Self-assembled multifunctional Fe₃O₄ hierarchical microspheres: high-efficiency lithium-ion battery materials and hydrogenation catalysts

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ABSTRACT Self-assembled Fe₃O₄ hierarchical microspheres (HMSs) were prepared by a one-pot synchronous reduction–self-assembling (SRSA) hydrothermal method. In this simple and inexpensive synthetic process, only glycerol, water, and a single iron source (potassium ferricyanide (K₃[Fe(CN)₆])) were employed as reactants without additional reductants, surfactants, or additives. The iron source, K₃[Fe(CN)₆], and glycerol significantly affected the synthesis of Fe₃O₄ HMSs. Fe₃O₄ HMSs with a self-assembled spherical shape readily functioned as high-performance anode materials for lithium-ion batteries with a specific capacity of > 1000 mA h g^{−1} at 0.5 A g^{−1} after 270 cycles. Further charging and discharging results revealed that Fe₃O₄ HMSs displayed good reversible performance (> 1000 mA h g^{−1}) and cycling stability (700 cycles) at 0.5 A g^{−1}. Furthermore, as multifunctional materials, the as-obtained Fe₃O₄ HMSs also exhibited high saturation magnetization (99.5 emu g^{−1}) at room temperature (25°C) and could be further employed as efficient and magnetically recyclable catalysts for the hydrogenation of nitro compounds.

Keywords: iron oxide, hierarchical structure, energy storage material, lithium-ion battery, hydrogenation catalyst

INTRODUCTION

Magnetic micro/nanoparticles are widely employed in various fields [1–4]. Fe₃O₄, a beneficial functional magnetic material, has attracted increased attention because of its excellent properties [5,6]. Therefore, various synthetic methods have been developed to prepare Fe₃O₄

micro/nanostructures (MNSs) with different morphologies and sizes. For example, in the coprecipitation method, Fe₃O₄ MNSs could be obtained from two different iron sources (ferrous and ferric salts), followed by the addition of alkali [7,8]. Generally, this method requires an inert atmosphere for the entire reaction process. Although the coprecipitation process is associated with advantages, such as its non-requirement of expensive precursor complexes, its good reproducibility, and eco-friendly reaction conditions, the sizes and morphologies of the products cannot be controlled without utilizing additives. Therefore, a precursor transformation method was developed to prepare Fe₃O₄ MNSs with controllable morphologies and sizes [9–12]. Moreover, it is well-known that the precursor transformation method requires two steps, namely the preparation of the precursors and the thermal transition in an inert atmosphere. Furthermore, Fe₃O₄ MNSs were prepared by a thermal decomposition method from the precursor complexes in high-boiling-point organic solvents at an elevated temperature [13–15]. As a beneficial synthetic strategy, the hydro/solvothermal method has been extensively employed in the synthesis of Fe₃O₄ MNSs [16–24]. In these cases, capping agents, such as surfactants, polymer stabilizers and/or complexing agents, reductants (hydrazine hydrate), or small organic molecules were required for the preparation process of Fe₃O₄ MNSs with specific shapes. Ultimately, tedious procedures, harsh reaction conditions, and/or additives were necessary to fabricate Fe₃O₄ MNSs

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with specific morphologies.

Fe_3O_4 MNSs with specific morphologies, such as a three-dimensional (3D) self-assembled structure have attracted immense attention because of their remarkable properties. Li *et al.* [25] reported a two-step method for the synthesis of chrysanthemum-like 3D hierarchical Fe_3O_4 NSs. The prepared NSs exhibited good adsorption capacity toward organic pollutants in water. Very recently, Lou and co-workers [26–28] developed a solvothermal method combined with subsequent annealing to prepare self-assembled sheaf-like [26] hollow microspheres (MSs) [27,28]. These self-organized structures displayed excellent lithium storage properties. The above reports revealed that the properties of Fe_3O_4 hierarchical MSs (HMSs) could be adjusted by controlling their specific structures.

Herein, a simple and inexpensive synchronous reduction–self-assembly (SRSA) hydrothermal method was designed to synthesize self-assembled Fe_3O_4 HMSs in the presence of glycerol. Additionally, various experimental conditions were applied to investigate the possible growth mechanism of the self-assembling of Fe_3O_4 HMSs. Electrochemical studies also revealed that the self-assembled Fe_3O_4 HMSs could be employed as high-capacity ($>1000 \text{ mA h g}^{-1}$) lithium-ion battery (LIB) materials with ultralong cycle life (700 cycles). Additionally, the magnetic behavior and catalytic hydrogenation performance of Fe_3O_4 HMSs were also studied.

EXPERIMENTAL SECTION

Synthesis of the self-assembled Fe_3O_4 HMSs

Fe_3O_4 micro/nanocrystals were synthesized by an SRSA hydrothermal method in mixed solutions at designated temperatures (Table S1, Supplementary information (SI)). In the typical synthesis of the self-assembled Fe_3O_4 HMSs, $\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.8 mmol, 263 mg) was added to a mixed solvent containing 37 mL of H_2O and 3 mL of glycerol. The clear solution was transferred to a Teflon-lined autoclave (60 mL) and kept at 180°C for 10 h. The self-assembled Fe_3O_4 HMSs were separated by the magnet and repeatedly washed by pure H_2O and absolute ethanol. Thereafter, the products were vacuum-dried overnight at 60°C . Additionally, the concentration of the iron ions (0.02 mol L^{-1}) and the volume of the mixture solvent (40 mL) remained unchanged when kept, and a series of comparative experiments were conducted by adjusting several reaction parameters, for example, the types of iron salts and polyols, the amount of glycerol, the different reaction temperatures, and time (the detailed procedures

are presented in Table S1).

