Synthesis and Characterization of Highly Efficient Oil-Water Separation, Recyclable, Magnetic Particles CoFe₂O₄/SDB

Cailin Liu (✉ liucailin2013@163.com)

SWUST: Southwest University of Science and Technology

Li Yu

SWUST: Southwest University of Science and Technology

Yue Fan

SWUST: Southwest University of Science and Technology

Chang Li

SWUST: Southwest University of Science and Technology

Xianyan Ren

SWUST: Southwest University of Science and Technology

Haijun Yang

SWUST: Southwest University of Science and Technology

Shudong Lin

SWUST: Southwest University of Science and Technology

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Abstract

In the oil-water separation, the difficulty to recover and low hydrophobicity are key limitation factors for practical applications. In this paper, we design Cobalt ferrite hybrid Polystyrene divinylbenzene microspheres ($\text{CoFe}_2\text{O}_4/\text{SDB}$), which were conducted through in-situ suspension copolymerization. The CoFe_2O_4 is prepared by low heat solid phase sol-gel method. It had been found that the $\text{CoFe}_2\text{O}_4/\text{SDB}$ have a spherical structure, good adsorption behavior, highly hydrophobicity and even superhydrophobicity. The adsorption capacity of $\text{CoFe}_2\text{O}_4/\text{SDB}$ composites could absorb kerosene up to 6 times of its own weight. Interestingly, kerosene can be easily separated from the surface of $\text{CoFe}_2\text{O}_4/\text{SDB}$ particles with ultrasonic operation. $\text{CoFe}_2\text{O}_4/\text{SDB}$ particles can still maintain good hydrophobicity and adsorption capacity of kerosene after 11 cycles after drying. With in situ polymerization of St-DVB and CoFe_2O_4 , $\text{CoFe}_2\text{O}_4/\text{SDB}$ as a promising absorbent of kerosene which has great potential in application of oil-water separation.

Introduction

With the development of the global economy, the demand for oil is also increasing and the risk of marine oil spill accidents continue to increase at the same time [1-3]. The oil spill accident and the discharge of a large amount of oily sewage have seriously damaged the ecological environment of lakes and oceans, which not only seriously disrupted people's lives, but also disrupted normal commercial production. Although oceans and lakes have the ability to self-purify oil pollution, this ability is limited [4]. Furthermore, oil pollution of water will directly affect the ecology and human health. Especially the oil leakage on the ocean will cause large-scale water pollution, removing oil spills from the water surface as quickly and effectively as possible should be the most important step in protecting the marine environment and life [5].

Recently, the desired oil-adsorption materials are getting much attention, which should have superhydrophobic and super oleophilic properties as oil absorbents. Many natural materials and man-made absorbents have been widely considered in the oil-water separation such as sponge [6-9], films [10], fiber [11-13], graphene [14-15]. Calcagnile et al [16] reported a PTFE powder and iron oxide nanoparticles modified polyurethane sponge, which is superhydrophobic, superoleophilic and shows magnetic response. The polyurethane sponge can be recovered by ultrasound in toluene, but with a low recovery rate of 80%. Sen Wang et al [17] reported a 3D porous polyoxometalate (POM)-hybridized GA (POM-GA) as a highly efficient and recyclable absorbent for oil/water separation, its oil-adsorption capacity retention rate is about 90% after 10 absorbing-squeezing cycles. Mo SiQi et al [18] have prepared a 3D porous sponge based on amino-terminated polydimethylsiloxane (PDMS) and graphene oxide (GO), over 80% strain of this material will occur after 20 compression cycles, demonstrating its weak compressive strength. Generally, these natural and synthetic materials show low adsorption capacity, low compressive strength, weak recoverability, and big difficult in recycle.

To overcome these limitations, more efforts should be paid in recent years to the high performances oil-adsorbent materials which have high oil adsorption capacity, low density, high porosity, large specific surface, and are hydrophobicity and environmentally friendly. As far as we know, the polystyrene divinylbenzene (SDB) porous microspheres have all the advantages mentioned above, and the suspension polymerization is one of the important methods to prepare SDB microspheres [19]. Therefore, it is reasonable to fabricate high oil-absorbent materials of magnetic particles modified SDB through in-situ suspension polymerization. We believe that with the simple polymerization method of magnetic SDB might be applied to the process of oil-water separation which could be recycled as the characteristics of magnetic materials that could response to external magnetic field. The CoFe_2O_4 is noticed due to its spinel-type and strong magnetic response in a wide variety of magnetic materials [20-21].

