

# Fabrication, characterization, and magnetic behavior of porous ZnFe<sub>2</sub>O<sub>4</sub> hollow microspheres

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**Abstract** Porous ZnFe<sub>2</sub>O<sub>4</sub> hollow microspheres with a diameter of about 100–210 nm were successfully prepared by simple template-free hydrothermal route in ethylene glycol (EG) solution. The formation mechanism and properties have been also demonstrated. The structural, morphological, and magnetic properties of ZnFe<sub>2</sub>O<sub>4</sub> hollow microspheres were investigated by means of X-ray powder diffraction (XRD), field emission scanning electron microscopy, Fourier transform infrared spectroscopy, and physical properties measurements system. The surface area was determined using the BET method. XRD and IR analyses confirm the cubic spinel phase of ZnFe<sub>2</sub>O<sub>4</sub> hollow microspheres. Every magnetic microsphere is made up of many ultrafine ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles with porous structure. The as-prepared porous magnetic hollow spheres have higher surface area and excellent magnetic properties at room temperature.

**Keywords** Hollow spheres · X-ray diffraction · SEM · FTIR · BET · Magnetic properties

## Background

The ecofriendly functional nanostructures, such as transition metal oxides with spinel structure MFe<sub>2</sub>O<sub>4</sub> (M = Mn, Fe, Co, Ni, Zn, etc.) have attracted considerable attention in the recent decade because of the fundamental scientific

interest in relation to size/shape effects and their potential technological applications in many important fields [1]. Among the family of ferrite materials, zinc ferrite (ZnFe<sub>2</sub>O<sub>4</sub>) has a normal spinel structure with the tetrahedral A sites preferentially occupied by Zn<sup>2+</sup> and octahedral B sites occupied by Fe<sup>3+</sup>, which results in anti-ferromagnetic properties at  $T_N = 10$  K [2].

In recent years, hollow micro-nano-materials have attracted broad attention due to their superior properties, such as low density, large specific area, distinct magnetic property, well-defined pore topology, and more appropriate pore size (>50 nm) compared with nanocrystalline materials, and have been proven to be promising in widespread applications in microelectronics, drug delivery, catalysis, energy storage, and gas sensing [3–6]. It has been found that nano-scaled materials exhibit promising properties that are quite different from their corresponding bulk materials [7]. Worldwide research efforts are underway to find new applications for ferrites in addition to improving their existing functional properties. In the past, various methodologies have been adopted for the preparation of hollow spheres [8–12]. However, the main process for the preparation of hollow spheres generally requires removable templates such as monodispersed silica, polystyrene latex spheres, metal nanoparticles, gas bubbles, and polymer spheres followed by sequential adsorption of magnetic nanoparticles on the templates [13–18]. The typical procedure is that the template is coated by either direct surface reaction utilizing special functional groups on the core or controlled precipitation of inorganic precursors on the surface of template to induce coating, followed by the removal of template core through calcination or solvent dissolution [19–21]. Definitely, the template or surfactant direct synthesis suffers from the disadvantages of low yield and high cost; template-free methods have drawn increasing attention.

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As the magnetic properties of these spinel ferrite nanocrystallines are affected by their morphology, shape-controlled synthesis of spinel ferrites has attracted much attention. The past two decades have seen a wealth of methods to synthesize different  $\text{ZnFe}_2\text{O}_4$  nanostructures with uniform size and shape, including nanoflowers [22], nanotubes [23], nanorods [24], and nanocubes [17].

However, there are still no reports for the preparation of porous zinc ferrite hollow microspheres. It appears that it remains a challenge to explore an economic, template-free, and effective strategy to synthesize magnetic  $\text{ZnFe}_2\text{O}_4$  with sphere morphology. The purpose of our study is to synthesize monodispersed purified hollow ferrite spheres in low temperature from EG solution with simple template-free hydrothermal method. Zinc chloride and ferric chloride were used as cation sources in the reaction system. EG and polyethylene glycol (PEG) were used as solvent and surfactant, respectively, and sodium acetate as a weak base. The phase structure, morphology, elemental, and magnetic behavior of the hollow microspheres were investigated in detail.

