# A Facile Method to Prepare Superhydrophobic and Flame-retardant Filter Paper for Effective Oil-water Separation

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A superhydrophobic and flame-retardant filter paper was prepared by a simple immersion process intended for effective oil-water separation. Superhydrophobicity and flame retardancy were achieved *via* a magnesium hydroxide ($Mg(OH)_2$) nanostructure formed on the filter paper surface and subsequent polydimethylsiloxane (PDMS) treatment. The surface chemical composition, phase structure, morphology, and wettability of the as-prepared paper were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffractometry (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and water contact angle (WCA) measurement. The as-prepared paper effectively separated both immiscible oil-water mixtures and oil-in-water emulsions while exhibiting good reusability and flame retardancy. Therefore, this study provided a simple method to prepare multifunctional filter paper, with promising potential applications in oily water treatment.

*Keywords: Superhydrophobic paper; Flame-retardance; Oil-water separation; $Mg(OH)_2$*

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## INTRODUCTION

Currently, clean-up of oil and organic contaminants from oily water is an important worldwide concern due to increasing oil pollution and oil leakage accidents (Wang *et al*. 2017). Superhydrophobic materials with water contact angles greater than 150° have attracted great attention in the field of oil-water separation because they can absorb only oil while repelling water completely, exhibiting high oil-water separation efficiency and selectivity (Guo *et al*. 2017). A diverse range of artificial superhydrophobic materials, such as porous metal mesh (Xu *et al*. 2018), sponge (Xia *et al*. 2018), polyester fabric (Liao *et al*. 2018), and polystyrene microspheres (Yu *et al.* 2017), have been produced for effective oil-water separation. Nevertheless, limitations such as high cost and poor recyclability still persist, and these materials are often difficult to properly dispose after use (Gu *et al*. 2017). Therefore, there is great demand to develop a cost-effective, reusable, and easily disposable superhydrophobic material (Zhou *et al*. 2016; Yu *et al.* 2019).

Filter paper is a low-cost, renewable, and biodegradable material, which is widely used for absorption of liquids and separation of solids and liquids due to its porous structure of microfibers (Piltan *et al.* 2016). However, filter paper cannot selectively remove oils and organic solvents from water due to its inherently high hydrophilicity, and this problem greatly influences its actual oil-water separation efficiency (Peng *et al.* 2016). Thus, it is necessary to modify filter paper for superhydrophobicity. In recent decades, many approaches have been proposed to prepare superhydrophobic paper, such as chemical

grafting (Wu *et al*. 2018), sol-gel process (Wang *et al*. 2019), plasma etching (Dimitrakellis *et al*. 2017), rapid expansion of supercritical $CO_2$ (Werner *et al*. 2010), and layer-by-layer processing (Li *et al*. 2019). However, most of the abovementioned methods are time-consuming and involve complex fabrication processes, toxic and expensive reagents, and sophisticated equipment, hindering their large-scale applications. Moreover, obtained superhydrophobic papers are mainly used for separation of immiscible oil-water mixtures but less used for emulsified oil-water mixtures (Yue *et al*. 2018). Therefore, development of a simple, green, and low-cost method to prepare superhydrophobic paper for separation of oil-water mixtures and emulsions is greatly needed.

This study examined a novel and facile method to fabricate superhydrophobic paper. The superhydrophobic paper was prepared by a simple solution-immersion process involving deposition of a magnesium hydroxide ($Mg(OH)_2$) nanostructure together with subsequent polydimethylsiloxane (PDMS) treatment. Considering the intrinsic flame retardancy of $Mg(OH)_2$, the as-prepared paper was expected to reduce the risk of fire and explosion when used for separation of flammable oils and organic compounds. The obtained superhydrophobic paper was applied to separate oil-water mixtures and oil-in-water emulsions, and the separation performance was evaluated.

## EXPERIMENTAL

### Materials

Filter papers were purchased from Hangzhou Whatman-Xinhua Filter Paper Co., Ltd. (Hangzhou, China). Polydimethylsiloxane (PDMS) pre-polymer (Sylgard 184A) and the curing agent (Sylgard 184B) were obtained from the Dow Corning Corporation (Midland, MI, USA). Analytical grade $MgCl_2$ and NaOH were used without any further purification.