In this work, we prepared a kind of high strength, environmentally friendly and recyclable oil-absorbent CoFe_2O_4 /SDB material, which is able to remove oils from water surface based on porous structure. Firstly, CoFe_2O_4 nanoparticles with uniform size and good magnetic property were prepared by the low heat solid phase sol-gel method. Then, magnetic CoFe_2O_4 /SDB particles were successfully prepared by in-situ suspension polymerization which have the high strength and superhydrophobic properties. In addition, the influence of different adding amounts of CoFe_2O_4 for the preparing of CoFe_2O_4 /SDB are discussed with the compressive stress, magnetic property, hydrophobicity and adsorption ability.

Experimental Section

Materials and Chemicals. Iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), Cobaltous nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Sodium dodecyl benzene sulfonate(LAS), and citrate were purchased by Kelon Chemical Co., Ltd., Chengdu, China. Divinylbenzene (DVB) and styrene (St) were purchased from Aladdin Reagent (Shanghai) Co., Ltd. Toluene, N-heptane, benzoyl peroxide (BPO) and acetone were received from Shanghai Siyan Reagent Chemical Co. Ltd. Poly(vinyl alcohol), Polyvinyl alcohol-1788(PVA) and Stearic acid(SA) were obtained from Xinglong Chemical Reagent Co. Ltd. All chemicals which were used were of analytical reagent grade and deionised water was used through the experiments.

Characterization of the prepared particles. X-ray diffraction (XRD) analysis was carried by using a Bruker D8 Advanced diffractometer with Cu K α radiation and the scanning angle ranged from 3° to 80° of 2 θ at 40 kV and 40 mA to classify the crystal structure of CoFeO_4 and CoFeO_4 /SDB. Morphologies of CoFeO_4 /SDB composites were investigated by using scanning electron microscope (SEM, Ultra55, Carl zeissNTS GmbH, Germany). Contact angles (CAs) were measured on contact angle measurement instrument (DSA30, Kluss. Co. Ltd., German). Thermal gravimetric (TG) analysis were carried out by SDTQ600 under a nitrogen atmosphere. The magnetic properties of CoFeO_4 and CoFeO_4 /SDB were measured by a vibrating sample magnetometer (VSM, LakeShore 7404). The nitrogen adsorption analyze was carried by an automatic specific surface and pore size distribution analyzer (Autosorb-iQ, Quantachrome).

Preparation of CoFe₂O₄ Nanoparticles.

CoFe₂O₄ nanoparticles were synthesized through the low heat solid phase sol-gel method. Specific synthesis steps were as follows: firstly, Fe(NO₃)₃·9H₂O (10.1 g) was grind with polyethylene glycol (20 g) for 30 minutes, then marked as A. Co(NO₃)₂·6H₂O (7.3 g) was grind with citrate acid (9.6 g) for 30 minutes, then marked as B. After that, grind A with B for 30 minutes and heat the mixture at 393.15 K for 2 hours in oven, forming a pale yellow homogeneous solution. Then, the mixed solution was transferred to a muffle furnace, with the temperature setting at 633.15 K and time setting at 1 h. After that, setting the temperature at 973.15 K and lasting 2 h. The prepared black products were washed three times by deionized water and ethanol. Then, get it to a vacuum drying oven in 333.15 K for 2 h. Finally, finally got the CoFe₂O₄ nanoparticles. For a better copolymerizing with St and DVB, CoFe₂O₄ nanoparticles was modified with SA.

Synthesis of CoFe₂O₄/SDB Composites with Different Amounts.

Briefly, to a beaker was added St (10 g), DVB (10 g), toluene (15.8 g), 1,2-dichloroethane (12.4 g), n-heptane (11.6 g), and BPO (0.2 g) with different amounts of CoFeO₄ and then, the solution was in ultrasonic oscillation for 30 min to form the black solution, giving liquid A. Then LAS (0.1 g) and PVA (2.0 g) were added into the deionized water (200 mL), giving liquid B. The liquid B and liquid A were mixed in a three-neck flask and set the temperature at 45°C in N₂ atmosphere with the mechanical stirring speed at 70 rad/min. Subsequently, the temperature was gradually raised to 70°C, and the N₂ was stopped. Finally, the temperature was turned to 88°C for 6 h. After the polymerization finished, the obtained CoFeO₄/SDB were collected with filtering. Then CoFeO₄/SDB were dried in vacuum at 60°C after being washed with ethanol and water for several times.

Consequently, the CoFe₂O₄/SDB were synthesized with different adding dosages of CoFe₂O₄ by in-situ polymerization which had the same crosslinking ratio of St : DVB=1:1 and named for S₁, S₂ S₃ and S₄ for the different CoFe₂O₄/SDB samples which were listed in Table 1.