## Methods

Magnetic  $\text{ZnFe}_2\text{O}_4$  hollow spheres were synthesized by simple template-free hydrothermal method. All of the reactants were analytical grade and were used without any further purification. The starting materials for the present study included  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ , sodium acetate ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ), ethylene glycol (EG), and PEG. A typical synthesis was performed as follows: 1.35 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 0.55 g  $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved into 40 mL EG. About 3.6 g NaAc and 2 g PEG were added into the solution and stirred under 50 °C for 30 min to form a homogeneous brown solution. The hydrothermal synthesis was carried out in a 100 mL Teflon-lined stainless steel autoclave cell without any agitation for 16 h at 180 °C. After being cooled to room temperature, the black products were collected by a magnet, washed several times with distilled water to remove the impurities, and finally dried at 80 °C for 8 h. The yield of  $\text{ZnFe}_2\text{O}_4$  microspheres is relatively high (85.9 %) for hydrothermal method.

The crystal structure was determined using X-ray diffraction (XRD, Bruker D2 Advanced Diffractometer with  $\text{Cu K}\alpha$  radiation). Morphological studies were conducted using field emission scanning electron microscope (FE-SEM, Hitachi S-4800). The element distribution and the content (wt%) of  $\text{ZnFe}_2\text{O}_4$  within the hollow spheres were detected by energy dispersive X-ray spectroscopy (EDX). The specific surface area of the obtained material was measured according to the Brunauer–Emmett–Teller (BET) method using Micromeritics ASAP-2020 V4.0

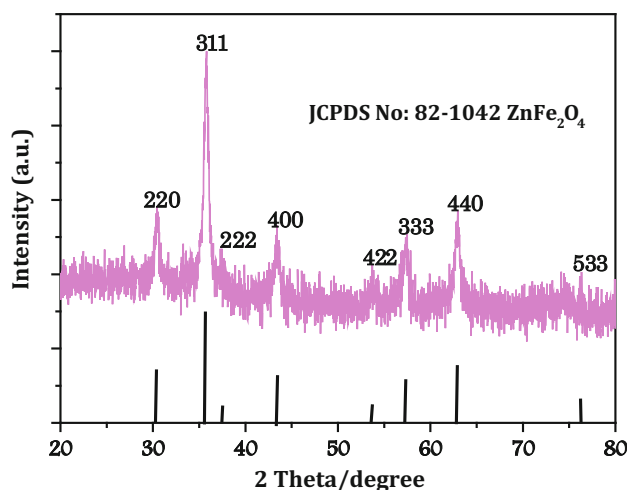
apparatus with liquid nitrogen at 77 K. BET surface area of  $\text{ZnFe}_2\text{O}_4$  was determined to be  $44.163 \text{ m}^2 \text{ g}^{-1}$ . The FTIR spectrum was recorded on a KBr pellet (Bruker Tensor 27). Magnetic studies at room temperature have been carried out using physical properties measurement system (PPMS).

