Fast and Selective Removal of Oils from Water Surface via Highly Hydrophobic Core−Shell Fe_2O_3@C Nanoparticles under Magnetic Field

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ABSTRACT The removal of oil spills or organic contaminants from water surface is of great technological importance for environmental protection. A major challenge is the fast distribution and collection of absorbent materials with high separation selectivity, good thermal stability, and excellent recyclability. Here we reported fast and selective removal of oils from water surface through core−shell Fe_2O_3@C nanoparticles under magnetic field. These nanoparticles combined with unsinkable, highly hydrophobic and superoleophilic properties, could selectively absorb lubricating oil up to 3.8 times of the particles' weight while completely repelling water. The oil-absorbed nanoparticles were quickly collected in seconds by applying an external magnetic field. More importantly, the oil could be readily removed from the surfaces of nanoparticles by a simple ultrasonic treatment whereas the particles still kept highly hydrophobic and superolephilic characteristics. Experiment results showed that the highly hydrophobic Fe_2O_3@C nanoparticles could be reused in water−oil separation for many cycles. Our results suggest a facile and efficient method that might find practical applications in the cleanup of oil spills and the removal of organic pollutants on water surface.

KEYWORDS: water−oil separation • Fe_2O_3@C nanoparticles • highly hydrophobic and superoleophilic properties • magnetic field • selectivity • recyclability

INTRODUCTION

Because of the increasing attention on environmental protection, there is a growing demand for materials capable of removing various forms of organic contaminants or oil spills from water surface. The existing absorbent materials used to achieve this goal include high-surface-area activated carbons, membranes (1) fabricated from polymers (2), carbon (3), or transition metal oxides (4), and highly porous materials (5), etc. Although widely applied in research and practical applications, these materials still have limitations. For example, activated carbons and porous materials have the disadvantages such as difficulty in collection due to small particle size, high regeneration temperatures (e.g., 800−850 °C for activated carbon), and low separation efficiency caused by the coadsorption of water (6−10). The conventional polymeric membranes will decompose at elevated temperatures and lack substantial selectivity. In addition, membranes are unsuitable for the cleanup of large-area oil spills or organic contaminants on a water surface.

Considering that an oil leakage will cause large-area water pollution in a very shot time (for example, 1 ton of oil will quickly spread on a water surface to form a film of 12 km^2 in area), efficient removal of oil spills from water surface as soon as possible should be a most important step for the protection of oceanic environment and livings. In this aspect, oil-absorbent materials can be fast distributed and collected will reduce this ecological impact. Recently, it was reported that materials with superhydrophobic and superoleophilic properties could selectively collect oils or organic chemicals from water, which provides a novel strategy for the water−oil separation techniques (11−19). More recently, magnetic porous materials were demonstrated to realize a fast separation of organic chemicals from water by applying an appropriate external magnetic field (20−25). However, little attention was paid to the materials combined with magnetic, highly hydrophobic, and superoleophilic properties. We believe that such kind of materials might be applied to the fast and selective cleanup of large-area oil spills under external magnetic field.

Here, we reported a kind of thermally stable, recyclable, environmentally friend, and highly selective oil-absorbent materials based on core−shell Fe_2O_3@C nanoparticles. The nanoparticles, composed of porous appearances and hydrophobic polysiloxane layers, exhibited highly hydrophobic and superoleophilic characteristics. These unique properties could be obtained or lost completely by coating with or removal of the polysiloxane layer at elevated temperatures. The nanoparticles were able to selectively absorb a broad range of oils and organic solvents while completely repelling water. More interestingly, the oil-absorbed nanoparticles could be quickly and thoroughly collected by a magnet bar (Scheme 1), which offers a possibility to fast removal oils or

