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Amphiphobic Nanocellulose-modified Paper: Fabrication and Evaluation

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Amphiphobic nanocellulose-modified paper with high durability is successfully fabricated by a facile two-step methods. Firstly, nanocellulose-modified paper is prepared by dipping filter paper, i.e., glass microfiber (GM) filter paper and polytetrafluoroethylene (PTFE) filter paper in dilute nanocellulose dispersed solution. Subsequently, the nanocellulose-coated paper is treated with Trichloro(1H,1H,2H,2H-tridecafluoro-n-octyl)silane (FOTS) by chemical vapor deposition. The obtained paper is found to have superhydrophobicity and oleophobicity which repelling both of polar and non-polar liquids, on which the drops of water and non-polar liquids with high molecular weight become marble shape, and the contact angles of water and n-hexadecane reach 156° and 144°, respectively. Furthermore, such amphiphobic nanocellulose-modified papers exhibit excellent surface durability in several environments including various temperatures, acid and alkaline solutions, salt solutions and seawater. In addition, such amphiphobic nanocellulose-modified papers show good repellent property for several kinds of liquids in our daily life. With the outstanding in protection from diversified liquids, the amphiphobic nanocellulose-modified paper can be applied in the self-cleaning, anti-bacteria, and anti-corrosion areas.

1 Introduction

In nature, lotus leaf shows self-cleaning property, on which water drop can be moved out quickly. This phenomenon inspire us to fabricate similar materials with water repellent property. A simple and quantitative indicator to evaluate the tendency of repelling or wetting property of liquid is contact angle of the liquid on the solid surface. The hydrophilic solid surface is the surface wetted from water spreads over without the formation of any droplets or the surface with a water contact angle less than 90°; in contrast, the hydrophobic solid surface which repels spreading of water generally with the water contact angle higher than 90°. Recently, the most attractive study is to develop a solid surface with superhydrophobicity, on which water forms apparently droplet, easily slides off, and the formed water droplet water has the contact angle larger than 150°.¹⁻⁷ On the contrary, a solid surface with oil repellent property is named as oleophobic surface. It is expected to develop materials with amphiphobic surface, on which both of water and oil can be repelled quickly. In other words, amphiphobic surface combines hydrophobicity and oleophobicity, resulting in the surface with super anti-wetting property. This anti-wetting property relates to the various advantages such as self-cleaning, anti-bacteria, anti-reflection, corrosion resistance and so on.⁸⁻⁹ However, development of such kinds of materials is full of more challenge since the lower

surface tension of oil generally leads to the higher solid surface attraction and as a result, the oil can easily wet on superhydrophobic surface.⁸⁻¹² To fabricate artificial superhydrophobic surface, two important factors, i.e., roughness and surface energy, need to be considered. For the surface roughness, Cassie *et al.*¹³ addressed the wetting theory modelling the wettability of rough surface. At the small protrusions of rough surface, it cannot be filled by liquid but can be filled by air, thus only on the top areas of rough surface are wetted by liquid.^{1,5-6} For the surface energy, liquid with lower surface tension than the critical surface tension of substrate will wet the surface.² Generally, the superhydrophobic surface shows the extremely low surface energy materials, especially lower than surface tension of water (72.1 mN/m)¹⁴, thus it will not be wetted by water. However, to fabricate superoleophobic surface, other factors which can protect oil from penetrating the texture should be concerned.^{8, 10-12} In addition, the lower surface tension of oil, i.e., n-hexadecane (27.47 mN/m)¹⁴, than water is another challenge for developing the low surface tension of superoleophobic surface. To fabricate superamphiphobic surface, it needs a specific combination of low surface energy and reentrant surface structure.¹⁰⁻¹² Li *et al.*¹¹ developed a method to design and create cellulose-based natural materials with superamphiphobic properties by combining the control of cellulose fiber size and structure using plasma etching and fluoropolymer deposition. The obtained handsheets exhibit contact angles greater than 150° for water, ethylene glycol, motor oil and n-hexadecane. Jin *et al.*¹⁵ also prepared amphiphobic cellulose-based materials using liquid treatments to generate the necessary roughness, followed by self-assembling 1H,1H,2H,2H-perfluorooctyl trimethoxysilane (PFOTMS) monolayer onto the surface.

