Assembly of magnetite nanocrystals into spherical mesoporous aggregates with a 3-D wormhole-like pore structure†

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Spherical mesoporous magnetite (Fe₃O₄) aggregates with a wormhole-like pore structure were successfully synthesized for the first time using a single iron precursor (iron(III) ethoxide) and an amphiphilic poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer (PEO₁₀₀–PPO₆₅–PEO₁₀₀) as a soft template. In this synthesis, the interaction between the iron precursor and the triblock copolymer self-assemblies in ethanol leads to the assembly of magnetite nanocrystals into spherical mesoporous aggregates. These aggregates were characterized using Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, field-emission scanning electron microscopy, standard and high-resolution transmission electron microscopy, ⁵⁷Fe Mössbauer spectroscopy, and X-ray diffraction, confirming the formation of pure-phase Fe₃O₄ particles with monodisperse morphology (about 130 nm in diameter), three-dimensional wormhole-like mesopores, and highly crystalline spinel structure. In addition, a formation mechanism for this material in the present system is proposed, based on the analysis of results. The mesoporous magnetite has a high specific surface area of 165.6 m² g⁻¹, and relatively large pores with a mean size of 5.2 nm. The magnetic susceptibility data demonstrate that this material exhibits superparamagnetic behavior.

Introduction

Mesoporous and mesoporous materials have generated considerable interest on account of their diverse compositions and morphologies (including shape and dimensionality), some with very high surface-to-volume ratios, making these materials useful in surface-related applications in fields such as catalysis,¹ sensors,² adsorption,³ dye-sensitized solar cells,⁴ and separation materials;⁵ etc. According to the IUPAC classification, inorganic solids, polymers and carbon that contain pores with diameters in the 2–50 nm scale are considered to be mesoporous materials.⁶ Historically, many researchers have focused on the development of techniques to produce mesoporous silica (SiO₂) and titania (TiO₂) based materials with large surface-to-volume ratios, to achieve superior catalytic properties and utilization efficiency.⁷ In comparison, there have been fewer studies of iron-based mesoporous materials, despite the enormous potential and novel properties of mesoporous iron oxide.

Iron oxide nanoparticles, including magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), and wüstite (FeO), are attracting growing interest because of their unique properties and broad range of applications in many fields.⁸ Magnetite, with space group Fm3m, has a face-centered cubic structure in the spinel series. There are two distinct iron sites in the spinel-type structure, ferrous (Fe²⁺) and ferric (Fe³⁺), which have tetrahedral and octahedral coordination, respectively (see Fig. S1†). Various properties of magnetite have been widely studied in the context of imaging,⁹ drug delivery,¹⁰ environmental catalysis,¹¹ recording devices,¹² solar cells,¹³ and environmental remediation,¹⁴ etc. Consequently, the synthesis of mesoporous magnetite with novel morphological properties, such as high surface area and porous structure, is both desirable and technologically important.

Many mesoporous materials, such as siliceous materials, metal oxides, carbon and polymers, have been prepared by either a nanocasting hard-template method or a surfactant self-assembly soft-templating approach.¹⁶ So far, a variety of approaches has been exploited in preparing magnetite spheres with particular properties. For example, Tang et al. prepared mesoporous magnetite hollow spheres using carboxyl-functionalized polystyrene (PS) spheres as hard templates, and studied their structure and magnetic properties.¹⁶ Wan et al. recently reported the preparation of magnetite microspheres on the basis of a two-step procedure involving the formation of ferrihydrite/urea and formaldehyde (UF) composite micro-spheres and subsequent reduction of the ferrihydrite to magnetite.¹⁷ Gao et al. have presented the synthesis of micrometre-sized magnetite spheres via coarsening (also known as Ostwald ripening) after prolonged hydrothermal treatment.¹⁸ More recently, Xia and
co-workers have described a method based on the cyclodextrin surfactant template-assisted synthesis of water-dispersible hollow clusters of magnetite nanoparticles.\textsuperscript{19} He et al. reported the synthesis of magnetic magnetite with mesoporous structure via the co-precipitation method using yeast cells as a template.\textsuperscript{20} However, in many of these studies the preparation of mesoporous magnetite is a complex multiple-step process. Moreover, the resulting particle size is generally more than 200 nm, with a specific surface area below 100 m² g⁻¹, which may limit their use in many applications. To the best of our knowledge, there have been no reports of a simple and economical synthesis and characterization of nanometre-scaled spherical mesoporous magnetite particles with a high specific surface area, particularly using a self-assembled block copolymer as a structure-directing agent. Block copolymers are suitable and versatile templates for fabricating mesostructured and mesoporous materials. In particular, nonionic amphiphilic copolymers as surfactants can form a large variety of three-dimensional (3D) structures through non-covalent interactions, which can be used to direct the nanocrystals into the desired mesostructure.\textsuperscript{21} They are also able to impart high effective surface areas, pore volumes, and well-controlled morphologies, as well as being industrially available, environmentally friendly, and easy to remove from the nanostructured framework.\textsuperscript{22}