Table 1. Different dosages of CoFe₂O₄

Name	SA-CoFe ₂ O ₄ (g)	St:DVB
S ₀	0	1:1
S ₁	0.5	1:1
S ₂	1.0	1:1
S ₃	2.0	1:1

Oil-Adsorption Experiments. The oil adsorption capacity of CoFe₂O₄/SDB particles was researched by weight measurement. Weighting the added CoFe₂O₄/SDB particles as M₁. Besides, to a watch-glass pour

water and kerosene in order which was clearly to see the kerosene were on the surface of water. Finally, $\text{CoFe}_2\text{O}_4/\text{SDB}$ were added into the watch-glass and it is obvious that the kerosene was quickly absorbed by the $\text{CoFe}_2\text{O}_4/\text{SDB}$ in a few minutes, Then, Weighting the mixture of the absorbed kerosene and $\text{CoFe}_2\text{O}_4/\text{SDB}$ particles as M_2 which were gathered through a magnet bar. Finally, the adsorption capacity (P) of $\text{CoFe}_2\text{O}_4/\text{SDB}$ particles were counted by this formula: . After the adsorption process, $\text{CoFe}_2\text{O}_4/\text{SDB}$ particles were washed by absolute alcohol three times and then dried in a oven at 45°C for 4 h. All the kerosene adsorption experiments were carried and repeated for three times to get the average value. The performance of recycled $\text{CoFe}_2\text{O}_4/\text{SDB}$ particles were examined to remove kerosene from water surface.

Results And Discussion

The structure and morphology of $\text{CoFe}_2\text{O}_4/\text{SDB}$ particles. As the FT-IR test results of $\text{CoFe}_2\text{O}_4/\text{SDB}$ (a), SA- CoFe_2O_4 (b) and CoFe_2O_4 powder (c) shown in Fig.1. In the CoFe_2O_4 powder (c) of Fig.1, the peak at 581 cm^{-1} is derived from the Fe-O vibration peak, and 1624 cm^{-1} is the characteristic peak of -OH on the surface of CoFe_2O_4 ; In the SA- CoFe_2O_4 (b) of Fig.1, the stretching vibration peaks at 2924 cm^{-1} and 2821 cm^{-1} were owing to methyl and methylene groups respectively, the adsorption peak at 1710 cm^{-1} is the stretching vibration adsorption peak of the carboxylic acid carbonyl group in SA, and the characteristic peak at 1434 cm^{-1} is the adsorption peak of Fe-O, which shows that SA has modified the surface of CoFe_2O_4 nanoparticles and the CoFe_2O_4 were successfully prepared; In the $\text{CoFe}_2\text{O}_4/\text{SDB}$ (a) of Fig.1, $1400\text{ cm}^{-1} \sim 2000\text{ cm}^{-1}$ are the characteristic peaks of stretching vibration of the benzene ring skeleton and the characteristic adsorption peak of CoFe_2O_4 can also be clearly seen in $\text{CoFe}_2\text{O}_4/\text{SDB}$ (a).

In Fig. 2, XRD patterns demonstrated that the diffraction peaks at $2\theta = 30.1^\circ$ (220) $\sim 35.5^\circ$ (311) $\sim 43.1^\circ$ (400) $\sim 57.0^\circ$ (511) and 62.6° (440) belonging to CoFe_2O_4 powder are the same as that in S_1 - S_3 samples (JCPDS file no. 22-1086). The average crystal diameter perpendicular to (220) planes of CoFe_2O_4 is about 39.71 nm calculated by the Scherrer equation. The results further prove that the CoFe_2O_4 nanoparticles were successfully introduced into the SDB microspheres without any transformation in the crystal forms.

The rough display of S_0 - S_1 were taken in Fig.3(a), with the increase of CoFe_2O_4 , the deeper color and rough surface were the S_0 - S_1 displayed. Without the adding of CoFe_2O_4 , S_0 demonstrate a white spherical surface and increase the adding amount of CoFe_2O_4 , getting the CoFe_2O_4 is unevenly distributed on the surface and inside of S_1 ; Then the S_2 were get a relatively uniform particle size distribution and a very bright surface. Due to the excessive content of CoFe_2O_4 in S_3 , the surface of the S_3 particles is not shiny and particle agglomeration occurs. To further characterize the morphology and size of the $\text{CoFe}_2\text{O}_4/\text{SDB}$ composites, SEM analysis of S_2 were carried out and shown in Figure 3(b, c, d). The diameter of $\text{CoFe}_2\text{O}_4/\text{SDB}$ is about 1~2 μm (Figure 3(b)) and the SA- CoFe_2O_4 nanoparticles was distributed on the surface of the SDB obviously (Figure 3(c)). In addition, the CoFe_2O_4 particles are easily to be found from the fracture surface of S_2 further elucidate the $\text{CoFe}_2\text{O}_4/\text{SDB}$ microspheres successfully prepared (Figure 3(d)).