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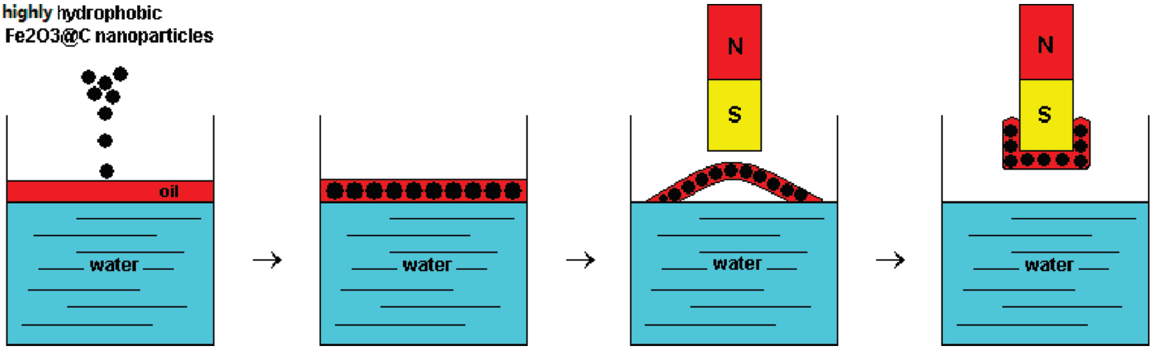
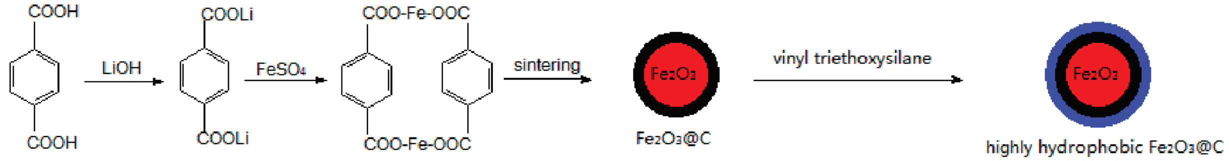
Scheme 1. Illustration for the Removal of Oil from Water Surface through Highly Hydrophobic Fe_2O_3@C Nanoparticles under External Magnetic Field



Scheme 2. Illustration for the Preparation of Highly Hydrophobic Fe_2O_3@C Nanoparticles



organic solvents from water surface. The nanoparticles also showed good structural stability in corrosive media and exhibited good recyclability in water and oil separation. Although Fe_2O_3 had been extensively used in the fields of pigments, environment protection (26), catalysts (27), gas sensors (28), magnetic storage media (29), clinical diagnosis (30), and lithium-ion batteries (31, 32), few studies applied the highly hydrophobic Fe_2O_3@C nanoparticles in the water−oil separation technology.

EXPERIMENTAL SECTION

First, 1.33 g of terephthalic acid ($C_8H_6O_4$, 8 mmol) and 0.67 g of lithium hydroxide monohydrate ($LiOH \cdot H_2O$, 16 mmol) were completely dissolved in 150 mL of distilled water. Then, 2.22 g of iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, 8 mmol) was added with stirring at ambient temperature for 5 h to obtain yellow ferric benzoate precursor. The preparation of Fe_2O_3@C nanoparticles was conducted by a thermal decomposition of the precursor in a sealed quartz tube at 600 °C for 6 h. Then the Fe_2O_3@C nanoparticles were treated with an ethanol solution containing 2 wt % vinyl triethoxysilane for 3 h (Scheme 2). After filtration, the obtained powder was dried at 140 °C for another 8 h. By these processes, the entire surfaces of the Fe_2O_3@C nanoparticles were coated with low-surface-energy polysiloxane layers.

Water contact angles (CAs) measurements were conducted by commercial instruments (OCA 20, DataPhysics Instruments GmbH, Filderstadt). Before measurements, the nanoparticles were placed on a slide and pressed into a flat film. A distilled water droplet and a N100 lubricating oil droplet of 6 μL were used as the indicators. Scanning electron microscopy (SEM) images were obtained with a FEI Quanta 200. X-ray diffraction (XRD) analysis was carried out using a Shimadzu XRD-6000. Transmission electron microscopy (TEM) measurements were conducted on an H-7650 (Hitachi) microscope. Size distribution measurements were carried out on a Mastersizer S (Malvern). Thermogravimetric analysis (TGA) was performed on a Netzsch STA-449F3 analyzer under an argon atmosphere at a heating rate of 10 °C min^{-1}. X-ray photoelectron spectroscope (XPS) was recorded on a PHI-5700ESCA. Brunauer−Emmett−Teller (BET) surface area of the nanoparticles was recorded by a Micromeritics ASAP2020. The magnetic property of the nanoparticles was measured by the physical measurement system (PPMS) of Quantum Design. The external magnetic field strength was recorded on a Gauss meter (Digital Measurement System SG-3-A).