## Results and discussion

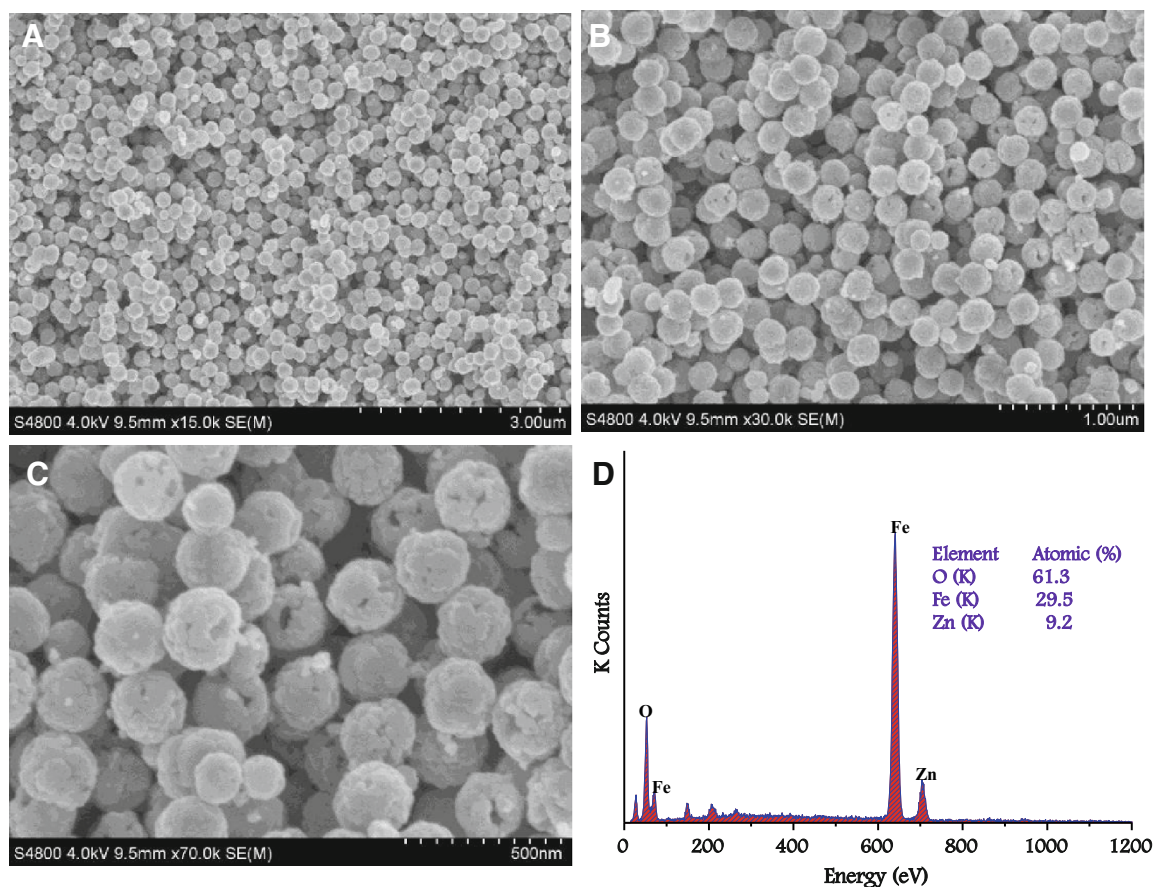
XRD patterns of all samples show very broad peaks, indicating poor crystallinity and ultrafine nature of the particles. The crystalline structure of the as-synthesized  $\text{ZnFe}_2\text{O}_4$  hollow sphere was characterized by powder XRD. As shown in Fig. 1, the diffraction peaks match well with the standard patterns of the cubic structure of spinel-phase Zn ferrite (JCPDS file no. 82–1042), where the diffraction peaks at  $2\theta$  values of 30.0°, 35.3°, 42.9°, 53.2°, 56.7°, 62.3°, and 76.6° can be attributed to the reflection of (220), (311), (400), (422), (333), (440), and (533) planes of the spinel  $\text{ZnFe}_2\text{O}_4$ , respectively. No additional peak of the impurity phase was observed in the XRD patterns, showing that the prepared ferrites are pure.

The general morphology of the as-prepared  $\text{ZnFe}_2\text{O}_4$  hollow sphere products observed by field emission SEM (FE-SEM) and typical images at different magnifications are shown in Fig. 2a–c, it was observed that the major morphological feature is a regular spherical shape with an average particle diameter of about 100–210 nm. The high-magnification FE-SEM image (Fig. 2c) reveals that each micro-hollow sphere is very similar to hollow spheres and it is actually composed of aggregates of more primary particles.

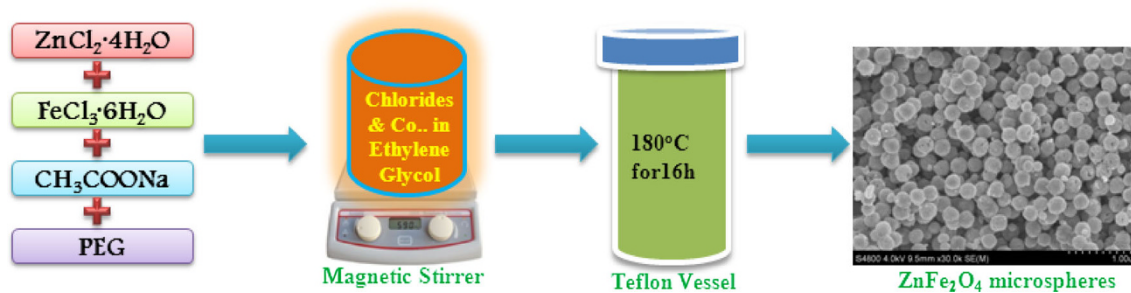
EDX results from hollow spheres showed that it was mainly composed of Zn, Fe, and O (Fig. 2d).



**Fig. 1** XRD patterns of the as-synthesized porous  $\text{ZnFe}_2\text{O}_4$  hollow microspheres



**Fig. 2** SEM (a–c) and EDS images of the as-synthesized porous  $\text{ZnFe}_2\text{O}_4$  hollow microspheres



**Fig. 3** The proposed preparation scheme of the porous  $\text{ZnFe}_2\text{O}_4$  hollow microspheres

Quantification of the EDX spectrum showed that the ratio of Zn, Fe, and O was about 1:2:4, suggesting that the porous hollow spheres had a chemical formula of  $\text{ZnFe}_2\text{O}_4$ .

