

Magnetically Driven Functionally Integrated Device for Continuous and Efficient

Collection of Oil Droplets from Water

Guannan Ju, Donglin Li, Yajun Zhang*

Institute of Plastic Machinery and Engineering, Beijing University of Chemical
Technology, Beijing 100029, China.

E-mail: zhyj@mail.buct.edu.cn

1. SEM images and corresponding energy dispersive X-ray (EDX) patterns of the copper foam and nickel foam respectively.

To check the surface composition and morphology of the magnetically driven functionally integrated device, SEM images and their corresponding EDX patterns were used in the stepwise treatment of copper foam and nickel foam. As shown in Fig. S1a-b, both the bare copper foam and bare nickel foam presented a relatively smooth surface (insets in Fig. S1a-b) and the major element in the selected region was copper and nickel respectively. After deposition in a solution of AgNO_3 , three dimensional microscale dendritic structures with nanoscale branches formed on the surface, which created a high surface roughness (insets in Fig. S1c,d); from the corresponding EDX pattern, we could observe that silver element showed a stronger absorption than that of copper element and nickel element (Fig. S1c,d) respectively, indicating that the major composition of the dendritic structure was silver. Subsequently, the surface modification of the thiol monolayer had little effects on the surface morphology of the as-prepared surface (insets in Fig. S1e,f) but the strong absorption of carbon element and sulfur element implied the presence of organic compounds (Fig. S1e,f).

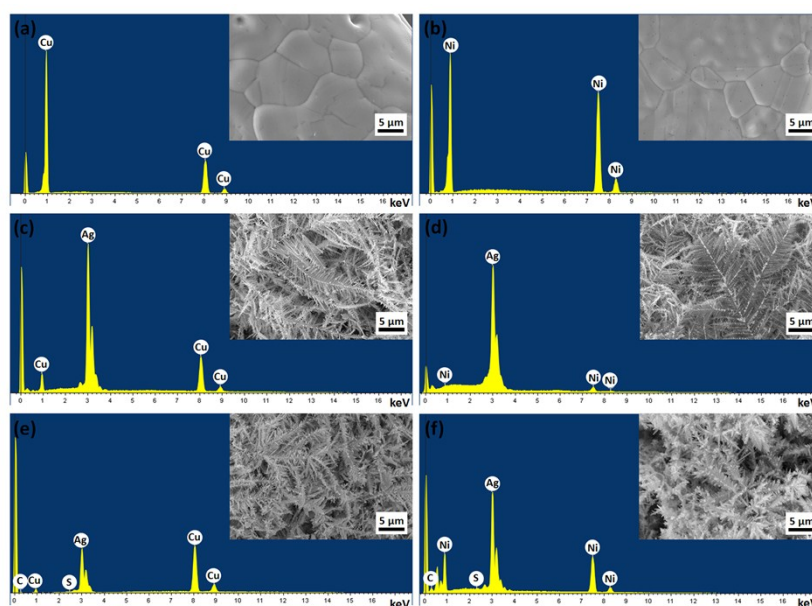


Fig. S1. SEM images and corresponding EDX patterns for (a) bare copper foam and (b) bare nickel foam, (c) copper foam and (d) nickel foam deposited in a AgNO_3 solution and (e-f) subsequently modified in an ethanol solution of $\text{SH}(\text{CH}_2)_{11}\text{CH}_3$ respectively.

2. Investigation into the superhydrophobicity and superoleophilicity of the as-prepared surface.

To verify the surface wettability of the as-prepared surface, both water droplets and toluene droplets were applied to the film which was deposited in an aqueous AgNO_3 (20 mM) solution at 50 °C for 15 min and modified with thiol molecules. When we dropped the toluene (dyed blue) to the as-prepared surface, the toluene droplets could be quickly absorbed by the foam surface and spread over the surface

as a result of the superoleophilicity (Fig. S2a). The toluene droplet dropped down after more toluene was added (Fig. S2b); however, the as-prepared surface showed superhydrophobicity for water droplets (dyed red) which rolled off the as-prepared foam surface even with a very small sliding angle instead of passing through the surface (Fig. S2c,d)

