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Underwater Low Adhesive Hydrogel-Coated Functionally Integrated Device by One-Step Solution-Immersion Method for Oil-water Separation

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To handle seriously oil spills, many strategies have been proposed to design novel materials for oil-water separation. Especially, conventional oil-water separation process with superhydrophobic-superoleophilic materials are easily fouled by adsorbed oils thus result in the quick decrease of flux and separation efficiency. However, superhydrophilic and underwater superoleophobic materials have shown advantages in overcoming above mentioned problems. In this paper, we developed a facile method for fabricating underwater low adhesive hydrogel-coated functionally integrated device. Due to its superhydrophilicity and underwater superoleophobicity, the separation of oil from oil-water mixtures was achieved by allowing water permeating through. The separation efficiency for various oils were above 98%, and for dichloromethane even reached 99.5%. What is more, the as-prepared device can be cycled 6 times and still had high separation efficiency. In addition to the underwater oil-repellent and water-absorbing capabilities, the as-prepared device exhibited also magnetic property and it can float easily on dichloromethane. Hence, by simply moving the device using a magnet, the device can absorb the floating little water from the dichloromethane, thereby purifying the oil underneath. It is expected that superhydrophilic and underwater superoleophobic oil-water separation materials achieve industrial scale production and be used for oily wastewater treatment in the near future.

Introduction

In recent years, the frequent occurrence of oil spills has been a serious threat to marine and aquatic ecosystems. The environmental and economic demands also emphasize the need for materials which can effectively separate oil and water. In order to handle these environmental issues caused by oil spills, all kinds of oil-water separation methods have been developed to recover spilt oil from marine environments, such as physical diffusion, bioremediation, [1-2] oil skimmers [3] and so on. Owing to the difference of interfacial effects for oil and water, utilizing the wetting behavior of solid surfaces to design an oil-water separating materials has attracted a great deal of attention in fundamental research and for potential application in the field of oil-water separation. Since the first report 2004, Jiang and coworkers fabricated a superhydrophobic mesh for separation of oil and water.[4] Meanwhile, a series of oil-water separating materials with both superhydrophobic and superoleophilic properties have been fabricated via various methods.[5-11] However, conventional oil-water separation process with superhydrophobic-superoleophilic materials are easily fouled, blocked up and even damaged by oils because of their intrinsic oleophilicity, resulting in a quick decrease in separation efficiency, flux, and film life, and even secondary pollution. These disadvantages have seriously restricted its practical application in oil-water separation. To solve these problems, a new strategy must urgently be found. Inspired by the underwater superoleophobicity of fish scales, several additional superhydrophilic-superoleophobic materials have been proposed [12–18] for oil-water separation. Compared with conventional superhydrophobic-superoleophilic oil-water separation materials, these superhydrophilic and underwater superoleophobic materials [19-21] can allow water infiltration but prevent oil penetration and may solve oil fouling during the separating process very well. Despite much progress in this field, some of these superhydrophilic and underwater superoleophobic materials with micro-nano structures are easily destroyed under severe environmental conditions, thus resulting in the reduction of flux and film life. Meanwhile, some of these fabrication processes are usually time-consuming which may have limited their practical application and their production on a large scale.

The best strategy for the facile and simple method is to introduce hydrogel coating on the material surface and then realize the separation of oil-water mixtures. Jiang and cowokers designed and fabricated a novel superhydrophilic and underwater superoleophobic polyacrylamide (PAM) hydrogel-coated mesh and then successfully applied it to the