The oil-absorbent capacity of the nanoparticles was determined by weight measurements. The weights of nanoparticles before and after oil absorbance were measured as m_1 and m_2 by an electronic balance, respectively. The weight of absorbed oil, m, was calculated by the difference between m_2 and m_1. The oil-absorbent capacity k of the nanoparticles was calculated by the formula $k = (m_2 - m_1)/(m_1)$.

The removal of lubricating oil from water surface was carried out according to the procedure illustrated in Scheme 1. First, the highly hydrophobic nanoparticles were scattered on the surface of water and oil mixture, and the particles absorbed the oil quickly. The nanoparticles soaked with oil were then separated from the water surface when a magnet bar approached the mixture. The oil was removed from the surfaces of the nanoparticles by ultrasonically washing in ethanol for 5 min. After being dried in an oven, the nanoparticles could be reused to separate the water and oil mixture and their recyclability was investigated by water contact angle measurements.

To investigate the stability of the polysiloxane coatings, we put highly hydrophobic Fe_2O_3@C nanoparticles on the surfaces of 0.1 M NaCl and aqueous solutions with pH values ranging from 1 to 14 for different times. After the coatings dried, the wettability of the resulting nanoparticles was investigated by water contact angle measurements.

RESULTS AND DISCUSSION

The structure and chemical composition of the resulting nanoparticles were investigated by SEM, XRD, and TEM. SEM images show that a large portion of nanoparticles (varying from 30 to 200 nm in size) assemble into agglomerations to form porous appearance. The BET surface area of the nanoparticles is 94.04 m^2/g. X-ray diffraction pattern of the nanoparticles confirmed the feature peaks of γ-Fe_2O_3 (JCPDS 39−1346) in the region of 10− 90° (see the Supporting Information, Figure S1). The nanoparticles have a strong magnetic response to an external magnetic field

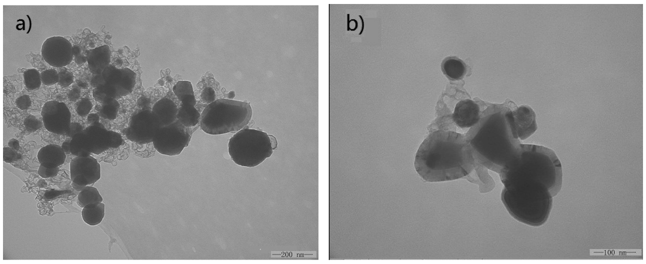


FIGURE 1. TEM images of the polysiloxane-coated Fe_2O_3@C nanoparticles: (a) 100 000 and (b) 200 000×.

according to the magnetization curve (see the Supporting Information, Figure S2).

Figure 1 shows transmission electron microscopy (TEM) images of the Fe_2O_3@C nanoparticles after polysiloxane modification. The surface of Fe_2O_3 particle is coated with a layer of carbon with a thickness of 7−36 nm, forming a core−shell nanostructure. The presence of polysiloxane layers on the surfaces of nanoparticles was demonstrated by X-ray photoelectron spectroscopy (XPS) (see the Supporting Information, Figure S3). The Si 2p and O 1s spectra show the feature peaks of the Si−O−Si bond, indicating the formation of polysiloxane layers on the particles after vinyl triethoxysilane modification. It should be noted that the modification of polysiloxane layers will reduce the aggregations particle size of Fe_2O_3@C nanoparticles, as proven by size distribution measurements (see the Supporting Information, Figure S2).

Contact angle measurements showed that the nanoparticles displayed highly hydrophobic and superoleophilic properties, as shown in Figure 2. The apparent contact angle of a water drop placed on a bed of the polysiloxane-coated Fe_2O_3@C nanoparticles was 162.9 ± 2° (Figure 2a), higher than that of the pristine Fe_2O_3@C nanoparticles (see the Supporting Information, Figure S4), confirming the high hydrophobicity of the nanoparticles after polysiloxane modification. In contrast, a drop of lubricating oil quickly spread on the bed of the highly hydrophobic nanoparticles, indicating superoleophilic property of the particles. The wetting time for an oil droplet (6 μL) added to the polysiloxane-coated particles was found to be 4.17 s, as evidenced by dynamic contact angle measurements (Figure 2b−e). The highly hydrophobic and superoleophilic properties of the polysiloxane-coated nanoparticles are believed to arise from the porous surfaces and the low-surface-energy polysiloxane