On the basis of the above experimental results and observations, a formation mechanism of the  $\text{ZnFe}_2\text{O}_4$  hollow spheres is designed, schematically illustrated in Fig. 3. The reaction begins with the mixture of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ , Sodium acetate ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ), EG, and PEG. In our system, the  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  ions were nucleated under hydrothermal conditions with the water generated from metal precursors to form nanosized

crystalline  $\text{ZnFe}_2\text{O}_4$ . PEG serves as a structure-directing template, as it can easily self-assemble to form spherical grains. The Ostwald ripening process also plays an important role in the formation of nanocrystals. According to the Ostwald ripening mechanism, crystalline particles will grow into crystalline nuclei, which aggregate isotropically to form spherical grains in ethanol solution and further to microspherical crystallites. During growth, the smaller, less crystalline particles will be dissolved gradually, while the larger, more crystalline particles will grow bigger. Eventually, the core can grow gradually to form a

solid sphere. As the crystal grows, the porous  $\text{ZnFe}_2\text{O}_4$  microsphere was formed at last. Finally, the massy porous  $\text{ZnFe}_2\text{O}_4$  microspheres are formed, as evidenced by XRD (Fig. 1), SEM (Fig. 2), TGA (Fig. 4), and FTIR (Fig. 6).

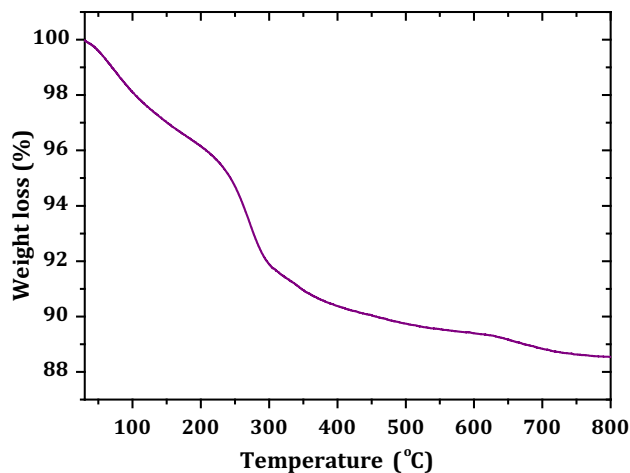
As shown in Fig. 4, the TG curve shows that porous  $\text{ZnFe}_2\text{O}_4$  hollow spheres have three weight loss steps from room temperature to 800 °C under air atmosphere. The first weight loss of about 3.7 % in the range 25–220 °C was due to the loss of residual water in  $\text{ZnFe}_2\text{O}_4$  hollow spheres. The combustion of carbon was complete at a relatively low temperature (<400 °C). From the weight change between 150 and 400 °C, the organic matter content (carbon and oxygen containing surface groups) was determined to be 40 wt%.

The nitrogen sorption isotherm of resultant  $\text{ZnFe}_2\text{O}_4$  hollow spheres and their corresponding pore-size distribution curve are exhibited in Fig. 5. The nitrogen adsorption-desorption isotherm belongs to type IV category according to international union of pure and applied chemistry classification, suggesting the presence of mesopores. The specific surface area was thus estimated, by BET equation [25], to be  $44 \text{ m}^2 \text{ g}^{-1}$ . In addition, the sorption exhibits type IV isotherm, and the pore analysis has revealed that the pore sizes in the porous microspheres mainly fall into 3–9 nm, as seen in the inset of Fig. 5. Hysteresis loops can be observed in the curve, attest to the existence of a mesoporous structure. The high surface area and pore volume further confirm that the hollow microspheres have porous structure which will broaden the application of the product.