Herein, we synthesized spherical mesoporous magnetite (Fe₂O₄) particles using a single iron precursor (iron(III) ethoxide) and a nonionic amphiphilic triblock copolymer (PEO₁₀₀–PPO₆₅–PEO₁₀₀, where PEO is poly(ethylene oxide) and PPO is poly(propylene oxide)). The triblock copolymer is used as the structure-directing and pore-forming agent, and the interaction between the iron precursor and the triblock copolymer self-assemblies in ethanol leads to the assembly of spinel-structured nanocrystals into spherical aggregates with wormhole-like porous structures. The mesoporous structure and wormhole-like channels are potentially important structural features for catalytic activity, because a high number of channels within the individual nanocrystals can expedite access to the reactive sites of the resulting particles.\textsuperscript{23} To study the chemical composition, morphology, crystal information, and properties of the synthesized material, a variety of techniques are employed, including Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, field-emission scanning electron microscopy, transmission electron microscopy, wide-angle X-ray diffraction, Fe Mössbauer spectroscopy, N₂ adsorption–desorption, and superconducting quantum interference device magnetometry. In addition, a reasonable model for the formation mechanism of these spherical aggregates is proposed and discussed in more detail.

**Experimental**

**Materials**

Amphiphilic poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) triblock copolymer (PEO₁₀₀–PPO₆₅–PEO₁₀₀, \(M_w = 14,600\)) was purchased from Aldrich. Iron(III) ethoxide (Fe(OCH₂CH₃)₃) was obtained from Alfa Aesar Co., Ltd. Ethanol (CH₃CH₂OH, stated purity: 99.8%) was obtained from Carlo Erba Reagents. All materials were used as received without any additional purification. Water used in all syntheses was distilled and deionized.

**Synthesis of spherical magnetite aggregates with wormhole-like pore structure**

The synthesis and assembly of mesoporous magnetite was carried out using the following procedure. First, 0.73 g (0.05 mmol) of PEO–PPO–PEO-based triblock-copolymer surfactant (as a structure-directing agent) in ethanol (30 mL) was stirred vigorously at a constant temperature of 40 °C to give a transparent solution. Next, iron(III) ethoxide (0.573 g, 3 mmol) was dissolved in ethanol (20 mL) in a separate beaker and added gradually to the surfactant solution with vigorous stirring. After addition, the reaction was allowed to proceed at 40 °C for 24 h without stirring. Initially no precipitation was observed, but after several minutes a brown–black powder was produced. When the reaction was complete, the solid product was isolated from the liquid phase by filtration and thoroughly washed with a large amount of ethanol and deionized water (2 or 3 times) to effectively remove excess polymeric surfactant and byproducts. The resulting particles were vacuum-dried at room temperature. Lastly, calcination was carried out at 500 °C for 3 h in nitrogen with a heating rate of 1 °C min⁻¹.