Nanocellulose has recently gained great attention from researchers and industry because it has some unique properties including high tensile modulus, high specific surface area, biodegradability, biocompatibility and sustainability.¹⁶⁻¹⁷ Especially,

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nanocellulose has nanoscale dimension and rich in hydroxyl group with good affinity to a variety of materials. Thus, it can be applied to make high quality paper with special surface properties or modify other solid surfaces.¹⁸ Using nanocellulose to increase roughness and reactivity on surface is an attractive idea to modify substrates for achieving amphiphobicity by natural source. Meanwhile, most of researches used hard particles such as SiO₂ particles¹⁹⁻²⁰, Perfluoropolyether (PFPE)²¹, and Al₂O₃ nanoparticles²² for surface modification to achieve superhydrophobicity and oleophobicity.

To decrease surface tension of substrates, silane is one kind of chemicals to interact with substrates for achieving the amphiphobicity. Silane is silicon chemicals consists of the hydrolytic center which can react with hydroxyl group and the long tail of organic substitution.² Many kinds of silanes were used for generated amphiphobic surface. Jin *et al.*²³ studied the superamphiphobic aerogel by chemical vapour deposition of membrane with various kinds of silane, in which 200 μL of (Tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane was used to meet amphiphobicity. Gonçalves *et al.*¹⁹ studied superhydrophobic cellulose nanocomposites by two kinds of fluorosiloxanes. 500 μL of 1H,1H,2H,2H-perfluorooctyl triethoxysilane was applied for obtaining 146.8° of water contact angle on their modified cellulose filter surface. Even silane is the active chemical for producing amphiphobic surface, the environmental issue from using it is in concern. Decreasing amount of silane used in the modification will be a selective way to reduce the harmfulness to nature.

In this study, to obtain amphiphobic papers with high durability, nanocellulose was used to modify two kinds of filter papers, i.e., glass microfiber (GM) filter paper and hydrophilic polytetrafluoroethylene (PTFE) filter paper, using dipping coating method at first and then, the nanocellulose-modified paper was treated by chemical vapor deposition with 50 μL of Trichloro(1H,1H,2H,2H-tridecafluoro-n-octyl)silane (FOTS). The as-obtained amphiphobic paper was characterized by contact angle meter, scanning electron microscope (SEM), and Fourier transform infrared spectroscopy (FTIR) for the investigation of its wettability, morphology, and chemical structure on the amphiphobic surface. The durability of the amphiphobic nanocellulose-modified paper was also tested in various environments including various temperatures, acid and alkaline solutions, salt solutions and seawater. In addition, 10 kinds of liquids in our daily life were used to test its repellent property. It is expected to develop a facile method to fabricate amphiphobic papers with high durability.

2 Experimental

2.1 Materials

Nanocellulose from bleached hardwood was provided by Daio Paper Corporation. GM filter paper (pore size: 1.6 μm; GF/A, Whatman) and hydrophilic PTFE filter paper (pore size: 0.1 μm; H010A047A, Advantec) were used as substrates. FOTS (98%, TCI, Japan) was used as received. Sulfuric acid aqueous solution (47 wt%), sodium hydroxide, sodium chloride, n-hexane, n-octane, n-hexadecane, toluene, ethylene glycol, and formamide were purchased from Wako Pure Chemical Ltd. and used without any further purification. Vacuum pump oil (ultragrade 15) was purchased from Edwards Ltd. Seawater was collected from Aomori bay, Aomori city, Japan, and also used for testing without any pretreatment.

2.2 Preparation of nanocellulose-modified substrates

The substrates (GM filter paper and hydrophilic PTFE filter paper) were cleaned by soaking them in ethanol for 5 h followed by drying them at 110 °C for 12 h. Various concentrations (0.01, 0.1, 0.5 wt%) of nanocellulose dispersions in distilled water were prepared at room temperature. A piece of cleaned substrate was dipped into the well-dispersed nanocellulose aqueous solution for 5 h at room temperature. Then, the substrate was taken out from the dispersion solution and dried overnight at 50 °C under vacuum state. As such, the nanocellulose-modified papers were obtained.

2.3 Amphiphobic treatment

A piece of nanocellulose-modified paper was further treated by 50 μL of FOTS in a 25 ml bottle, which was sealed with a cap and placed in an oven at 90 °C for various periods (1-9 h). Then, the FOTS-treated paper was vacuumed at 50 °C overnight for the removal of the unreacted chemical.