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separation of oil-water mixtures.[15] Because most superhydrophiliic materials can only collect water on the oil surface, it is urgent for a device to be designed and produced which will enable the targeted recovery of water. The best strategy for the directional locomotion of an object on the oil surface is to introduce magnetically responsive materials into the system and then apply a magnetic field to drive the object to the targeted position. In the presence of an external magnetic field, this device can easily remove water droplets located at different places. To the best of our knowledge, there are few reports about the fabrication of functionally integrated device consisting of superhydrophilic and underwater superoleophobic coating to clean up and collect oil spills. Therefore, in this paper, we have developed a facile and simple strategy to prepare a low-adhesive and hydrogel-coated functionally integrated device on magnetic nickel foam for highly efficient oil-water separation. For the as-prepared device, the superhydrophilicity and underwater superoleophobicity of the hydrogel coating just allowed the water layer to infiltrate while the oil layer was prevented from passing through. In this way, the device could selectively and efficiently separate oil from a variety of oil-water mixtures without external power. What is more, the as-prepared device can selectively absorb water droplet from the oil interface. In the presence of an external magnetic field, the as-prepared device can easily remove water droplets located at different places, remove and collect the little water into the interior of the device, exhibiting a directionality and selectivity. This novel method may provide a facile and simple strategy for separating complex oil-water mixtures in oil spill accidents.

Results and discussion

We had obtained a magnetic material, with highly efficient oil-water separation capability, using a facile and easily scalable fabrication technique based on inexpensive materials. The starting material is commercially available and poriferous nickel foam, which is widely used for various applications such as catalyst material, electrode material, etc. The porous and 3D textural nickel foam can provide more contact area for PAM-hydrogel. The underwater low adhesive hydrogel-coated functionally integrated device was fabricated as the following process. First, the nickel foam was folded to a rectangular box without top roof with an edge length of 3cm × 3cm × 1cm; the as-prepared box was washed by dipping in ethanol three times, 10 min each time, and dried carefully under nitrogen flow. Second, the one-step process used to obtain the superhydrophilicity and underwater superoleophobicity were realized by immersing the topless nickel foam box into a mixture solution of acrylamide and sonicated under a power of 0.3 kW for 15 min at room temperature and ambient pressure, followed by sufficient washing with deionised water. In this step, PAM was chosen as the coating material, in which N,N'-Methylenebisacrylamide (BIS) served as the chemical cross-linker. Compared to other polymerization method, the ultrasonic polymerization was relatively simple and easy to operate. The as-prepared nickel foam box coated hydrogel had been wetted by the deionised water right now. In order to check whether the immersion process provided a layer of PAM hydrogel, we characterized the surface morphology of the nickel foam before and after immersion with scanning electron microscopy (SEM). Fig. 1a showed a typical SEM image of nickel foam surface, the average diameter of pores was around 300 µm. In order to clearly see the topography of the porous hydrogel layer, we had carried on the freeze drying for the sample. From Fig. 1b indicated a large-area of staggered holes covered with a thick and compact porous hydrogel layer, forming the superhydrophilic surface. The surface elements were detected by energy dispersive xray spectrom (EDX) before and after modification. As shown in Fig. 1c, before the immersion step, nickel was the dominant element on the surface and there were almost no signals detected from carbon or oxygen atoms. After the immersion step, the signal of carbon and oxygen atoms, which were contained in PAM hydrogel, appeared clearly in the EDX spectra. The detailed EDX element-distribution pattern showed that the C and O atoms were distributed homogeneously on the surface of the nickel foam, indicating the presence of the PAM hydrogel layer, as shown in Fig. 1d.

Surface morphology and chemical composition are two important factors which significantly affect the wettability of a solid surface. The chemical composition determines whether the surface is hydrophilic or not, while the morphological structure will amplify this surface property to superhydrophilicity or superhydrophobicity. Hydrogel with excellent water-absorbing and water-retaining capacities is one of the most typical hydrophilic materials and is considered to be promising candidate for designing novel water-removing materials for oil-water mixtures separation. After we obtained the nickel foam box covered by PAM hydrogel, we expiored its surface wetting properties through dropping a drop of water onto the surface of nickel foam box. The water droplet easily spreaded and penetrated the surface when it was in contact with the surface coated by hydrogel, and the water droplet dropped down when more water was added. The surface was superhydrophilic, with contact angle (CA) about 0° (Fig. 2a). However, the water droplet CA on bare nickel foam surface was less than 90°, indicated the hydrophilicity of surface, as shown in Fig. 2b. Obviously, a water droplet standing on the surface of nickel foam and cannot penetrate through spontaneously because of the negative capillary effect. So these phenomena indicated that superhydrophilicity had generated on the nickel foam surface after modification by hydrogel. This difference of wettability provided a possibility for water-oil separation through the as-prepared surface.