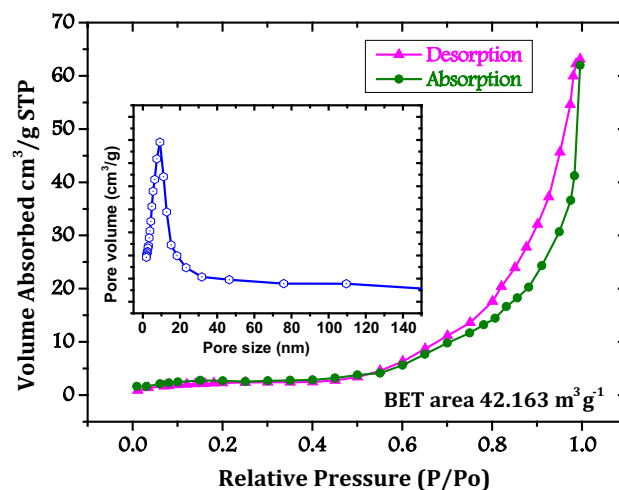
Theoretically, all  $\text{MFe}_2\text{O}_4$  either normal or inverse spinel oxides of transition metals have four infrared active modes. These vibrations occur at frequencies of  $\nu_1$  ( $650\text{--}550 \text{ cm}^{-1}$ ),  $\nu_2$  ( $525\text{--}390 \text{ cm}^{-1}$ ),  $\nu_3$  ( $380\text{--}335 \text{ cm}^{-1}$ ), and  $\nu_4$  ( $300\text{--}200 \text{ cm}^{-1}$ ) [26].

The  $\nu_1$  and  $\nu_2$  bands are generated due to intrinsic vibrations of tetrahedral and octahedral coordination compounds. Absorption of  $\nu_1$  happens due to the bond stretching of tetrahedral metal ions and oxygen, while  $\nu_2$  vibration is observed due to the vibration of oxygen in the direction perpendicular to the axis joining the tetrahedral ions and oxygen. The  $\nu_3$  mode is obtained from the  $\text{Fe}^{3+}\text{--O}$  complexes at octahedral sites [27]. The frequency of  $\nu_4$  vibration depends on the mass of tetrahedral metal ion complexes, which gives information about the vibration of ions occupying at tetrahedral site.

In order to make sure of its chemical compositions, the Fourier transform infrared spectrometry (FTIR) spectrum of the  $\text{ZnFe}_2\text{O}_4$  hollow sphere product was verified. As shown in Fig. 6, the two bands at  $582$  and  $435 \text{ cm}^{-1}$  represented the characteristic peaks of tetrahedral and octahedral Fe–O stretching for  $\text{ZnFe}_2\text{O}_4$ . The appearance of bands at  $1,081$  and  $2,925 \text{ cm}^{-1}$  is assigned to the stretching



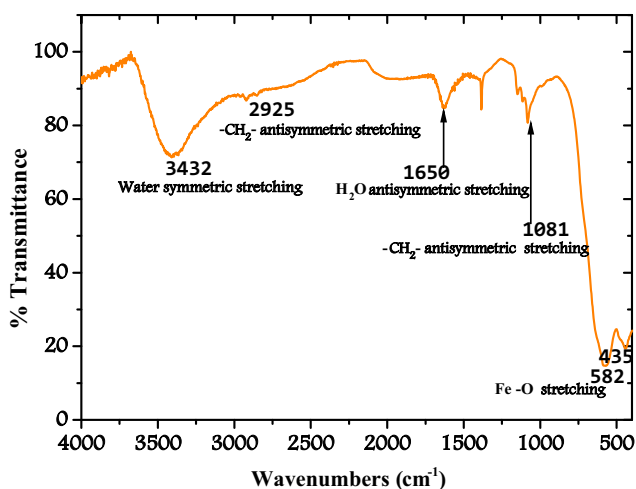
**Fig. 4** TG curve of the as-synthesized porous  $\text{ZnFe}_2\text{O}_4$  hollow microspheres



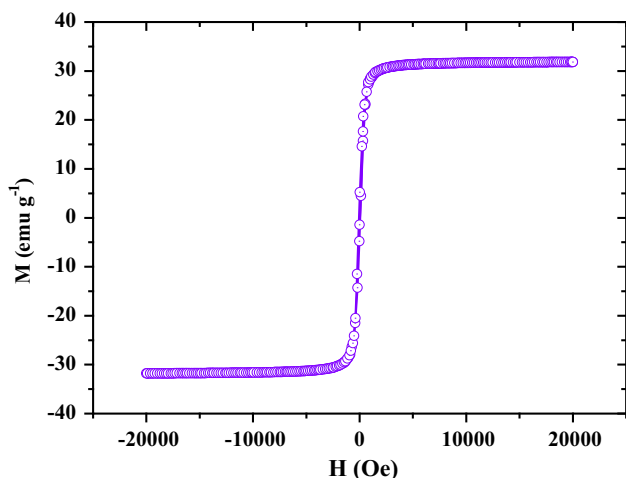
**Fig. 5**  $\text{N}_2$  sorption isotherm of the porous  $\text{ZnFe}_2\text{O}_4$  hollow microspheres. The inset shows the corresponding BJH pore-size distribution