### Preparation of Superhydrophobic Filter Paper

The filter paper was first immersed into the $MgCl_2$ solution (3 M) for 5 min, and it was then immersed into 1 M NaOH solution for 5 s. Finally, the $Mg(OH)_2$-deposited filter paper ($Mg(OH)_2$ filter paper) was immersed into tetrahydrofuran solution containing the PDSM pre-polymer and curing agent (weight ratio of 10:1) for 5 min and subsequently dried at 80 °C for 3 h.

### Characterization

The surface chemical composition of the sample was investigated using X-ray photoelectron spectroscopy (XPS) (Kratos Analytical Ltd., Manchester, UK). The phase structure of the sample was studied using X-ray diffractometry (XRD) (Bruker D8 Advance, Karlsruhe, Germany). The surface morphology of the sample was observed by field-emission scanning electron microscopy (SEM) (FESEM, Hitachi S-4800, Tokyo, Japan) and atomic force microscopy (AFM) (Nanoscope IIIa Multimode, Veeco Co., Santa Barbara, CA, USA). The water contact angle (WCA) of the sample was measured by a contact angle goniometer (OCA20, DataPhysics Instruments GmbH, Filderstadt, Germany) equipped with video capture at ambient temperature with 5 μL testing liquid droplets. Thermogravimetry (TG) and derivative thermogravimetry (DTG) analysis of the sample were performed on a SDT-Q600 modulus thermogravimetric analyzer (TA instruments,

Dekaware, USA). The sample was heated from room temperature to 800 °C at a heating rate of 20 °C/min and under a nitrogen flow rate of 100 mL/min.

### Oil-water Separation Process

The oil-water separation process was performed using a simple filtration method. First, a piece of the paper sample was folded into a "V" shape and put into a funnel. Then, an oil-water mixture (volume ratio of 1:1) was poured into the paper funnel, and the separated oil was collected using a beaker. After separation, the water in the funnel was collected and weighed. The separation efficiency was calculated by the ratio of the weight of water collected and that initially added to the mixture. The separation flux was determined by calculating the volume of oil permeated within 1 min. The entire separation process was solely driven by gravity.

## RESULTS AND DISCUSSION

### Characterization of As-prepared Paper

The surface chemical compositions of the original and modified paper samples were studied by XPS, as shown in Fig. 1(A). As expected, C and O were the only elements detected for the original filter paper, the C/O ratio was 1.51. A new peak at a binding energy of 1304.4 eV, belonging to Mg 1s, was observed after deposition of $Mg(OH)_2$, while a peak at 199.0 eV (Cl 2p) originated from $MgCl_2$. The C/O ratio of $Mg(OH)_2$ filter paper of 0.83 was lower than that of original filter paper. This was due to that the deposition of $Mg(OH)_2$ decreased the content of carbon. After PDMS treatment, two new peaks appeared at binding energies of 101.0 eV (Si 2p) and 153.0 eV (Si 2s), while the peaks of Mg 1s and Cl 2p disappeared, and the C/O ratio increased to 1.42, indicating the formation of a PDMS film on the surface of the $Mg(OH)_2$ filter paper. The phase structures of the paper samples were characterized by XRD, as presented in Fig. 1(B).