2.4 Characterization

The contact angle measurement was carried out using a contact angle meter (DMe-201, Kyowa Interface Science). A 5 μL drop of liquid (water, n-hexane, n-octane, or n-hexadecane) was applied on the surface of substrates. The contact angle was analyzed by the FAMES software version 3.5.0. All surface contact angle values reported here were the average values of at least three measurements made on different positions of the sample surface.

Surface morphology of paper was examined by a scanning electron microscope (SEM, SU8010, Hitachi) at an acceleration voltage of 1.0 kV. A small piece of paper was fixed on the carbon tape. Then, the sample was sputter-coated with Pt at 15 mA for 20 seconds to avoid charging.

Chemical compositions of substrate was characterized by Fourier transform infrared spectroscopy (FTIR) which was recorded by using Jasco FT/IR-4200 infrared spectrophotometer with wavelengths in the range of 500-4000 cm⁻¹. The sample was cut into a small piece and placed between two mini-KBr plates, following by pressing into a thin pellet for characterization.

2.5 Durability test

To test the effects of various environments on the amphiphobic property of FOTS-treated nanocellulose-modified paper. The selected papers were firstly placed at different environmental temperatures (-30, 9, 30, and 50 °C) for 6 h; various concentrations of NaCl solutions (1, 3, and 5 wt%) for 6 h at room temperature, various solutions with different pH values (1, 3, 5, 7, 9, 11, and 14; prepared by 47 wt% sulfuric acid and sodium hydroxide) for 6 h at room temperature, and seawater in different periods (6, 12, and 24 h) at room temperature, respectively. Then, the pretreated papers were dried at 50 °C overnight under vacuum state for the contact angle measurement.

The FOTS-treated nanocellulose-modified papers were also tested by dropping the 5 μL of ten different kinds of liquids directly for measuring their contact angles. Ten different liquids included seawater, sodium chloride solution (5 wt%), distilled water (7 °C), distilled water (50 °C), sulfuric acid solution (pH = 1), sodium hydroxide solution (pH = 14), toluene, ethylene glycol, formamide, and vacuum pump oil.

Table 1 Contact angles of various liquids on FOTS treated and untreated nanocellulose-modified GM filter papers.

Samples	Average contact angle (°)			
	water	n-hexane	n-octane	n-hexadecane
GM filter paper	0	0	0	0
FOTS treated for 1 h	142	0	128	135
FOTS treated for 5 h	145	0	128	138
FOTS treated for 9 h	148	0	117	137
1.0 wt% nanocellulose/ GM filter paper	0	0	0	0
FOTS treated for 1 h	151	0	81	134
FOTS treated for 5 h	155	0	93	136
FOTS treated for 9 h	154	0	100	120
0.1 wt% nanocellulose/ GM filter paper	0	0	0	0
FOTS treated for 1 h	134	0	53	90
FOTS treated for 5 h	156	0	118	144
FOTS treated for 9 h	154	0	106	140
0.5 wt% nanocellulose/ GM filter paper	0	0	0	0
FOTS treated for 1 h	134	0	43	83
FOTS treated for 5 h	139	0	40	58
FOTS treated for 9 h	128	0	74	95

3 Results and Discussion

3.1 Wettability

Table 1 demonstrates the contact angles of water, n-hexane, n-octane, and n-hexadecane on the FOTS-treated nanocellulose-modified GM filter papers with various loading amounts of nanocellulose and various FOTS treatment periods, comparing with the untreated samples. One can see that the GM filters without nanocellulose modification and FOTS treatment can be wet by water and other three types of non-polar liquids. This is because the GM filter paper is made of borosilicate with the fine capillary structure, which can absorb water and other liquids in fast flow rates for enabling its filtration quality. Moreover, the surface energy of unmodified GM filters should be higher than surface tension of water and other three types of non-polar liquids. For the nanocellulose-modified GM filter papers with various concentrations of nanocellulose but without FOTS treatment, they also show good affinity to water and the three non-polar liquids since the loaded nanocellulose also has a number of hydroxyl groups, which can