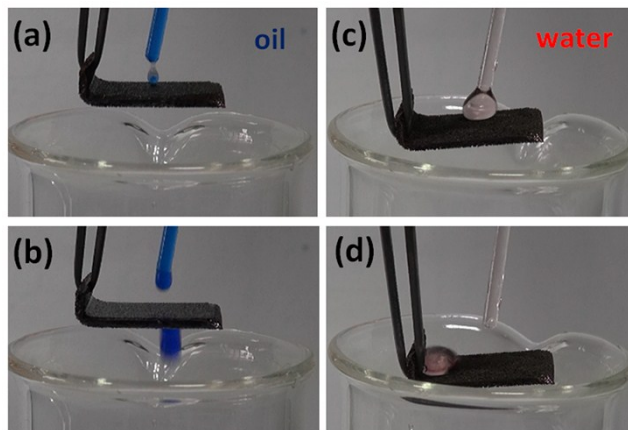


Fig. S2. Optical snapshots displayed the different wettability of the as-prepared surface. (a) The toluene droplets (dyed blue) could be absorbed immediately. (b) The excessive toluene could penetrate the surface after adding toluene droplets continuously. (c-d) A drop of water (dyed red) stood on the surface instead of passing through it.

3. Folding process of a seamless functionally integrated device.

The seamless functionally integrated device was folded as the following steps, as shown in Fig. S3. The dotted lines were used to fold. The copper foam was flexible and easy to fold and seal. For the possible applications, we developed a well-connected seamless functionally integrated device without safety pins.

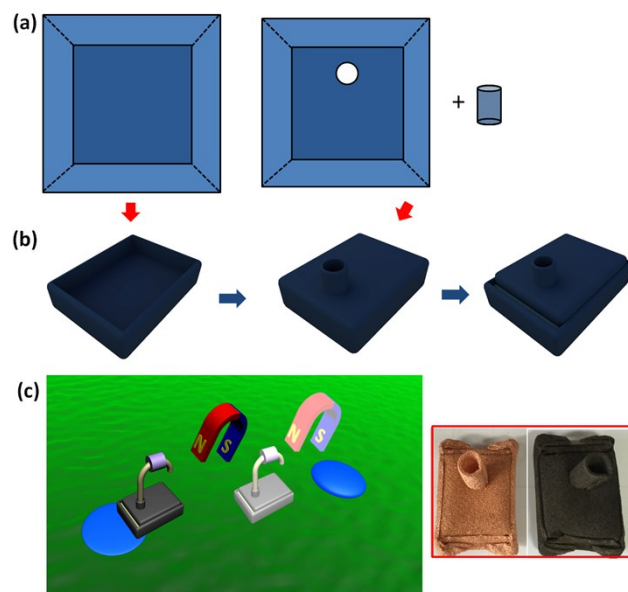


Fig. S3. Illustration of the folding process of a seamless device (a,b). Fold in the dotted line, followed by a simple assembly process. (c) Facile configuration of in situ

continuous oil-water separation and snapshots of the device before (left, yellow) and after (right, grey) modification.

4. Magnetically-actuated oil collecting progress.

To demonstrate the magnetically driven separating progress of the oil, further design and experiment were carried out. As shown in Fig. S4a, the as-prepared device was put on water surface and kept still. At this time, the as-prepared device could not absorb the floating oil droplets located in different areas automatically. After applying a magnetic field, the as-prepared device could be easily controlled to move to the targeted site and absorb the oil spills quickly (Fig. S4b,c). After continuous locomotion of the as-prepared device under magnetic control, all the oil droplets on water surface were cleaned up within a short time (Fig. S4d), which indicated the satisfactory superhydrophobicity and superoleophilicity.

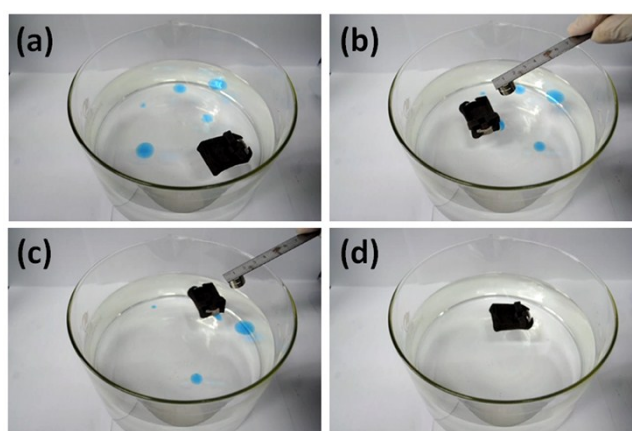


Fig. S4. (a) The as-prepared device was placed far from the oil droplets and could not absorb oil automatically. (b,c) The as-prepared device moved toward the oil droplet and absorbed it by the introduction of an external magnetic field. (d) Oil droplets were cleaned up.