Characterizations

The crystal phases and purities of the obtained powders were confirmed by X-ray diffraction (XRD). The Raman spectra were obtained on an InVia spectrometer (Renishaw) at room temperature. The structure, morphology, and composition of the products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The elemental mapping results were also measured by a field-emission electron microscope (JEM-2100F). The Fourier-transform infrared (FT-IR) spectra were recorded on an IR Prestige-21 spectrometer. The thermogravimetric (TG) analysis was conducted on a thermal analyzer in an air atmosphere. The N_2 sorption measurement was conducted on an ASAP 2460 instrument. The magnetic measurement was examined by a superconducting quantum interference device (SQUID). The detailed characterization and test conditions are presented in the SI.

Electrochemical measurements

The electrochemical lithium storage performance was tested utilizing 2032-type coin cells on a Neware battery test system. The coin cells were assembled in a glove box. The employed electrolyte was $1 \text{ mol L}^{-1} \text{ LiPF}_6$ in an ethylene carbonate mixture of ethylene carbonate and diethyl carbonate. The galvanostatic discharge–charge experiments were evaluated at potentials of 0.01–3.0 V. Additionally, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed. The detailed electrochemical measurements are presented in the SI.

Evaluation of the catalytic performance

The typical catalytic processes are as follows: 20 mg of the self-assembled Fe_3O_4 HMS catalyst, 1 mmol substrate (nitro compounds), and 3 mL of ethanol were added to a thick-walled pressure bottle (15 mL) with a Teflon cover by ultrasonic dispersion for 10 min. Sequentially, 2 mL of hydrazine hydrate (80 wt%) and a Teflon-coated magnet were added to the above thick-walled pressure bottle with a Teflon cover, after which the mixture reacted at 60°C for 5 h. After the reaction, the catalyst was separated utilizing a magnet. The conversion and selectivity of the products were detected by gas chromatography–mass spectrometry (GC–MS) and GC (*n*-dodecane was employed as a standard) after the reacting solution was filtered through a membrane.

RESULTS AND DISCUSSION

The phase and chemical compositions of the self-assembled Fe_3O_4 HMSs were determined by XRD and XPS. Fig. 1a shows the XRD pattern of the product obtained by the addition of 3 mL of glycerol (the total volume of the aqueous solution was 40 mL) to $0.02 \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ at 180°C for 10 h. All the characteristic peaks could be indexed to the pure phase of Fe_3O_4 (JCPDS No. 89-0691). To characterize the crystal phase of Fe_3O_4 HMSs, their Raman spectra were obtained at excitation wavelengths of 633 and 532 nm, respectively. Fig. 1b shows the Raman spectrum (black line) of Fe_3O_4 HMSs that was excited at 633 nm with 5% power. The wavenumber at $\sim 670 \text{ cm}^{-1}$ was assigned to the characteristic peak of the symmetric breathing A_{1g} mode of Fe–O in magnetite [16,29]. Fig. 1b also shows the Raman spectrum (red line) of Fe_3O_4 HMSs that was excited at 532 nm with 10% power. Evidently, the phase transformation occurred on the surface of Fe_3O_4 HMSs because the high laser energy (excitation wavelength at 532 nm with 10% power) resulted in the oxidation of Fe^{2+} to Fe^{3+} [29]. Further, no typical peak for $\gamma\text{-Fe}_2\text{O}_3$ at either $\sim 1,430$ or $1,580 \text{ cm}^{-1}$ was observed [16]. These results indicated that Fe_3O_4 HMSs were oxidized in the air under laser irradiation at 532 nm with 10% power and stabilized under laser irradiation at 633 nm with 5% power [29], further confirming that the as-prepared products were in a pure phase. Moreover, the as-obtained samples were further examined by XPS, and the Fe and O signals were observed (Fig. S1a). The highly magnified Fe 2p and O 1s spectra are shown in Fig. S1b and S1c. The binding energies relating to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ were ~ 711 and 724 eV , respectively (Fig. S1b), and these results are consistent with those of previous reports [30,31]. The binding energies at 710.2 and 711.2 eV corresponded to Fe $2p_{3/2}$ for Fe^{2+} and Fe^{3+} , and the binding energies at 723.3 and 724.3 eV corresponded to Fe $2p_{1/2}$ for Fe^{2+} and

Fe^{3+} , respectively. The quantitative analysis was based on the Fe $2p_{3/2}$ spectra (Fig. S1b) and the area ratio of Fe^{3+} to Fe^{2+} was 2.06:1, which was very close to 2:1. Further, there were no evident peaks of N (Fig. S1d) and K (Fig. S1e) in the sample. Therefore, the XRD pattern, Raman spectra, and XPS results proved that the as-prepared samples were pure Fe_3O_4 crystals.

