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# Smart Enrichment and Facile Separation of Oil from Emulsions and Mixtures by Superhydrophobic/Superoleophilic Particles

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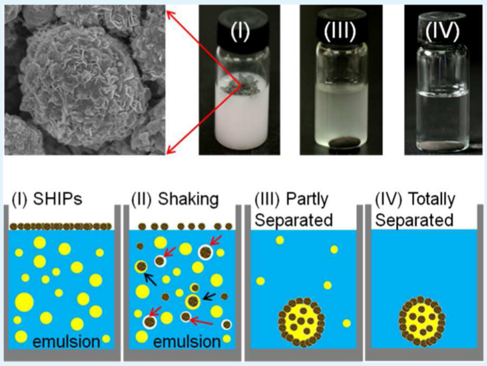
S *Supporting Information*

**ABSTRACT:** The separation and removal of oil or organic pollutants from water is highly imperative. The oil phases in surfactant-free oil-in-water emulsions or in free oil/water mixtures can be smartly enriched and transported by using superhydrophobic/superoleophilic iron particles (SHIPs) under a magnetic field. For water-in-oil emulsion, SHIPs-based composite membranes selectively allow the oil to pass through. Their convenient and scalable preparation, excellent separation performance, and good reusability are of great advantages for practical applications in wastewater treatment, the cleanup of oil spills, emulsion concentration, and fuel purification.



**KEYWORDS:** *superhydrophobicity, superoleophilicity, oil/water separation, nanostructured, magnetic particles*

## 1. INTRODUCTION

The environmental and economic demands for the separation and removal of oil or organic pollutants from water are highly imperative, because of the worldwide oil-contaminated water caused by industrial wastewater and oil spill accidents.[1−4] Jiang et al. first explored a superhydrophobic and superoleophilic mesh to separate oil and water from a mixture.[5] Because of the special surface wettability, the mesh can smartly allow oil to pass through but prevent water from leaching. Since then, the separation of oil and water, based on the special wettability of various materials, has attracted considerable attention.[6−19] Generally, a "superhydrophobic surface" is defined by a water contact angle of >150° and a roll-off angle of <10°;[20,21] moreover, a "superoleophilic surface" refers to the surface on which an oil droplet spreads quickly with a final oil contact angle of ∼0°.[21−24] The special wettable materials can be mainly divided into three types: porous bulks, films, and particles. Superhydrophobic and superoleophilic foams[25−29] (or sponges[30−35]) and aerogels[36−39] are typical porous bulks that can selectively absorb oil but repel water when being exposed to an oil/water mixture. These materials can be regenerated by washing, distillation, squeezing, or even burning after absorption. Superhydrophobic films[40,41] allow oil to permeate while superhydrophilic films with underwater superoleophobicity[42,43] only let water pass, thus continuous separation of water and oil from their mixtures can be achieved. The separation efficiency depends on surface wettability and pore size of the films. Besides, smart films with switchable superoleophilicity and superoleophobicity in aqueous circumstances have been developed for controllable oil/water separation.[44] As far as particles are concerned, superhydrophobic magnetic particles have been successfully applied to transport oil from water under magnetic field with good reusability.[45−47]

The above-mentioned materials have good performance, with regard to the separation of free oil/water mixtures where the diameter ($d$) of the dispersed phase is >150 $\mu$m. Until now, there have been only a few works concerning the separation of oil/water dispersions (20 $\mu m \leq d \leq 150$ $\mu$m) or emulsions ($d <$ 20 $\mu$m).[48] Superhydrophobic/superoleophilic nanofibrous membranes,[49] carbon nanotube network films,[50] and superoleophilic PVDF membranes[51] have been successfully used to separate water-in-oil (W/O) emulsions. However, these membranes have no effect on separating oil-in-water (O/W) emulsions. For O/W emulsions, inorganic membranes with underwater superoleophobicity were developed.[52] In addition, Jiang et al. reported a continuous collection of silicon oil droplets from a surfactant-free emulsion by oleophilic conical needles.[53] Yet, these materials are incapable of treating W/O emulsions. Therefore, it is still a challenge to prepare materials

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that are versatile for the oil/water separation, including water-rich or oil-rich free water−oil mixtures, and O/W and W/O emulsions or dispersions. A breakthrough has been achieved by Tuteja and co-workers,[54] who fabricated a fluorodecyl POSS and x-PEGDA coated hygro-responsive mesh membrane showing superhydrophilicity and superoleophobicity both in air and under water. This membrane is capable of separating surfactant-free and surfactant-stabilized W/O and O/W emulsions. Very recently, Xue and Liu[55] have developed an intelligent PVDF membrane with underwater superoleophobicity and under-oil superhydrophobicity, which can separate various O/W and W/O emulsions.

Herein, we report a facile preparation of superhydrophobic/superoleophilic iron particles (SHIPs) that can separate not only free oil/water mixtures, but also surfactant-free O/W and surfactant-stabilized W/O emulsions, with a high separation efficiency, magnetic tracking efficiency, and good reusability. To the best of our knowledge, this is the first report on using superhydrophobic particles for emulsion separation. The facile, low-cost, and scalable preparation procedure and the efficient performance promise a potential application of SHIPs in wastewater treatment, fuel purification, and the separation of emulsions and dispersions.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Carbonyl-iron powder (Fe) was obtained from Sigma−Aldrich Company. Copper sulfate ($CuSO_4$), hydrochloric acid (HCl, 37 wt %), xylene, chloroform, kerosene, toluene, ethanol, and acetone were purchased from Beijing Chemical Reagent Company. Span80, Tween80, cetyltrimethylammonium bromide (CTAB), and 1-dodecanethiol were obtained from Alfa Aesar. Corn oil was purchased from Wal-Mart. Silicone oil (DY-OH 502) was provided by Shangdong Dayi Chemical Company. Paraffin wax (melting point (mp), 53−57 °C) was purchased from Sigma−Aldrich. All reagents were used without further purification.

