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Three-Dimensionally Macroporous Fe/C Nanocomposites As Highly Selective Oil-Absorption Materials

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Supporting Information

ABSTRACT: In this study, three-dimensionally macroporous Fe/C nanocomposites were investigated as highly selective absorption materials for removing oils from water surface. The macroporous nanocomposites were synthesized by sintering a mixture of closely packed polystyrene microspheres and ferric nitrate precursor. These nanocomposites exhibited superhydrophobic and superoleophilic properties without the modification of low-surface-energy chemicals. And the pore size of the nanocomposites, which is crucial for the oil-absorption capacity, was tuned by varying the diameter of polystyrene microspheres. The macroporous nanocomposites fast and selectively absorbed a wide range of oils and hydrophobic organic solvents on water surface, and the removal of the absorbed oils from the water surface was readily achieved under a magnetic field. Moreover, the nanocomposites still kept highly hydrophobic and oleophilic characteristics after repeatedly removing oils from water surface for many cycles. Because of frequently occurring environmental pollution arising from oil spills and chemicals leakage, the results of this study might offer a kind of efficient and selective absorbent materials for removing oils and nonpolar organic solvents from the surface of water.

KEYWORDS: *three-dimensionally macroporous, Fe/C nanocomposites, superhydrophobicity and superoleophilicity, oil absorption, magnetic field*

INTRODUCTION

In recent years, the frequent occurrence of oil spillage on water surface causes a severe crisis of ecology environment.[1−3] Therefore, much attention was paid on developing facile methods for fast and selective removal of oils from water surface. Traditionally, oil spillage can be cleaned by mechanical collection,[4] absorbent materials,[5−7] chemical dispersants,[8] bioremediation,[9] in situ burning,[10] etc. The use of absorbent materials is considered to be one of the most effective approaches because of its low cost in operation and ready availability. Generally, an ideal absorbent material should have the properties such as high oil-absorption capacity, high selectivity, low density, excellent recyclability, environmental friendliness, and so on. Synthetic and natural absorbent materials[5,11,12] had been investigated for the oil-removal purpose. However, it is still a challenge to increase the water-repelling property as well as oil-absorption capacity of the materials for the purpose of practical application. Recently, superhydrophobicity and superoleophilicity were introduced to synthetic absorbent materials in order to improve the selectivity (i.e., water repelling but oil absorptive) and efficiency. For example, superhydrophobic and superoleophilic carbon nanotubes,[13] polymer films,[14] ZnO mesh film,[15] metallic meshes,[16−19] MnO_2 nanowires,[20] filter paper,[21] magnetic nanoparticles,[22] etc., were reported to selectively and efficiently separate oils from water. Nevertheless, complicated processes involved constructing micro−nanoarchitectures and subsequent modification with low-surface-energy chemicals were needed for these absorbent materials. In addition, the dependence of oil-absorption capacity on the microstructure (e.g., pore size) of absorbent materials needs further investigations.

Here, we presented a kind of three−dimensionally macroporous Fe/C nanocomposites for removing oils from water surface under magnetic field. The macroporous nanocomposites were synthesized by sintering a mixture of closely packed polystyrene (PS) microspheres and $Fe(NO_3)_3$ precursor (Scheme 1). Interestingly, the as−prepared macroporous nanocomposites exhibited superhydrophobic and superoleophilic properties without the modification of low−surface−energy chemicals. Therefore, the nanocomposites fast removed a wide range of oils and hydrophobic solvents from water surface with high selectivity and efficiency under a magnetic field. Although three−dimensionally ordered macroporous (3DOM) materials[23−32] were synthesized in the fields of photonics, catalysis, sensors,[33−35] etc., few studies reported three-dimensionally macroporous Fe/C nanocomposites for oil-absorption. The finding of this study might provide a kind of absorbent materials for fast and selective removal of oils from water surface.