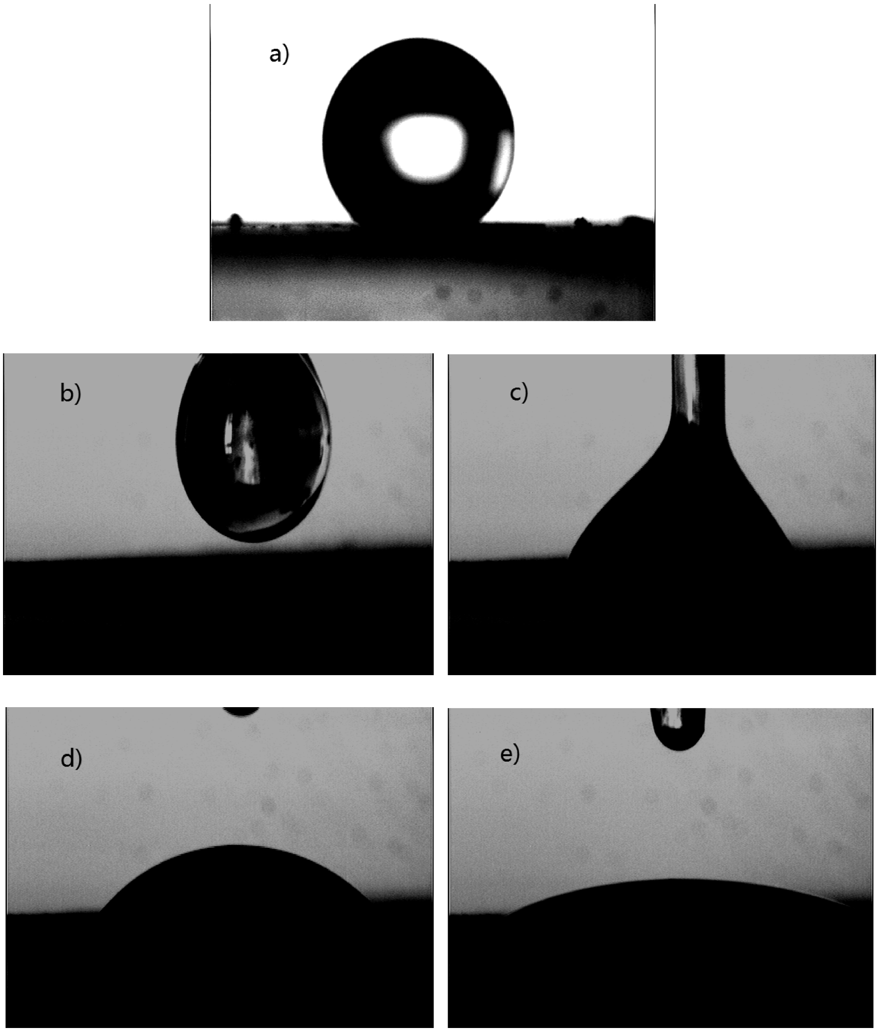


FIGURE 2. (a) Optical image of a water droplet placed on a bed of the polysiloxane-coated Fe_2O_3@C nanoparticles; and (b−e) video snapshots of the wetting of an oil droplet on the bed of polysiloxane-coated Fe_2O_3@C nanoparticles.

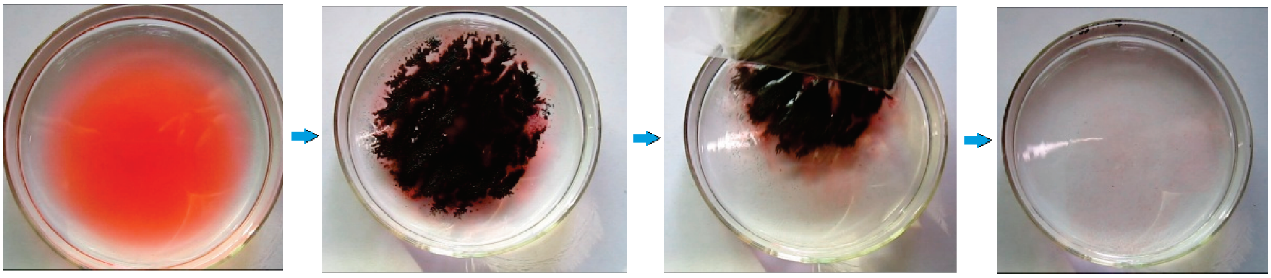


FIGURE 3. Removal of lubricating oil from water surface by the polysiloxane-coated $Fe_2O_3@C$ nanoparticles under magnetic field. The lubricating oil was labeled by oil red III dye for clarity.