**2.2. Fabrication of Superhydrophobic/Superoleophilic Iron Particles (SHIPs).** Iron powder was decorated by copper via a typical hydrometallurgy method. First, HCl (1 mL) was added to a 500 mL $CuSO_4$ solution (0.05 M) to make a reaction solution. Second, iron powder (0.2 g) was added into 30 mL reaction solution and the mixture was shaken for 2 min. Third, the reaction solution was poured out while the modified iron powder was left behind by a magnet. The modified iron particles were washed with deionized water three times, followed by washing with ethanol, and then was dried at 60 °C.

Modification of the copper-decorated iron powder with mercaptan was conducted in ethanol as reported.[47] Copper decorated iron (1.0 g) was added into a 50 mL ethanol solution of 1-dodecanethiol (volume content: 0.1%). The mixture was shaken for 5 h. The powder then was washed with ethanol three times and dried at 60 °C.

**2.3. Preparation of Sandwich-Like Membrane for Separating Water-in-Oil Emulsion.** A quantity of SHIPs (0.15 g) was dispersed in 10 mL of ethanol. The mixture was filtrated under a reduce pressure on a nylon filter membrane with a diameter of 4.0 cm. The diameter of particle-deposited area was ~3.8 cm. The particles-deposited membrane was covered by another membrane to form the sandwich-like membrane.

**2.4. Preparation of Emulsions.** Surfactant-free oil-in-water emulsions with an oil content ($C_{oil}$) of 2 and 5 wt % were prepared as reported.[53] Specifically, 2 g (or 5 g) of silicone oil and 98 g (or 95 g) of deionized water were mixed and stirred vigorously. The mixture then was treated under ultrasonication until a uniform emulsion was obtained. Emulsions of corn oil and olive oil were prepared in the same way.

For CTAB-stabilized O/W emulsion, CTAB (100 mg) was dissolved in 50 g of water, and then silicone oil (3.75 g) was added. The mixture was homogenized at 10 000 rpm for 20 min, then sonicated for 3 h. Tween80 (0.65 g), $H_2O$ (50 g), and silicone oil (3.0 g) were mixed using the same method to obtain a Tween80-stabilized O/W emulsion.

A water-in-toluene emulsion was obtained using a method reported elsewhere.[51] Span80 (0.44 g) was added into 100 mL toluene, and then 0.88 mL water was added. The mixture was stirred for 3 h and sonicated for 3 h.

**2.5. Separation of Free Oil−Water Mixture and Emulsion.** The dosage of SHIPs for separating the free oil−water mixture was measured as follows: water (5 mL) was added to a beaker of 10 mL, then 200 μL of oil was added and the weight of oil ($m_{oil}$) was noted. SHIPs were added slowly to the oil until all the oil was absorbed by SHIPs and could be transported out by a magnet. The total weight of SHIPs ($m_{SHIP}$) was recorded. The absorption capacity was equal to $m_{oil}/m_{SHIP}$.

Separation of the oil-in-water emulsion was carried out as above. Emulsion (2 g) was added to a vial of 10 mL, and then a small amount of SHIPs was added. The mixture was shaken for 10 s. The process was repeated until the water phase became clear. The absorption capacity of emulsion is equal to $m_{emulsion}/m_{SHIP}$, and the absorption capacity of oil in emulsion is equal to $(c_{oil}m_{emulsion})/m_{SHIP}$.

The sandwich-like membrane was fixed between two polytetrafluoroethylene (PTFE) flanges, which connected a glass tube and a Büchner Flask. The freshly prepared water-in-toluene emulsion was poured onto the membrane, and the separation process was carried out under a reduced pressure. The filtrate was collected for purity tests.

**2.6. Preparation of Solidified Paraffin Marble.** This process was carried out in an oven at 80 °C. Paraffin wax (1.0 g) was liquified beforehand and kept in the oven. Water of 80 °C (5 mL) was added to a beaker of 10 mL, then 200 μL of liquid paraffin was added. SHIPs (200 mg) were added to the liquid paraffin. A magnet was used to draw the SHIPs/paraffin phase under water to form paraffin marble. After that, the beaker was taken out of the oven and cooled to room temperature. A solidified paraffin marble was obtained as a result.

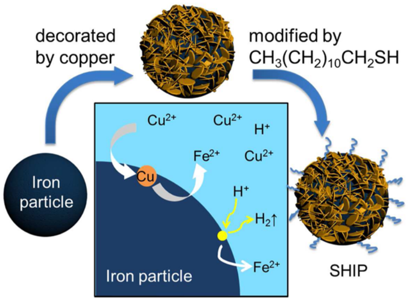
**2.7. Characterization.** Scanning electron microcopy (SEM) was performed on a JEOL Model JSM-7500F at an accelerating voltage of 5 kV. Size distribution of the pristine iron particles was analyzed from the SEM image containing 357 particles, using Nano Measure software. Contact angle data were obtained on a Krüss Drop Shape Analysis System-100 (DSA 100), using a sessile water drop method with 5−10 μL liquid drops. Before the contact angle test, particles were affixed onto a glass slide by double-sided adhesive. The adhesive was completely covered to avoid the influence of the adhesive on the measurement of water contact angles. A microscope (Olympus, Model IX71) was used to observe droplets in emulsions. An IKA mini shaker was used to shake the samples. An IKA T25 digital ultraturrax disperser was used to emulsify oil/water mixtures. The X-ray diffraction (XRD) measurement was performed on a Empyrean X-ray diffractometer, using Cu Kα radiation. The magnetic hysteresis loops were measured using a vibrating sample magnetometer (LakeShore, Model 7307). Infrared spectra were obtained from a Fourier transform infrared (FT-IR) spectrophotometer (Bruker, Model Tensor 27). A sample for FT-IR analysis was deposited dropwise onto a silicon wafer and dried under an infrared lamp. The purity of toluene was measured using a moisture titrator (Karl Fischer).