of ether groups and the characteristic absorptions of alkyl ( $\text{R-CH}_2$ ) stretching modes. In addition, the bands at  $3,432$  and  $1,650 \text{ cm}^{-1}$  are attributed to the surface hydroxyl and the adsorbed water molecules, respectively [28]. Hydroxyl group contribution was observed at  $3,432 \text{ cm}^{-1}$ . The appearance of these peaks in the spectrum confirmed the presence of PEG and adsorbed EG on the surface of particles. The above FTIR analysis matches well with the XRD result, which confirms that the as-obtained products are pure-phase spinel Zn ferrite.

Such porous oriented  $\text{ZnFe}_2\text{O}_4$  hollow spheres exhibited good magnetic property [29]. Magnetic measurements of the samples were carried out at room temperature using a PPMS with a peak field of 20 kOe. The hysteresis loops for porous zinc ferrite hollow microspheres are shown in Fig. 7. As clearly shown, the variation of magnetization as



**Fig. 6** FTIR spectra of the as-synthesized porous  $\text{ZnFe}_2\text{O}_4$  hollow microspheres



**Fig. 7** Magnetization hysteresis loop of the porous  $\text{ZnFe}_2\text{O}_4$  hollow microspheres

a function of the applied field presents a narrow cycle, and the observed hysteresis loops are a characteristic behavior of soft magnetic materials. The saturation magnetization ( $M_s$ ) of the zinc ferrite hollow spheres is about  $32 \text{ emu g}^{-1}$ , which is close to the value of bulk  $\text{ZnFe}_2\text{O}_4$  ( $36 \text{ emu g}^{-1}$ ) [30]. The low saturation magnetization of the ferrite NPs is generally believed to be due to the decreased particle size and the presence of an anti-ferromagnetic layer on the surface. In the close-up view (not shown in Figure), the curve presents a very small hysteresis loop with a remnant magnetization ( $M_r$ ) of  $1.3 \text{ emu g}^{-1}$  and a coercivity ( $H_c$ ) of 16 Oe, denoting the ferromagnetic behavior of the sample. Table 1 shows the previously reported saturation magnetization values for zinc ferrite nanocrystallines synthesized by various methods [31–37],

**Table 1** Comparison of the saturation magnetization ( $M_s$ ) values for  $\text{ZnFe}_2\text{O}_4$  hollow spheres with literature values

Number	Method of synthesis	Temp (K)	Size (nm)	$M_s$ (emu/g)	Ref
1	Hydrothermal method	300	210	32	This study
2	Hydrothermal in ammonia solution	300	80	61.87	[31]
3	Hydrothermal in supercritical methanol	5–20	4.2	38	[32]
4	Oil-in-water micelles	3.7	3	70	[33]
5	Co-precipitation at 373 K	55	4.2	46.9	[34]
6	Sol-gel method	30	300	7.8	[35]
7	Ultrasound-assisted emulsion	12	5	25	[36]
8	Hydrothermal method	8	250	17.5	[37]

from which we could conclude that our present  $M_s$  value at ambient temperature is obviously higher than that of most of the reported uniform  $\text{ZnFe}_2\text{O}_4$  nanocrystallines through the facial hydrothermal synthesis.

## Conclusions

$\text{ZnFe}_2\text{O}_4$  hollow microspheres with diameters of about 210 nm were successfully synthesized under low temperature through template-free hydrothermal method. These  $\text{ZnFe}_2\text{O}_4$  porous hollow spheres have excellent magnetic properties and higher surface area. The proposed method is easy, nontoxic, and reproducible. EG plays a key role in the synthesis of hollow spheres. Further work to investigate and fabrication of Co, Mn, and  $\text{NiFe}_2\text{O}_4$  hollow microspheres is in progress. This method may provide a simple and scalable synthesis approach for preparing advanced materials based on various multicomponent hollow structures for multipurpose application.

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**Author's contributions** MLPR is a postdoctoral scientist who performed the experiment and prepared the manuscript. XBZ is a doctoral student who studied on nanostructures. SD and QH supervised in conducting this work. All authors read and approved the final manuscript.

**Conflict of interest** The authors declare that they have no competing interests.

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