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Abstract

"In this report, hollow mesoporous silica (HMS) and iron oxide-hollow mesoporous silica (FexOy@HMS) core-shell composite were prepared by a one-step facile fabrication method. Transmission electron microscopy, X-ray diffraction, N₂ adsorption-desorption isotherms, and vibrating sample magnetometer were used to characterize the morphology, microstructure, and magnetic properties of the HMS and core-shell composite. The magnetic separability of FexOy@HMS core-shell composite was tested in Rhodamine B (Rh. B) dye solution. The results indicate that the core-shell composite can absorb Rh. B dyes molecules effectively up to 90.1%. (C) 2012 American Institute of Physics. [doi:10.1063/1.3670049]"

Keywords

silica, separation, mesoporous, composite, oxide, applications, iron, microstructures, properties, magnetic, shell, core, dye

Disciplines

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Magnetic properties and microstructures of iron oxide@mesoporous silica core-shell composite for applications in magnetic dye separation

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In this report, hollow mesoporous silica (HMS) and iron oxide-hollow mesoporous silica ($\text{Fe}_x\text{O}_y\text{@HMS}$) core-shell composite were prepared by a one-step facile fabrication method. Transmission electron microscopy, X-ray diffraction, N_2 adsorption-desorption isotherms, and vibrating sample magnetometer were used to characterize the morphology, microstructure, and magnetic properties of the HMS and core-shell composite. The magnetic separability of $\text{Fe}_x\text{O}_y\text{@HMS}$ core-shell composite was tested in Rhodamine B (Rh.B) dye solution. The results indicate that the core-shell composite can absorb Rh.B dyes molecules effectively up to 90.1%. © 2012 American Institute of Physics. [doi:10.1063/1.3670049]

I. INTRODUCTION

Hollow mesoporous (HM) materials exhibit attractive physical and chemical properties, such as large adsorption capacity, good selectivity, and high catalytic activity, because of their high surface area, well-defined porous structure, and large tunable inner hollow size.¹⁻³ The comparatively large inner hollow core provides potential carrier space, and the mesoporous shell provides the passage between the inside and the outside. HM materials have potential applications in absorbents,⁴ drug delivery,⁵ and catalyst support.⁶ The absorbents are broadly used in water purification by adsorption of pollutants due to their simplicity and low cost.⁷ The microstructure of HM materials is suitable for absorbents. However, it is so far still a challenge to separate HM materials from solution after purification, which possibly induces a secondary source of environmental pollution. The development of a facile separation method is very important for mesoporous absorbents in industrial applications.⁸ Recently, it was found that incorporating magnetic nanoparticles (MNs) into HM materials can provide a new strategy to develop novel absorbents for environmental purification.^{9,10} The MNs@HM core-shell structure combines the advantages of both mesoporous materials and magnetic particles, in which the mesoporous shell can effectively absorb pollutant molecules due to its high surface area and uniform pores, and the magnetic particles simplify the separation process in the liquid-phase system on application of an external magnetic field. Some efforts have been made to develop MNs@HM core-shell materials for absorbent application. It has been reported that $\text{Fe}_3\text{O}_4\text{@SiO}_2$ core-shell materials could be used as an absorbent for 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) Methylene Blue (MB), Acridine Orange (AC), and Rhodamine B (Rh.B) dyes, respectively.^{8,11,12} Hollow mesoporous carbon spheres with magnetic cores were also found to show good adsorption property for bilirubin.¹³

The conventional approaches to fabricating the MNs@HM core-shell nanostructures are the coating method and infiltration method.^{8,11-13} One important process in both approaches is the removal of the by-products or purification of products, which complicates the preparation and limits their applications. Cracked hollow nanostructures are also unavoidable during the synthesis process. In this work, we report the adsorption properties of $\text{Fe}_x\text{O}_y\text{@HMS}$ core-shell nanoparticles prepared by a one-step fabrication method. The microstructures and magnetic properties of the hollow mesoporous silica (HMS) and the $\text{Fe}_x\text{O}_y\text{@HMS}$ core-shell composite were studied. The adsorption properties and magnetic separability of $\text{Fe}_x\text{O}_y\text{@HMS}$ core-shell composite were tested in Rh.B dye solution.