EXPERIMENTAL SECTION

1. Preparation of Three-Dimensionally Macroporous Fe/C Nanocomposites. Initially, monodispersed polystyrene (PS) microspheres were synthesized through an emulsion polymerization method.[36] Then three−dimensionally closely packed colloidal crystals were fabricated by gravity sedimentation[24,37] and used as templates. The closely packed PS templates were immersed in an aqueous solution of ferric nitrate (2.5 M) for 5 min, and the excessive solution was removed by filtration. The resulting solid mixtures were dried at 50 °C for 4 h. Finally, the PS templates were removed by calcination at

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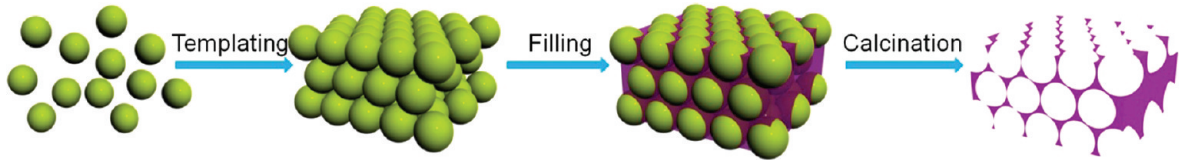
Scheme 1. Illustration for the Synthesis of Three-Dimensionally Macroporous Fe/C Nanocomposites



600 °C for 7 h in an argon atmosphere. The obtained samples were called three-dimensionally macroporous Fe/C nanocomposites. The PS microspheres used in this study and as-prepared Fe/C samples were listed in Table 1.

Table 1. Diameters of PS Microspheres and the Pore Sizes of Macroporous Fe/C Nanocomposites

sample	diameter of PS microsphere (μm)	pore size (μm)
Fe/C−1	0.67	0.35
Fe/C−2	1.7	1.1
Fe/C−3	2.5	1.8
Fe/C−4	4.2	3.0

2. Characterization of Macroporous Fe/C Nanocomposites. Morphologies of macroporous Fe/C nanocomposites were investigated by scanning electron microscopy (SEM, FEI Sirion 200). Contact angles (CAs) were measured on an OCA20 (DataPhysics Instruments GmbH, Filderstadt) at room temperature by using 6 μL distilled water or lubricating oil droplet as an indictor. X-ray diffraction (XRD) analysis was performed by using a Shimadzu XRD−6000. Brunauer−Emmett−Teller (BET) surface area of the macroporous nanocomposites was measured by an ASAP 2020 (Micromeritics). Thermogravimetric analysis (TGA) was measured by Netzsch STA−449F3 in an air or argon flow. The X-ray photoelectron spectroscope (XPS) was measured by PHI−5700ESCA.

3. Oil-Absorption Experiments. First, five kinds of oils and organic solvents including lubricating oil, crude oil, bean oil, dodecane and decane were poured on the surface of water contained in a beaker, respectively. Then macroporous Fe/C nanocomposites were gently placed on the surface of the oil−water mixtures. The oils and organic solvents were fast and selectively absorbed by the macroporous nanocomposites in a few seconds. Later, the absorbed oils together with the macroporous Fe/C nanocomposites were collected by a magnet bar and weighed. The oil−absorption capacity of the nanocomposites was calculated by the formula described in reference.[22] After absorption process, the macroporous Fe/C nanocomposites were washed by ethanol to collect the oils. After being filtered and dried at 50 °C for 5 h, the regenerated nanocomposites were reused to remove oils from water surface for many cycles. The purity of the collected oils and the selective absorption characteristics of macroporous Fe/C nanocomposites were investigated by thermal gravimetric analysis (TGA). All the experiments were repeated for three times.

RESULTS AND DISCUSSION

First, the chemical composition of the as−prepared macroporous Fe/C nanocomposites was confirmed by XRD analysis. Pure metallic phase of α−Fe (2θ = 43.8, 65.2, and 82.6°, JCPDS 06−0696) and iron carbide (Fe_3C, JCPDS 75−0910) phase are detected in the XRD pattern (Figure 1a), indicating the formation of Fe/C nanocomposites. The amorphous carbon was also detected, which is ascribed to the decomposition of the PS template. The carbon content in the macroporous Fe/C nanocomposites was determined to be 43 wt % (Fe/C-2 sample) by TGA measurement performed in an air flow (Figure 1b). To further confirm the chemical composition of the as-prepared macroporous Fe/C nanocomposites, we conducted XPS measurement and analyzed its results (see the Supporting Information, Figure S1).