create hydrogen bonds with water and organic molecules, and making the liquids spread over the surface.¹⁻² In contrast, for the FOTS-treated papers, the wettability is in the level of hydrophobicity and oleophobicity. Interestingly, for 0.1 wt% nanocellulose-modified GM filter paper, after it is treated by FOTS for 5 h, its surface exhibits superhydrophobicity with a water contact angle as large as 156° and water droplet on the surface becomes marble (Fig. 1A and B). In addition, the nanocellulose concentration has effect on achieving the amphiphobicity. Furthermore, its surface also repels from the non-polar liquids with high molecular weights, i.e. n-hexadecane and n-octane, and the contact angles reach 144° and 118°, respectively (Fig. 1C and D)). It indicates that the obtained surface has both superhydrophobicity and near superoleophobicity in this case. However, it should be noted that it has no oleophobicity for the non-polar liquids with low molecular weight such as n-hexane (Fig. 1E). The different wettability between low and high molecular weights of non-polar liquids comes from the distinctive liquid surface tensions at 20 °C of n-hexane, n-octane, and n-hexadecane which are 18.40, 21.62, and 27.47 mN/m, respectively¹⁴. Here, because the surface energy of the obtained paper is decreased, it cannot be wetted by water, n-hexadecane, and n-octane. However, the surface energy is

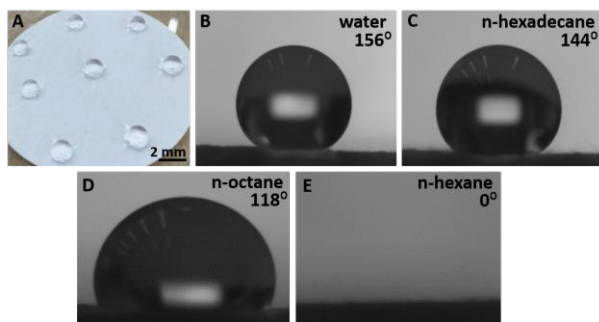


Fig. 1 Liquid droplets on the amphiphobic surface of FOTS treated 0.1wt% nanocellulose-modified GM filter paper. A: water droplets in marble shape; B: water; C: n-hexadecane; D: n-octane; E: n-hexane.

still higher than liquid surface tension of n-hexane, so it can be still wetted by n-hexane.

The contact angles of water, n-hexane, n-octane, and n-hexadecane on the FOTS-treated nanocellulose-modified PTFE filter papers with various loading amounts of nanocellulose and various FOTS treatment periods were also measured. As shown in Table S-1 in supplementary information, the results are similar with those of the FOTS-treated nanocellulose-modified GM filter papers. For 0.1 wt% nanocellulose-modified PTFE filter paper, after it is treated by FOTS for 5 h, its surface also exhibits superhydrophobicity with a water contact angle as large as 153° and water droplet on the surface becomes marble (Fig. S-1A and B)). However, for the three non-polar liquids, its surface only repels from n-hexadecane with a contact angle of 92° (Fig. S-1C). It indicates that this surface also has superhydrophobicity but only have oleophobicity for some non-polar liquids with larger molecular weight. For the non-polar liquids with lower molecular weight, i.e. n-octane and n-hexane, the contact angles are 43° and 26° , respectively (Fig. S-1D and E). Herein, it should be noted that the applied GM filter paper has an average pore diameter of $1.6 \mu\text{m}$ whereas PTFE filter paper has an average pore diameter of $0.1 \mu\text{m}$, which could have some effects on their amphiphobic properties. In this study, the FOTS-treated nanocellulose-modified papers with the best amphiphobic properties are selected for further characterization and testing.

3.2 Surface morphology

Fig.2A, B and C show the morphologies of original GM filter paper, 0.1 wt% nanocellulose-modified GM filter paper and FOTS-treated 0.1 wt% nanocellulose-modified GM filter paper, respectively. One can see that the original GM filter paper is composed of various straight fibers with smooth surface (Fig.2A). After modified with 0.1 wt% of nanocellulose, the glass fibers are found to be significantly covered with nanocellulose (Fig. S-3 A) so that the surfaces of the fibers become rough (Fig. 2B). For the FOTS-treated paper, no significant difference can be found on the morphology (Fig. 2C). However, as shown in the insets of Fig.2, the contact angles of water and n-hexadecane on it have obvious distinction.

Fig. S-2A, B and C show the morphologies of original PTFE filter paper, 0.1 wt% nanocellulose-modified PTFE filter paper and FOTS-treated 0.1 wt% nanocellulose-modified PTFE filter paper, respectively. Comparing with GM filter paper, original PTFE filter paper has denser structure with smaller PTFE fibers and less porosity.

