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# Facile synthesis of magnetic hollow mesoporous silica spheres with assembled shell by nanosheets as an excellent adsorbent

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ABSTRACT

Adsorption technology has been widely employed to deal with wasterwater. In order to enhance adsorption rate and capacity, magnetic hollow mesoporous silica spheres (MHMSS) was synthesized by a facile solvothermal method, which $SiO_2$ sheets assembled as the shell. Monodispersed nanosized Zn-doped $Fe_3O_4$ particles (about 2–3 nm) were synthesized on the $SiO_2$ sheets. MHMSS exhibits superior adsorption capacity and high selectivity toward cationic dye of MB adsorption. Significantly, it took about only 1 min to reach the adsorption equilibrium. The experimental results indicate that this kind of structure may be a promising adsorbent for highly effective pollutant removing.



## 1. Introduction

Among pollutes in water, synthetic dyes are considered as an important pollutant source for their wide applications, casual and uncontrolled release, as well as their potential toxic, mutagenic and carcinogenic activities [1]. Among different approaches for wasterwater purified, adsorption technology is regarded as a promising strategy due to its high efficiency, economic feasibility and simplicity of operation [2]. Magnetic spinel ferrites have been employed in designing composite adsorbents for the convenient separation from wasterwater by an external magnetic field [3].

Primary requirements for adsorbents adopted in the industry process include sufficient adsorptive capacity, high adsorption rate, and reproducibility [4]. Hollow mesoporous silica spheres (HMSS) show excellent features as large pore volume, high surface area, narrow pore size distribution, open pore structure and reliable desorption performance [5]. In this work, synergistic functions of magnetic materials and the hollow structure with ordered mesoporous shell were employed. MHMSS with flake-sheet network shells were synthesized, which show an excellent adsorption property for methylene blue (MB) with high adsorption capacity and rate.

## 2. Experimental

All the chemicals were of analytical grade and used as received without further purification. MHMSS were synthesized as the following, 0.036 mmol of $Zn(NO_3)_2{\cdot}6H_2O$ and 0.504 mmol of $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in 1.5 mL of anhydrous ethylene glycol. 0.54 mmol of $CH_3COONa$ was added into the solution. 0.1 g of HMSS was added in the solution, transferred into a 10 mL teflon-lined stainless steel autoclave, heated to 200 °C with about a rate of 5 °C/min, and maintained for 24 h, where HMSS were synthesized according to our previous report [6]. The autoclave was allowed to cool down to room temperature naturally. The obtained products were washed with pure water and ethanol, and dried under vacuum at 60 °C for 12 h.

Batch adsorption experiments were conducted in 250 mL glass bottles with 10.0 mg of MHMSS in 100.0 mL of a MB solution, and the pH was adjusted to 11.0 with NaOH solution at 25 °C. The concentration of MB was determined calorimetrically by an UV–vis spectrophotometer at $\lambda = 664$ nm. To study the selective adsorption of dyes mixture, initial concentration ratio of each mixed dyes (MO/MB, PR/MB and Rh B/MB) in solution was controlled at 20:20 (mg/L).

The amount of adsorbed dye on adsorbents ($q_e$ mg/g) was calculated as follows

Wwhere $C_0$ and $C_e$ present the dye concentrations at the beginning and equilibrium (mg/L), respectively. $V$ is the initial solution volume (L), and $m$ is the adsorbent weight (g).

X-ray powder diffraction (XRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer with Cu Ka radiation. Magnetic characterization was carried out with a superconducting quantum interference device (SQUID) (MPMS-XL-7). $N_2$ adsorption–desorption measurements were carried out on an Omnisorp 100 CX gas adsorption analyzer. Standard and high-resolution transmission electron microscopy (TEM and HRTEM)

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measurements were performed on a JEOL-2010 TEM. SEM image was observed on a Hitachi S-4800 field emission scanning electron microscope.

## 3. Results and discussion

MHMSS consisted of interlaced flakes can be found from SEM and TEM images in Fig. 1. The flake thickness is about 15–20 nm as shown in Fig. 1a. The diameter of the sphere and the thickness of the shell were determined about 1000 and 75 nm, respectively, as shown in Fig. 1b. The loading monodispersed magnetic Zn-doped $Fe_3O_4$ particles can be easily seen on the flakes as shown in Fig. 1c, which the diameter of these particles was about $2 \sim -3$ nm based on a HRTEM image (Fig. 1d). The distances between two adjacent planes were about 0.30 and 0.25 nm as shown in Fig. 1d, which correspond to (311) and (220) planes of the spinel Zn-doped $Fe_3O_4$, respectively.