**Characterization**

Fourier transform infrared (FT-IR) spectra in the range 4000 to 600 cm⁻¹ were recorded on a Thermo Scientific Nicolet 6700 IR spectrophotometer with a spectral resolution of 4 cm⁻¹. X-Ray photoelectron spectroscopy (XPS) measurements were acquired on a KRATOS AXIS with Mg-Kα X-rays as the excitation source (1253.6 eV). The spectra were recorded with a background pressure of 1.0 × 10⁻⁹ torr. The thermogravimetric transition studies were performed over the temperature range 25–600 °C using a TA Instruments Q500 thermogravimetric analysis (TGA) and Q1000 differential scanning calorimetry (DSC) system under flowing nitrogen with a heating rate of 10 °C min⁻¹. The morphology of the material was determined by field-emission scanning electron microscopy (FE-SEM, Carl Zeiss SUPRA 55VP), operated at an accelerating voltage of 3.0 kV and equipped with energy-dispersive spectroscopy (EDS) capabilities. All samples were coated with platinum under vacuum prior to microscopy. Standard and high-resolution transmission electron microscopy (TEM and HR-TEM, respectively) were performed using a JEOL JEM-2000EXII instrument operated at 200 kV. Samples for the TEM experiments were prepared by dispersing dried samples in absolute ethanol. A drop of the sample suspension was placed on a copper grid coated with a carbon film and then dried in air. The crystal structure and crystallite size of the mesoporous magnetite were determined using wide-angle X-ray diffraction (WXRd, MAC/Sci. MXP 18XHF–22SRA) with Cu-Kα radiation (\(λ = 1.541 \text{ Å}\)) at room temperature. An accelerating voltage of 50 kV and an emission current of 100 mA were used. Scans were recorded for 2θ values between 15° and 80° with a scanning speed of 5° min⁻¹. The average crystallite size was determined by the Debye–Schererr equation, \(D = \frac{Kλ}{βcosθ}\),\textsuperscript{24} where \(D\) is the average crystal diameter, \(K (= 0.89)\) is a constant related to the shape of the crystal,
Another absorption band at 2985 cm\(^{-1}\) is the stretching vibration of the terminal hydroxyl (–OH) group. The PEO–PPO–PEO-based triblock copolymer corresponds to the range of applied fields from 10 to +10 kOe. The magnetic moment of each sample was measured over a range of 10 to +10 kOe. Zero-field-cooled (ZFC) magnetization measurements were performed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-XL). Samples were weighed and placed in a gelatin capsule for magnetic studies. For FC magnetization measurements, the magnetite sample was first cooled to 5 K without an applied magnetic field and then the magnetization of the sample was measured from 5 to 350 K in an applied magnetic field. For FC magnetization measurements, the sample was cooled to 5 K with an applied magnetic field and then the measurement of magnetic moments was carried out. Magnetic studies were conducted in the solid state at room temperature using a vibrating sample magnetometer (VSM).

### Results and discussion

Fig. 1 shows two FT-IR spectra: (a) triblock copolymer, and (b) magnetite after calcination at 500 °C for 3 h. In Fig. 1(a), the broad absorption band at around 3480 cm\(^{-1}\) corresponds to the stretching vibration of the terminal hydroxyl (–OH) group. Another absorption band at 2985 cm\(^{-1}\) is due to \(sp^3\) C–H stretching. Many intense and sharp bands are observed in the range 1460–1113 cm\(^{-1}\), which are associated with methylene (–CH\(_2\)) and methyl (–CH\(_3\)) group bending and C–O stretching.\(^{25}\) In the magnetite sample, the peaks from the triblock copolymer are absent after washing and calcination at 500 °C, as evident from Fig. 1(b), showing the complete removal of the polymeric surfactant from the pores of the mesoporous magnetite particles. The spectrum of magnetite contains characteristic low frequency bands. Generally, the band around 600 cm\(^{-1}\) corresponds to the Fe–O bond vibration of iron cations at the tetrahedral site, whereas the band around 400 cm\(^{-1}\) corresponds to iron cations in the octahedral site. It is widely known that the Fe–O bond length of tetrahedral iron cations is smaller than that of octahedral iron cations.\(^{26}\) In our experimental data, these two absorption bands occur at 563 cm\(^{-1}\) and 439 cm\(^{-1}\), respectively, which indicates formation of pure magnetite in the present system.\(^{27}\)