## 3. RESULTS AND DISCUSSION

The fabrication of SHIPs is schematically shown in Scheme 1. Commercially available carbonyl-iron particles are modified in a reaction system containing $CuSO_4$ and HCl, in which the reduction of the Cu ion and the acid corrosion of iron occur simultaneously.

The pristine iron particles, 0.5−5 μm in diameter (size distribution shown in Figure S1a in the Supporting Information), have a featureless surface (see Figures 1a and 1b). After the reaction, however, many nanoflakes appear on the particle surface (Figures 1c and 1d). Energy-dispersive X-

**Scheme 1. Fabrication of the Superhydrophobic/ Superoleophilic Iron Particles (SHIPs)**



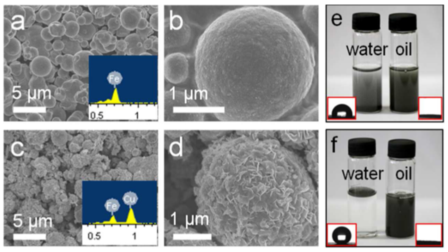


**Figure 1.** SEM images of iron powders (a, b) before and (c, d) after the superhydrophobic modification. Insets in panels a and c are the EDX results. (e, f) Digital photos showing the pristine iron particles and the SHIPs in water and oil, respectively. Insets are the respective profiles of water and kerosene on the surfaces of the powders. The size distribution of the SHIPs is shown in Figure S1b in the Supporting Information.

ray (EDX) results show the formation of copper (see insets in Figures 1a and 1c) and X-ray diffraction (XRD) patterns indicate the copper nanoflakes have a face-centered cubic structure (see Figure S2a in the Supporting Information).[8] Thus, hierarchically structured particles with microsized iron cores and copper nanoflakes shells are formed (size distribution shown in Figure S1b in the Supporting Information). The magnetic hysteresis loops show only a minor decrease after the modification (see Figure S2b in the Supporting Information). Note that the existence of acid is important for the formation of copper nanoflakes on the surface of the carbonyl-iron, because of the lower reactivity of carbonyl-iron, relative to that of pure iron. In a control experiment without introducing acid in the reaction system, no copper was observed on the particle surface (see Figure S3 in the Supporting Information for details).

The as-formed particles were then reacted with 1-dodecanethiol to reduce the surface energy. Because of the hierarchical morphology and low surface tension, SHIPs are obtained, since the water and oil contact angles on the SHIPs coatings are ~160° and ~0°, respectively, compared to the values of 110° and almost 0° on the coatings of the untreated iron particles (see insets in Figures 1e and 1f).[56−61] The roll-off angle of water on the SHIPs coating was <3°. A kerosene droplet of 5 μL spread on the surface of SHIPs within 2 s and reached a final contact angle of 0° (see Figure S4 in the Supporting Information). The contact angle data show that SHIPs have superhydrophobicity and superolephilicity. Therefore, SHIPs disperse in oil but float on a water surface, because of its selective wettability, while the pristine iron particles disperse both in water and oil.

Based on the selective wettability and the magnetic response, SHIPs can smartly collect oil microdroplets from surfactant-free O/W emulsions and controllably transport the oil phase under a magnetic field. Figures 2a–d show the process of separating a silicone oil-in-water emulsion. A certain amount of SHIPs is added into the emulsion and the mixture is shaken on a mini-shaker for 10 s. An aggregate of silicone oil and SHIPs then forms under water, which we termed as oil marble, corresponding to the "liquid marble".[47,62,63] The separating efficiency is dependent on the amount of SHIPs used. Insufficient SHIPs leads to a translucent liquid after shaking, implying that there are still oil droplets remaining in the water (Figure 2c). After adding additional SHIPs and shaking the system again, clean water is obtained (Figure 2d). The as-formed oil marble (in the bottom) can be easily transported by a magnet. The oil droplets, once dispersed in the emulsion (with a diameter of ~1−10 μm, the size distribution of the oil droplets is shown in Figure S5a in the Supporting Information), cannot be observed via fluorescence microscopy after the separation (see Figures 2e and 2f), and the characteristic peaks of silicone oil also disappear in the infrared spectrum of the clean water after separation, showing a high separation efficiency (Figure 2g). It has been found that 1 g of SHIPs can clean up to 10.5 g (2 wt %) or 5.5 g (5 wt %) emulsions, respectively.

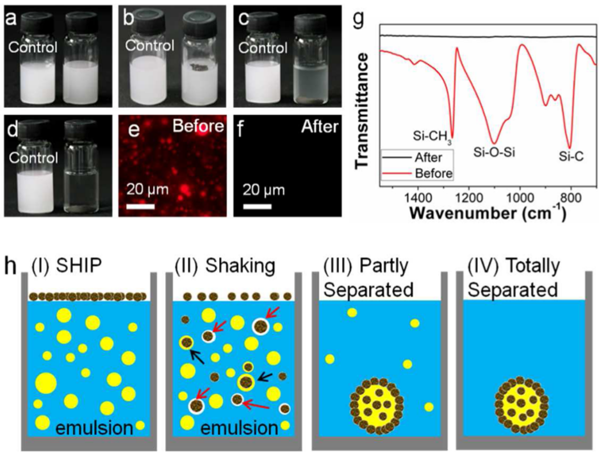


**Figure 2.** (a–d) Photographs showing the separation of the surfactant-free emulsion of silicone oil-in-water. Panels c and d reflect the incomplete and complete separation, respectively, depending on the amount of SHIPs used. Alsos hown are fluorescence microscope images of the emulsion (e) before and (f) after the separation. (Red droplets in panel e are silicone oil dyed by fluorescent dye.) (g) FT-IR spectra of the emulsion and the clean water left after the separation. (h) Schematic illustration of the separation of the silicone oil-in-water emulsion.