5. The controllable pumping oil instead of water in the oil-water separation.

In order to illustrate this hypothesis that the system just pumped the oil instead of water, we used the device to collect the oil (toluene) located in different areas in the crystallizing dish. The device could float due to its superhydrophobicity and its lower density than that of water, as shown in Fig. S5a. The device started to absorb the oil droplets and the oil was pumped into the collecting beaker by the peristaltic pump (Fig. S5b). The pressure of the peristaltic pump (BT300-2J) used in our experiment was about 0.05 MPa and the speed was 30 rpm. In Fig. S5c, continuous air bubbles instead of water were pumped into the collected oil after most of oil was collected, which was mainly attributed to the hydrophobicity and superoleophilicity. Under this pressure of the peristaltic pump, the water would not be pumped out (for the details, please see Movie S3 in Supporting Information). Adjusting the pumping speed to 40 rpm, 50 rpm, 60 rpm, 70 rpm and 80 rpm, the identical results were obtained.

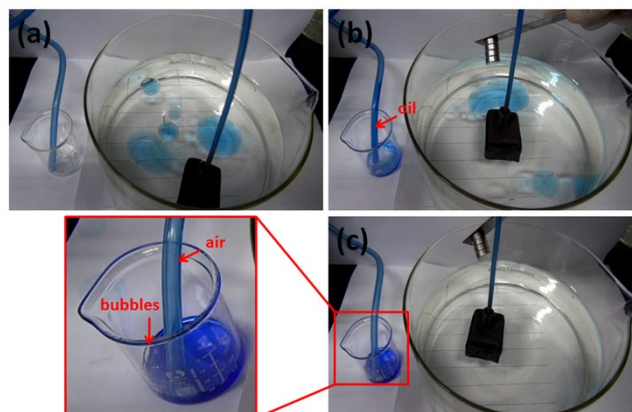


Fig. S5. The process for the clean-up of floating oil droplets. (a) Some toluene droplets spilt on water. (b) The device was driven towards the oil droplet by a magnet (c) leaving a clean water surface with continuous air bubbles instead of water in dyed toluene.

6. Directional oil collection under the water surface.

We designed a system featuring a water layer containing dyed dichloromethane droplets at the bottom of the vessel. Afterwards, the as-prepared device was placed on the water surface (Fig. S6a). To pull it down to the bottom directionally towards the spilt oil, we applied an external magnetic field at the bottom of the vessel. Guided by the movement of the magnet, the device could directionally clean up the dyed oil efficiently and quickly in a controlled way (Fig. S6b,c). After the removal of the external magnetic field, the device refloated on the surface of the water, as shown in Fig. S6d (for the details, please see Movie S4 in the Supporting Information).

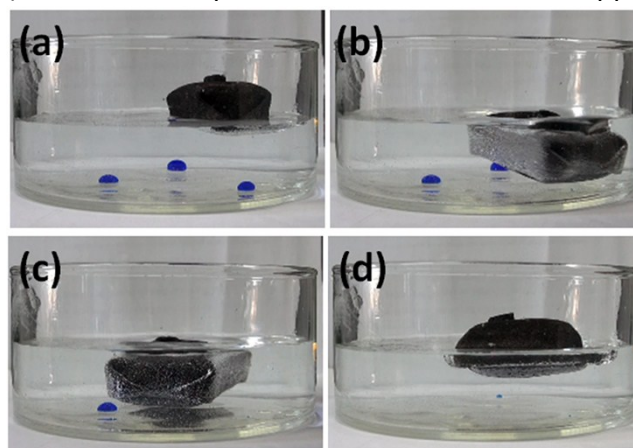


Fig. S6. Optical snapshots of the dichloromethane droplets absorbing process under the water surface. (a) The as-prepared device floated on the water surface. (b) The device sank to the bottom by the introduction of an external magnetic field. (c) Directional removal of the oil droplets located on different sites underwater with the control of the magnetic field. (d) In the absence of the magnetic field, the device rised to the water surface again.

7. The evaluation of separating efficiency of the as-prepared device.

In the continuous oil collecting process, the residual oil within the walls of the as-prepared device as well as the pipe was not counted after one oil collection. To exclude the effects of the residual oil on the separating efficiency, we carried out the following experiment to evaluate the optimized oil-water separating efficiency. After one round of oil-water separating and collecting process, we re-added 60 mL oil into the same system and did the oil collecting following the identical procedure as shown in Fig. S7a,b. The collecting volume was about 56.5 mL at the moment, which indicated the separating efficiency to be about 94.2% (Fig. S7c) (for the details, please see Movie S5 in the Supporting Information). The process of oil-water separation was cycled 6 times and the average separating efficiency was about 95%. Finally, the as-prepared device could be picked up slowly by tweezers and no redundant oil overflowed, which indicated that there was almost no oil in the interior of the as-prepared device, as shown in Fig. S7d-f.