The chemical composition of the prepared magnetite was additionally confirmed by energy dispersive spectroscopy (EDS). EDS spectra were taken at a number of different positions on the sample. In Fig. 2(a), EDS analysis shows the presence of Fe (111), Fe (200), O (111), and C (111). The high-resolution Fe 2p XPS spectrum shows the peaks at 710.7 eV and 726.5 eV, which are associated with Fe\(_{3}O\(_{4}\)\). The high-resolution O 1s XPS spectrum shows the peak at 531.2 eV, which is associated with O\(_{2}\).
and O elements only, with an atomic ratio Fe : O of 3 : 4, in agreement with the expected stoichiometry. To study the surface nature of the synthesized magnetite, the sample was characterized by X-ray photoelectron spectroscopy (XPS). Fig. 2(b–d) shows various regions of the XPS spectrum for mesoporous magnetite (Fe₃O₄) particles, clearly indicating the presence of Fe and O. The Fe 2p spectrum shows peaks at 710.7 and 724.5 eV, corresponding to the 2pₓ/ᵧ and 2pᵧ/ₓ spin-orbital components, respectively, and the single O 1s peak is observed at 531.2 eV. The nature of the characteristic peaks of Fe 2p and O 1s is close to that the report for magnetite. These results all indicate that the synthesis of Fe₃O₄ particles was successful.

In a separate series of experiments, before calcining the magnetite sample at 500 °C, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) profiles of as-synthesized magnetite were measured, as shown in Fig. S2 (see ESIF†). Below 100 °C, an endothermic DSC peak can be attributed to the elimination of residual water and ethanol. The single broad exothermic peak at 257.3 °C relates to an amorphous-to-crystalline phase transition. A slight weight loss in the range of 200–350 °C can be ascribed to the decomposition of the remaining polymeric surfactant, which is accompanied by an exotherm at around 330 °C. From the TGA analysis, it is observed that above 340 °C most of the surfactant has been evaporated. No further weight losses are observed at higher temperatures. Moreover, according to TGA and DSC analysis, the mesoporous magnetite sample calcined at 500 °C possesses good thermal stability. It is evident that at 500 °C, the chosen calcination temperature, all organic matter including surfactant has been eliminated, thus maximizing the available porosity.

Wide-angle X-ray diffraction (WXRD) was used to determine the purity and crystal structure of magnetite in the assembled spheres. Fig. 3 shows the WXRD patterns of magnetite samples calcined at 300 and 500 °C for 3 h. The mesoporous magnetite particles produce several relatively strong and well-defined reflection peaks in the 2θ region of 20–70°, quite similar to those of pure-phase magnetite particles reported by other groups, indicating that the prepared particles have the magnetite crystal structure. The diffraction peaks corresponding to the (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 3) planes provide clear evidence for the spinel cubic structure (space group: Fd3m), confirming the crystallization of the standard magnetite (Joint Committee on Powder Diffraction Standards, JCPDS file, No. 19-0629), as shown in Table S1†. The Bragg reflection peaks are relatively broad because of the small dimensions of the magnetite nanocrystals. No peaks of any other phases, for example, maghemite (γ-Fe₂O₃), are detected, indicating that the resulting material is pure magnetite (see Table S2 and Fig. S3 in the ESI†). With increasing calcination temperature the diffraction peaks of the spinel structure become noticeably sharper and stronger, revealing increasing primary crystal size; partial crystallization occurs in the magnetite sample calcined at 300 °C (Fig. 3(b)), whereas the sample calcined at 500 °C displays most of the diffraction peaks of the spinel phase (Fig. 3(a)). On the basis of the WXRD results, the crystallite domain size of the calcined mesoporous magnetite particles is determined from the breadth of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) reflection, based on the Debye–Scherrer formalism, giving an average crystal size of 5.79 nm (see Table S3 in the ESI† for details). This is consistent with the transmission electron microscopy (TEM) results within experimental error.