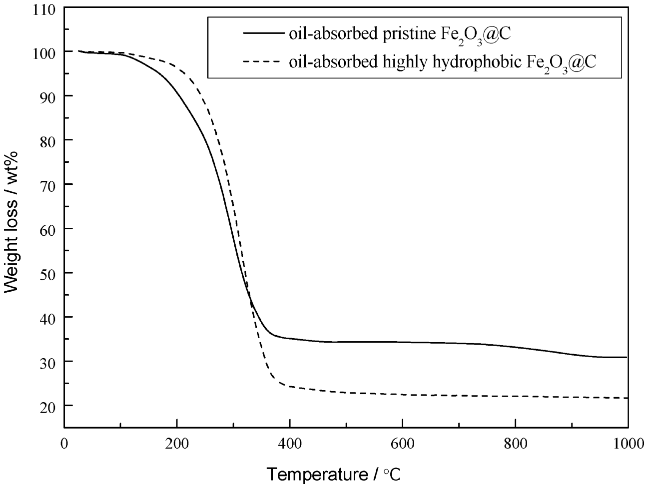


FIGURE 4. TGA curves of oil-absorbed pristine and polysiloxane-coated $Fe_2O_3@C$ nanoparticles under an argon atmosphere.

layers (33−36). It is notable that the polysiloxane-coated nanoparticles remained their highly hydrophobic property after floating on the surfaces of corrosive media for a long time, indicating good corrosive-resistance of the polysiloxane coatings on the particles (see the Supporting Information, Figure S5). For example, the nanoparticles exhibited almost no change in contact angle when they were placed on a 0.1 M NaCl solution for 24 h. More importantly, the nanoparticles still showed contact angles larger than 150° after floating on the aqueous solutions with pH values ranging from 3 to 14 for 14 h. Only a slight decrease in contact angle was observed for the solution having pH 1.

As expected, the highly hydrophobic and superoleophilic nanoparticles exhibited a property called selective absorbance. When brought into contact with a layer of lubricating oil on a water surface, the nanoparticles quickly absorbed the oil while repelling the water, as shown in Figure 3. More interestingly, the oil-absorbed nanoparticles could be readily moved with a magnet bar over the water surface and then quickly be collected in seconds (see the Supporting Information, Movie M1). The strength of the magnetic filed in this study was 0.35T. The oil-absorbent capacity *k* of the polysiloxane-coated particles was up to 3.70 times of their weight, whereas that of the pristine particles was 2.18. The values are very close to the results of TGA, as shown in Figure 4. The polysiloxane-coated particles showed oil uptake capacity up to 3.8 times of their weight, whereas the pristine particles only exhibited a value of 1.8, confirming the importance the highly hydrophobic and superoleophilic coatings for the selective adsorption. TGA results also confirmed that only oil was absorbed by the highly hydrophobic nanoparticles because there was no weight loss associated with water at 100 °C. Considering that these particles can be facile dispersed (e.g., by spray method) over a water surface, they might be useful for the removal of organic contaminants on large scale by applying an external magnetic field. Therefore, this method offers a novel approach for the removal of hydrophobic organic pollutants and oil-spills on water surface. Notably, the removal of organic chemicals on the water surface by this method can be extended to many organic solvents and oils if they can be effectively adsorbed onto the nanoparticles, making these nanoparticles ideal candidate for oil-absorbent materials.

Interestingly, the nanoparticles showed unsinkable property when they were put on the both surfaces of the mixture and water under vigorous agitation conditions, as illustrated in Figure 5 and Figure S6 (see the Supporting Information). The polysiloxane-coated particles still floated over the water surface after vigorous stirring, while no particles sunk to the bottom of the water (see the Supporting Information, Movie M2). After being collected by a magnet bar, the weight of the particles remained unchanged, confirming the high hydrophobicity of the particles' surfaces. The unsinkable property of the polysiloxane-coated nanoparticles might be related to the highly hydrophobic coatings, which could repel the water surface to increase the water displace volumes of the particle s (37−41). These results are of practical importance for the application of the nanoparticles under oceanic conditions.