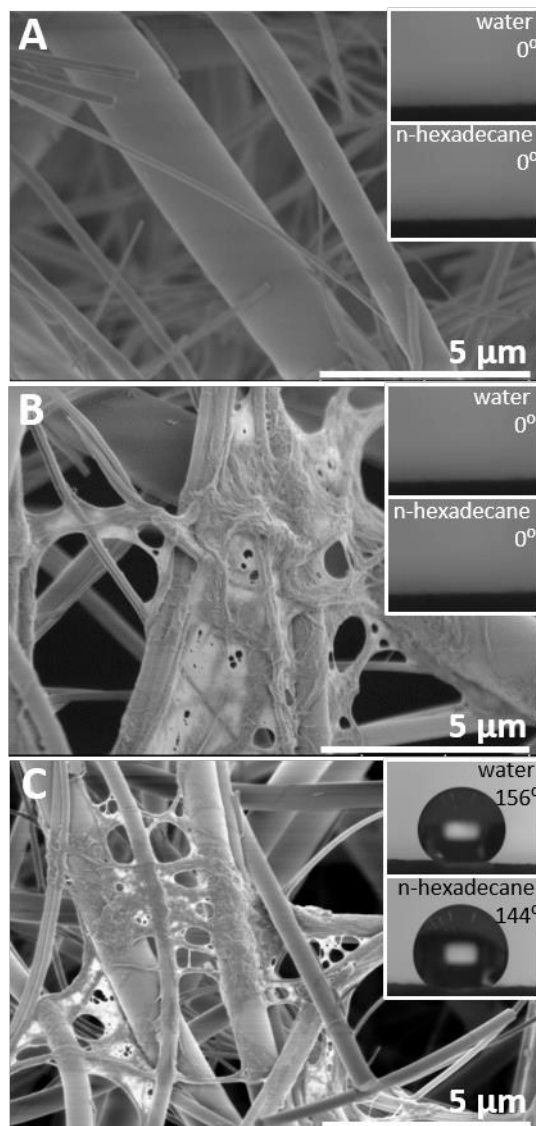


Fig. 2 SEM images of A: GM filter paper; B: 0.1wt% nanocellulose-modified GM filter paper; C: FOTS treated 0.1wt% nanocellulose- modified GM filter paper. Insets: contact angles of water and n-hexadecane.

Similar to the nanocellulose-modified GM filter paper, for the FOTS-treated nanocellulose-modified PTFE filter paper, no significant difference can be found on the morphology (Fig.S-2B and C). However, as shown in the insets of Fig.S-2, the contact angles of water and n-hexadecane on it have obvious distinction, and the FOTS-treated nanocellulose-modified PTFE filter paper also shows superhydrophobicity and oleophobicity. In this study, one main advantage of loading nanocellulose on GM filter paper or PTFE filter