The ⁵⁷Fe Mössbauer spectra of the resulting material recorded at room temperature are given in Fig. 4. As shown, the Mössbauer spectra have confirmed that the two sextuplets are due to the small difference between the hyperfine fields of the Fe³⁺ and Fe²⁺ ions in the sublattices for octahedral and tetrahedral sites, and no signals due to the existence of other phases such as maghemite are observed (see Fig. S4 in the ESI†). As listed in Table 1, the values of internal magnetic fields, Hₑ, obtained were 492.3 kOe (Fe³⁺ tetrahedral A-site) and 451.8 kOe (Fe³⁺/Fe²⁺ octahedral B-site), respectively. The isomer shift (IS) value of 0.28 mm s⁻¹ confirms the presence of Fe³⁺ ions in A and B-sites, the other IS value (0.61 mm s⁻¹) is attributed to the

![Fig. 3](image-url) X-Ray diffraction patterns of mesoporous magnetite as a function of the scattering angle: (a) calcined at 500 °C for 3 h; (b) calcined at 300 °C for 3 h; and (c) as-prepared.

![Fig. 4](image-url) ⁵⁷Fe Mössbauer spectra of the mesoporous magnetite at room temperature. Full circles are the experimental data while the solid lines represent the best fit with two sextets.
presence of Fe$^{2+}$ ions in $B$-site. The values of the hyperfine parameter are reasonably close to the reported values for magnetite, ideal composition Fe$_{tet}^{3+}$[Fe$^{2+}$Fe$^{3+}$]$_{oct}$O$_4$. The morphology of the mesoporous magnetite was investigated by field-emission scanning electron microscopy (FE-SEM). Fig. 5(a) shows a typical FE-SEM image of the magnetite particles. The spherical aggregates retain their shape and size after calcination. Interestingly, the particles display highly monodisperse morphology with an average diameter of around 130 nm. A detailed FE-SEM image in Fig. 5(b) indicates that the Fe$_3$O$_4$ spherical structure consists of tightly interconnected individual nanoparticles, and that the discernible pores extend to the outer surface of the spheres.

TEM was used to further examine the morphology, particle size and crystallinity of the mesoporous magnetite particles. Representative TEM micrographs of mesoporous magnetite at low and high magnification are presented in Fig. 6(a) and (b), respectively, in which the pores can be seen as white spots in a wormhole-like array. As can be clearly observed, the mesoporosity is mainly due to the interparticle connections between agglomerated nanocrystals of about 4–5 nm, producing 3D spherical mesoporous particles of around 130 nm in diameter. These spherical aggregates are integrated and not easily fragmented. These results are consistent with the FE-SEM images. In Fig. 6(b), the high-resolution TEM (HR-TEM) micrograph and the fast Fourier transform (FFT) diffractogram of a selected area in the sample show that the mesoporous magnetite sample is well crystallized with an interplanar distance of ca. 0.48 nm, which is consistent with the lattice spacing of the (1 1 1) spinel planes of the magnetite crystal structure. Within an individual aggregate, the mesopore surface openings are surrounded by several primary nanoparticles. In addition, dynamic light scattering (DLS) analysis supports these TEM results. Fig. 7 depicts the particle size distribution of mesoporous magnetite in ethanol. The correlation functions were analyzed by means of the constrained regularization (CONTIN algorithm) method to determine the distribution decay rates (see Fig. S5 in the ESI† for details). The DLS results show that the mesoporous magnetite particles are well dispersed in ethanol, and the mean particle size for mesoporous magnetite particles is 157 nm in diameter with a size distribution standard deviation of 34 nm, which is in agreement with FE-SEM and TEM observations.

The large surface area generated by mesopores can promote chemical activities. The specific surface area and the porosity of the mesoporous magnetite particles were measured in order to demonstrate their potential use as catalytic materials. To determine the porosity of the calcined magnetite, standard N$_2$ adsorption–desorption tests were performed, as shown in Fig. 8. A large hysteresis loop between the adsorption and desorption isotherms, which is characteristic of highly porous materials, confirms the formation of mesopores in the magnetite particles. The isotherms can be considered as essentially type-IV curves, which typically illustrate the presence of mesopores. Estimation of the Brunauer–Emmett–Teller (BET) specific surface area and the Barrett–Joyner–Halenda (BJH) pore-size distribution demonstrates that the magnetite aggregates have a high specific surface area of up to 165.6 m$^2$/g and pores with an average size of 5.2 nm. The pore-size distribution plot (inset of Fig. 8) shows