A reasonable mechanism is shown in Figure 2h. SHIPs initially float on the emulsion surface, because of its ultrahigh water repellency (step I). The particles will be forced into the emulsion under shaking. The particles may exist as four types: free particles floating on the surface, particles capsulated by an air layer (red arrow, in Cassie state[56]), and particles wetted by oil (black arrow) and by water (in Wenzel state[56]) (step II). Because of the superhydrophobicity and superoleophilicity of SHIPs and the collision between the oil droplets and particles, the SHIPs are more preferably to be wetted by oil during the further shaking. To reduce the total surface energy of the system, a big oil marble will be formed under the magnetic field with most of the SHIPs located at the water/oil interface (step

III). That is why the separation efficiency is dependent on the amount of SHIPs used. A complete separation can be achieved only with sufficient SHIPs (step IV). In the separation process, the greatly reduced oil/water interface area contributes mainly to the free energy decrease of the entire system.

SHIPs can also be used to effectively separate other surfactant-free O/W emulsions (see Figures S5b and S5c in the Supporting Information). Although surfactant-free emulsions are temporarily stable and have a tendency to be destabilized with time, the separation process requires a relatively long time. The time required for complete demulsification of the above-mentioned emulsions was more than 5 days (Figure S5d in the Supporting Information). Such a long demulsification time is not tolerable in some cases, like treating the oily water in an incident of toxic organic leakage. By using the SHIPs, however, the separation is completed within tens of seconds. Since surfactant-free emulsions are common in chemical engineering, the use of superhydrophobic/superoleophilic particles to separate surfactant-free emulsions is a more effective and environmentally benign method.

SHIPs cannot be used directly for separating W/O emulsions in the above-mentioned manner, since the particles disperse well in the continuous oil phase. The dispersed water droplets in oil will be absorbed, along with oil, by the particles if they are placed into the emulsions directly, resulting in a noneffective separation (see Figure S6 in the Supporting Information). Here, W/O emulsions can be separated by a simple device, shown in Figure 3a, where a sandwich-like composite membrane of nylon-SHIPs-nylon (Figure 3b) is fixed between two PTFE flanges. Toluene or kerosene in Span80-stabilized W/O emulsions is allowed to permeate the membrane while water droplets are prevented from passing through (see Figures 3c–e), showing selective penetration. The purity of the filtrate is above 99.9% for both toluene and kerosene, suggesting a high separation efficiency. The initial membrane flux of separating the Span80-stabilized water-in-kerosene emulsion was ~270 L $m^{-2}$ $h^{-1}$, under a pressure difference of 90 kPa. The amount of SHIPs was 0.15 g, and the diameter of particle-deposited area was ~3.8 cm. It should be noted that the amount of SHIPs affects the separation performance. The nylon film cannot be completely covered if the amount is <0.15 g, leading to an ineffective separation. An excess amount increases the thickness of the membrane, resulting in a lower flux.

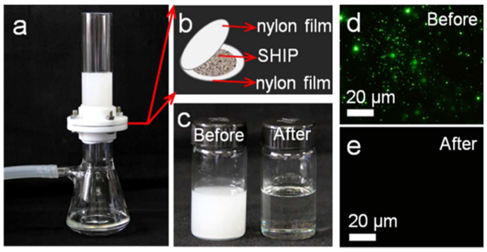


**Figure 3.** (a) Picture showing the separation of a Span80-stabilized water-in-toluene emulsion. The composite membrane allows toluene to permeate while preventing water droplets from passing through. (b) Illustration of a nylon–SHIPs–nylon composite membrane with a sandwich-like structure, using 100 mg of SHIPs per membrane. The diameters of the nylon membrane and particle-deposited area are 4.0 and 3.8 cm, respectively. (c) Photograph of emulsion before and after separation. Also shown are corresponding fluorescence microscope images (d) before and (e) after separation. Green droplets in panel d are water dyed by fluorescent dye.

The separation process is quite similar to that using superhydrophobic membranes, in which the surface wettability and pore size of the membrane are the critical parameters.[50,51,55] Herein, because of the superoleophilicity and superhydrophobicity of the particles, the oil phase in the W/O emulsion was allowed to pass through the gaps between the particles while the dispersed water droplets were blocked on the membrane surface. Demulsification of the emulsion is more likely to occur under a reduced pressure during the separation process, since the fluorescence microscope images show that the particles in the top layer were polluted by water (Figure S7 in the Supporting Information). The demulsified water droplets will foul the membrane by blocking the pores. As a result, the flux rate of the emulsion decreases with time (see Figure S8 in the Supporting Information). The pollution can be washed away by filtrating ethanol, and the composite membrane returns to normal and the separation rate recovers. It has been demonstrated that most of the surfactant remained in the good solvent after the separation.[50,54] Therefore, in our case, Span80 was more likely found in toluene after the separation. This method enlarges the application scope of superhydrophobic particles in the oil/water separation.