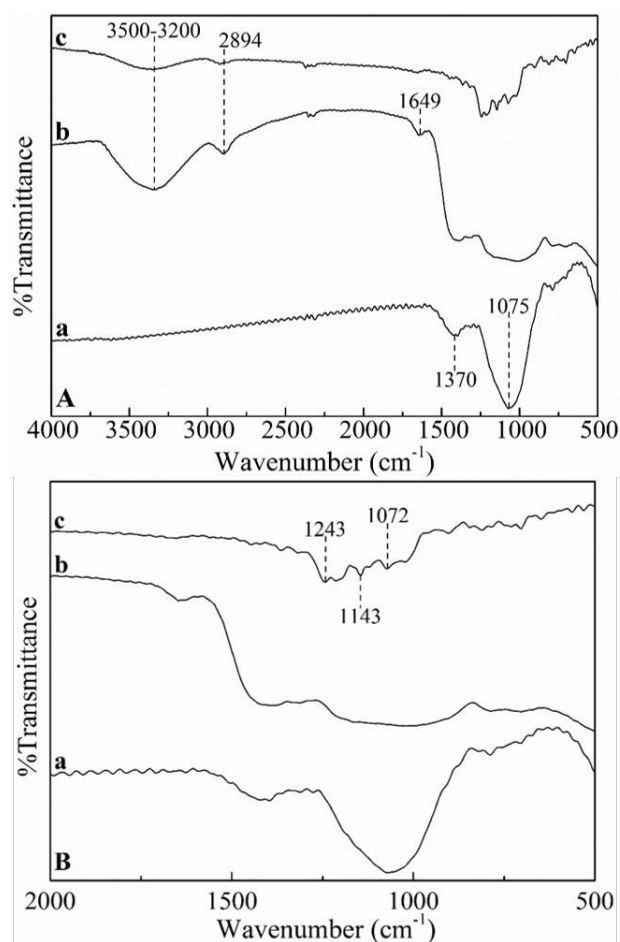


Fig. 3 A: FT-IR spectra of (a) GM filter paper, (b) 0.1wt% nanocellulose-modified GM filter paper, and (c) FOTS treated 0.1wt% nanocellulose-modified GM filter paper; B : Enlargement between 500-2000 cm^{-1} .

paper is to increase the roughness of fibers in the filter paper, which is benefit to modify the wettability of them from hydrophilicity and oleophilicity to superhydrophobicity and oleophobicity.^{1,3,11,13,15,19,24} Arbatan *et al.*²⁴ fabricated superhydrophobic paper by using cellulose nanofibers as binder to coat precipitated calcium carbonate on filter paper, followed by treating with a solution of alkyl ketene dimer in n-heptane, and found that water contact angle on the obtained paper was much larger than that without using cellulose nanofiber as binder. This result is similar as the present study, in which nanocellulose is an effective material for the substrate modification. It should be noted that nanocellulose can be solely used for increasing the roughness on substrate due to its high surface area, which leads to the strong adhesion on the fibers of substrate²⁵, which is the positive for amphiphobicity.

3.3 Chemical structure

Fig. 3 shows FT-IR spectra of (a) GM filter paper, (b) 0.1 wt% nanocellulose-modified GM filter paper, and (c) FOTS-treated 0.1 wt% nanocellulose-modified GM filter paper. Since the GM filter

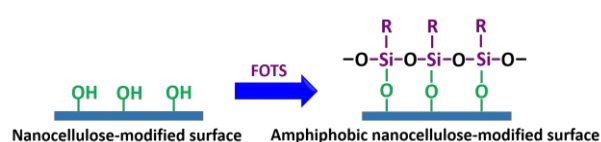


Fig. 4 Schematic of chemical vapor deposition of nanocellulose-modified surface with FOTS ($\text{R} = \text{C}_8\text{H}_{13}\text{F}_4$).

paper is made of 100% of borosilicate glass, its main chemical compositions are silicon dioxide (SiO_2), boric oxide (B_2O_3), and other alkali oxide.²⁶ In its FT-IR spectrum (Fig.3-a), the detected peak at 1370 cm^{-1} is associated with the B-O stretching vibration band while the absorption peak at 1075 cm^{-1} is the asymmetric stretching vibration of Si-O-Si.²⁷ After it is modified by nanocellulose, the absorption peaks at $3500\text{-}3200$ and 2894 cm^{-1} are attributed to the O-H stretching and C-H stretching of nanocellulose, respectively²⁸⁻²⁹ (Fig.S-3 B). In addition, the appearance of the absorption peak at 1649 cm^{-1} indicates the water absorption by nanocellulose. This result confirms that the modification by nanocellulose successfully increases the O-H amounts on the modified substrate. After FOTS treatment, the new absorption peaks are detected at around 1243 and 1143 cm^{-1} (Fig. 3B-c), which are the C-F stretching and symmetric CF_2 stretching of FOTS, respectively.²² Another new absorption peak at 1072 cm^{-1} is associated to Si-O-Si asymmetric stretching vibration of FOTS, indicating that FOTS has reacted with -OH bonds of nanocellulose. Moreover, the intensity of O-H group at $3500\text{-}3200 \text{ cm}^{-1}$ is also decreased due to the less of -OH bonds after amphiphobic treatment. This result confirms that the surface of nanocellulose-modified GM filter paper has been successfully modified by FOTS, resulting in the improvement of wettability to superhydrophobicity and oleophobicity.