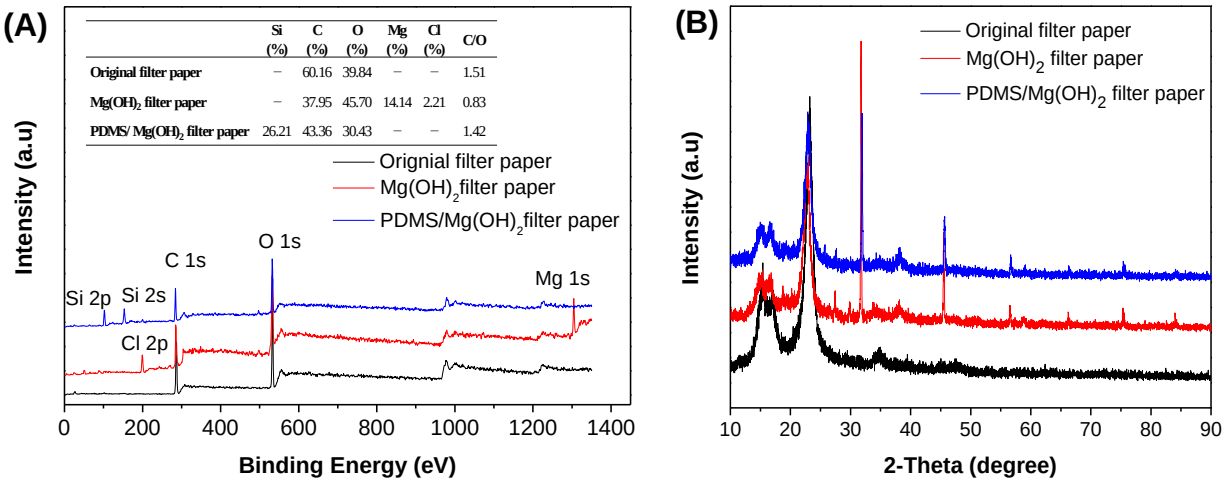


**Fig. 1.** (A) XPS spectra of original and modified filter paper; (B) XRD patterns of original and modified filter paper

The XRD pattern of the original filter paper exhibited three obvious diffraction peaks at 15.4°, 17.1°, and 23.2°, which were attributed to the natural crystallization of

cellulose. The diffraction peaks at approximately 7.7°, 18.8°, 31.8°, 38.2°, 45.5°, 56.5°, 66.2°, 75.3°, and 84.1° in the XRD spectrum of the $Mg(OH)_2$ filter paper were assigned to $Mg(OH)_2$ (JCPDS 83-0114). After PDMS modification, all the characteristic diffraction peaks of $Mg(OH)_2$ were still detected at similar angles, implying no substantive change in the phase structure of the $Mg(OH)_2$. The slight decreases in diffraction peak intensities in the PDMS/$Mg(OH)_2$ filter paper were observed due to the formation of the PDMS coating.

The surface morphologies of the original and modified paper samples were investigated by SEM and AFM, and the representative SEM and 3D AFM images are shown in Fig. 2. The original filter paper was completely composed of cellulose fibers, and the surface of cellulose fibers was relatively smooth, with a arithmetic average roughness ($R_a$) of 10.2 nm (Fig. 2(A) and 2(D)). After the paper was successively immersed into the $MgCl_2$ solution and the NaOH solution, many $Mg(OH)_2$ particles covered the cellulose fiber surface, making the surface rougher with an $R_a$ value of 23.7 nm (Fig. 2(B) and 2(E)). Subsequently, the $Mg(OH)_2$ filter paper was further treated with PDMS, and a uniform film with many nanoscale protuberances appeared on the cellulose fiber surface (Fig. 2(C)). The $R_a$ value increased to 45.3 nm (Fig. 2(F)), which played an important role in the fabrication of the superhydrophobic surface. The original and $Mg(OH)_2$ filter papers were highly hydrophilic and rapidly absorbed water. However, the water droplets on the PDMS/$Mg(OH)_2$ filter paper surface were nearly spherical, and its WCA reached 152.1° (inset in Fig. 2(C)), indicating achievement of a superhydrophobic surface. In contrast, filter paper treated only with PDMS was highly hydrophobic, with a WCA of 128.7°, demonstrating that the synergistic effect of $Mg(OH)_2$ particles and low-surface-energy PDMS was crucial for the preparation of the superhydrophobic surface.