It is well-known that superhydrophobic surface originate from the special formation of a water-air-solid system. According to the theory developed by Cassie et al., [22] stable air molecules exist on the surface of micro-nanostructures, forming a water-air-soild interface. This strategy will help us study the wetting behavior in the oil-water-soild system. When hydrogel coated on nickel foam contacted with the oil-water mixture, water molecules were trapped in the hydrogel coating, forming an oil-water-solid interface. This new

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composite interface showed superhydrophilic and underwater superoleophobic properties. To verify the surface wettability and low adhesive property underwater, the oil droplets were applied to the as-prepared hydrogel-coated functionally integrated device underwater. From Fig. 3a, we can observe that a round oil droplet formed on the surface of the as-prepared device with an oil contact angle (OCA) of 150.1°, which indicated the underwater superoleophobicity of the surface. With slowly moving the injection syringe, we can take notice of the paralleled movement of the oil droplet without any residual oil droplet on the surface. The shape of the oil droplet was spherical during the whole movement, which indicated the surface had a low adhesion property to the employed oil (Fig. 3b,c). To further study the oil wettability of the as-prepared device surface, another oil droplet was also utilized on the inclined surface. The OCA measurement results of as-prepared device with oil droplet sliding angle 3° ± 0.5°were presented in Fig. 3d-f. Accordingly, the oil-water mixture can be well separated via the hydrogel-coated functionally integrated device due to the different wettabilities of its surface including superhydrophilicity and underwater superoleophobicity.

After fabricating the underwater low adhesive hydrogel-coated functionally integrated device and demonstrating the superhydrophilicity and underwater superoleophobicity, the device was evaluated with regard to oil-water separation. An oil-water mixture was constructed by adding 5 mL of deionized water into 5 mL of blue-dyed dichloromethane, forming separate upper and bottom layers composed of water and oil phases, respectively. The as-prepared device was positioned over the top of a beaker, and the oil-water mixtures was poured into the interior of the device, as shown in Fig. 4a, b. Driven by gravity only, the superhydrophilic property of hydrogel allowed the water to pass quickly through the device and into the supporting beaker (Fig. 4c). From the amplifying Fig. 4c, we can observe that the blue oil layer was still stored in the device. No leakage of oil was observed in the supportive beaker, which was due to the underwater superoleophobic surface of the device. By taking advantage of the difference in wettability between oil and water, the oil-water mixtures were separated successfully without any external force, indicating its easy operation and low energy consumption.

In order to understand the separation efficiency of the as-prepared device, we have taken a dichloromethane-water mixture as an example to separate dichloromethane from water. A total of 5ml dichloromethane labeled with blue dye (Fig. 5a, a') was added to a beaker containing 5ml of water. Since the density of water was lower than that of dichloromethane, the added water finally floated on the dichloromethane surface (Fig. 5b). When we poured the dichloromethane-water mixture into the as-prepared device, water was soon taken up by the device, infiltrated through the walls, and finally gathered into the beaker due to gravitational effects (Fig. 5c). And then, the collected dichloromethane in the device was transferred to the original pipette, as shown in Fig. 5c'. According to the original added volume of the dyed dichloromethane (5 mL), we could calculate the collecting efficiency to be 99.5%.

As oil spill accidents occur frequently throughout the world, it is crucial to extend the application of the device for different oil-water mixtures, such as toluene, dichloromethane, canola oil and n-hexane. Separation efficiency was used to quantitatively describe the separation ability of device. It can be defined according to the ratio between the volume of collected oil after separation and that of original. As shown in Fig. 5d, the separation efficiencies of the as-prepared device for various oils were all above 98%, nearly no visible oil existed in the permeated water, demonstrating the high efficiency of the as-prepared device in oil-water separation. What is more, the as-prepared device can be reused 6 times and still had high separation efficiency, for each time of separation, the collection efficiency of dichloromethane-water mixture was over 97%, which demonstrated its reproducibility, as shown in Fig. 5e. These results indicated that this novel superhydrophilic and underwater superoleophobic device was a potential candidate for oil-water separation, which would provide promising possibilities in industrial applications.

