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One-step solvothermal synthesis of Fe_3O_4 @C core-shell nanoparticles with tunable sizes

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Abstract

We report the synthesis of Fe_3O_4 @C core-shell nanoparticles (FCNPs) by using a facile one-step solvothermal method. The FCNPs consisted of Fe_3O_4 particles as the cores and amorphous uniform carbon shells. The content of Fe_3O_4 is up to 81.6 wt%. These core-shell nanoparticles are aggregated by primary nanocrystals with a size of 10–12 nm. The FCNPs possess a hollow interior, high magnetization, excellent absorption properties and abundant surface hydroxyl groups. A possible growth mechanism of the FCNPs is proposed. The role of glucose in regulating the grain size and morphology of the particles is discussed. The absorption properties of the FCNPs towards Cr(VI) in aqueous solution is investigated. We demonstrate that the FCNPs can effectively remove more than 90 wt% of Cr(VI) from aqueous solution.

(Some figures may appear in colour only in the online journal)

1. Introduction

Fe_3O_4 @C core-shell nanoparticles (FCNPs) are the subject of intensive research owing to their scientific and technological importance [1–4]. Core-shell particles are more stable than pure magnetic particles because the shell not only protects the magnetic core nanoparticles from environmental degradation, but also prevents agglomeration [5, 6]. In addition, a magnetic field they can easily be separated from the medium for recycling. Various approaches have been developed for synthesizing Fe_3O_4 @C core-shell nanostructures. The common approach is two-step hydrothermal assembly; firstly magnetic particles are prepared as a template by various methods, then the magnetic templates are coated with carbon [7–11]. Chemical vapor deposition [12], hybrid laser-magnetron method [13, 14] and microwave synthesis [15] are also used to prepare FCNPs. These

approaches are usually complicated, energy consuming, and require special equipment. In 2007, Xuan *et al* [16] first successfully fabricated carbon-encapsulated Fe_3O_4 core/shell composites via a one-step hydrothermal reaction. In that work, glucose is both the carbon source for formation of carbon shells and the reducing agent for the reduction of Fe^{3+} . However, they had no success in trying to regulate the particle diameters. Recently, Wang *et al* [17] synthesized magnetite/carbon nanoparticles with an average size of about 190 nm via a one-step solvothermal process using ferrocene as the reactant at 240 °C. The obtained core/shell particles were composed of small crystal size (8 nm) magnetite nanocrystals as the core and a carbon shell with oxygen-containing functional groups.

Heavy metals such as chromium, mercury and lead have harmful effects on human physiology and other biological systems when they exceed the tolerance levels [18].

Adsorption is probably the most common method in practical use to remove heavy metals from wastewater [19]. However, for traditional sorbents, an additional separation step is required to remove such adsorbing material from solution. Via a magnetic field, the magnetic nanoparticles can be a facile tool for removal of heavy metals from solution [20]. It has been reported that carbonaceous coatings containing functional groups such as hydroxyl on the surface of nanoparticles can enhance the linkage of other species to the particle surface [21, 22]. For example, Fe_3O_4 @carbon core-shell microspheres could effectively adsorb TiO_2 or tin species to synthesize Fe_3O_4 @C@ SnO_2 [22] and Fe_3O_4 @ TiO_2 [23]. Herein, we describe a facile one-step solvothermal synthesis of FCNPs using glucose, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CO}(\text{NH}_2)_2$ and ethylene glycol (EG) as raw materials. Compared with previous work [16], the water used as a solvent was substituted by EG. It acted both as a high boiling point solvent and a reducing agent. Besides, smaller amounts of glucose are used in the reaction and for regulating the grain size and morphology of the particles. Fe_3O_4 nanocrystals can be easily encapsulated in a carbon shell and the hybrid nanoparticles possess a hollow interior. The particle size of FCNPs can be simply tuned by changing the amount of glucose. The FCNPs with a diameter of about 80 nm and a shell thickness of around 8 nm exhibited a favorable performance for the removal Cr (VI) in aqueous solution.