The corresponding size and morphology of the self-assembled Fe_3O_4 HMSs were further observed by SEM. The as-obtained products consisted of hierarchical MSs (HMSs) (Fig. 2a–d) that were assembled from the nanoparticles (inner) and nanoplates (surface), i.e., the building blocks. HMSs all possessed similar structures, and their diameters were $1.5\text{--}3 \mu\text{m}$. Furthermore, the self-assembled Fe_3O_4 HMSs were further characterized by TEM (Fig. 2e), which revealed that the self-assembled HMSs comprised two parts: the inner part, which consisted of self-aggregating Fe_3O_4 nanoparticles, and the surface, which consisted of Fe_3O_4 nanoplates with their one-side inset on the surface layers of the inner part. From the SEM (Fig. 2a–d) and TEM results (Fig. 2e), the Fe_3O_4 spherical structures were constructed by subunits of the nanoparticles (inner) and nanoplates (outer) through self-assembling. Further structural characterization of Fe_3O_4 HMSs was performed by HRTEM. The HRTEM image (Fig. 2f) captured from Fig. 2e (bottom left) revealed that the nanoplates at the surface of the self-assembled Fe_3O_4 HMSs exhibited evident lattice fringes. The lattice spacing, which was measured from the HRTEM image, was 0.253 nm . It fitted well with the (311) planes of the cubic Fe_3O_4 structure (JCPDS No. 89-0691). The related selected-area electron diffraction pattern (Fig. S2) consisted of diffraction spots and rings, which are attributable to the complex surface structure of the self-assembled Fe_3O_4 HMSs. From the inner to the outer parts, the clear diffraction spots and rings could be indexed to the (311),

Figure 1 (a) XRD pattern and (b) Raman spectra of the self-assembled Fe_3O_4 HMSs.

Figure 2 (a–d) Low- and high-resolution SEM images, (e) TEM image, (f) high-resolution TEM (HRTEM) image, (g) high-angle annular dark-field scanning transmission microscopy (HAADF-STEM) image, and (h, i) energy-dispersive X-ray (EDX) elemental mapping of the as-obtained self-assembled Fe_3O_4 HMSs.

(331), and (442) crystal planes of Fe_3O_4 (JCPDS No. 89-0691). The EDX elemental mappings indicated that the Fe and O elements were uniformly distributed over the entire self-assembled Fe_3O_4 HMSs (Fig. 2g–i and Fig. S3). As shown in Fig. S3, a weak C signal was observed in the sample. The FT-IR results (Fig. S4, red line) indicated that glycerol was not present in the FT-IR spectra. The results also indicated that the glycerol molecules were not observed on the surface of the self-assembled Fe_3O_4 HMSs. The TG-differential thermal analysis (DTA) data (Fig. S5) revealed that two evident valleys were observed in the DTA curve. The first valley at $< 200^\circ\text{C}$ was ascribed to the loss of water. The other evident valley at 350°C was from the chemical reaction, which was attributable to the oxidation of the glycerol molecule and Fe^{2+} by O_2 . A slight decrease in the sample mass at $> 400^\circ\text{C}$ was attri-

butable to the large size of the self-assembled structure. The glycerol molecules adsorbed by the Fe_3O_4 nanoparticles in the core could not be simultaneously oxidized because of the gradual oxidation process from the outside to the inside. Additionally, the inner ultrafine Fe_3O_4 nanoparticles could also combine with some water molecules to afford a stable binding form, which was a challenge to release at a low temperature. Resultantly, the combined water was released at high temperatures. The FT-IR and DTA results also indicated that the glycerol molecules were detected in the inner part of the self-assembled Fe_3O_4 HMSs. To evaluate the specific surface areas and porosities of the obtained Fe_3O_4 HMSs, the N_2 adsorption-desorption isotherms were obtained. The Brauner-Emmett-Teller (BET) surface area of the self-assembled Fe_3O_4 HMSs was $31.8 \text{ m}^2 \text{ g}^{-1}$. Fe_3O_4 HMSs

(Fig. S6) exhibited a type-IV isotherm characteristic. They displayed microporous and mesoporous properties (Fig. S6b) centered at ~ 1 and ~ 7 nm based on the Barrett–Joyner–Halenda (BJH) method, respectively.

In this SRSA hydrothermal process, $K_3[Fe(CN)_6]$ and glycerol played critical roles in the formation of the self-assembled Fe_3O_4 HMSs (Table S1). When $K_3[Fe(CN)_6]$ was replaced with $FeCl_3$ and $Fe(NO_3)_3$, the products with plate-like (Fig. S7a) and particle (Fig. S7b) shapes were obtained, respectively. The XRD patterns (Fig. S7c) indicated that the as-obtained products were rhombohedral $\alpha-Fe_2O_3$ (JCPDS No. 86–2368), and no Fe_3O_4 phase was observed. Here, when the iron source was $FeCl_3$ or $Fe(NO_3)_3$, glycerol could not form chelating intermediates with the iron ions because of the rapid release of iron ions from this source. Rather, it directly formed precipitates with the hydroxyls that were ionized from water, thereby failing to form Fe_3O_4 HMSs (Fig. S7). In our typical SRSA hydrothermal route, glycerol was selected as the reducing and assembling agent. To expound the roles of the two-in-one functional molecule, a series of experiments were performed by adjusting the volume of the utilized glycerol while keeping other conditions constant (Table S1). Without glycerol, the as-prepared samples were red powders with a dendritic shape (Fig. S8a) and a rhombohedral phase structure (Fig. S8b) [32,33]. When a small quantity of glycerol was added (2 mL), the samples with imperfect self-assembled MSs (Fig. S9a) were observed in low yield but the XRD pattern (Fig. S9dI) indicated that the products consisted of both cubic Fe_3O_4 and rhombohedral $\alpha-Fe_2O_3$. When 5 mL of glycerol was utilized, the as-prepared samples with a perfect self-assembled structure (Fig. S9b) and pure cubic Fe_3O_4 (Fig. S9dII) were observed. However, when the volume of glycerol was further increased to 10 mL, only monodispersed Fe_3O_4 nanoparticles were observed (Fig. S9c and S9dIII). Generally, the optimal quantity of glycerol was 3–10 mL for the synthesis of the self-assembled Fe_3O_4 HMSs. Therefore, we observed that a low concentration of glycerol resulted in an insufficient reduction, which made it challenging to form the pure phase of the self-assembled Fe_3O_4 structure (Fig. S9a and S9dI). Conversely, a high concentration of glycerol could not complete the assembling process because of its strong reduction ability and high growth speed, although it formed monodispersed Fe_3O_4 nanoparticles (Fig. S9c and S9dIII).