II. EXPERIMENTAL

FeCl_2 , FeCl_3 , tetraethyl orthosilicate (TEOS), cetyltrimethyl ammonium bromide (CTAB), ammonia, and ethanol were obtained from Beijing Chemical Reagent Corporation of the Chinese Medicine Group. All materials were of analytical grade and were used as received without any further purification. 0.1 g FeCl_2 and 0.2 g FeCl_3 were dissolved into 20 ml H_2O , which was then added to a 40 ml ethanol solution containing 0.1 g CTAB and 3 ml TEOS. The mixed solution was then added into 200 ml 0.225 M ammonia under vigorous magnetic stirring at room temperature. A brown precipitate was formed and collected after aging the suspension for 2 h. The product was calcined at 600 °C with a heating rate of 1 °C min^{-1} under N_2 atmosphere. The sample was outgassed at 300 °C under N_2 atmosphere for 3 h prior to the measurement.

X-ray diffraction (XRD) and small angle XRD (SAXRD) patterns were collected on a Rigaku RINT D/Max-2400 powder diffraction system using $\text{Cu K}\alpha$ radiation at 1.54 Å. Nitrogen sorption experiments were performed at 77 K on a Micromeritics ASAP 2010 system. Transmission electronic microscopy (TEM) measurements were performed on a JEOL 2100 F microscope operated at 200 kV. All samples subjected to TEM measurements were ultrasonically dispersed in methanol and drop-cast onto copper grids. The magnetic properties

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were characterized by a vibrating sample magnetometer (VSM; LakeShore7410) at room temperature. The magnetic separability of $\text{Fe}_x\text{O}_y\text{@HMS}$ was characterized by adsorption of Rh.B solution. In the measurement, 0.5 g $\text{Fe}_x\text{O}_y\text{@HMS}$ was added into 250 mL 1 mg/L Rh.B. Ultraviolet-visible (UV-Vis) absorption spectra of the solution were collected on a Hitachi U3010 spectrophotometer after 1 min adsorption.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the $\text{Fe}_x\text{O}_y\text{@HMS}$ core-shell nanocomposite. The XRD peaks are indexed with Fe_3O_4 (Ref. 14) and $\gamma\text{-Fe}_2\text{O}_3$.¹⁵ The broad peak at 22° can be assigned to the characteristic reflection from amorphous SiO_2 . The XRD results indicate that Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, and amorphous silica were formed simultaneously. TEM images of the microstructures and morphologies of HMS and of the composite are shown in Fig. 2. We can see that the mesoporous silica (Fig. 2(a)) consists of hollow spheres 100–220 nm in diameter and about 25 nm in shell thickness. For the $\text{Fe}_x\text{O}_y\text{@HMS}$ sample (Fig. 2(b)), it can be seen that there is a strong contrast difference in all of the spheres between the dark centers and the bright edges of the spheres, confirming that the Fe_xO_y particles completely fill the hollow silica particles when ferric halide precursors are incorporated into the reaction system. The thickness of the mesoporous shell remains unchanged. The observed blurry silica shells indicate the decay of the mesoporous structure symmetry, which is due to the incorporation of iron oxide.

The adsorption properties of core-shell materials depend on the mesoporous structure of the silica shell. The porous structure of the as-prepared particles was assessed by SAXRD and N_2 adsorption isotherms. From the SAXRD patterns (as shown in Fig. 3(a)), the intensity of the (100) peak decreases while the full width at half maximum (FWHM) increases, indicating the decay of the mesoporous structure symmetry.¹⁶ This is in accordance with the results observed from TEM images. The nitrogen absorption isotherm provides further information on the hollow core variation. As shown in Fig. 3(b), the N_2 adsorption-desorption isotherms

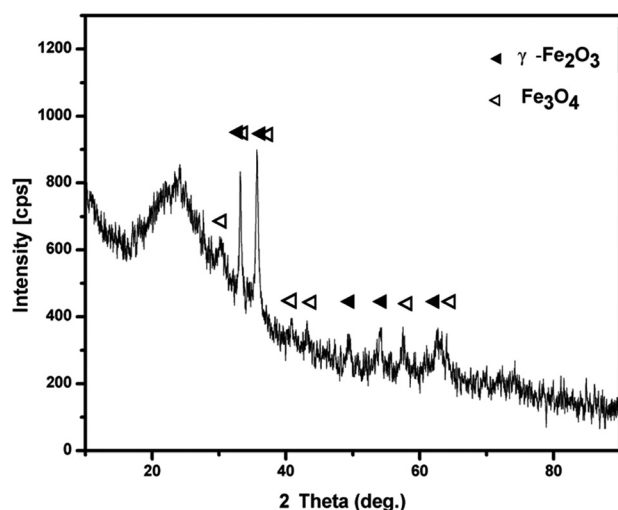


FIG. 1. XRD pattern of $\text{Fe}_x\text{O}_y\text{@HMS}$ core-shell structure.