For oil-water separation, a series of immiscible oil-water mixtures were poured onto the as-prepared device. Water immediately permeated through the surface and oils were retained above. The oil content in water after only one separation was measured by total organic carbon analyzer. During the course of the experiment, the solubility of oil in water is different with the oil type. The oil content in water also existed large difference. As shown in Fig. 6a, for the immiscible oil-water mixtures（dichloromethane, toluene, n-hexane）, the oil contents were respectively 961.5 ppm, 267.5ppm, 194.1ppm. The water flux were calculated by measuring the time for different kinds of oil-water mixtures, as shown in Fig. 6a. The highest fluxes of 425 and 384.1 $Lm^{-2}h^{-1}$ were achieved for the hexane-water and dichloromethane-water mixtures, respectively. This result indicated that the type of oils had little effect on permeating flux. For canola oil, after making it and water stirred thoroughly, the oil-water mixtures need take a long time to stratify. So the oil content in water was high (5055ppm) and the water flux was relatively low (36.67 $Lm^{-2}h^{-1}$). In order to verify the repeatability of the as-prapared device, we had relized the test of the water flux for every cycle. During the six cycles experiments, the water flux was about 380 $Lm^{-2}h^{-1}$ and kept stable. This is because the as-prepared device only allows water to permeate, as shown in Fig. 6b.

Besides their ideal underwater superoleophobic property and high water-absorption capacity, the as-prepared device can also be actuated onto oil zones by means of a weak magnetic field. To confirm the hypothesis, we designed a system featuring a dichloromethane layer containing drops of dyed water at the surface of the beaker. The system was constructed by adding 0.1ml of dyed water, whose density is lighter than dichloromethane, at different places at the surface of beaker (Fig. 7a). Afterwards, the as-prepared device was placed on the surface of the system. At the beginning, the as-prepared device was floating over the oil surface, as shown in

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Fig. 6a. In this case, the as-prepared device remained immobile and could not absorb the blue water automatically. To pull the as-prepared device to directionally towards the dyed water, we applied an external magnetic field above the beaker. Guided by the movement of the magnet, the as-prepared device can directionally clean up the dyed water (Fig. 7b,c). When just coming into contact with the blue water droplets, the device quickly absorbed them. No blue water droplets were left on the surface (Fig. 7d), indicating the excellent capability of the device to directionally clean up the little water on the oil surface. The result demonstrated that the as-prepared device performed well, not only in the directional water collection, but also in the controlled magnetically responsive water absorption, exhibiting integrated functions. This design had broadened the application of as-prepared device in water-oil separation by the additional magnetic field. Meanwhile, the as-prepared device may be applied to closed-system to clean up little water, such as gas tanks, petroleum pipeline.

Experimental

Materials and instruments

Oil Blue 35 (Askul Co., Ltd., Japan), canola oil (Nisshin Oillio Co., Ltd., Japan), nickel foam (Anping Huirui Wire Mesh Manufacture Co., Ltd., China). Toluene, dichloromethane, n-hexane, alcohol, Acrylamide (C_3H_5NO, 97%), N,N'-Methylenebisacrylamide ($C_7H_{10}N_2O_2$), Ammonium persulfate ($H_8N_2O_8S_2$) and N,N,N',N'-Tetramethylethylenediamine ($C_6H_{16}N_2$) were purchased from Nacalai tesque and Alfa Aesar, used as received.

Scanning electron microscopy (SEM) measurements were carried out on an EVO MA 25 instrument at 20.0 kV. Photographic images were taken with a Nikon camera (D5000). Total organic carbon analyzer were carried out on a TOC-V CPH instrument (SHIMADZU). The CA was characterized on the OCA20 instrument (Data Physics Instruments Gmbh, Filderstadt).