Previous studies have reported that polyol functioned both as a solvent and as a reducing agent in the polyol process [16,34]. When glycerol was replaced with other polyols, such as 1,2-propanediol (Fig. 3a), 1,3-propane-

diol (Fig. 3b), 1,4-butanediol (Fig. 3c), and ethylene glycol (Fig. 3d), only irregular particles were obtained, and the XRD patterns (Fig. S10) revealed that they were all rhombohedral phase $\alpha-Fe_2O_3$ microcrystals (JCPDS No. 86–2368). These results also revealed that the Fe_3O_4 crystals could be formed only in the presence of glycerol in the mixed solvent. It is well-known that glycerol possesses a stronger reducing ability than the other polyols (1,2-propanediol, 1,3-propanediol, 1,4-butanediol, and ethylene glycol) under an alkaline condition. In this SRSA process, glycerol could be oxidized into intermediate products, such as glyceraldehyde, glyceric acid, dihydroxyacetone, and hydroxypyruvate aldehyde. Since CN^- ionized by $K_3[Fe(CN)_6]$ decomposes to form ammonium ions, which affords an alkaline-like environment to the reaction system, the glycerol molecules could react with the iron ions under hydrothermal conditions to partly reduce Fe^{3+} to Fe^{2+} , thus availing a prerequisite for the formation of Fe_3O_4 . At the same hydrothermal reaction temperature, the reduction abilities of the other polyols were weaker than that of glycerol. Therefore, Fe_2O_3 precipitate was directly formed under the alkaline condition, although the reduction of Fe^{3+} to Fe^{2+} could not be achieved. Therefore, when other polyols were employed, irregular microstructures with a Fe_2O_3 phase were produced (Fig. 3 and Fig. S9). Additionally, the reaction temperature affected the shape and purity of the

Figure 3 SEM images of the samples obtained from different polyols: (a) 1,2-propanediol, (b) 1,3-propanediol, (c) 1,4-butanediol, and (d) ethylene glycol with polyol/ H_2O = 3:37 (v/v) while keeping the other conditions constant.

products. Although the self-assembled structures were observed at low temperatures, such as 140 (Fig. S11a) and 160°C (Fig. S11b), the XRD patterns (Fig. S11dI and S11dII) indicated that the mixed phases were also obtained. At a high temperature, like 200°C, pure Fe_3O_4 with self-assembled structures were obtained (Fig. S11c and S11III), which were like those of the products obtained at 180°C (Figs 1 and 2).

The formation process of the self-assembled Fe_3O_4 HMSs was investigated in-depth based on the time-dependent experiments. Simultaneously, the pH values (Table S2) during the reaction process were also detected. First, we dissolved 0.8 mmol $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 37 mL of H_2O to form a uniform solution with a pH value of 5.64. After 3 mL of glycerol was added to the aforementioned solution, the pH value became 5.60, signifying only a very slight change. In this case, most of the H^+ ions existed in the solution. When the reaction was performed in an autoclave and kept at 180°C for 2.5 h, irregular sub-MSs assembled from the nanoparticles (Fig. S12a and Fig. 4I) were obtained. The pH value of the solution increased to 6.93, indicating that the H^+ ions were consumed by the CN^- ions. When the reaction times were 5 (Fig. S12b and Fig. 4II) and 7.5 h (Fig. S12c and Fig. 4III), the as-prepared samples exhibited hierarchical spherical structures composed of two parts: the inner (nanoparticles) and outer (nanoplates) parts. After the times were extended to 10 (Fig. 2) and 12.5 h (Fig. S12d), the perfect self-assembled HMSs were observed. The pH values of the solutions were 8.83 for 5 h, 9.40 for 7.5 h, 9.51 for 10 h, and 9.50 for 12.5 h. The increasing pH values indicated that the OH^- ions were gradually produced in the reaction system. The XRD patterns (Fig. S13) indicated that the products with mixed phases of cubic Fe_3O_4 and rhombohedral $\alpha\text{-Fe}_2\text{O}_3$ were obtained at 2.5 (Fig. S13a) and 5 h (Fig. S13b) while the pure Fe_3O_4 phases were obtained at 7.5 (Fig. S13c), 10 (Fig. 1a), and 12.5 h (Fig. S13d).