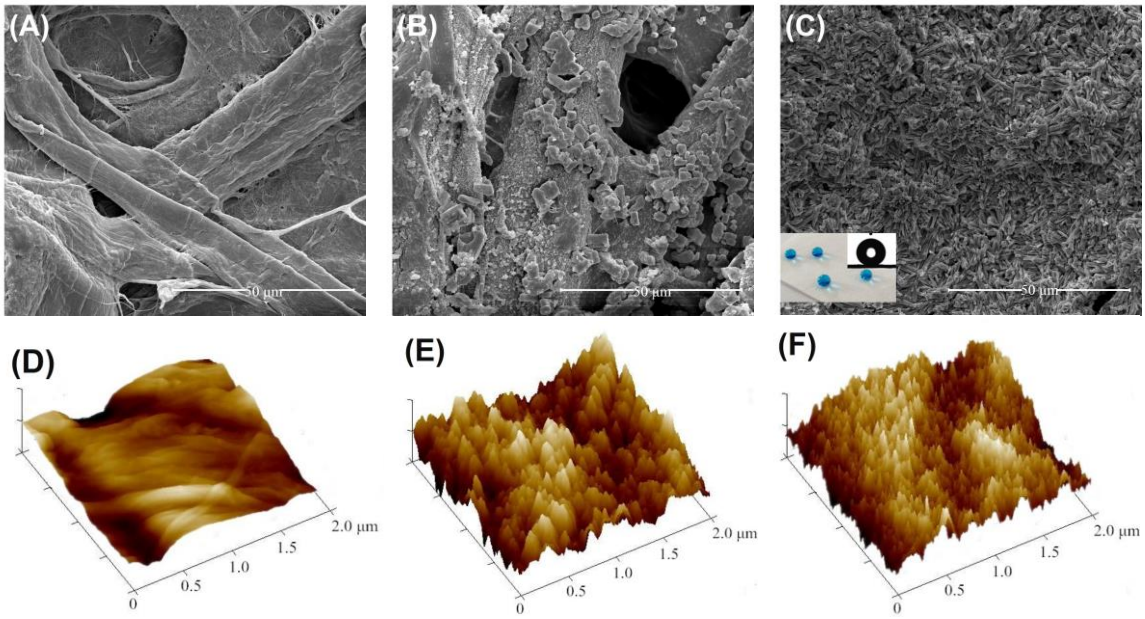


**Fig. 2.** SEM and 3D AFM images of (A and D) the original filter paper, (B and E) the $Mg(OH)_2$ filter paper, and (C and F) the PDMS/$Mg(OH)_2$ filter paper, where the inset shows water droplets on the PDMS/$Mg(OH)_2$ filter paper and the corresponding WCA

## Oil-water Separation

The oil-water separation process was performed as illustrated in Fig. 3(A). When the mixture of n-hexane (dyed by Oil Red O) and water (dyed by methylene blue) was poured into the as-prepared filter paper funnel, the red n-hexane was rapidly absorbed by the paper funnel at first and then passed through the paper funnel into the beaker, while the blue water completely remained in the paper funnel because of its superhydrophobicity. The same separation process was also performed for the petroleum ether-water mixture, the chloroform-water mixture, the dichloromethane-water mixture, and the toluene-water mixture, and all the separation processes were as good as that of the n-hexane-water mixture. The results indicated good separation performance for both water-on-top and oil-on-top mixtures of the as-prepared superhydrophobic filter paper. The separation efficiency for all the tested mixtures was greater than 98.5%. The separation flux values were 7334 mL/($m^2$·h), 5556 mL/($m^2$·h), 6875 mL/($m^2$·h), 6286 mL/($m^2$·h), and 7639 mL/($m^2$·h) for the n-hexane-water, petroleum ether-water, chloroform-water, dichloromethane-water, and toluene-water mixtures, respectively. The separation flux values differed for the tested mixtures due to the viscosity differences among the oils.

The reusability of the superhydrophobic paper also plays an important role in lowering oil cleanup cost. The reusability of as-prepared paper for different oil-water mixtures was investigated, the paper was cleaned thoroughly with ethanol and water after each cycle, and the results are shown in Fig. 3C. It can be found that the reusability was similar for five different oil-water mixtures and the separation efficiceny slightly decreased throughout the whole cycles. After 30 cycles, the separation efficiency of the as-prepared paper for all the tested mixtures remained greater than 98%, indicating good reusability of the as-prepared superhydrophobic paper.