The SHIPs are also applicable for separating free oil/water mixtures. As shown in Figures 4a and 4b, for both kerosene floating on the water surface and chloroform lying under water, the oil phase can be exclusively enriched by the SHIPs and the particles/oil phase can be facilely taken out under magnetic force with clean water left. When the particle/oil phase was drawn under water and then the magnet was removed, a sphere was formed spontaneously with the solid particles encapsulating the oil droplet, which we referred as "oil marble" (corresponding to the "liquid marble").[47,62] To analyze the distribution of SHIPs in the resultant oil marble, paraffin wax is employed in a

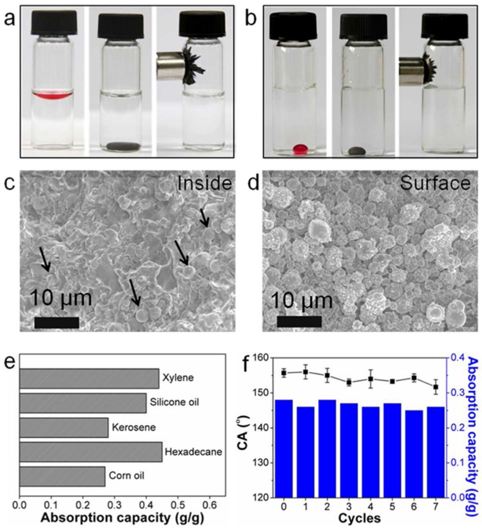


**Figure 4.** Pictures showing the effective enrichment and transportation of (a) kerosene and (b) chloroform from the free oil–water mixtures by using SHIPs under a magnetic field. Oil red is used as a colorant. Also displayed are SEM images showing the distribution of SHIPs (c) inside and (d) on the surface of the solidified paraffin marble. The arrows indicate the SHIPs. (e) Absorption capacities of SHIPs for different oils. (f) Change of the water contact angle (CA) and kerosene absorption capacity of the SHIPs with different cycles.

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control experiment. The separation process was performed at 80 °C, above the melting point of paraffin (53−57 °C), making paraffin floating on water surface as a liquid. "Paraffin marble" could be obtained as described above. The system then was cooled, resulting in the formation of a solid paraffin marble. The structure of the marble is fixed. A core−shell structure can be observed from the SEM images (Figures 4c and 4d; also see Figure S9 in the Supporting Information). Only a small number of SHIPs disperse inside of the marble, while most of the particles locate on the surface of the oil marble. This morphology is similar to that of the "liquid marbles" reported by Quéré,[62] in which a water droplet is capsulated by hydrophobic particles. In our case, it is assumed that most of the SHIPs prefer to remain at the interface between oil and water, to minimize the surface free energy of the entire system. The absorption capacity, which is defined as the weight of oil that can absorbed by SHIPs per unit weight of SHIPs, is in the range of 0.27−0.45 g/g for various organic solvents and oils (see Figure 4e). The adsorption capacity is low, because the density of SHIPs is pretty high (the density of carbonyl-iron powder is 7.86 g/mL). The absorption capacities for the free mixtures and the silicon oil in water emulsions are comparable, possibly because of similar oil marbles that are formed after the separation. The used SHIPs can be easily regenerated by washing with organic solvents. For example, as shown in Figure 4f, the absorbed kerosene can be washed away by acetone and no obvious change can be found in the absorption capacity and contact angle of the regenerated SHIPs after seven cycles, implying good stability and reusability.

Herein, the selective wettability of SHIPs plays an important role for the separation. The pristine carbonyl-iron powders cannot separate the oil/water mixture (see Figure S10 in the Supporting Information). For surfactant-stabilized O/W emulsions, SHIPs are easily wetted by water, because the surfactants in the water reduce the surface tension of the water, leading to the loss of the selective wettability to the continuous phase and the dispersed phase in O/W emulsions (CTAB- and Tween80-stabilized emulsions of silicon oil in water; see Figure 5).[64−66] Therefore, the surfactant-stabilized O/W emulsions cannot be separated by using SHIPs.

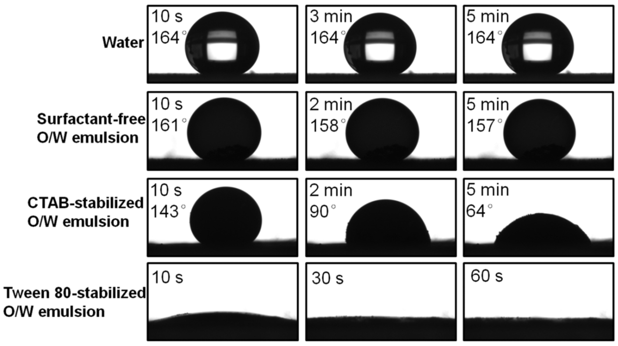

**Figure 5.** Variation of contact angles (CAs) of different liquids on the SHIPs surfaces with time.

Compared to the reported superhydrophobic porous materials,[30−39] the advantages of SHIPs are applicable for different oil−water mixtures, including surfactant-free oil-in-water emulsions that superhydrophobic porous materials cannot separate. The disadvantages of SHIPs are magnetic dependence (for free oil/water mixture and surfactant-free oil-in-water emulsion) and driving pressure dependence (for sandwich membrane).

## 4. CONCLUSION

In conclusion, here, we have demonstrated a facile preparation of hierarchically structured superhydrophobic/superoleophilic iron particles (SHIPs). The oil phase in surfactant-free O/W emulsions or in free oil/water mixtures can be smartly enriched to form oil marbles by using the SHIPs and then transported under magnetic field. In addition, a SHIPs-based composite membrane has been developed to separate W/O emulsions with an efficiency of >99.9%. The convenient and scalable preparation, efficient separation, and outstanding reusability are of great advantages for practical applications in wastewater treatment, cleanup of oil spills, emulsion concentration, and fuel purification.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Size distribution of pristine iron particles, XRD patterns, magnetic hysteresis loops, SEM images of particles with or without acid corrosion, fluorescence microscope images of the SHIPs in the composite membrane contacing with the emulsion, SEM images showing the fracture section of the solidified paraffin marble, pictures showing futile separation by using pristine iron powders. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01901.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

(1) Shannon, M. A.; Bohn, P. W.; Elimelech, M.; Georgiadis, J. G.; Marinas, B. J.; Mayes, A. M. Science and Technology for Water Purification in the Coming Decades. *Nature* **2008**, *452*, 301−310.