It is well-known that the super hydrophobicity of the solid surface depends on the layered roughness and lower surface energy [23-24]. Owing to the CoFe_2O_4 nanoparticles that anchored on the surface, the $\text{CoFe}_2\text{O}_4/\text{SDB}$ particles possess a rough surface and present highly hydrophobic property. The contact angle of $\text{CoFe}_2\text{O}_4/\text{SDB}$ surface was tested as shown in table 2, the water contact angles on the surface of the $\text{CoFe}_2\text{O}_4/\text{SDB}$ are increased with the CoFe_2O_4 , which are 78.94° , 83.84° , 127.00° , and 154.70° , respectively for S_0 , S_1 , S_2 and S_3 . The intrinsic hydrophobicity of an absorbent is critical to improve oil adsorption property when used to oil-water separation due to a fact that the absorbent can selectively adsorb oil and repel water.

Table 2. The contact angel and compressive strength of S_0 - S_3 samples

Samples	Degree($^\circ$)	Compressive Strength(N)
S_0	78.84	32.10
S_1	83.84	181.36
S_2	127.00	197.69
S_3	154.70	221.91

The compressive strength tests were carried three times to get the average value and the results are shown in Table 2. $\text{CoFe}_2\text{O}_4/\text{SDB}$ is prepared by in-situ polymerization, the $\text{SA-CoFe}_2\text{O}_4$ were embedded in a cross-linked structure composed of St and DVB to enhance the strength owing to the ultrahard characteristic of CoFe_2O_4 . In Table 2, the compressive strength of S_1 sample, S_2 sample and S_3 sample can reach 5.66 times, 6.16 times and 6.92 times of the compressive strength of S_0 sample, respectively. The reinforcement of $\text{CoFe}_2\text{O}_4/\text{SDB}$ make it can be used many times without deformation.

The magnetic properties of the $\text{CoFe}_2\text{O}_4/\text{SDB}$ particles ($\text{S}_1\sim\text{S}_3$) were measured at room temperature and the results are shown in Figure 4. The saturation magnetization of the S_1 - S_3 samples at an external field of 2 T are 0.6119 emu/g, 1.19538 emu/g and 1.73652 emu/g, respectively. This result states the magnetic $\text{CoFe}_2\text{O}_4/\text{SDB}$ have been successfully synthesized and the adding amounts of CoFe_2O_4 in the $\text{CoFe}_2\text{O}_4/\text{SDB}$ particles can affect the magnetism property. It is well known that $\text{CoFe}_2\text{O}_4/\text{SDB}$ could be easily separated from the mixture of water and kerosene with the external magnetic field. Owing to the magnetic property of $\text{CoFe}_2\text{O}_4/\text{SDB}$ material could be positively correlated with handling the removal of different types water and kerosene.

N_2 adsorption-desorption experiments were performed at 77 K to examine the specific surface area and the pore volume of $\text{CoFe}_2\text{O}_4/\text{SDB}$ (S_2 -Figure 5). When the relative pressure of the system is low, the adsorption-desorption curve of S_2 does not close, indicating that there are micropores in the structure of S_2 , which may be due to the chemical adsorption between the S_2 itself and N_2 , resulting in the incomplete

removal of N₂. In terms of pore size distribution, S₂ mainly has micropores that are about 2 nm. The small pore size makes N₂ difficultly to be removed from the pore of CoFe₂O₄/SDB resulting in the retention of N₂ in the pores. At the same time, the N₂ adsorption-desorption experiments were applied to determine the pore structure of the S₀, S₁ and S₃, the results show that the S₂ possess the largest pore volume of 2.1948 cm³/g, as shown in Table 3, which suggest that the S₂ is the best candidate for the oil apportion.