Then the morphologies of the as-prepared macroporous Fe/C nanocomposites were observed by SEM. As shown in Figure 2, macropores interconnect each other to form three-dimensionally macroporous structures. We also revealed that the size of the macropores could be tuned by varying the diameter of PS microspheres. For example, macroporous Fe/C composites with pore sizes of 350 nm and 1.1, 1.8, and 3.0 μm were fabricated by using PS microspheres with diameters of 670 nm

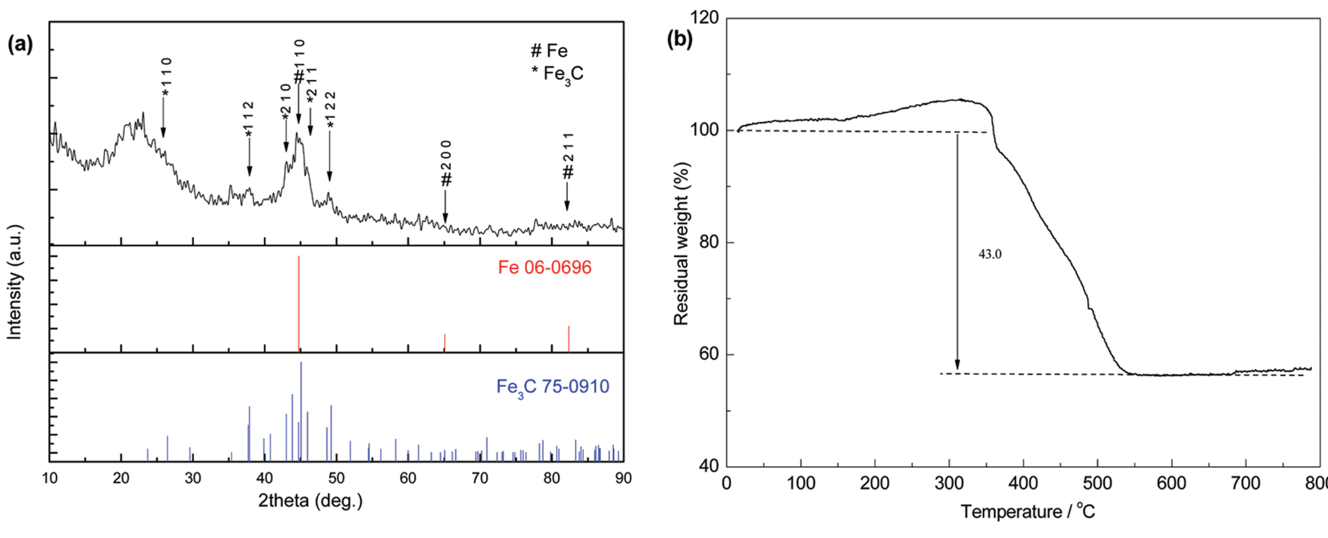


Figure 1. (a) XRD pattern and (b) TGA curve of Fe/C-2 sample; the standard diffraction peaks of Fe and Fe_3C are marked with red and blue bars in the XRD pattern; TGA was performed in an air flow at a rate of 10 °C min^{-1}.