(2) Farrington, J. W. Oil Pollution in the Marine Environment Inputs, Big Spills, Small Spills, and Dribbles. *Environment* **2013**, *55*, 3−13.

(3) Kintisch, E. Gulf Oil Spill an Audacious Decision in Crisis Gets Cautious Praise. *Science* **2010**, *329*, 735−736.

(4) Montgomery, M.; Elimelech, M. Water and Sanitation in Developing Countries: Including Health in the Equation. *Environ. Sci. Technol.* **2007**, *41*, 17−24.

(5) Feng, L.; Zhang, Z.; Mai, Z.; Ma, Y.; Liu, B.; Jiang, L.; Zhu, D. A Super-Hydrophobic and Super-Oleophilic Coating Mesh Film for the Separation of Oil and Water. *Angew. Chem., Int. Ed.* **2004**, *43*, 2012−2014.

(6) Zhang, J.; Huang, W.; Han, Y. A Composite Polymer Film with Both Superhydrophobicity and Superoleophilicity. *Macromol. Rapid Commun.* **2006**, *27*, 804−808.

(7) Yuan, J.; Liu, X.; Akbulut, O.; Hu, J.; Suib, S.; Kong, J.; Stellacci, F. Superwetting Nanowire Membranes for Selective Absorption. *Nat. Nanotechnol.* **2008**, *3*, 332−336.

(8) Wang, S.; Song, Y.; Jiang, L. Microscale and Nanoscale Hierarchical Structured Mesh Films with Superhydrophobic and Superoleophilic Properties Induced by Long-Chain Fatty Acids. *Nanotechnology* **2007**, *18*, 015103.

(9) Zhou, Y.; Chen, L.; Hu, X.; Lu, J. Separation of Oil from Oily Wastewater by Modified Resin. *Water Sci. Technol.* **2009**, *59*, 957−963.

(10) Wang, C.; Yao, T.; Wu, J.; Ma, C.; Fan, Z.; Wang, Z.; Cheng, Y.; Lin, Q.; Yang, B. Facile Approach in Fabricating Superhydrophobic and Superoleophilic Surface for Water and Oil Mixture Separation. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2613−2617.

(11) Su, C. Highly Hydrophobic and Oleophilic Foam for Selective Absorption. *Appl. Surf. Sci.* **2009**, *256*, 1413−1418.

(12) Howarter, J.; Youngblood, J. Amphiphile Grafted Membranes for the Separation of Oil-in-Water Dispersions. *J. Colloid Interface Sci.* **2009**, *329*, 127−132.

(13) Wang, S.; Li, M.; Lu, Q. Filter Paper with Selective Absorption and Separation of Liquids that Differ in Surface Tension. *ACS Appl. Mater. Interfaces* **2010**, *2*, 677−683.

(14) Shang, Y.; Si, Y.; Raza, A.; Yang, L.; Mao, X.; Ding, B.; Yu, J. An In Situ Polymerization Approach for the Synthesis of Superhydrophobic and Superoleophilic Nanofibrous Membranes for Oil−Water Separation. *Nanoscale* **2012**, *4*, 7847−7854.

(15) Kwon, G.; Kota, A.; Li, Y.; Sohani, A.; Mabry, J.; Tuteja, A. On-Demand Separation of Oil−Water Mixtures. *Adv. Mater.* **2012**, *24*, 3666−3671.

(16) Wu, C.; Huang, X.; Wu, X.; Qian, R.; Jiang, P. Mechanically Flexible and Multifunctional Polymer-Based Graphene Foams for Elastic Conductors and Oil−Water Separators. *Adv. Mater. (Deerfield Beach, Fla.)* **2013**, *25*, 5658−5662.

(17) Wang, Y.; Tao, S.; An, Y. A Reverse Membrane Emulsification Process Based on a Hierarchically Porous Monolith for High Efficiency Water−Oil Separation. *J. Mater. Chem. A* **2013**, *1*, 1701−1708.

(18) Han, Y.; Xu, Z.; Gao, C. Ultrathin Graphene Nanofiltration Membrane for Water Purification. *Adv. Funct. Mater.* **2013**, *23*, 3693−3700.

(19) Guix, M.; Orozco, J.; Garcia, M.; Gao, W.; Sattayasamitsathit, S.; Merkoci, A.; Escarpa, A.; Wang, J. Superhydrophobic Alkanethiol-Coated Microsubmarines for Effective Removal of Oil. *ACS Nano* **2012**, *6*, 4445−4451.

(20) Abraham, M. Superhydrophobic and Superhygrophobic Surfaces: from Understanding Non-Wettability to Design Considerations. *Soft Matter.* **2013**, *9*, 7900−7904.

(21) Drelich, J.; Chibowski, E.; Meng, D. D.; Terpilowski, K. Hydrophilic and Superhydrophilic Surfaces and Materials. *Soft Matter* **2011**, *7* (21), 9804−9828.

(22) Darmanin, T.; Guittard, F. Wettability of Conducting Polymers: From Superhydrophilicity to Superoleophobicity. *Prog. Polym. Sci.* **2014**, *39* (4), 656−682.

(23) Nishimoto, S.; Bhushan, B. Bioinspired Self-Cleaning Surfaces with Superhydrophobicity, Superoleophobicity, and Superhydrophilicity. *RSC Adv.* **2013**, *3* (3), 671−690.