Based on the above results, the formation of Fe_3O_4 crystals and their self-assembly into HMSs are elaborated

in Fig. S14. We found that the iron source, $\text{K}_3[\text{Fe}(\text{CN})_6]$, and the polyol, glycerol, were key to the synthesis of the self-assembled Fe_3O_4 HMSs. Here, four steps were observed in the SRSA hydrothermal process (Fig. 4 and Fig. S14). First, the Fe^{3+} and CN^- ions were formed according to Equations (S1) and (S2) in Fig. S14. In this step, $\text{K}_3[\text{Fe}(\text{CN})_6]$ dissociated into K^+ and $[\text{Fe}(\text{CN})_6]^{3-}$ ions and further dissociated slowly into Fe^{3+} and CN^- ions (Equation (S2)) [32,33]. Secondly, the pH value of the aqueous solution increased according to Equations (S3–S6) (Fig. S14). The H^+ ions from the ionization of H_2O combined with the CN^- ions in the aqueous solution and further decomposed into NH_3 under the hydrothermal condition at a suitable temperature, thus resulting in the production of OH^- ions. Thirdly, Fe^{2+} was formed from the reduction of Fe^{3+} by glycerol according to Equation (S7) (Fig. S14). Finally, the Fe_3O_4 nanocrystals were formed with the self-assembly according to Equation (S8) (Fig. S14). Fig. 4 illustrates the formation processes of the self-assembled Fe_3O_4 HMSs, namely nucleation, self-assembling, and secondary growth [35]. In an alkaline environment, the Fe_3O_4 nanocrystals were prepared from Fe^{2+} and Fe^{3+} through coprecipitation [36]. With the aid of a glycerol molecule [34,37] and through dipole–dipole interactions [37], these Fe_3O_4 nanocrystals aggregated to form highly self-assembled Fe_3O_4 MS (Fig. 4I). In the secondary growth stage, a few nanoplates were formed on the self-assembled Fe_3O_4 MS (Fig. 4II) with the aid of a glycerol molecule. As the growth proceeded, an increased number of nanoplates were produced on the surface of Fe_3O_4 MS (Fig. 4III). Finally, the self-assembled Fe_3O_4 HMSs with subunits of nanoparticles (inner) and nanoplates (outer) were obtained (Fig. 4IV).

The electrochemical performance of the self-assembled Fe_3O_4 HMSs was investigated. As shown in Fig. S15, the charge storage capacity of the 80 wt% Super-P conductive additive and 20 wt% CMC/SBR binder as the working electrode was $\sim 200 \text{ mA h g}^{-1}$ at a current density of

Figure 4 Schematic illustration of the formation process of the self-assembled Fe_3O_4 HMSs: (I) fast nucleation and self-assembling and (II–IV) further growth and secondary growth (further self-assembling).

0.5 A g^{-1} . This result indicated that the Super-P conductive additive and CMC/SBR binder contributed to the battery capacity. Therefore, the total capacity (Q_{total}) of the battery in this work was calculated as follows: $Q_{\text{total}} = Q_{\text{Fe}_3\text{O}_4 \text{ HMSs}} + Q_{\text{conductive agent + binder}}$. First, the electrochemical properties of the working electrode with 60 wt% active materials, 20 wt% Super-P conductive additive, and 20 wt% CMC/SBR binder were investigated (Fig. 5). Fig. 5a shows the CV curves of the self-assembled Fe_3O_4 HMSs for the initial three cycles. During the first cycle, the peaks at ~ 0.6 and ~ 0.72 V represented the conversion of Fe_3O_4 to Fe^0 and the formation of amorphous Li_2O [38]. Moreover, in the anodic process, the wide peaks at ~ 1.63 and ~ 1.85 V represented the reversible oxidation of Fe to Fe^{3+} [39–41]. During the following second and third cycles, the CV curves overlapped very well, indicating high electrochemical reversibility [39,41]. The charge–discharge profiles of the self-assembled Fe_3O_4 HMSs are shown in Fig. 5b. The Li–Fe–O compounds were formed at the step-voltage range of 3–0.8 V [41,42]. Subsequently, the Li–Fe–O compounds were converted to Fe^0 and Li_2O at a long voltage plateau at 0.72 V [41–43]. The charge–discharge capacities of the self-assembled Fe_3O_4 HMSs were 823.3 and $1070.6 \text{ mA h g}^{-1}$ for the first cycle, 817

and $848.3 \text{ mA h g}^{-1}$ for the second cycle, and 807.8 and $839.1 \text{ mA h g}^{-1}$ for the third cycle.