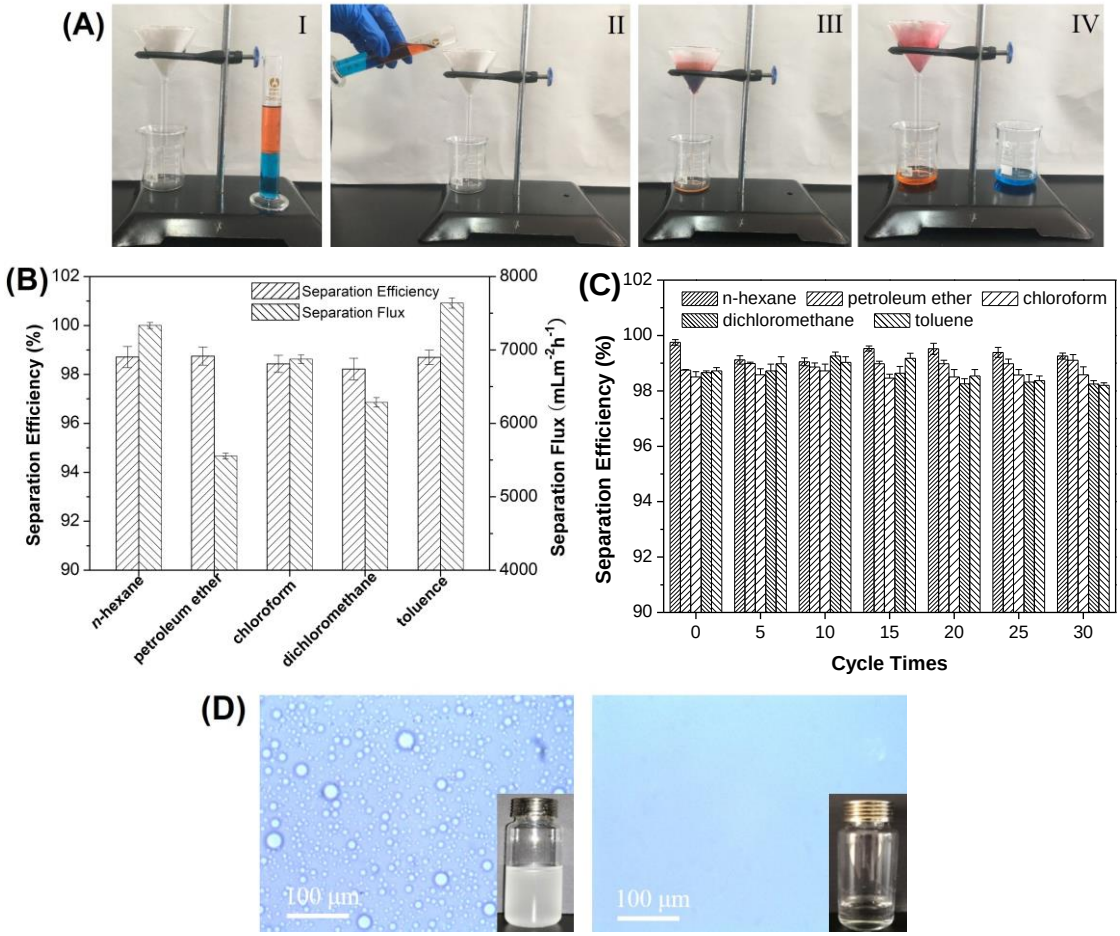


**Fig. 3.** (A) Separation process for n-hexane and water mixture using the as-prepared superhydrophobic filter paper; (B) separation efficiency and separation flux for different oil-water mixtures; (C) effect of number of cycles on the separation efficiency of the as-prepared superhydrophobic filter paper; (D) optical microscopy images of the oil-in-water emulsion before and after separation

Furthermore, the obtained superhydrophobic paper could also separate surfactant-free oil-in-water emulsions. The oil-in-water emulsion was prepared by mixing n-hexane and water in a volume ratio of 1:9 with intense ultrasonic dispersion for 2 h to produce a stable emulsion. When poured into the filter paper funnel, the oil-in-water emulsion was immediately demulsified upon contact with the paper. The oil wetted and permeated through the paper funnel, while the water was retained in the paper funnel. The feed emulsion was milky white, while the collected filtrate was transparent. This result indicated the oil-in-water emulsion separation capability of the obtained superhydrophobic paper. Light microscopy showed that there were almost no water droplets present in the oil filtrate (Fig. 3D), further indicating that the oil-in-water emulsion was successfully separated by the superhydrophobic filter paper.