(24) Tettey, K. E.; Dafinone, M. I.; Lee, D. Progress in Superhydrophilic Surface Development. *Mater. Express* **2011**, *1* (2), 89−104.

(25) Calcagnile, P.; Fragouli, D.; Bayer, I.; Anyfantis, G.; Martiradonna, L.; Cozzoli, P.; Cingolani, R.; Athanassiou, A. Magnetically Driven Floating Foams for the Removal of Oil Contaminants from Water. *ACS Nano* **2012**, *6*, 5413−5419.

(26) Cheng, M.; Ju, G.; Jiang, C.; Zhang, Y.; Shi, F. Magnetically Directed Clean-Up of Underwater Oil Spills Through a Functionally Integrated Device. *J. Mater. Chem. A* **2013**, *1*, 13411−13416.

(27) Zhang, X.; Li, Z.; Liu, K.; Jiang, L. Bioinspired Multifunctional Foam with Self-Cleaning and Oil/Water Separation. *Adv. Funct. Mater.* **2013**, *23*, 2881−2886.

(28) Chen, N.; Pan, Q. Versatile Fabrication of Ultralight Magnetic Foams and Application for Oil-Water Separation. *ACS Nano* **2013**, *7*, 6875−6883.

(29) Liu, C.; Yang, J.; Tang, Y.; Yin, L.; Tang, H.; Li, C. Versatile Fabrication of the Magnetic Polymer-Based Graphene Foam and Applications for Oil−Water Separation. *Colloids Surf., A* **2015**, *468*, 10−16.

(30) Wang, H.; Wang, E.; Liu, Z.; Gao, D.; Yuan, R.; Sun, L.; Zhu, Y. A Novel Carbon Nanotubes Reinforced Superhydrophobic and Superoleophilic Polyurethane Sponge for Selective Oil−Water Separation Through a Chemical Fabrication. *J. Mater. Chem. A* **2015**, *3* (1), 266−273.

(31) Ke, Q.; Jin, Y.; Jiang, P.; Yu, J. Oil/Water Separation Performances of Superhydrophobic and Superoleophilic Sponges. *Langmuir* **2014**, *30* (44), 13137−13142.

(32) Liu, Y.; Ma, J.; Wu, T.; Wang, X.; Huang, G.; Liu, Y.; Qiu, H.; Li, Y.; Wang, W.; Gao, J. Cost-Effective Reduced Graphene Oxide-Coated Polyurethane Sponge as a Highly Efficient and Reusable Oil-Absorbent. *ACS Appl. Mater. Interfaces* **2013**, *5*, 10018−10026.

(33) Sun, H.; Li, A.; Zhu, Z.; Liang, W.; Zhao, X.; La, P.; Deng, W. Superhydrophobic Activated Carbon-Coated Sponges for Separation and Absorption. *ChemSusChem* **2013**, *6*, 1057−1062.

(34) Zhu, Q.; Chu, Y.; Wang, Z.; Chen, N.; Lin, L.; Liu, F.; Pan, Q. Robust Superhydrophobic Polyurethane Sponge as a Highly Reusable Oil-Absorption Material. *J. Mater. Chem. A* **2013**, *1*, 5386−5393.

(35) Zhu, Q.; Pan, Q. Mussel-Inspired Direct Immobilization of Nanoparticles and Application for Oil−Water Separation. *ACS Nano* **2014**, *8*, 1402−1409.

(36) Hayase, G.; Kanamori, K.; Fukuchi, M.; Kaji, H.; Nakanishi, K. Facile Synthesis of Marshmallow-like Macroporous Gels Usable under Harsh Conditions for the Separation of Oil and Water. *Angew. Chem., Int. Ed.* **2013**, *52*, 1986−1989.

(37) Cervin, N.; Aulin, C.; Larsson, P.; Wagberg, L. Ultra Porous Nanocellulose Aerogels as Separation Medium for Mixtures of Oil/Water Liquids. *Cellulose* **2012**, *19*, 401−410.

(38) Bi, H.; Yin, Z.; Cao, X.; Xie, X.; Tan, C.; Huang, X.; Chen, B.; Chen, F.; Yang, Q.; Bu, X.; Lu, X.; Sun, L.; Zhang, H. Carbon Fiber Aerogel Made from Raw Cotton: A Novel, Efficient and Recyclable Sorbent for Oils and Organic Solvents. *Adv. Mater.* **2013**, *25*, 5916−5921.

(39) Wu, Z.; Li, C.; Liang, H.; Chen, J.; Yu, S. Ultralight, Flexible, and Fire-Resistant Carbon Nanofiber Aerogels from Bacterial Cellulose. *Angew. Chem., Int. Ed.* **2013**, *52*, 2925−2929.

(40) Tian, D.; Zhang, X.; Wang, X.; Zhai, J.; Jiang, L. Micro/Nanoscale Hierarchical Structured ZnO Mesh Film for Separation of Water and Oil. *Phys. Chem. Chem. Phys.* **2011**, *13*, 14606−14610.

(41) Wu, J.; Chen, J.; Qasim, K.; Xia, J.; Lei, W.; Wang, B. A Hierarchical Mesh Film with Superhydrophobic and Superoleophilic Properties for Oil and Water Separation. *J. Chem. Technol. Biotechnol.* **2012**, *87*, 427−430.

(42) Xue, Z.; Wang, S.; Lin, L.; Chen, L.; Liu, M.; Feng, L.; Jiang, L. A Novel Superhydrophilic and Underwater Superoleophobic Hydrogel-Coated Mesh for Oil/Water Separation. *Adv. Mater.* **2011**, *23*, 4270−4273.