Fig. 5c shows that the rate capabilities of the self-assembled Fe_3O_4 HMSs were estimated at different current densities from 0.5 – 3 A g^{-1} at 0.01 to $3.0 \text{ V Li}^+/\text{Li}$. The discharge capacities were kept constant at ~ 1040 , ~ 790 , ~ 580 , ~ 470 , ~ 430 , and $\sim 375 \text{ mA h g}^{-1}$ at currents of 0.5 , 1 , 1.5 , 2 , 2.5 , and 3 A g^{-1} , respectively. By comparison, the lithium storage properties of the self-assembled Fe_3O_4 HMSs were better than those previously reported at different rate capabilities (Tables S3–S7). However, when the current density was restored to 0.5 A g^{-1} after 60 cycles, the self-assembled Fe_3O_4 HMSs still delivered $\sim 996 \text{ mA h g}^{-1}$, which was $\sim 84.3\%$ of the initial capacity. Furthermore, the cycling performances of Fe_3O_4 HMSs tested from 0.01 to 3.0 V at a current density of 0.5 A g^{-1} was up to 700 cycles. The capacities faded rapidly to $< 500 \text{ mA h g}^{-1}$ in the initial 64 cycles (Fig. 5d). However, they increased in the 65th cycle. This result indicated that the morphological changes during the charging process increased the number of active sites in the working electrode [52, 53]. Thereafter, the capacity of HMSs increased to $> 900 \text{ mA h g}^{-1}$ under the current density of 0.5 A g^{-1} after 200 cycles, and the specific capacity further

Figure 5 (a) Cyclic voltammograms of the initial three cycles of the self-assembled Fe_3O_4 HMSs electrode at a scan rate of 0.1 mV s^{-1} ; (b) charge–discharge profiles of the self-assembled Fe_3O_4 HMSs; (c) rate capabilities and cycling performance of the self-assembled Fe_3O_4 HMSs at various current densities; (d) typical charge–discharge curves of the self-assembled Fe_3O_4 HMSs cycled between 0.01 and 3.0 V under a current density of 0.5 A g^{-1} ; (e) Nyquist plots of the self-assembled Fe_3O_4 HMSs before and after 700 cycles.

increased to 1000 mA h g^{-1} from the 270th to the 700th cycles at 0.5 A g^{-1} . We knew that the ratio of the active materials, conductive additive, and binder exerted a great influence on the lithium storage performance. Contrarily, the electrochemical properties of the working electrode with 80 wt% active materials, 10 wt% Super-P conductive additive, and 10 wt% CMC/SBR binder were studied. As shown in Fig. S16, the rate capabilities and cycling performances of the self-assembled Fe_3O_4 HMSs with a high active material load also displayed a similar phenomenon as that of the working electrode with low active material load (Fig. 5d). In the first 60 cycles, the capacity also decreased (Fig. S16). After 570 cycles, the capacity increased to 500 mA h g^{-1} (Fig. S16). The capacity further increased to 560 mA h g^{-1} after 700 cycles (Fig. S16). The lithium storage performances of the working electrode with a high load (80 wt% active materials) were lower than that with low load (the working electrode (60 wt% active materials)). Although the working electrode with high active material load was thicker, its effective utilization rate was low, resulting in a decrease in the specific capacity. Additionally, the diffusion path of the ions in the liquid phase increased in the working electrode with a high load, resulting in an increase in the diffusion resistance of the electrolyte and the worse rate performance of the battery. Therefore, the optimal compositions of the working electrode were 60 wt% active materials, 20 wt% Super-P conductive additive, and 20 wt% CMC/SBR binder. Fig. 5d shows that the structure of the self-as-

sembled MSs may be broken during the cycles (the first 64 cycles), resulting in a decrease in the capacity. More lithium storage sites are exposed to the destruction of the structure of the self-assembled MSs, thereby increasing the lithium storage capacity. Fig. 5d shows that in the first 64 cycles, CEs were maintained at 96%, while with the subsequent cycles, CEs were $> 98\%$. In 700 cycles, the average CE attained 98.3%. The results further prove that the self-assembled Fe_3O_4 HMSs exhibited highly efficient lithium-ion utilization. Compared with others (Table 1), the self-assembled Fe_3O_4 HMSs demonstrated higher capacity and ultralong-cycle-life lithium storage performance. Furthermore, EIS measurements were conducted before and after the 700th cycle. As shown in Fig. 5e, the electrode-electrolyte interfaces (R_{ct}) of the fresh self-assembled Fe_3O_4 HMSs electrode were ~ 75 and $\sim 50 \Omega$ before and after the 700th cycle, respectively. This change in R_{ct} may be due to the activation of the electrode material during the circulation process, which formed the channel for the lithium-ion to be embedded and removed, thereby resulting in a decrease in R_{ct} . Here, the low R_{ct} was beneficial to the enhancement of the electron kinetics and the diffusivity of the lithium ions in the electrode materials [40,41]. The high capacity and ultralong cycle life for Fe_3O_4 HMSs, which was applied in LIB, should be due to the following reasons: (i) the self-assembled hierarchical microstructures composed of nanoparticle (inner) and nanoplate (outer) subunits availed more contact positions for the electrolyte and Li^+ [52–57];

Table 1 Comparison of the lithium storage properties of different Fe_3O_4 -based materials