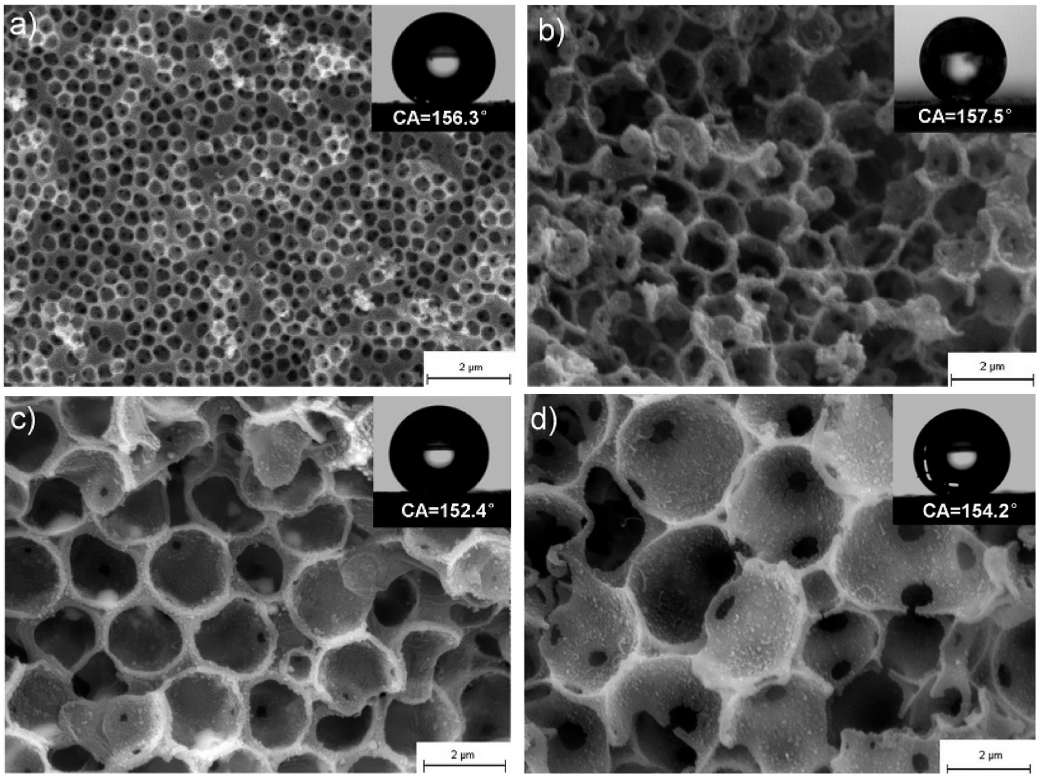


Figure 2. SEM images of (a) Fe/C-1, (b) Fe/C-2, (c) Fe/C-3, and (d) Fe/C-4 samples; inset images are the water contact angles of the corresponding macroporous nanocomposites.

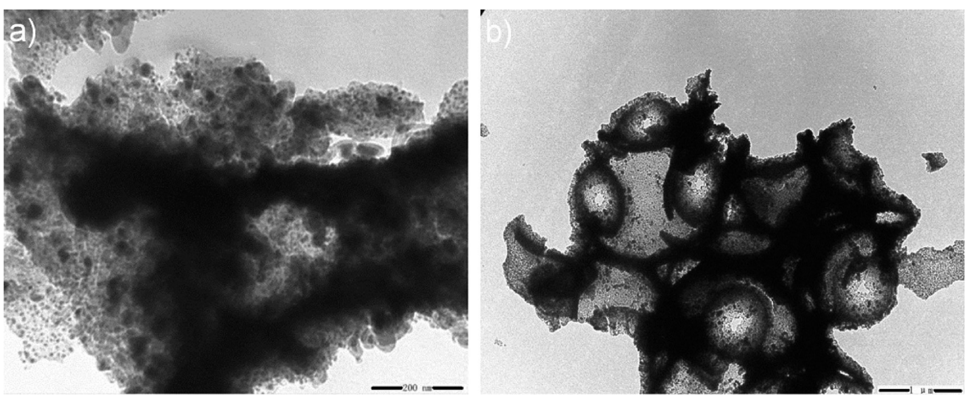


Figure 3. TEM images of Fe/C-2 sample; (a) ×150 000, (b) ×30 000.

and 1.7, 2.5, and 4.2 μm as the templates, respectively (Table 1). It is believed that these interconnected macropores are beneficial for constructing a highly hydrophobic surface as well as increasing oil-absorption capacity.

The microstructure of the macroporous Fe/C−2 nanocomposite was further investigated by TEM. A low magnification TEM image reveals the presence of 3D interconnected Fe skeleton (Figure 3b). And the outer surface of the Fe skeleton is coated with amorphous carbon layers, as illustrated by a high magnification image (Figure 3a).