EDX element mappings exhibit that Fe and Zn elements are uniformly distributed throughout the flake shells as shown in Fig. 2. These results further indicate that the as-prepared Zn-doped $Fe_3O_4$ distributed homogeneously in MHMSS.

The structure of Zn-doped $Fe_3O_4$ was confirmed by XRD as shown in Fig. 3A. All diffraction peaks can be indexed to the standard reflection (PDF#221012), which can be indexed as the pure cubic phase [space group: Fd3m (227)]. No diffraction peak corresponding to $SiO_2$ was observed except the broad peaks around 23°, which indicated the amorphous $SiO_2$ shell formation. $N_2$ adsorption–desorption isotherms and pore size distributions of this sample are presented in Fig. 3B. The isotherm shape of MHMSS sample is type IV with H3-type hysteresis loop [7]. The specific surface area of this sample was about 191 $m^2/g$. The pore size is primarily between 2 and 60 nm with an average of 11 nm as shown as an inset in Fig. 3B. The magnetic hysteresis loop of MHMSS was determined (not shown here). The saturation magnetization of MHMSS

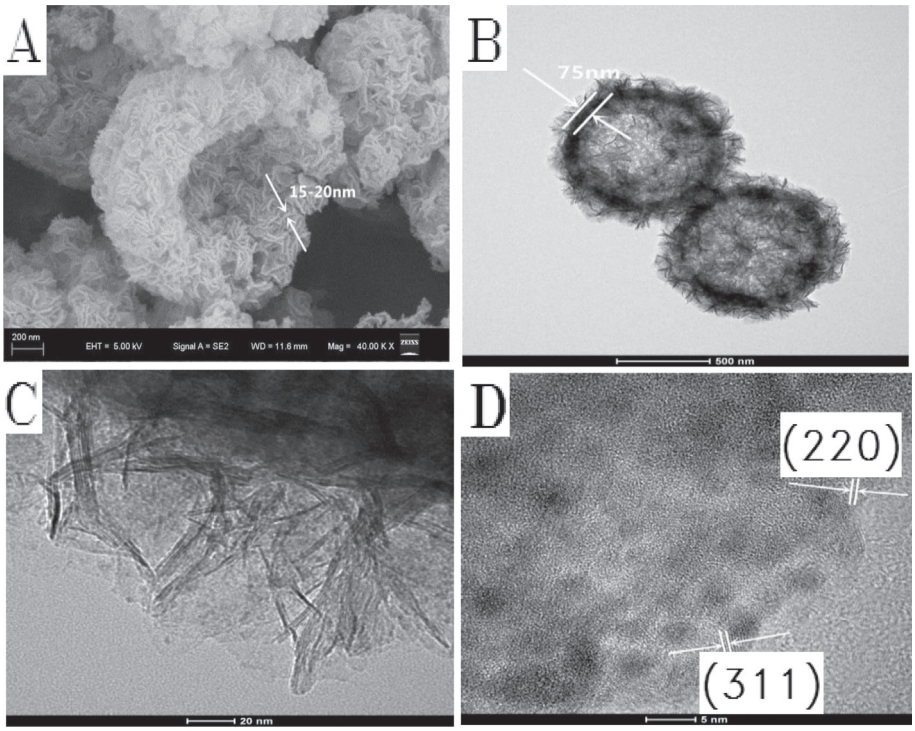


**Fig. 1.** A SEM image (A), TEM images (B and C) and HRTEM image (D) of MHMSS.

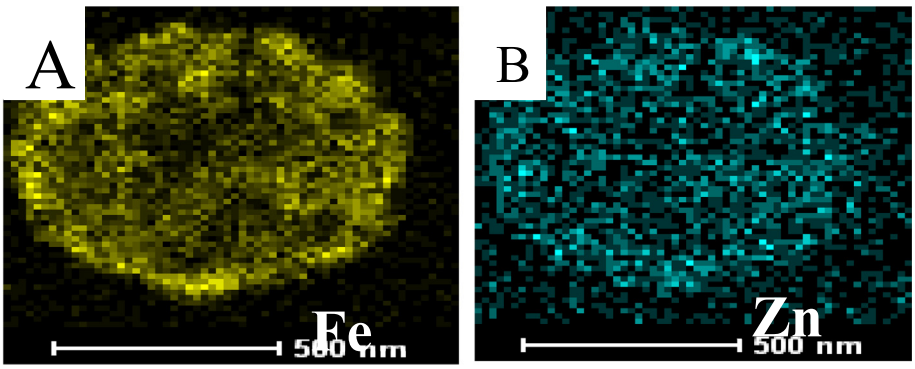


**Fig. 2.** EDX mapping of elements Fe (A) and Zn (B) for MHMSS.