Fabrication of the superhydrophilic and underwater superoleophobic nickel foam

The superhydrophilic and underwater superoleophobic surface was fabricated by one-step solution-immersion method. A topless nickel foam box was immersed into a mixture aqueous solution of acrylamide (35 mmol), N,N'-Methylenebisacrylamide (0.2 mmol), ammonium persulfate (0.1 mmol) and N,N,N',N'-Tetramethylethylenediamine (10 µl). Afterward, the mixture solution was sonicated under a power of 0.3 kW for 15 min. Then, the topless nickel foam box was taken out of the mixture solution and rinsed three times by deionised water.

Separation of dichloromethane from oil-water mixture

In order to distinguish dichloromethane from oil-water mixture, we dyed the layer with Oil Blue 35 to indicate the directional delivery. The labeled dichloromethane (5 mL) and 5 mL of water were added into a beaker forming the oil-water mixture solution. After the as-prepared device put on the top of the supporting beaker, water was allowed to penetrate the surface rapidly while dyed dichloromethane was prevented. Then the dichloromethane was collected and measured its volume.

Magnetically driven floating device for the removal of little water from oil

The system was constructed by adding water, whose density is lighter than dichloromethane, at different places on the surface of watch glass. We dyed the water to a blue colour, to distinguish the dichloromethane from water. Afterwards, the as-prepared device was placed on the surface of the system, which floated due to its underwater superoleophobicity. By employing an external magnetic field, the as-prepared device can be driven and directionally clean up dyed water.

Conclusions

In summary, we develop a facile method for fabricating underwater low adhesive hydrogel-coated functionally integrated device to separate oil from mixtures with water. In particular, the commercially available nickel foams are functionalized by means of hydrogel coating. Compared with other preparation methods, the nickel foams coated by hydrogel are also a promising approach in oil-water separation. The technique is simple and easy to be scaled up, while the employed materials are inexpensive and some of them can be recycled. Therefore, we propose the use of the developed systems in the selective removal of little water from oil surface by means of a magnetic field, underwater superoleophobic, and water-absorbing nickel foams from a distance toward the targeted areas with minimal energy consumption. By taking advantage of the superhydrophilic and underwater superoleophobic properties, we have realized the effective separation of oil-water mixtures, which demonstrated a re-collecting efficiency as high as 99.5%. What is more, it also can be reused 6 times and still had high separation efficiency. We believe that the as-prepared device will provide a novel strategy for handling oil spills under various conditions and can be applied in other oil-water separating systems.

Notes and references

1 R. Z. Hoff, *Pollut. Bull*., 1993, **26**, 476.
2 R. M. Atlas, *Biotechnol.*,1991, **52**, 149.
3 M. Fingas, *Chem. Ind.*, 1995, **24**, 1005.
4 L. Feng, Z. Y. Zhang, Z. H. Mai, Y. M. Ma, B. Q. Liu, L. Jiang and D. B. Zhu, *Angew. Chem., Int. Ed.*, 2004, **43**, 2012.
5 T. Darmanin, M. Nicolas and F. Guittard, *Phys. Chem. Chem. Phys.*, 2008, **10**, 4322.
6 Q. Zhu, N. Chen, F. Tao and Q. M. Pan, *J. Mater. Chem.*, 2012, **22**, 15894.
7 J. Li, L. Shi, Y. Chen, Y. B. Zhang, Z. G. Guo, B. L. Su and W. M. Liu, *J. Mater. Chem.*, 2012, **22**, 9774.
8 X. M. Liu and J. H. He, *Langmuir*, 2005, **25**, 11822.