Interesting, the as−prepared macroporous Fe/C nanocomposites displayed superhydrophobilic and superoleophilic properties at ambient temperature without the modification of low-surface-energy chemicals. The water contact angles of Fe/C-1, Fe/C-2, Fe/C-3, and Fe/C-4 samples are 156.3,157.5,152.4, and 154.2°, and the contact angles for lubricating oil are 4.0, 2.5, 2.9, and 5.0°, respectively. At the same time, the wetting time of Fe/C-2 sample for a lubricating oil drop was found to be 8.64 s (see the Supporting Information, Figure S3), The superhydrophobicity of macroporous Fe/C nanocomposites is believed to arise from the 3D porous structure and the amorphous carbon layers. The 3D macroporous structure traps a large amount of air, whereas the carbon layers on the outer surface of the 3D skeleton reduce the surface free energy. Therefore, a water droplet does not fully contact with the nanocomposites' surface but rather suspends on the air layer formed by the interconnected macropores. As a result, the water droplets minimizes its surface tension by keeping a spherical shape.[38] In contrast, an oil droplet is adsorbed first on the surface of the macroporous materials through van der Waals force, and then it penetrates into the macropores of the nanocomposites by capillary action.

As expected, the three-dimensionally macroporous Fe/C nanocomposites showed excellent selective adsorption characteristics for a wide range oils and hydrophobic organic solvents because of high porosity, superhydrophobicity and superoleophilicity. Five kinds of oils and hydrophobic solvents including lubricating oil, bean oil, crude oil, dodecane and decane were investigated in this study. For instance, lubricating oil was quickly absorbed by Fe/C-2 sample in a few seconds when the nanocomposites were placed onto the surface of the oil−water mixture. The oil-absorption capacity of Fe/C-2 sample for the oils and organic solvents is in order of lubricating oil > bean oil > crude oil > dodecane > decane, which is related to the density and viscosity of the oils (see the Supporting Information, Table S1). Generally, for the Fe/C samples have a given pore size, an increase in oil density means that a larger amount of oils can be stored in the macropores of the nanocomposites. The viscosity of the oils has two effects on the oil absorption capacity. On the one hand, an increase in viscosity enhances the adherence of the oils to the nanacomposites, which is beneficial for the improvement in oil absorption capacity. On the other hand, high viscosity will impede the permeation of the oils into the inner pores of the nanocomposites, which will decrease the oil absorption capacity. In this study, we revealed that the oil absorption capacities increase for the oils with higher density and viscosity (see the Supporting Information, Figure S7).

The pore size is also an important factor affecting the oil-absorption capacity of the nanocomposites. The oil−absorption capacities of Fe/C-1, Fe/C-2, Fe/C-3, and Fe/C-4 samples for lubricating oil are 4.8, 7.5, 8.0, and 9.4, respectively. We compared the present results with that of core−shell Fe_2O_3@C nanoparticles reported previously.[22] Although the BET surface areas of Fe/C-2 (67.58 m^2/g) and Fe/C-4 and (50.59 m^2/g) are smaller than those of Fe/C−1 (172.23 m^2/g) and Fe_2O_3@C nanoparticles (94.04 m^2/g), the formers still exhibit higher oil−absorption capacities under the same conditions, suggesting that the interconnected macropores are beneficial for oil−storage. This result is due to the fact that oils are mainly stored in the macropores rather than in the micropores or mesopores of the nanocomposites. Although the later contributes greatly to the BET surface area of the nanocomposites, the total volume of these small pores is much lower than that of the macropores. In addition, it is difficult for oils to permeate into these micropores and mesopores, especially for the pores with closed openings. Therefore, the oil-absorption capacity of the nanocomposites is increased by a larger pore size.

More interesting, the absorbed oils together with the nancomposites could be readily removed from the water surface by a magnetic bar, as shown in Figure 4 (also see the Supporting Information, Movie M1). Notably, no macroporous composites sink to the bottom of the container even under vigorous stirring, indicating that they can be used on water surface without sinking (see Supporting Information, Figure S4 and Movie M2).