Another feature of the highly hydrophobic nanoparticles was their excellent recyclability in the oil-absorbent capacity, which would significantly reduce the materials waste and operation cost. After absorbance, the particles could be regenerated by ultrasonic washing in ethanol for 5 min. Only slight changes in water contact angles were observed in each cycle (six times for the study shown in Figure 6), as proven by keeping water contact angles above 150°. It should be noted that the highly hydrophobic and superoleophilic coatings could sustain a temperature up to 450 °C, indicating good thermal stability of the highly hydrophobic nanoparticles (see the Supporting Information, Figure S7). At a temperature of 600 °C, the polysiloxane coatings on the surfaces of nanoparticles were easily removed. After recoating the particles with polysiloxane layers, the particles regained highly hydrophobic property. Although the oil

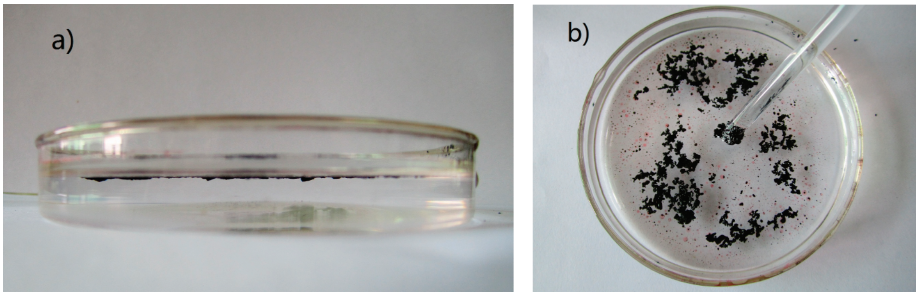


FIGURE 5. Optical images of the polysiloxane-coated Fe_2O_3@C nanoparticles on the surface of oil and water mixture after vigorous agitation: (a) side view, (b) top view.

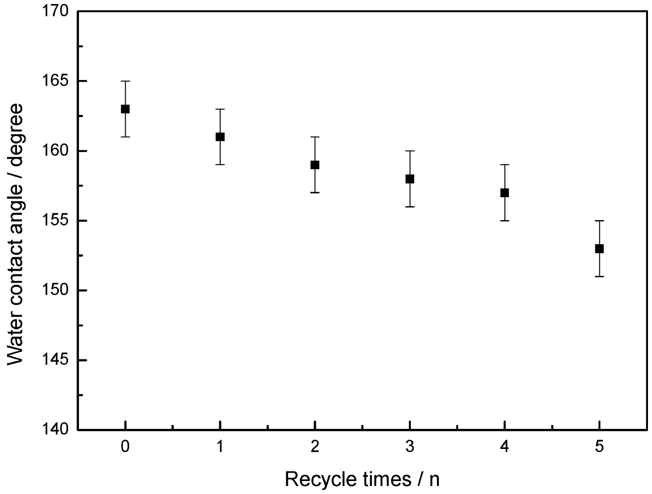


FIGURE 6. Water contact angles of highly hydrophobic Fe_2O_3@C nanoparticles after water−oil separation for six cycles.

uptake capacity of the nanoparticles was lower compared to the reported membranes (2−4) or porous materials (5), they still possessed the advantages of easy production and storage, fast distribution and collection, low cost, good recyclability, high resistance to corrosion, thermal stability, and environmental friendliness. We believe that a careful design on the morphology and porosity of the particles might further improve the oil-absorbent capacity of this kind of materials.

CONCLUSIONS

In summary, the present finding provided an alternative method for the fast and selective removal of hydrophobic organic contaminants from water surface via highly hydrophobic core−shell Fe_2O_3@C nanoparticles under external magnetic field. The nanoparticles showed an oil-absorbent capacity up to 3.8 times of their weight and good stability in corrosive media for a long time. In particular, the nanoparticles exhibited unsinkable property under agitation conditions and excellent recyclability, which are of importance in practical applications. Given the global attention on severe water pollution, a more immediate application for this method might be in the removal of large-area contaminants on water surface arising from oil spills and industrial organic pollutants.

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Supporting Information Available: Videos showing the removal of oil from water surface and the behavior of polysiloxane-coated Fe_2O_3@C nanoparticles on the water surface under agitation condition (AVI); SEM images, XRD pattern, XPS spectra, TGA curves, size distributions, and magnetic property of the polysiloxane-coated Fe_2O_3@C nanoparticles; the wettability of the pristine and polysiloxane-coated Fe_2O_3@C nanoparticles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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