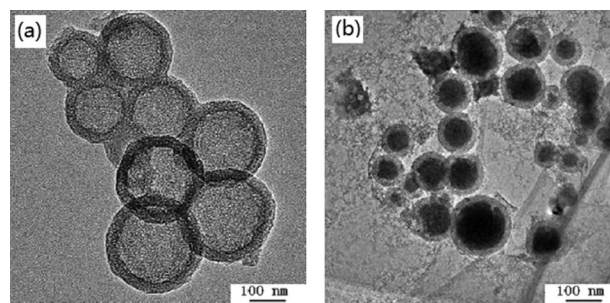


FIG. 2. TEM images of (a) HMS and (b) $\text{Fe}_x\text{O}_y\text{@HMS}$ core-shell composite.

of the samples present typical type-IV adsorption,¹⁷ which show an apparent capillary condensation step at relative pressure (P/P_0) of 0.3. The pore size was calculated as 2.4 nm by the Barrett-Joyner-Halenda (BJH) method. H4-type hysteresis loops¹⁸ at relative pressure (P/P_0) above 0.5 for the samples suggest that the inner hollow core and the outer surface are connected through the mesoporous structure, which results in the adsorption of N_2 molecules in the hollow core. The reduction of the H4-type loop for the composite is ascribed to the incorporation of Fe_xO_y particles into the inner hollow spaces. The decay of symmetry and the occupation of

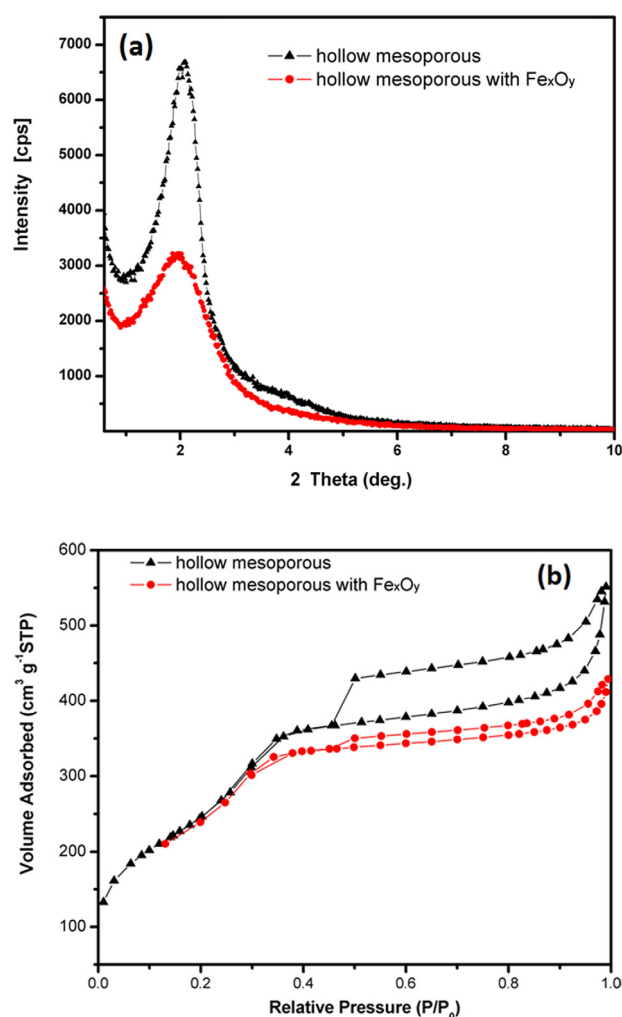


FIG. 3. (Color online) (a) SAXRD patterns and (b) N_2 adsorption isotherms of HMS and $\text{Fe}_x\text{O}_y\text{@HMS}$ core-shell composites.

