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Facile removal of oils from water surfaces through highly hydrophobic and magnetic polymer nanocomposites

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ABSTRACT

In this study, magnetic polymer nanocomposites were investigated as highly selective absorbent materials for removing oils from water surfaces. The nanocomposites with highly hydrophobic and superoleophilic surface were synthesized through a low-cost emulsion polymerization, and exhibited some practical properties including unsinkability, thermal stability and corrosive-resistance for real applications. These as-prepared nanoparticles could effectively absorb three kinds of oils up to above 3.63 times of the particles' weight while completely repelling water. It is very easy to collect the oil-absorbed nanoparticles by applying an external magnetic field. Besides, the oil could be readily removed from the surfaces of nanoparticles by a simple ultrasonic treatment, and the nanocomposites still kept highly hydrophobic and oleophilic characteristics after repeatedly removing oils from water surface for many cycles. The findings of this study might provide a convenient method for fast and selective removal of oils from the surface of water.

1. Introduction

Because of the frequent occurrence of water pollution caused by oil spillages in recent years, there is a growing demand to develop facile methods for fast and selective removal of oils from water surface. The conventional methods used to solve these problems include oil containment booms, mechanical extraction [1], chemical dispersants [2], membranes [3], bioremediation [4], absorbent materials [5], in situ burning [6], etc. To date, as a result of the possibility to remove and collect oils, a large number of natural and synthetic absorbent materials have been widely employed in practical applications such as activated carbon [7], wool fibers [8], zeolites [7,9], straw [5,9], fly ash [10], and so forth. However, these absorbent materials still have some shortcomings including environmental incompatibility, low absorption capacity, poor recyclability, and so on. Most importantly, these materials may absorb not only oils but also water, leading to the reduction of absorbent selectivity and separation efficiency.

Recently, surfaces with highly hydrophobic or superhydrophobic and superoleophilic properties have attracted considerable interests in the field of oil–water separation [11–26], which allow for the proper disposal of oil and does not cause secondary pollution. Several methods had been reported for constructing highly or super hydrophobic surfaces, including sol-gel process [11–13], chemical vapor deposition [16–18], solution-immersion process [20,21], and layer-by-layer (LbL) technique [24–26], etc. Nevertheless, the preparation processes were always either time consuming or high energy consumption. Moreover, costly fluoride was often involved in the process so as to achieve the superhydrophobic property of material. These limitations inhibited the materials to be produced in large-scale and widely used in practical applications. Therefore, a simple, economic and practical approach for preparing surfaces with low energy, considerable stability, high hydrophobicity and superoleophilicity is very desirable.

It is well-known that emulsion polymerization is one of the most important and widely applied industrial polymerization processes all over the world [27]. Thus, it is essential to investigate the possibility of creating highly hydrophobic or superhydrophobic surfaces through emulsion polymerization for potential scalable production in the future. Nowadays, magnetic materials have been paid much attention because of their special response to external magnetic field in dispersion. In order to realize a fast separation of oils from water, the synthesis of magnetic oil absorbents will be an alternative technology. In this study, magnetic Fe_3O_4 nanoparticles were initially coated with a layer of poly(St/DVB) via emulsion polymerization and subsequently modified with highly hydrophobic

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and superoleophilic poly(MMA/St/DVB) coating through secondary polymerization in the previous emulsion system. The hydrophobicity, buoyancy, thermal stability and corrosive resistance of the as-prepared nanoparticles were evaluated. In addition, the nanocomposites were used to remove three kinds of oil films from water surface with high selectivity and efficiency under a magnetic field. These findings of this study might offer a facile method for the cleanup of oil spillages on the water surface.

2. Experimental

2.1. Chemicals and materials

Except for the chemically pure of methyl methacrylate (MMA), all the other chemicals were analytic reagent grade and used without further treatment. Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), anhydrous ammonium acetate (NH_4OAc), styrene (St), methyl methacrylate (MMA) and sodium dodecyl benzene sulfonate (SDBS) were received from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Divinylbenzene (DVB) was purchased from Aladdin. Ethylene glycol ($(CH_2OH)_2$) and azobisisobutyronitrile (AIBN) were purchased from Shanghai No. 4 Reagent & HV Chemical Co. Ltd., Shanghai, China. Polyethylene glycol (PEG4000) was from Xilong Chemical Reagent Co. Ltd., Shantou, China. Anhydrous ethanol was supplied by Nanjing Chemical Reagent Co. Ltd., Nanjing, China. Deionized water was used throughout.

2.2. Preparing magnetic polymer nanocomposites

2.2.1. General process for preparing Fe_3O_4@poly (St/DVB) as core

Initially, Fe_3O_4 nanoparticles were synthesized through a hydrothermal method [28]. A typical experiment for the synthesis of Fe_3O_4@poly(St/DVB) core–shell nanoparticles is as follows: 150 mg of Fe_3O_4 was dispersed into 50 mL of deionized water with sonication for 5 min. Then 500 mg of SDBS and 1 mL of St were sequentially added into the solution under continuous sonication for another 5 min. The resulting mixture was then transferred into a three-necked flask which was equipped with a mechanical stirrer, a condenser and a nitrogen gas inlet. The mixture was stirred at 30 °C for 30 min while being purged with nitrogen. After that, the temperature was raised to 70 °C, slowly added dropwise a mixed solution of 3 mL of St, 0.4 mL of DVB and 20 mg of AIBN in 20 min, and this reaction was continued for 6 h at 70 °C to form a stable emulsion system consisted of Fe_3O_4@poly(St/DVB) nanocomposites. These magnetic nanoparticles were labeled as MPSD-I.