Fig. S-4 shows FT-IR spectra of (a) PTFE filter paper, (b) 0.1 wt% nanocellulose-modified PTFE filter paper, and (c) FOTS-treated 0.1 wt% nanocellulose-modified PTFE filter paper. As shown in Fig.S-4-a, the characteristic peaks of PTFE at 1205 , 1150 , and 636 cm^{-1} indicate the stretching of CF_2 group.³⁰ For 0.1 wt% nanocellulose-modified PTFE filter paper, the new peaks at $3500\text{-}3200$, 2894 , and 1649 cm^{-1} are detected, which indicate the existence of nanocellulose (Fig. S-4-b). However, for FOTS-treated 0.1 wt% nanocellulose-modified PTFE filter paper, the peaks corresponding to FOTS and Si-O-Si cannot be detected obviously even though the wettability has been improved from hydrophilicity and oleophilicity to amphiphobicity (Fig. S-4-c). This is because the spectra of new structures such as Si-O-Si from the chemical vapor deposition have been hidden by the main spectra of PTFE, i.e. at the wavelenghtes of 1205 , and 1150 cm^{-1} . Based on these FTIR results, the possible reaction occurred on the nanocellulose-modified filter paper should be as shown in Fig. 4. The filter paper modified by nanocellulose can not only increase the roughness of nanofibers, but also increase the active hydroxyl groups on the paper. With the chemical vapor deposition of FOTS a thin film composed of covalent linkage as shown in Fig.4 leads to the amphiphobicity of nanocellulose-modified papers.^{2, 6, 21-22, 31-32}

3.4 Durability

The durability of amphiphobic surface of FOTS-treated 0.1 wt% nanocellulose-modified GM filter paper was evaluated by measuring the contact angle after putting it in various environments. Fig. 5A shows the contact angles of water and n-hexadecane on it after 6 h soaking in various concentrations of NaCl. The results indicate that the contact angles have no obvious change after soaking in 1, 3, and 5 wt% of NaCl and the wettability still remains in the level of superhydrophobic and oleophobic states. Fig. 5B shows the effect of environmental temperature on the amphiphobicity. One can see that

Fig.5-5 shows the durability of amphiphobic surface of FOTS-treated 0.1 wt% nanocellulose-modified PTFE filter paper, which was also evaluated by measuring the contact angle after putting it in same environments. Almost the similar results were obtained. Thus, it can conclude that the obtained amphiphobic filter papers have excellent durability in various environments.

Table 2 and Fig. 6 represent the contact angles of different kinds of liquids dropped on the amphiphobic surface of 0.1 wt% nanocellulose-modified GM filter paper. One can see that all contact angles of seawater, sodium chloride solution (5 wt%), distilled water (7 °C), distilled water (50 °C), sulfuric acid solution (pH = 1), sodium