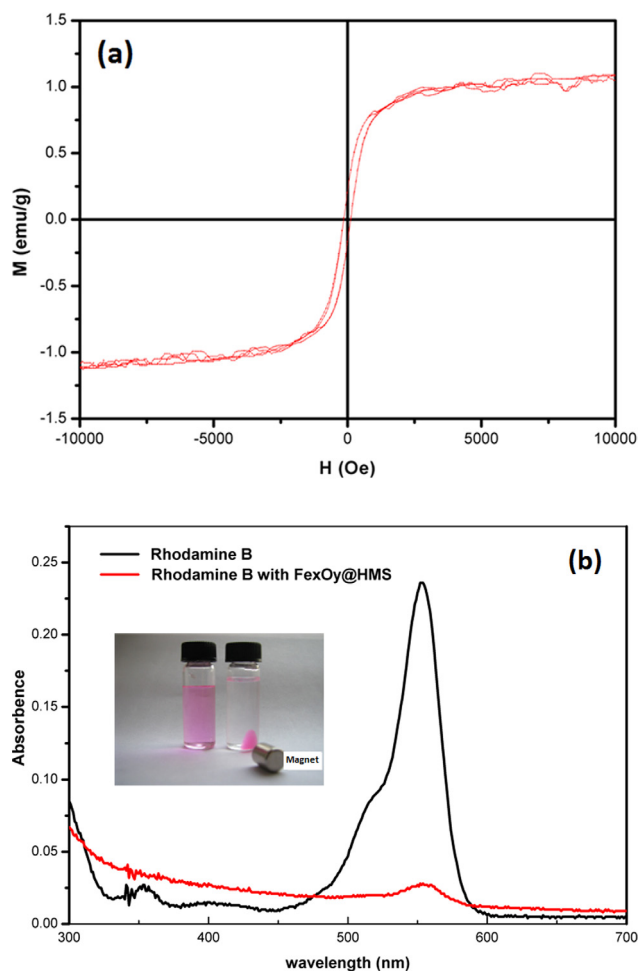


FIG. 4. (Color online) (a) M-H hysteresis loop measured at room temperature, (b) adsorption test for Rh.B dye solution, with the inset illustrating the magnetic separation of absorbent from the final solution by an external magnetic field.

inner spaces lead to reduction of the surface area of composite sample. The Brunauer-Emmett-Teller (BET) surface area is $896 \text{ m}^2 \text{ g}^{-1}$ and $128 \text{ m}^2 \text{ g}^{-1}$ for HMS and $\text{Fe}_x\text{O}_y@$ HMS composite, respectively. The surface area of the core-shell material is quite large, even if it shows a decrease compared with HMS.

The separation performance of the $\text{Fe}_x\text{O}_y@$ HMS composite depends on the magnetic properties of the Fe_xO_y core. The magnetization (M) as a function of magnetic field (H) was measured for $\text{Fe}_x\text{O}_y@$ HMS at room temperature, as shown in Fig. 4(a). There is a clear M-H hysteresis loop with saturated magnetization of 1.1 emu/g , which indicates that the core-shell material has a good response to an external magnetic field. The magnetic separability of $\text{Fe}_x\text{O}_y@$ HMS was tested by adsorption of Rh.B solution, which is regarded as general dye pollution waste. After 1 min adsorption, a magnet was placed near the waste solution with $\text{Fe}_x\text{O}_y@$ HMS particles, A clear solution was obtained immediately, as shown in inset of Fig. 4(b). The separated solution was characterized by UV-Vis absorption spectra of the Rh.B solution before and after magnetic separation (Fig. 4(b)).

The adsorption capability can be expressed by the concentration variation of $(C_0 - C)/C_0$ (where C_0 is the initial concentration and C is the final concentration of Rh.B dye). The concentration variation is about 90.1%, which indicates that the core-shell material exhibits a high adsorption capacity. The results demonstrate that $\text{Fe}_x\text{O}_y@$ HMS core-shell material can be a potential candidate as a magnetic separation absorbent.

IV. CONCLUSIONS

In summary, we have successfully fabricated $\text{Fe}_x\text{O}_y@$ HMS core-shell composite with uniform shell thickness of 25 nm via a facile one-step method. The inner iron oxide core has a good response to external magnetic field. The high surface area and porous structure of the outer mesoporous silica shell leads to high adsorption capacity of the core-shell material. The magnetic separability of the $\text{Fe}_x\text{O}_y@$ HMS core-shell composite was confirmed by adsorption testing in Rh.B dye solution.

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