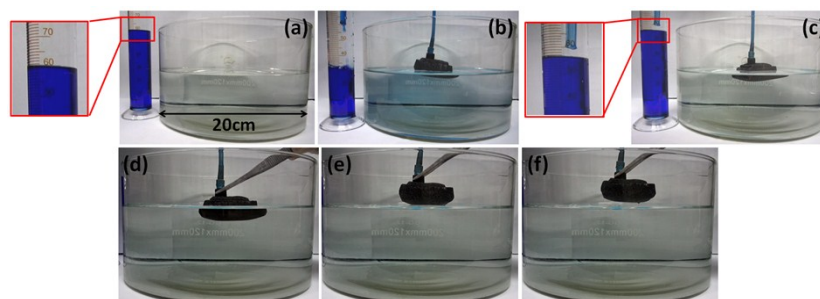


Fig. S7. (a) The toluene dyed blue with the origin volume of 60 mL. (b) Adding the toluene into the water in the crystallizing dish. (c) The spilt oil was separated and collected. (d-f) No redundant oil overflowed when the device was picked up slowly by tweezers.

8. Chemical stability of the as-prepared device in the oil-water separation.

To test the durability and stability of the superhydrophobicity, we performed the following experiment. First, the modified copper foam box with a WCA of 151° was positioned over the top of a beaker, as illustrated in Fig. S8a. Second, the toluene dyed blue could pass through the device as a result of superoleophilicity (Fig. S8b). Then some water was added but blocked perfectly in the interior of the device in Fig. S8c. In spite of the fact that the modified copper foam box had absorbed oil, the inset of Fig. S8d also indicated the WCA of 147.8° . The as-prepared device also showed stable superhydrophobicity, even in many corrosive solutions, such as acidic or basic solutions, and also in oxidizing solutions (hydrogen peroxide). It could withstand weak acidic or alkaline environmental conditions for a long time. Water or aqueous solutions (pH 2~13) have WCA of 151° on the treated surfaces of the as-prepared device, as shown in Fig. S8e. Furthermore, we measured the WCA after every cycle experiment carefully. The device was washed with copious ethanol and dried before the next cycle. After recycling for 10 times, the as-prepared device remained satisfactory superhydrophobicity with WCA around 148.5° as shown in Fig. S8f, which illuminated the as-prepared device could be recycled and still had stable

superhydrophobicity. The as-prepared device was placed on the surface of oil-water mixtures keeping afloat and moved by the external magnetic field, as shown in Fig.8 h-j (for the details, please see Movie S6 and Movie S7 in the Supporting Information).

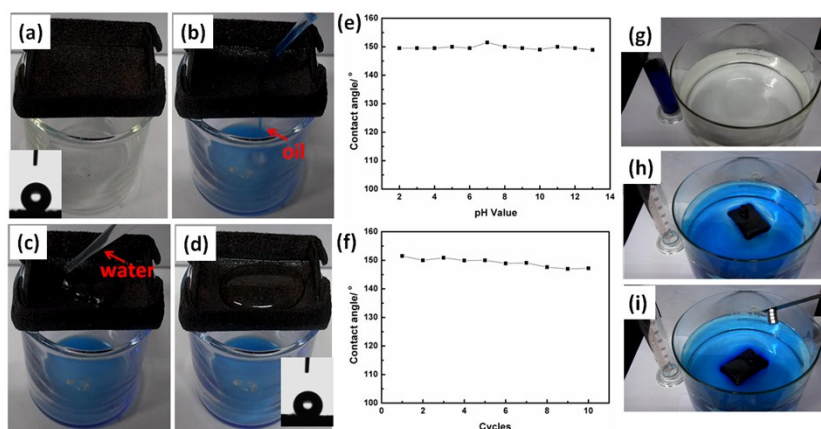


Fig. S8. Optical snapshots and WCA showed the stable superhydrophobicity and superoleophilicity using the as-prepared device. (a) The as-prepared device was positioned over the top of a beaker. (b) The toluene dyed blue passed through into the supporting beaker. (c,d) The water was blocked in the interior of the device. (e) WCA as a function of pH value on the surface of the as-prepared device which was modified with $\text{SH}(\text{CH}_2)_{11}\text{CH}_3$. (f) The WCA of every cycle experiment for oil-water separation. (g-i) The as-prepared device was placed on the surface of oil-water mixtures (60 mL toluene dyed blue).