2.2.2. General process for preparing poly(MMA/St/DVB) as shell

The emulsion mentioned above was allowed to cool to room temperature, and 0.5 mL of MMA was directly added at 30 °C under vigorous stirring for further polymerization. After 30 min stirring, the mixture was heated to 70 °C, and then 0.5 mL of St, 1.5 mL of MMA, 0.2 mL of DVB and 10 mg of AIBN were added dropwise into the emulsion to carry out polymerization once again. The reaction mixture was allowed to continue at 70 °C for another 4 h. The prepared core–shell nanoparticles were purified by deionized water and ethanol for several times, and finally dried in a vacuum oven at 60 °C for 8 h. By these processes, the surfaces of MPSD-I were coated with poly(MMA/St/DVB) layer as shell, and this material was named as PMSD-II. For comparison, the same method for preparing MPSD-I was used to synthesize magnetic poly(MMA/St/DVB) without the secondary polymerization, and the product was labeled as MPMSD.

2.3. Characterization

Powder X-ray diffraction (XRD) analyses were carried out on a Bruker D8 Advanced diffractometer (Bruker D8 Super Speed) with Cu Kα radiation and the scanning angle ranged from 10° to 80° of 2θ. Transmission electron microscopy (TEM) images were taken with Model Tecnai 12. Thermal stability of the sample was measured by thermogravimetric analysis (TGA, Model TA2100, TA Instruments, USA) at a heating rate of 10 °C/min in N_2 over the range of 50–600 °C. Field-emission scanning electron microscopy (FESEM) images were performed with a Model-S4800 (Hitachi, Japan). Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vector 22 spectrometer using the KBr pellet technique. Water contact angles (CAs) measurements were conducted by contact angle measurement instrument (SL200B, Solon Tech. Co. Ltd., Shanghai).

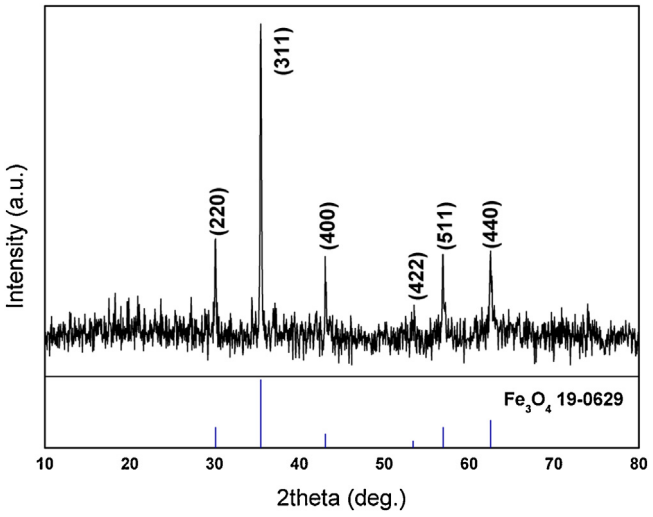

Fig. 1. XRD pattern of pure Fe_3O_4, the standard diffraction peaks of Fe_3O_4 is marked with blue bars.

2.4. Oil-absorption experiments

First, three kinds of oils including diesel oil, salad oil, and lubricating oil were poured on the surface of water contained in a beaker. Then nanocomposites were gently placed on the surface of the oil–water mixtures. After the nanoparticles were entirely wetted by oils, the nanocomposites together with the absorbed oils were collected by a magnet bar and weighted by an electronic balance. The oil-absorption capacity of the nanocomposites was calculated by the formula:

$$k = \frac{m_2 - m_1}{m_1}$$

where k is the sorption capacity (g/g), m_1 and m_2 are the weight of the materials before and after oil absorbance, respectively. All the absorption experiments were repeated for three times. The absorbed oil was removed from the surfaces of nanocomposites by ultrasonically washing in ethanol for 3 min. After being dried in a vaccum oven, the nanocomposites could be reused to separate the water and oil mixture and their reusability was evaluated by water contact angle (CA) measurements.

3. Results and discussion

First, Fig. 1 shows the XRD diffraction pattern of Fe_3O_4. It is found that all the reflection peaks are assigned to the diffraction from (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) crystal planes of cubic structure of Fe_3O_4 (JCPDS no. 19-0629), indicating the formation of magnetite nanoparticles. Then the nanostructures of Fe_3O_4, MPMSD, MPSD-I and PMSD-II were further investigated by TEM, respectively. It can be clearly seen in Fig. 2a that the Fe_3O_4