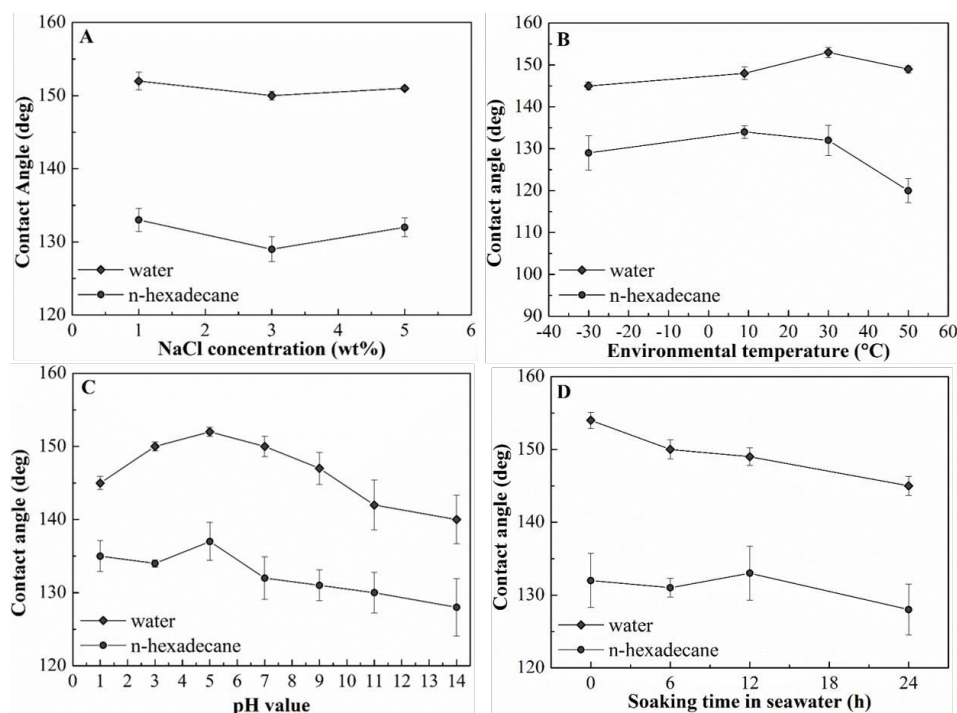


Fig. 5 Durability of the contact angles of water and n-hexadecane on the amphiphobic surface of FOTS treated 0.1wt% nanocellulose-modified GM filter paper in various environments. A: soaking in various NaCl solutions for 6 h ; B: various environmental temperatures ; C: soaking in various solutions with different pH values ; D: soaking in real seawater for different periods.

the amphiphobicity has almost no change at cold environments, and at hot environment (50 °C) contact angles of water and n-hexadecane are decreased less than 10% but still remain in the range of amphiphobicity. Fig. 5C shows the durability of the amphiphobic surface after soaking in various solutions with different pH values. One can see that the water contact angles decrease around 3% and 7% after 6 h soaking in strong acid solution (pH = 1) and strong basic solution (pH = 14), respectively, but still remain in the range of ultrahydrophobicity while the contact angle of n-hexadecane decrease around 3% after soaking in strong basic solution but still remain in the range of ultraoleophobicity. Fig. 5D shows the stability of amphiphobic surface soaked in real seawater for 6, 12, and 24 h. One can see that that the contact angles after 24 h soaking decrease only around 3% and also remain in the range of amphiphobicity.

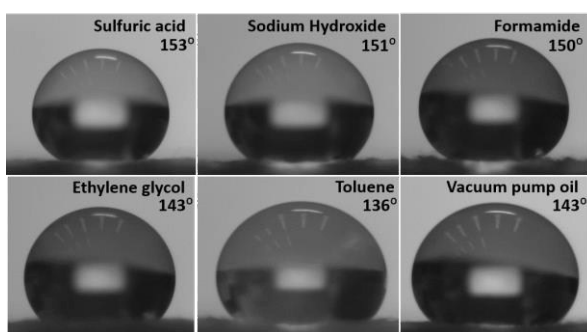


Fig. 6 Various liquid droplets on the amphiphobic surface of FOTS treated 0.1wt% nanocellulose-modified GM filter paper.

hydroxide solution (pH = 14), toluene, ethylene glycol, formamide,

Table 2 Contact angles of various liquids on FOTS treated 0.1wt% nanocellulose-modified GM filter paper

Liquid	Average contact angle (°)
Seawater	153
Sodium chloride solution (5 wt%)	152
Distilled water (7 °C)	150
Distilled water (50 °C)	148
Sulfuric acid solution (pH = 1)	153
Sodium hydroxide solution (pH = 14)	151
Toluene	136
Ethylene glycol	143
Formamide	150
Vacuum pump oil	143

and vacuum pump oil are higher than 135°, indicating that the amphiphobicity is retained for different kinds of liquids. Similarly, as shown in Table S-2 and Fig. S-6, for the amphiphobic surface of 0.1 wt% nanocellulose-modified PTFE filter paper, except for toluene and vacuum pump oil, the contact angles of other liquids are larger than 120°, also indicating that amphiphobicity can be retained for different kinds of liquids.

4 Conclusions

Amphiphobic nanocellulose-modified papers with high durability have been successfully fabricated by a facile two-step methods, in which nanocellulose-modified paper can be prepared by dipping the filter paper such as GM filter paper and PTFE filter paper in dilute nanocellulose dispersed solution and then, the nanocellulose-coated paper is further treated with FOTS by chemical vapor deposition. The obtained paper is found to have superhydrophobicity and oleophobicity which can repel various polar and non-polar liquids. In the optimum condition, the contact angles of water and n-hexadecane reach 156° and 144°, respectively on the amphiphobic surface of 0.1 wt% nanocellulose-modified GM filter paper. Furthermore, the obtained amphiphobic nanocellulose-modified papers exhibit high surface durability in several environments including various temperatures, acid and alkaline solutions, salt solutions and seawater. The novelty of this work is using the advantage of solely nanocellulose which comes from nature to increase the roughness and hydroxyl groups of filter paper for amphiphobic treatment. Meanwhile, the less amount of FOTS used

in reaction is another point that support to decrease harmfulness to environment.

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