2. Experimental section

2.1. Synthesis of the FCNPs

All chemicals used were analytical-grade and without further purification. FCNPs were fabricated by an improved solvothermal reaction [16, 17] of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, glucose and $\text{CO}(\text{NH}_2)_2$ in EG solvent. In a typical experiment, 2.5 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 30 ml of EG to form a clear solution. Under vigorous stirring, 25 mmol $\text{CO}(\text{NH}_2)_2$ and 0.5 mmol glucose were added to the solution. After the mixture was vigorously stirred for 30 min, it was transferred into a Teflon-lined stainless steel autoclave and heated at 200 °C for 12 h. After that, the solid products were washed (with de-ionized water and absolute ethanol) and dried (at 60 °C for 6 h). In order to tune the particle size and morphology of the FCNPs, controlled experiments were carried out. The initial amounts of glucose—0 mmol (for pure Fe_3O_4 particles), 0.25, 0.5 and 1.0 mmol—in the system were varied and the other raw materials kept unchanged. The experimental conditions in each batch were maintained the same as those in the typical experiment.

2.2. Characterization

X-ray powder diffraction pattern (XRD) for the structure and phase composition was done on a Philips X'pert PRO diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm), with an accelerating voltage of 40 kV and tube current 40 mA. Raman data were collected on a Renishaw InVia microRaman system with a 514 nm Ar ion laser attached

to a Lecica DMLM microscope. Field emission scanning electron microscopy (FE-SEM) images were obtained using a Hitachi S-3400 field emission electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM), high-resolution transmission electron microscope (HRTEM), high-angle annular dark field scanning TEM (HAADF-STEM) photographs and energy dispersive spectrometry (EDS) maps were taken on a Tecnai G² F20 S-Twin microscope at an accelerating voltage of 200 kV. Fourier transform infra red (FT-IR) spectra were collected on a Bruker Tensor 27 FT-IR spectrometer with KBr pellets. The resolution was 4 cm^{-1} and 16 scans. Thermal analysis of FCNPs was conducted on a Q500 TGA analyzer (TA Instruments) under air at a heating rate of 15 °C min^{-1} . The magnetic properties of the samples were investigated using a vibrating sample magnetometer (VSM; 7407, LakeShore, USA) with applied magnetic fields between -18 and 18 kOe at 300 K.

2.3. Adsorption measurement

The adsorption properties of FCNPs were studied using a batch method. The concentration of Cr(VI) was determined by the 1,5-diphenylcarbazide (DPC) method as described before [24]. Typically, 50 mg of FCNPs was added to 200 ml of 500 $\mu\text{g L}^{-1}$ Cr(VI) solution to obtain a dispersion at room temperature. Then this mixture was stirred to accelerate the equilibrium between FCNPs and Cr(VI). After 2 h stirring, the concentration of Cr(VI) was determined with the Vis Spectrophotometer in a 5 cm cuvette (volume approx. 25 ml) and performed at 540 nm for the colored Cr-DPC complex. By correlating the absorbency of the solution to the established standard curve, the concentration of residual Cr(VI) was determined. The experiment was carried out in triplicate and the average values were used in the calculations. The standard deviation among them was less than 3%.

3. Results and discussion

3.1. Morphology, structure and properties

Figure 1(a) shows a typical TEM image of the FCNP sample. The FCNPs consist of nearly spherical particles with a size range from 70 to 100 nm. On close inspection of the image it can be seen that the particles consist of smaller primary magnetic particles. The structural nature of the FCNPs can be observed in a high-magnification TEM image of a isolated particle shown in figure 1(b). The FCNP is an aggregation of small primary crystals with a size of 10–12 nm. Some similar superstructures aggregated from nanoparticles were presented in previous reports [25–28]. Besides, it is clearly seen that the particle has a magnetite/carbon core-shell structure and the shell thickness ranges from about 5 to 10 nm. Furthermore, the bright center of the nanoparticle indicates that the FCNPs have a hollow interior [29–31]. The high-resolution TEM (HRTEM) image shown in figure 1(c) revealed that the resolved spacing of about 0.48 nm corresponds to the (111) lattice planes of cubic Fe_3O_4 crystal (JCPDS 75-1609). The