## Thermal Stability and Flame Retardancy

The flame retardancy of the as-prepared superhydrophobic paper can improve its environmental adaptability when it is used in a flammable environment. Flame-retardant paper could delay ignition and hinder flame propagation, thus reducing the risk of fires. As

the decomposition process of materials is closely related to their flammability, TG and DTG were used to investigated the thermal stability of the as-prepared paper. The TG and DTG curves of the paper samples are presented in Fig. 4.

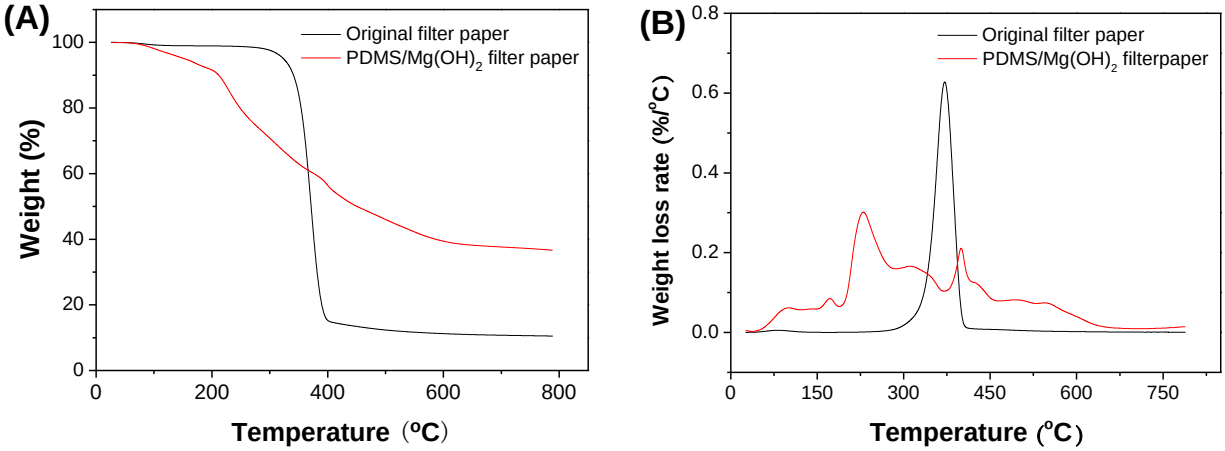


**Fig. 4.** (A)TG and (B) DTG curves of the original and as-prepared superhydrophobic filter papers

The starting decomposition temperature ($T_{-10\%}$) of the original filter paper was about 340 °C, and the maximum weight loss temperature ($T_{max}$) occurred at 374 °C due to the depolymerization of cellulose with the generation of $CO_2$ and volatile hydrocarbons. However, the PDMS/$Mg(OH)_2$ filter paper showed a reduced $T_{-10\%}$ at 212 °C and $T_{max}$ at 232 °C presumably due to the earlier degradation of $Mg(OH)_2$ or PDMS. Furthermore, there was obvious difference of residue weight percentage at 800 °C for this two paper samples. The residue weight percentage of original paper was only 10%, but the residue weight percentage of as-prepared superhydrophobic paper increased to 38% due to the presence of flame retardant $Mg(OH)_2$ and PDMS. These results indicated that thermal stability was improved by the introduction of $Mg(OH)_2$ and PDMS coating.