TGA measurement was conducted on Fe/C-2 sample absorbed lubricating oil in order to investigate its absorption efficiency and selectivity. Figure 5 shows that only lubricating oil was absorbed by Fe/C-2 sample because no weight loss ascribed to water evaporation is observed at 100 °C, indicating high selectivity and efficiency of macroporous nanocomposites for removing oils from water surface.

Macroporous Fe/C nanocomposites also showed excellent recyclability in the removal of oils from water surface. Figure 6 illustrates the water contact angles and oil−absorption capacities of Fe/C−2 sample after 10 successive water−oil separation cycles. The sample still kept a high water contact angle of 142.1° (Figure 6a) and an oil−absorption capacity of 5.7 (Figure 6b) even after the 10th cycle.

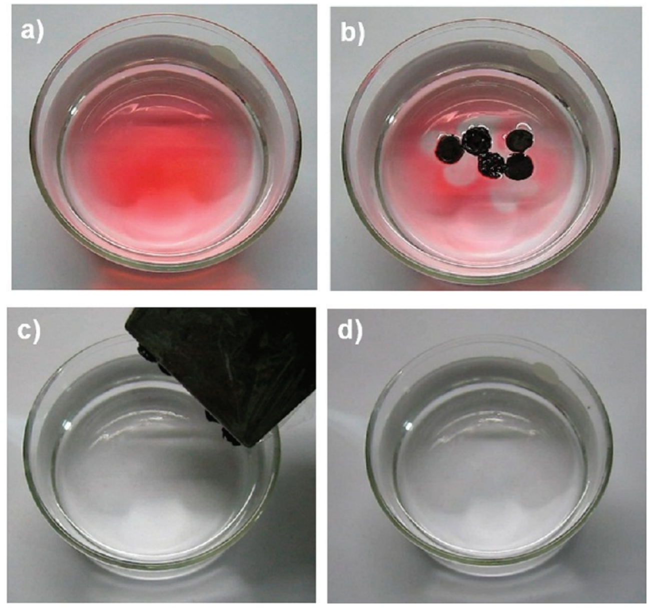


Figure 4. Removal of lubricating oil from water surface by Fe/C-2 sample under magnetic field. The oil was dyed with oil red 24 for clear observation.

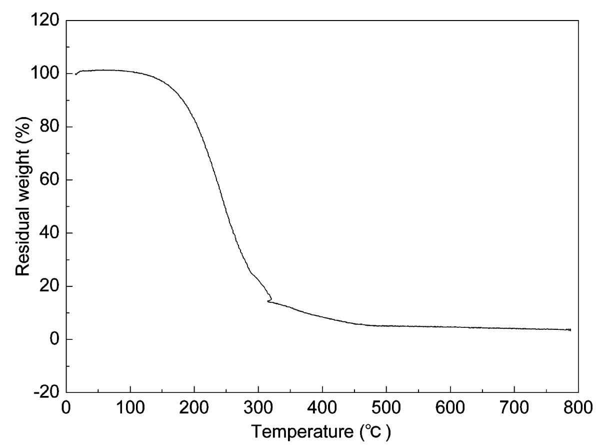


Figure 5. TGA curve for the Fe/C-2 sample that absorbed lubricating oil in an argon flow at a rate of 10 °C min^{-1}.

Moreover, macroporous Fe/C nanocomposites exhibited high corrosion resistance in 3.5 wt % NaCl and aqueous solutions with pH values ranging from 2 to 14 for 24 h. The water contact angles of Fe/C-2 sample after put on the surface of the corrosive media were plotted (see Figure S8 in the Supporting Information). The XRD pattern of Fe/C-2 sample exhibits almost no change after they were put on the surface of solution with pH 2 for 24 h (see Figure S9 in the Supporting Information).

In addition, we also demonstrated that three-dimensionally macroporous Co/C and Ni/C nanocomposites synthesized by the same method displayed superhydrophobic and superoleophilic properties, highly selective absorption characteristics, desirable oil-absorption capacities and excellent recyclability (see Table S2 and Figures S5−S8 in the Supporting Information).