### Table 1

<table>
<thead>
<tr>
<th>Mössbauer spectra components</th>
<th>$H_{hf}$/kOe (±0.5)</th>
<th>$\delta$/mm s$^{-1}$ (±0.01)</th>
<th>$\Delta$/mm s$^{-1}$ (±0.01)</th>
<th>$\Gamma$/mm s$^{-1}$ (±0.01)</th>
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</thead>
<tbody>
<tr>
<td>Fe$^{3+}$ in $A$-sites</td>
<td>492.3</td>
<td>0.28</td>
<td>0.00</td>
<td>0.48</td>
</tr>
<tr>
<td>Fe$^{3+}$, Fe$^{2+}$ in $B$-sites</td>
<td>451.8</td>
<td>0.61</td>
<td>0.02</td>
<td>0.71</td>
</tr>
</tbody>
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Fig. 5 (a) FE-SEM image of mesoporous magnetite spheres, and (b) a more detailed view.

Fig. 6 (a) TEM image of a mesoporous magnetite particle, and (b) HR-TEM image of the boxed region shown in image (a) and corresponding Fourier transform pattern (inset).

Fig. 7 DLS histogram of the mesoporous magnetite particle size distribution.
a relatively narrow mesopore-size distribution, which corresponds well to the TEM results. We believe that the combination of high specific surface area with 3D wormhole-like mesoporous structure is advantageous for catalytic and environmental applications.

In accordance with these results, a proposed mechanism for triblock-copolymer-based synthesis of three-dimensional spherical mesoporous magnetite is schematically illustrated in Fig. 9. As shown, when symmetrical triblock copolymer (PEO₁₀₀–PPO₆₅–PEO₁₀₀) is dissolved in ethanol solution at a constant temperature of 40 °C, a large number of spherical micelles are formed due to the interaction of the two segment types (hydrophilic PEO and hydrophobic PPO) of the triblock copolymer (stage A). It is generally accepted that the micelles are spherical in shape with a dense core consisting mainly of PPO and a swollen corona of hydrated PEO. The aggregation behavior of the triblock copolymer under thermodynamic equilibrium conditions is known to depend on both the concentration and the temperature, which may affect the formation of the mesophase as well as the particle morphology (including shape and dimensionality). Below a reaction temperature of 40 °C, irregular particle morphology of materials were obtained. As the concentration of surfactant increased in the reaction, the SEM image shows that as-made magnetite is mainly composed of short rods on the nanometre scale (see Fig. S6(B), (C) in the ESI†). Accordingly, preparation of spherical magnetite particles with mesopores requires suitable choice of synthesis parameters including temperature, reaction time, and molar ratio of triblock copolymer and magnetite precursors. These parameters are particularly important in generating high surface area and the desired mesopore structure. We therefore studied the role of various synthesis parameters in determining the magnetite mesostructure, as illustrated in Fig. S6 (see ESI†). Further hydrolysis and polycondensation (nucleation and growth) of the iron precursor leads to the formation of primary nanoparticles (stage B), which spontaneously aggregated to form the large spherical clusters in the solvent due to the strong surface tension. The main driving force for aggregation of the nanoparticles is a decrease in the high surface energy of the tiny nanoparticles. It is assumed that micelles surround the magnetite nanoparticles, playing a crucial role in the formation of spherical morphology (stage C). In addition, it is generally accepted that the functional groups of the surfactant have coordination bonds with the nanocrystals. In this system, surface hydroxyl groups in the surfactant coordinate with primary magnetite nanoparticles in ethanol solution. A subsequent washing and calcination would remove surfactant species in the mesostructured surfactant–magnetite composite, forming surfactant-free mesoporous magnetite (stage D). Therefore, it is believed that the use of
micelles as pore-forming template is a useful method to prepare the mesoporous structure, and the wormhole-like mesoporosity is due to the interparticle connections between agglomerated nanocrystals. On the other hand, no pore structure was formed in the as-synthesized particles without the addition of the surfactant, because magnetite species were distributed almost randomly without aggregation center for the formation of mesopore, as shown in Fig. S6(d) (see ESI†). Consequently, the individual magnetite nanocrystals (~5 nm in diameter) self-assemble into spherical aggregates (~130 nm in diameter) with a disordered wormhole-like mesopore structure. Similar mechanisms involving the aggregation of magnetite nanoparticles resulting in mesoporous spheres or hollow microspheres were proposed by Ohta et al., Gu et al. and Yu et al. From our analysis, this mode of formation may explain the growth mechanism of spherical mesoporous magnetite particles in this system. The FE-SEM and TEM images in Fig. 5 and 6 show that the mesoporous magnetite is composed of magnetite nanocrystals, which supports this mechanism.