RSC Advances Accepted Manuscript

9 J. Wu, J. Chen, K. Qasim, J. Xia, W. Lei and B. P. Wang, J. Chem. Technol. *Biotechnol.*, 2012, **87**, 427.
10 Q. P. Ke, Y. X. Jin, P. Jiang and J. Yu, *Langmuir*, 2014, **30**, 13137.
11 D. L. Tian, X. F. Zhang, X. Wang, J. Zhai and L. Jiang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 14606.
12 L. B. Zhang, Y. J. Zhong, D. Y. Cha and P. Wang, *Sci. Rep.*, 2013, **3**, 2326.
13 L. P. Xu, J. Zhao, B. Su, X. L. Liu, J. T. Peng, Y. B. Liu, H. L. Liu, G. Yang, L. Jiang, Y. Q. Wen, X. J. Zhang and S. T. Wang, *Adv. Mater.*, 2013, **25**, 606.
14 X. L. Liu, J. Zhou, Z. X. Xue, J. Gao, J. X. Meng, S. T. Wang and L. Jiang, *Adv. Mater.*, 2012, **24**, 3401.
15 Z. X. Xue, S. T. Wang, L. Lin, L. Chen, M. J. Liu, L. Feng and L. Jiang, *Adv. Mater.*, 2011, **23**, 4270.
16 H. L. Liu, P. C. Zhang, M. J. Liu, S. T. Wang and L. Jiang, *Adv. Mater.*, 2013, **25**, 4477.
17 Y. Cai, L. Lin, Z. X. Xue, M. J. Liu, S. T. Wang and L. Jiang, *Adv. Funct. Mater.*, 2014, **24**, 809.
18 F. Zhang, W. B. Zhang, Z. Shi, D. Wang, J. Jin and L. Jiang, *Adv. Mater.*, 2013, **25**, 4192.
19 X. F. Gao, L. P. Xu, Z. X. Xue, L. Feng, J. T. Peng, Y. Q. Wen, S. T. Wang and X. J. Zhang, *Adv. Mater.*, 2014, **26**, 1771.
20 M. H. Jin, S. S. Li, J. Wang, Z. X. Xue, M. Y. Liao and S. T. Wang, *Chem. Commun.,* 2012, **48**, 11745.
21 L. P. Xu, J. T. Peng, Y. B. Liu, Y. Q. Wen, X. J. Zhang, L. Jiang and S. T. Wang, *ACS nano*, 2013, **7**, 5077.
22 A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.*, 1944, **40**, 546.

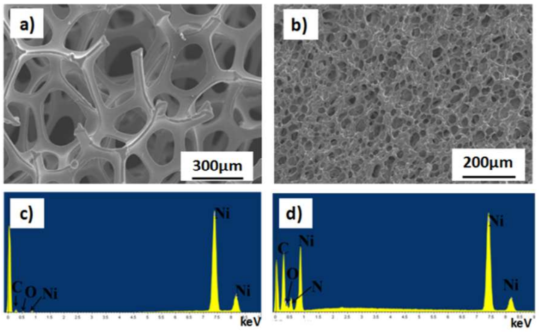

Fig. 1. SEM images of the nickel foam a) before and b) after modification by PAM hydrogel; the corresponding EDX patterns for c) bare nickel foam and d) modification by PAM hydrogel.

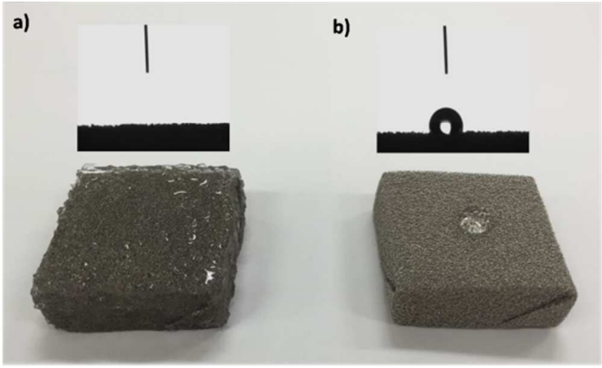

Fig. 2. CA and photographs of water droplets on different surfaces: a) PAM hydrogel coated nickel foam and b) bare nickel foam

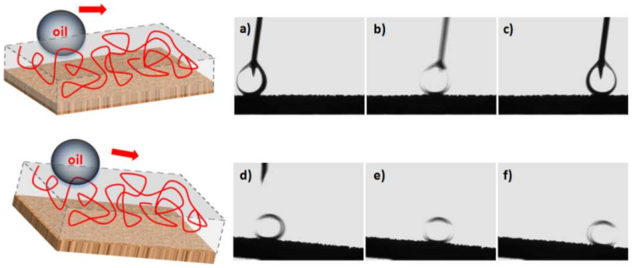

Fig. 3.The dynamic underwater oil adhesion measurement on as-prepared divice surface: a-c) An oil droplet was applied to contact the surface and can be moved easily; d-f) The slant surface showed an ultralow affinity to the oil droplet.