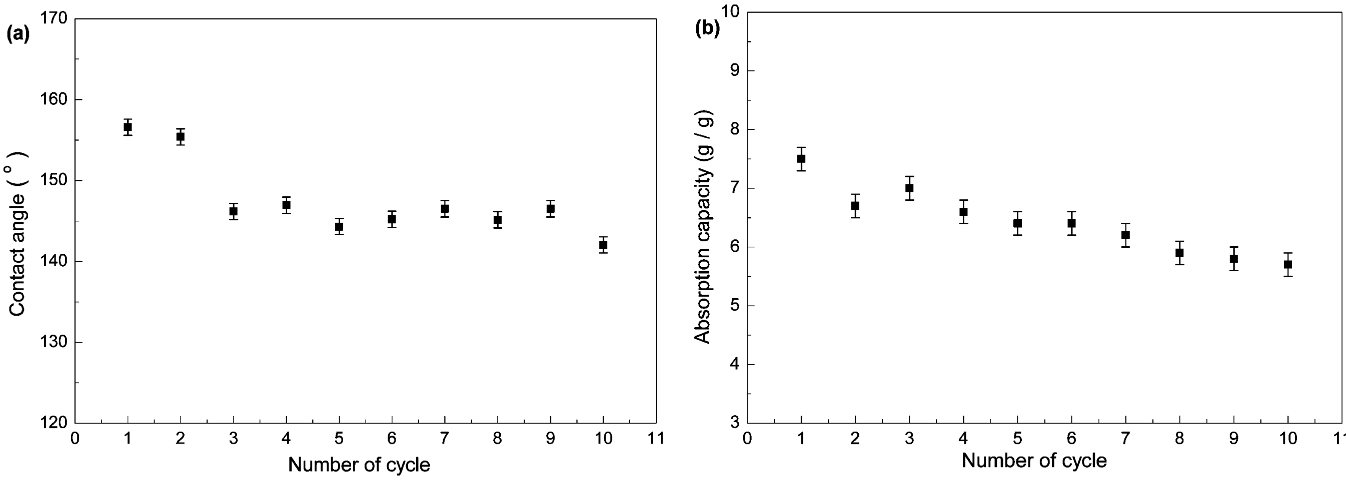


Figure 6. (a) Water contact angle and (b) oil-absorption capacity of Fe/C-2 sample recorded after different water−oil separation cycles. Lubricating oil was used in this experiment.

■ CONCLUSIONS

In summary, three-dimensionally macroporous Fe/C nanocomposites were fabricated through calcination processes by using closely packed polystyrene microspheres as the template. The macroporous nanocomposites not only exhibited interesting superhydrophobicity and superoleophilicity without the modification of low-surface-energy chemicals, but also fast and selectively removed a variety of oils and hydrophobic organic solvents from water surface under magnetic field. The oil-absorption capacity of the nanocomposites, which are much higher than that of reported Fe_2O_3@C nanoparticles, could be tuned by varying the diameter of macropores. Because of their good corrosion resistance, unsinkable property, excellent recycleability, environmental friendliness, and easy operation, these three-dimensionally macroporous Fe/C nanocomposites might be a kind of promising absorbent materials for removing oils and hydrophobic organic solvents from water surface.

■ ASSOCIATED CONTENT

Supporting Information

Information on XPS results, photograph and SEM images, dynamic wetting behavior of macroporous Fe/C nanocomposites for lubricating oil, properties of oils and organic solvents, surface areas, contact angles, structural characterizations, morphologies of three−dimensionally macroporous Ni/C and Co/C nanocomposites, oil-absorption capacities for different kinds of oils and organic solvents, corrosion resistance of macroporous Fe/C, Ni/C, and Co/C nanocomposites, structural characterization of macroporous Fe/C nanocomposites after corrosion test, the removal of lubricating oil from the water surface, the floating behavior of macroporous Fe/C nanocomposites that absorbed lubricating oil on the water surface under stirring conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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