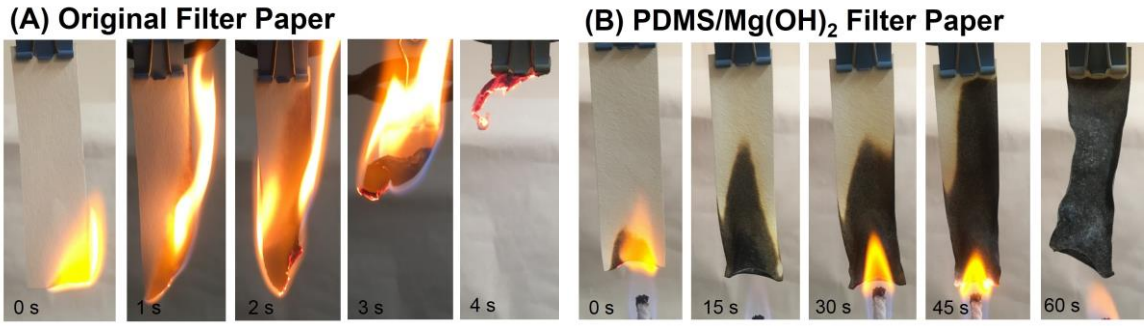


**Fig. 5.** Flame retardancy tests of the original and as-prepared superhydrophobic filter papers based on the vertical combustibility method

In addition, the paper samples were subjected to flammability tests using a vertical combustibility method in order to further test their flame-retardant properties. As shown in Fig. 5, the original filter paper was used as the control sample. As expected, the original filter paper easily burnt within 5 s. In contrast, when the as-prepared superhydrophobic

paper was exposed to the fire, there was no obvious flame on the paper, and the paper could preserve its structural integrity for at least 1 min. This result indicated that the as-prepared superhydrophobic paper had good flame retardancy.

## CONCLUSIONS

1. A superhydrophobic and flame-retardant filter paper was successfully prepared by deposition of $Mg(OH)_2$ onto the paper surface using a simple solution-immersion method and subsequent hydrophobic treatment with PDMS.
2. The synergetic effect of the rough $Mg(OH)_2$ nanostructure and the low-surface-energy PDMS was essential for the construction of the superhydrophobic surface.
3. The obtained superhydrophobic filter paper exhibited good performance for both water-on-top and oil-on-top mixtures, and the separation efficiency reached 98.5% for all the tested mixtures. After 30 cycles, the obtained paper retained high separation efficiency, indicating excellent reusability. The obtained superhydrophobic filter paper could also separate oil-in-water emulsions and exhibited good flame retardancy.

## ACKNOWLEDGMENTS

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## REFERENCES CITED

Dimitrakellis, P., Travlos, A., Psycharis, V. P., and Gogolides, E. (2017). "Superhydrophobic paper by facile and fast atmospheric pressure plasma etching," *Plasma Process. Polym.* 14(3). DOI: 10.1002/ppap.201600069

Gu, J., Xiao, P., Chen, P., Zhang, L., Wang, H., Dai, L., Song, L., Huang, Y., Zhang, J., and Chen, T. (2017). "Functionalization of biodegradable PLA nonwoven fabric as superoleophilic and superhydrophobic material for efficient oil absorption and oil/water separation," *ACS Appl. Mater. Inter.* 9(7), 5968-5973. DOI: 10.1021/acsami.6b13547

Guo, F., Wen, Q., Peng, Y., and Guo, Z. (2017). "Simple one-pot approach toward robust and boiling-water resistant superhydrophobic cotton fabric and the application in oil/water separation," *J. Mater. Chem. A* 5(41), 21866-21874. DOI: 10.1039/C7TA05599D

Li, H., Wang, X., He, Y., and Peng, L. (2019). "Facile preparation of fluorine-free superhydrophobic/superoleophilic paper *via* layer-by-layer deposition for self-cleaning and oil/water separation," *Cellulose* 26(3), 2055-2074. DOI: 10.1007/s10570-018-2187-3

Liao, X., Li, H., Zhang, L., Su, X., Lai, X., and Zeng, X. (2018). "Superhydrophobic mGO/PDMS hybrid coating on polyester fabric for oil/water separation," *Prog. Org. Coat.* 115, 172-180. DOI: 10.1016/j.porgcoat.2017.12.001