Macroscopically, mesoporous magnetite particles in a vial are attracted by a conventional magnet placed close to the vial wall, and can be redispersed when the magnet is removed. This is illustrated in the photograph (inset of Fig. 11). The mesoporous magnetite was also investigated by field-dependent magnetization measurements using standard zero-field-cooling (ZFC) and field-cooling (FC) procedures. The magnetization curves were measured as a function of temperature with an applied magnetic field of 200 Oe between 5 and 350 K using a superconducting quantum interference device (SQUID) magnetometer, as shown in Fig. 10. In this figure, the ZFC and FC curves coincide at high temperature and separate as the temperature decreases, with a maximum in the ZFC curve at around 40 K. The peak in the temperature shows nonlinear, reversible characteristics with no hysteresis, exhibiting only superparamagnetic behavior. In the present system, considering that magnetic particles are spherical, the anisotropy constant of the assembled magnetite nanocrystals is 1.36 × 10⁶ erg cm⁻³. Fig. 11 shows the magnetization (M–H) curve of mesoporous magnetite measured using a vibrating sample magnetometer (VSM) at ambient temperature, with the applied field sweeping from −10 to +10 kOe. In this figure, the magnetization curve of mesoporous magnetite particles at room temperature shows nonlinear, reversible characteristics with no hysteresis, exhibiting only superparamagnetic behavior. In particular, the value of the magnetic saturation, $M_s$, for the magnetite sample, obtained from the VSM data, is 69.3 emu g⁻¹, which is lower than that of the bulk phase (84.5 emu g⁻¹). It is mostly due to the surface contribution of small nanoparticles. In addition, the average magnetic particle size can be obtained by fitting the slope of magnetization near zero-field region, $(dM/dH)_{H=0}$, from the M–H curve, shown in Fig. 11. The magnetic domain size, $D_m$, can be calculated from magnetization curve with the following equation:

$$D_m = \left( \frac{18k_B T}{\pi} \frac{(dM/dH)_{H=0}}{\rho M_s^2} \right)^{1/3}$$

where $\rho$ is the density (the density of magnetite phase is generally given in 5.1 g cm⁻³), $M_s$ represents the saturation magnetization. In light of the experimental data, the magnetic domain size of magnetite is around 4.2 nm. In general, the magnetic particle size is smaller than those of the sample observed from the WXRD and TEM analyses. From the experimental results, the mesoporous magnetite aggregates could be considered as a potential candidate as a reusable catalytic material by use of an external magnetic field.

**Conclusion**

In this study, a direct triblock-copolymer templating approach is demonstrated for the successful synthesis of spherical mesoporous magnetite ($\text{Fe}_3\text{O}_4$). The triblock copolymer is the
determining factor in the morphology of the resulting material, and the individual magnetite nanocrystals (about 5 nm in size) have a strong tendency to self-assemble during synthesis into spherical aggregates (about 130 nm in diameter) with a disordered wormhole-like mesopore structure. This process is spontaneous. Extensive characterization of the resulting material confirmed that these particles possess a uniform 3D spherical morphology, high specific surface area (∼165.6 m² g⁻¹), narrow particle-size distribution (with mean diameter of about 5.2 nm), and superparamagnetic susceptibility. In particular, with effective control of the mesoporous structure and the crystalline phase, and subsequent magnetic behavior, the synthesized mesoporous magnetite particles have great potential for applications in carbon dioxide (CO₂) decomposition. Additionally, this approach could be extended to the fabrication process of other iron oxides with complex metal oxidation states, which is currently underway.

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Notes and references