(43) Zhang, S.; Lu, F.; Tao, L.; Liu, N.; Gao, C.; Feng, L.; Wei, Y. Bio-Inspired Anti-Oil-Fouling Chitosan-Coated Mesh for Oil/Water Separation Suitable for Broad pH Range and Hyper-Saline Environments. *ACS Appl. Mater. Interfaces* **2013**, *5*, 11971−11976.

(44) Zhang, L.; Zhang, Z.; Wang, P. Smart Surfaces with Switchable Superoleophilicity and Superoleophobicity in Aqueous Media: Toward Controllable Oil/Water Separation. *NPG Asia Mater.* **2012**, *4*, e8.

(45) Chu, Y.; Pan, Q. Three-Dimensionally Macroporous Fe/C Nanocomposites as Highly Selective Oil-Absorption Materials. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2420−2425.

(46) Xu, L.; Wu, X.; Meng, J.; Peng, J.; Wen, Y.; Zhang, X.; Wang, S. Papilla-like Magnetic Particles with Hierarchical Structure for Oil Removal from Water. *Chem. Commun.* **2013**, *49*, 8752−8754.

(47) Zhang, L.; Wu, J.; Wang, Y.; Long, Y.; Zhao, N.; Xu, J. Combination of Bioinspiration: A General Route to Superhydrophobic Particles. *J. Am. Chem. Soc.* **2012**, *134*, 9879−9881.

(48) Cheryan, M.; Rajagopalan, N. Membrane Processing of Oily Streams. Wastewater Treatment and Waste Reduction. *J. Membr. Sci.* **1998**, *151*, 13−28.

(49) Huang, M.; Si, Y.; Tang, X.; Zhu, Z.; Ding, B.; Liu, L.; Zheng, G.; Luo, W.; Yu, J. Gravity Driven Separation of Emulsified Oil-Water Mixtures Utilizing In Situ Polymerized Superhydrophobic and Superoleophilic Nanofibrous Membranes. *J. Mater. Chem. A* **2013**, *1*, 14071−14074.

(50) Shi, Z.; Zhang, W.; Zhang, F.; Liu, X.; Wang, D.; Jin, J.; Jiang, L. Ultrafast Separation of Emulsified Oil/Water Mixtures by Ultrathin Free-Standing Single-Walled Carbon Nanotube Network Films. *Adv. Mater.* **2013**, *25*, 2422−2427.

(51) Zhang, W.; Shi, Z.; Zhang, F.; Liu, X.; Jin, J.; Jiang, L. Superhydrophobic and Superoleophilic PVDF Membranes for Effective Separation of Water-in-Oil Emulsions with High Flux. *Adv. Mater.* **2013**, *25*, 2071−2076.

(52) Zhang, F.; Zhang, W.; Shi, Z.; Wang, D.; Jin, J.; Jiang, L. Nanowire-Haired Inorganic Membranes with Superhydrophilicity and Underwater Ultralow Adhesive Superoleophobicity for High-Efficiency Oil/Water Separation. *Adv. Mater.* **2013**, *25*, 4192−4198.

(53) Li, K.; Ju, J.; Xue, Z.; Ma, J.; Feng, L.; Gao, S.; Jiang, L. Structured Cone Arrays for Continuous and Effective Collection of Micron-Sized Oil Droplets from Water. *Nat. Commun.* **2013**, *4*, 2276.

(54) Kota, A.; Kwon, G.; Choi, W.; Mabry, J.; Tuteja, A. Hygro-responsive Membranes for Effective Oil−Water Separation. *Nat. Commun.* **2012**, *3*, 1025.

(55) Tao, M.; Xue, L.; Liu, F.; Jiang, L. An Intelligent Superwetting PVDF Membrane Showing Switchable Transport Performance for Oil/Water Separation. *Adv. Mater. (Deerfield Beach, Fla.)* **2014**, *26*, 2943−2948.

(56) Lafuma, A.; Quéré, D. Superhydrophobic States. *Nat. Mater.* **2003**, *2*, 457−460.

(57) Sun, T. L.; Feng, L.; Gao, X. F.; Jiang, L. Bioinspired Surfaces with Special Wettability. *Acc. Chem. Res.* **2005**, *38*, 644−652.

(58) Gao, L.; McCarthy, T. The "Lotus Effect" Explained: Two Reasons Why Two Length Scales of Topography are Important. *Langmuir* **2006**, *22*, 2966−2967.

(59) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J.; Mazzella, S.; Rutledge, G.; McKinley, G.; Cohen, R. Designing Superoleophobic Surfaces. *Science* **2007**, *318*, 1618−1622.

(60) Quéré, D. Wetting and Roughness. *Annu. Rev. Mater. Res.* **2008**, *38*, 71−99.

(61) Roach, P.; Shirtcliffe, N.; Newton, M. Progess in Superhydrophobic Surface Development. *Soft Matter* **2008**, *4*, 224−240.

(62) Aussillous, P.; Quéré, D. Liquid Marbles. *Nature* **2001**, *411*, 924−927.

(63) Bormashenko, E. Liquid Marbles: Properties and Applications. *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 266−271.

(64) Shirtcliffe, N.; McHale, G.; Newton, M.; Perry, C.; Roach, P. Superhydrophobic to Superhydrophilic Transitions of Sol−Gel Films for Temperature, Alcohol or Surfactant Measurement. *Mater. Chem. Phys.* **2007**, *103*, 112−117.

(65) Ferrari, M.; Ravera, F.; Rao, S.; Liggieri, L. Surfactant Adsorption at Superhydrophobic Surfaces. *Appl. Phys. Lett.* **2006**, *89*, 053104.

(66) Mohammadi, R.; Wassink, J.; Amirfazli, A. Effect of Surfactants on Wetting of Super-Hydrophobic Surfaces. *Langmuir* **2004**, *20*, 9657−9662.

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