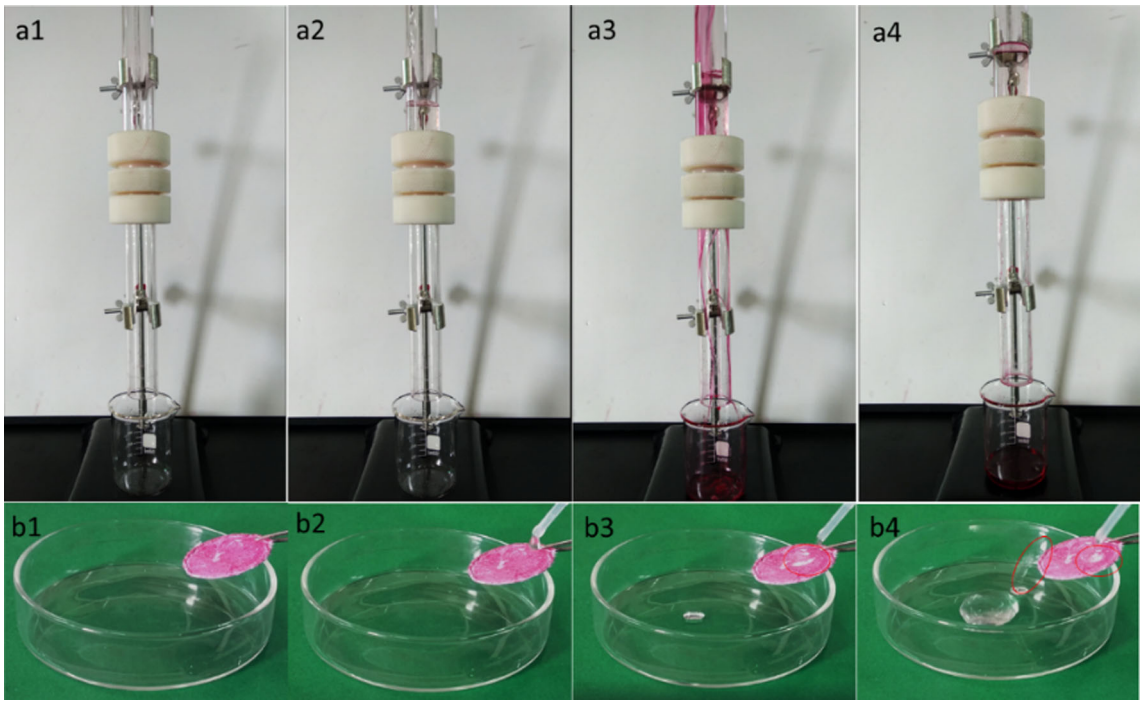



**Figure 8** **a** Sequential snapshots of the as-prepared paper used for oil/water separation process of water and red oil dyed chloroform; **b** optical pictures of superhydrophobic cellulose-based paper after oil–water separation test.

below, while the water was intercepted and retained above the funnel. Moreover, the paper after oil–water separation still maintained excellent superhydrophobic property, which implied that the paper showed durable superhydrophobicity even under oil immersion (Fig. 8b, Movie S5).

## Conclusion

In summary, a simple and eco-friendly strategy to develop durable superhydrophobic paper based on $TiO_2$-functionalized cellulose fiber as building block was demonstrated. The surface morphology of the $TiO_2$-functionalized cellulose fiber could be well controllable by adjusting the amount of HAc used. After papermaking and HDTMS modification, the obtained paper showed excellent superhydrophobicity with WCA of $152.3° \pm 1.3°$. It also showed excellent self-cleaning, antifouling and oil/water separation ability. Moreover, the paper also presented durable water-resistant property against finger-wiping and sandpaper-abrasion tests for over 50 times. The whole process was with eco-friendly and low-cost raw materials, simple operational procedure and mild reaction conditions, which provide new opportunities to develop novel superhydrophobic cellulose-based functional materials.

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## Compliance with ethical standards

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

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