Anode materials	Current density (A g^{-1})	Cycle numbers	Specific capacity (mA h g^{-1})	Ref.
Self-assembly Fe_3O_4 HMSs	0.5	700	~ 1000	This work
$\text{Fe}_3\text{O}_4/\text{C-FSA}$	1	1000	938.7	[12]
Octahedral Fe_3O_4	0.04	50	~ 445	[17]
$\text{Fe}_3\text{O}_4/\text{C}$ microrods	0.5	200	~ 837	[26]
Fe_3O_4 hollow microspheres	0.2	100	~ 580	[27]
Fe_3O_4 hollow spheres	0.5	100	~ 1063	[28]
MWCNTs- Fe_3O_4 -rGO	0.2	100	~ 800	[38]
Fe_3O_4 -C nanorods	0.1	50	~ 820	[41]
$\text{Fe}_3\text{O}_4/\text{GN}$	0.1	100	~ 925	[44]
$\text{Fe}_3\text{O}_4/\text{C}$	1	300	~ 840	[45]
Fe_3O_4 nanocubes	0.2	60	~ 221.9	[46]
3D net-like FeO_x/C composite	0.2	50	~ 851.3	[47]
$\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4/\text{FeCO}_3$ composite	0.5	80	~ 779	[48]
NaBO_2 -coated Fe_3O_4	0.1	400	~ 1228	[49]
$\text{Fe}_3\text{O}_4/\text{C}/\text{RGO}$	1	1000	971	[50]
$\text{Fe}_3\text{O}_4/\text{CNTs}/\text{rGO}$ composite	1	450	1080	[51]

(ii) the self-assembled hierarchical architecture based on the nanoparticle (inner) and nanoplate (outer) units optimized the electrochemical reaction kinetic process [26–28,52,53], which facilitated the fast diffusion of Li^+ ; and (iii) the self-assembled hierarchical microstructures resisted the huge volume changes that occurred during the Li^+ -insertion/extraction processes [26–28,52,53].

As important functional materials, we also studied their magnetic and catalytic properties. To investigate the magnetic behavior of self-assembled Fe_3O_4 HMSs, the magnetic measurement was conducted at 25°C by SQUID with an applied field of $-30\text{ kOe} < H < 30\text{ kOe}$. The magnetization–hysteresis (M – H) loop is shown in Fig. 6, and their magnetic data are listed in Table S8. As shown in Fig. 6, Fe_3O_4 HMSs exhibited a ferromagnetic behavior. The saturation magnetization (M_s), remnant magnetization (M_r), coercivity (H_c), and M_r/M_s were 99.5 emu g^{-1} , 11.1 emu g^{-1} , 90.8 Oe , and 0.11 , respectively. Compared with previous reports (Table S9), the self-assembled Fe_3O_4 HMSs revealed a higher M_s of 99.5 emu g^{-1} . Previous reports indicated that M_s of the particles could be affected by their structures, such as defects, impurities, crystallinities, sizes, and couplings. The possible reasons for high M_s of the self-assembled Fe_3O_4 HMSs are summarized as follows: (i) the specific self-assembled hierarchical structures composed of nanoparticles (inner) and nanoplates (outer) in which the interparticle exchange interaction decreased resulted in high M_s [31,36,58]; (ii) lesser amounts of impurities enhanced M_s [59–61], such as slight adsorption of the glycerin molecules in the internal particles of Fe_3O_4 HMSs; (iii) high-quality crystalline nanoparticles resulted in higher magnetization [61–63]; (iv) the larger sizes of the self-assembled hierarchical structures may be the other reason for a higher M_s value [65]. Based on the above possible reasons, the self-as-

sembled hierarchical structures exhibited good magnetic performance. The reasons for the enhanced M_s in Fe_3O_4 HMSs were fascinating and not yet clear. Further research is required to identify the exact cause of the high M_s of the self-assembled Fe_3O_4 HMSs. However, because of its excellent magnetic properties, it was possible to study its application as a magnetic-separable catalyst.

In previous studies, the iron-based compounds can be applied to organic catalysis [1,3,6,64,65]. Because the self-assembled Fe_3O_4 HMSs displayed good magnetic properties, it could be employed as a magnetic recyclable catalyst. Here, the catalytic performances of Fe_3O_4 HMSs were evaluated in the hydrogenation of nitro compounds. The catalytic process for the hydrogenation of nitrobenzene is as follows: the self-assembled Fe_3O_4 HMSs as a catalyst (20 mg), ethanol as the solvent (3 mL), and 1 mmol nitrobenzene as the substrate were added into a thick-walled pressure bottle (15 mL) with a Teflon cover by ultrasonic dispersion for 10 min. Afterward, 2 mL of hydrazine hydrate (80 wt%) was added to the thick-walled pressure bottle with a Teflon cover, and the mixture reacted at 60°C at different reaction times. The catalytic process was tracked by GC–MS. As a contrary experiment, nitrobenzene could not be hydrogenated in the absence of the self-assembled Fe_3O_4 HMSs catalyst or hydrazine hydrate (80 wt%). The catalytic kinetic process of hydrogenating nitrobenzene at different reaction times was studied. Regarding the kinetic curve (Fig. 7a), the nitrobenzene was gradually converted into aniline, and the conversion rate approached 100% in 5 h. At a low concentration of hydrazine hydrate (40 wt%), the reaction lasted for 8 h to fully convert nitrobenzene to aniline. When the concentration of hydrazine hydrate was up to 98 wt%, the conversion rate from hydrogenated nitrobenzene to aniline was only 78% after 8 h. The above

Figure 6 (a) Room temperature magnetic hysteresis loops of the self-assembled Fe_3O_4 HMSs and (b) magnified hysteresis loop from -110 to 110 Oe .

Figure 7 (a) Conversion rate curve vs. reaction time and (b) cyclic catalytic experiments for the hydrogenation reduction of nitrobenzene employing the self-assembled Fe_3O_4 HMSs as a catalyst.