Table 3. The pore structure data of S₀-S₃ samples

Sample number	Pore size(nm)	Pore volume(cm ³ /g)
S ₀	1.326	1.214
S ₁	1.688	0.8175
S ₂	1.435	2.1948
S ₃	4.427	0.00478

We can clearly observe the initial decomposition temperatures of S₀-S₃ samples from Figure 7, which are 360 °C, 410 °C, 490 °C and 500 °C, respectively. The final decomposition temperature of S₀~S₃ gradually increases while the adding amount of CoFe₂O₄ were increased in the meantime. The main reason is that the inorganic material CoFe₂O₄ were in-situ polymerized with the long crosslinking chain of St and DVB which form the strong interaction between two phases of inorganic material and organic material to hampered bodily movement of CoFe₂O₄/SDB particles and since CoFe₂O₄ itself occupies a certain steric hindrance, this action impedes the thermal motion of the molecular chain of CoFe₂O₄/SDB. With the increased adding amount of CoFe₂O₄, the stronger force of interaction between two phases and sterically hindered were demonstrated, thereby the thermal stability of the CoFe₂O₄/SDB is increased by improving the thermal decomposition energy.

The kerosene adsorption capacity of CoFe₂O₄/SDB. The CoFe₂O₄/SDB particles prepared in this study were used for handling the kerosene on the surface of water. The weight measurement methods were carried to study the kerosene adsorption efficiency of SDB and CoFe₂O₄/SDB (S₀~S₃). Results of weight measurement are obviously seen in Fig. 7 due to the highest pore volume, S₂ demonstrate the best oil adsorption capability and the adsorption capacities (P) of S₀, S₁, S₂ and S₃ are 5.723, 6.356, 6.526 and 5.625, respectively. Furthermore, the residual big π bond in SDB which could have reaction with the π bond in the kerosene is another drive for the adsorption process. And with the existence of CoFe₂O₄, the π-π interaction between benzenes and the kerosene can be improved [25]. Taking the pore volume and the effect of CoFe₂O₄, into consideration, the S₂ should perform well when applied to absorb oil.

As we expected, the S₂ adsorbed kerosene quickly in a few minutes when they were added into watchglass with a layer of kerosene on a water surface. Because of the presence of magnetic CoFe₂O₄ nanoparticles, the S₂ could be taken to the assigned mixture region of water and kerosene by external magnetic field. Furthermore, the S₂ can be separated easily from the oil-water system and regenerated by washing in ethanol with a help of ultrasonic which was flowed by drying steps. Moreover, as shown in Fig. 9 the regenerated S₂ still show good performances in oil adsorption capacity which reach 6.021 times even after the 11th cycle. The recoverability and durability of the absorbent as well as the efficiency of kerosene removal play an important role in controlling the extent of pollution and protecting the environment.

Interestingly, the magnetic CoFe₂O₄/SDB particles did not sink even when they were put on the surface of oil and water mixture under oscillation for one night. This is due to their low density, excellent hydrophobicity which can overcome their own weight and prevent them from immersing in water surface to increase the water displace volumes. We believe that CoFe₂O₄/SDB particles would be used widely for the treatment of the oil spillage.

RESULTS

In sum, CoFe₂O₄ nanoparticles with uniform particle size (about 39.71 nm) and strong magnetism was prepared via the low heat solid phase sol-gel method, which played an important role in construction of CoFe₂O₄/SDB particles. CoFe₂O₄/SDB particles were prepared through in-situ polymerization, which had advantages of strong magnetism, high pore volume, unsinkability and low density. The kerosene was quickly adsorbed by the prepared CoFe₂O₄/SDB in a few minutes and have a good adsorption capability which could be reused under the existing of external magnetic field and washing by absolute alcohol. Moreover, S₂ sample showed the best oil-adsorbent capacity up to 6.526 times of their weight and we could also learn that the S₂ could be regenerated at least 11 times. All in all, the excellent hydrophobicity, large pore volume and pore diameter, superoleophilicity, recovery of magnetic medium and environmental- friend are the advantages of CoFe₂O₄/SDB particles which shows a highly promising absorbent for oil and water separation.

Declarations

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Figures

Figure 1

The FT-IR spectra of (a) CoFe₂O₄/SDB, (b) SA- CoFe₂O₄ and (c) CoFe₂O₄ powder

Figure 2

The XRD patterns of CoFe_2O_4 powder and S_0 - S_3

Figure 3

(a) The rough display of S0-S3 samples, (b) the SEM images of CoFe₂O₄/SDB (S₂), (c) the surface of CoFe₂O₄/SDB (S₂) and (d) the fracture surfaces of CoFe₂O₄/SDB (S₂)

Figure 4

VSM curves of S1-S3 samples in the room temprature

Figure 5

N₂ adsorption and desorption isotherms (the inset is the corresponding pore size distribution) of S2

Figure 6

the TGA curves of S0-S3

Figure 7

The oil adsorption capacity curves of S0-S3

Figure 8

The oil adsorption capacity of S2 recorded after 11th cycles

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