Peng, H., Wang, H., Wu, J., Meng, G., Wang, Y., Shi, Y., Liu, Z., and Guo, X. (2016). "Preparation of superhydrophobic magnetic cellulose sponge for removing oil from water," *Ind. Eng. Chem. Res.* 55(3), 832-838. DOI: 10.1021/acs.iecr.5b03862

Piltan, S., Seyfi, J., Hejazi, I., Davachi, S. M., and Khonakdar, H. A. (2016). "Superhydrophobic filter paper *via* an improved phase separation process for oil/water separation: Study on surface morphology, composition and wettability," *Cellulose* 23(6), 3913-3924. DOI: 10.1007/s10570-016-1059-y

Wang, Q., Xiong, J., Chen, G., Xinping, O., Yu, Z., Chen, Q., and Yu, M. (2019). "Facile approach to develop hierarchical roughness fiber@$SiO_2$ blocks for superhydrophobic paper," *Materials* 12(9). DOI: 10.3390/ma12091393

Wang, Q., Yu, M., Chen, G., Chen, Q., and Tai, J. (2017). "Facile fabrication of superhydrophobic/superoleophilic cotton for highly efficient oil/water separation," *BioResources* 12(1), 643-654. DOI: 10.15376/biores.12.1.643-654

Werner, O., Quan, C., Turner, C., Pettersson, B., and Wågberg, L. (2010). "Properties of superhydrophobic paper treated with rapid expansion of supercritical $CO_2$ containing a crystallizing wax," *Cellulose* 17(1), 187-198. DOI: 10.1007/s10570-009-9374-1

Wu, H., Wu, L., Lu, S., Lin, X., Xiao, H., Ouyang, X., Cao, S., Chen, L., and Huang, L. (2018). "Robust superhydrophobic and superoleophilic filter paper *via* atom transfer radical polymerization for oil/water separation," *Carbohyd. Polym.* 181, 419-425. DOI: 10.1016/j.carbpol.2017.08.078

Xia, C., Li, Y., Fei, T., and Gong, W. (2018). "Facile one-pot synthesis of superhydrophobic reduced graphene oxide-coated polyurethane sponge at the presence of ethanol for oil-water separation," *Chem. Eng. J.* 345, 648-658. DOI: 10.1016/j.cej.2018.01.079

Xu, Z., Jiang, D., Wei, Z., Chen, J., and Jing, J. (2018). "Fabrication of superhydrophobic nano-aluminum films on stainless steel meshes by electrophoretic deposition for oil-water separation," *Appl. Surf. Sci.* 427, 253-261. DOI: 10.1016/j.apsusc.2017.08.189

Yue, X., Zhang, T., Yang, D., Qiu, F., and Li, Z. (2018). "Janus ZnO-cellulose/$MnO_2$ hybrid membranes with asymmetric wettability for highly-efficient emulsion separations," *Cellulose* 25(10), 5951-5965. DOI: 10.1007/s10570-018-1996-8

Yu, M., Wang, Q., Yang, W., Xu, Y., Zhang, M., Deng, Q., and Liu, G. (2019). "Facile fabrication of magnetic, durable and superhydrophobic cotton for efficient oil/water separation," *Polymers* 11(3), 442. DOI: 10.3390/polym11030442

Yu, M., Wang, Q., Zhang, M., Deng, Q., and Chen, D. (2017). "Facile fabrication of raspberry-like composite microspheres for the construction of superhydrophobic films and applications in highly efficient oil–water separation," *RSC Adv.* 7(63): 39471-39479. DOI: 10.1039/C7RA07250C

Zhou, S., Liu, P., Wang, M., Zhao, H., Yang, J., and Xu, F. (2016). "Sustainable, reusable, and superhydrophobic aerogels from microfibrillated cellulose for highly effective oil/water separation," *ACS Sustain. Chem. Eng.* 4(12), 6409-6416. DOI: 10.1021/acssuschemeng.6b01075

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