Table 2 Hydrogenation reduction of nitro compounds employing self-assembled Fe_3O_4 HMSs as the catalyst^a

Entry	Substrate	Product	Time (h)	Conv. (%) ^b	Sel. (%) ^b
1			4	> 99	> 99
2			4	> 99	> 99
3			4	> 99	> 99
4			5	> 99	> 99
5			5	> 99	> 99
6			5	> 99	> 99
7			6	> 99	> 99
8			4	> 99	> 99
9			4	> 99	> 99
10			4	> 99	> 99
11			3.5	> 99	> 99
12			4	> 99	> 99
13			5	> 99	> 99
14			6	> 99	> 99

a) Reaction conditions: 20 mg of the self-assembled Fe_3O_4 HMSs catalyst, 1 mmol substrate, 3 mL of ethanol, 2 mL of hydrazine hydrate (80 wt%), 60°C. b) Qualitative and quantitative analyses by GC-MS and GC (*n*-dodecane was employed as the standard).

results confirm that a low concentration of hydrazine hydrate and the low water content of hydrazine hydrate were uncondusive to the hydrogenation of nitrobenzene.

To further test the catalytic performance of the self-assembled Fe_3O_4 HMS catalyst, the catalytic hydrogenations of other nitro compounds were conducted

(Table 2). The results confirmed that many nitro compounds could be hydrogenated by Fe_3O_4 HMSs as the catalyst at different reaction times. The self-assembled Fe_3O_4 HMSs exhibited similar catalytic activity as those of CeO_2 nanorods [66] and Co–CoO@N-doped porous carbon [67] catalysts. No azo compound (Entries 1–14) and dehalogenation (Entries 7–9) were observed in the catalytic products, indicating that the Fe_3O_4 HMS catalyst displayed high selectivity as well as high catalytic activity. To examine the stability and recycling ability of the catalyst, cyclic experiments were performed employing nitrobenzene hydrogenation as the reaction model. After five consecutive cyclic tests (Fig. 7b), the stability and chemoselectivity did not significantly change. The above catalytic results prove that the self-assembled Fe_3O_4 HMSs were excellent catalysts with good stability and recyclability. It also confirmed their positive potential industrial application value.

CONCLUSIONS

Summarily, a simple and inexpensive one-pot glycerol-assisted surfactant-free synchronous reduction—self-assembling hydrothermal route was developed to prepare multifunctional self-assembled Fe_3O_4 HMSs employing potassium ferricyanide as the only iron source. Fe_3O_4 HMSs with a self-assembled spherical shape readily functioned as high-performance anode materials for LIBs and displayed good reversible performance ($> 1000 \text{ mA h g}^{-1}$) and cycling stability (700 cycles) at a current density of 0.5 A g^{-1} . Magnetic measurements indicated that the self-assembled Fe_3O_4 HMSs exhibited high M_s of 99.5 emu g^{-1} with soft magnetic properties. Furthermore, the obtained self-assembled Fe_3O_4 HMSs could be utilized as high-efficiency and magnetically recyclable catalysts for the hydrogenation of nitro compounds. We believe that SRSA availed a new route for the preparation of hierarchical self-assemblies of other metal oxide materials.

Received 12 May 2020; accepted 21 September 2020;
published online 25 December 2020

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Acknowledgements We gratefully acknowledge the financial support from the National Natural Science Foundation of China (21501004, 21771003, 21901007 and 21671005), and Anhui Provincial Natural Science Foundation for Distinguished Youth (1808085J27).

Author contributions Wu K, Chen Z and Wei X designed and conceived the whole work. Wu K, Ling M, Wu T and Guan P carried out the syntheses and characterizations of the samples, and their performances for hydrogenation of nitro compounds, analyzed the data and wrote the manuscript. Zeng P and Zhang L tested the electrochemical lithium storage properties. Fang Z revised the paper and give suggestions. Cheong WC performed the TEM-EDX-mapping characterization and revised the paper. All the authors commented on the manuscript and have given approval to the final version of the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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自组装多功能 Fe_3O_4 分级微球: 高效的锂离子电池材料和加氢催化剂

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摘要 本论文发展了一种简单、低成本的一步“同步还原-自组装(SRSA)”水热法并制备了自组装 Fe_3O_4 分级结构的微球(Fe_3O_4 HMSs)。在合成过程中, 仅使用甘油、水和铁氰化钾作为反应物, 而无需任何其他还原剂、表面活性剂或添加剂即可获得自组装 Fe_3O_4 HMSs。其中, $\text{K}_3[\text{Fe}(\text{CN})_6]$ 和甘油是合成自组装 Fe_3O_4 HMSs的两个重要因素。自组装 Fe_3O_4 HMSs可以作为高性能的锂离子存储材料, 在 0.5 A g^{-1} 的电流密度下, 经过270次循环后比容量大于 1000 mA h g^{-1} 。进一步充电和放电结果表明自组装 Fe_3O_4 HMSs表现出良好的可逆性能(放电比容量维持在 1000 mA h g^{-1} 以上)和循环稳定性(700次循环)。此外, 作为多功能材料, 自组装 Fe_3O_4 HMSs的饱和磁化强度达到 99.5 emu g^{-1} , 其可以进一步作为高效、磁性可回收的催化剂用于高效的硝基化合物加氢反应。