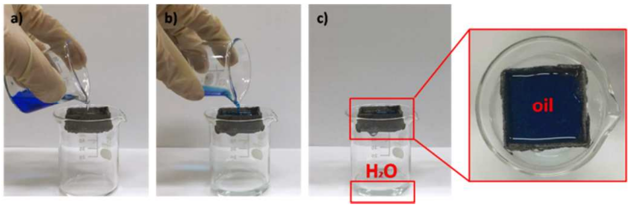

Fig. 4. The oil-water separation process: a) A mixture of water and blue-dyed oil was poured into the device. b) Water passed through the device, c) while oil was prevented from permeating into the hydrogel and remains in the device.

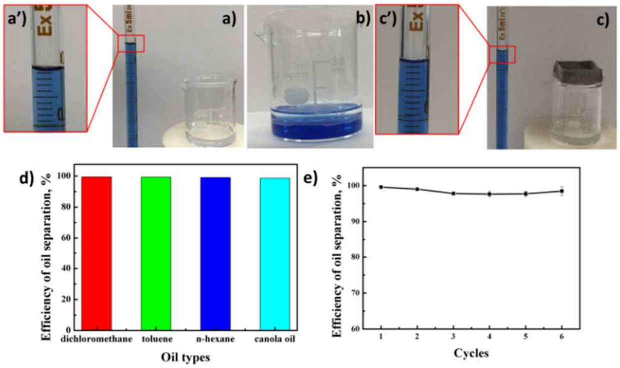

Fig. 5. The process a-c) of evaluating the separation efficiency of the dichloromethane-water mixture by as-prepared device; The magnification of a) and c) indicate the volumes in the pipette; d) Separation efficiency of the as-prepared device for different oil-water mixtures; e) Recycled experiments for separating oil from water by as-prepared device.

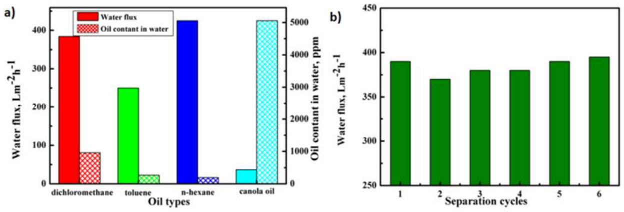

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Fig. 6. Oil-water separation results of the as-prepared device. a) Oil content and the water flux after permeating a series of immiscible oil-water mixtures. b) Water flux for permeating oil-water mixture through the as-prepared device with different cycle index.

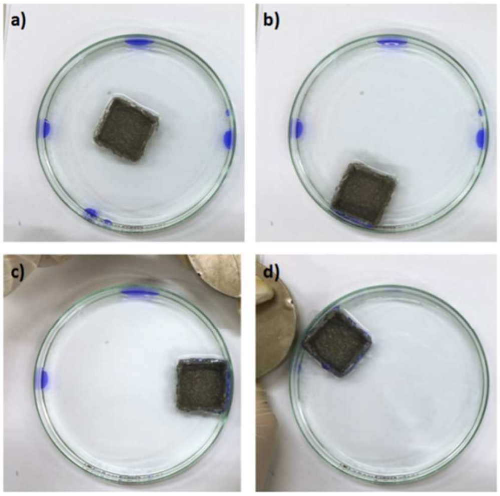

Fig. 7. a) Dye-colored water on the surface of the dichloromethane in a watch glass; b,c) subsequent removal of the little water by the magnetically driven the as-prepared device; d) Cleaned oil surface after the process.

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