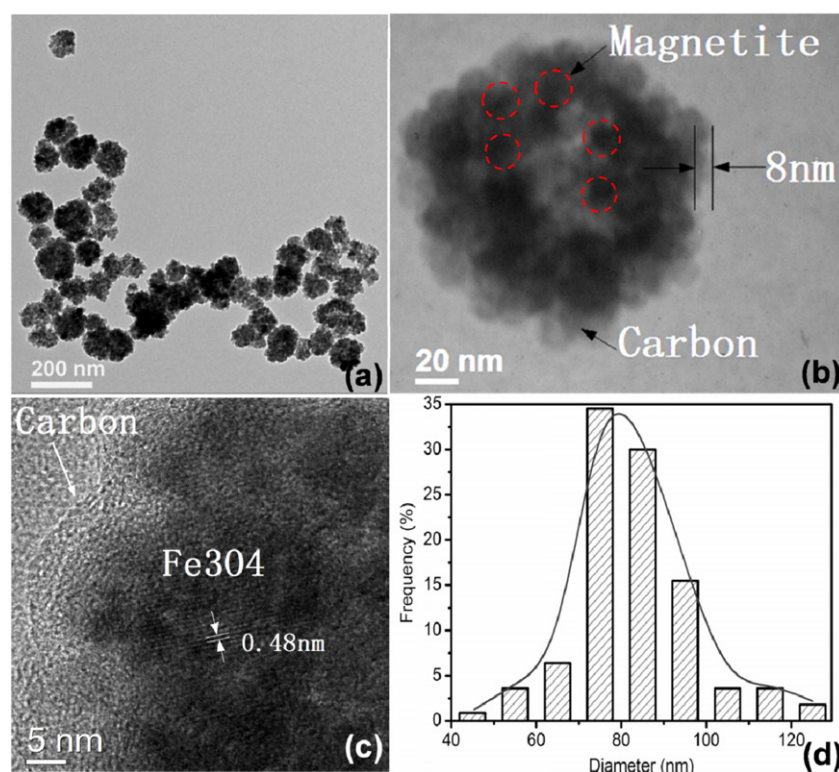


Figure 1. (a) Typical TEM images of FCNPs. (b) High-magnification TEM image of a typical obtained nanoparticle. (c) HRTEM of FCNPs. (d) Size distribution of FCNPs.

disordered carbon coating on the Fe_3O_4 particle is evident and the mean thickness of the carbon shell is around 8 nm. Figure 1(d) gives the size distribution of FCNPs and indicates the mean particle size is about 80 nm.

HAADF-STEM is a powerful method for finding the nanoparticles of interest. Image contrast in HAADF-STEM becomes brighter as the atomic mass of the element in the particle becomes heavier [32, 33]. It is possible to distinguish the presence of a core-shell structure in figure 2(a), in which the Fe_3O_4 core is bright in the interior and the carbon shell shows a relatively dark edge. In order to study the elemental composition and distribution throughout the FCNPs, a detailed chemical analysis was carried out using EDS mapping. The images correspond to the Fe K-edge signals (figure 2(b)), O K-edge signals (figure 2(c)) and C K-edge signals (figure 2(d)), respectively. It can be seen that the Fe is located in the inner part of the FCNPs except the central region, which is further confirmation of the hollow core-shell structure. The O signal is found throughout the nanoparticles, from the inner core to the periphery, possibly owing to the Fe_3O_4 in the core and the $-\text{OH}$ on the carbon shell. In the C K-edge map it is distributed on the outer surface of the FCNPs shown in figure 2(d). Additionally, the faint red light throughout the image is a thin layer of amorphous carbon which creates a coating on the FCNPs during the electron microscope experiment [34].

The crystalline structures of FCNPs and pure Fe_3O_4 particles were characterized by XRD. As shown in figure 3(a), the patterns of both samples can be easily indexed to Fe_3O_4

(JCPDS 75-1609). There is neither a hematite phase nor an iron hydroxide phase in the two samples. Compared with the XRD patterns of pure Fe_3O_4 , the decrease in the peak intensity of FCNPs may arise from the shielding effect of these surface carbon species [35]. Calculations with the Debye-Scherrer equation for the five strongest peaks (220, 311, 400, 511 and 440), gave mean grain sizes of 10.20 nm for FCNPs. This agrees with the TEM result that FCNP is composed of small primary crystals with a size of 10–12 nm. The weak and broad peak from FCNPs at a low degree may be attributed to the amorphous carbon coating on the Fe_3O_4 particles [36]. Figure 3(b) displays the thermo-gravimetric analysis (TGA) curve in air of FCNPs. The weight loss curve exhibits the inflection at 40–200 °C, due to the endothermic loss of surface hydroxyls and water molecules in the composite nanoparticles [37]. The maximum weight loss occurs in the second step. The combustion of amorphous carbon begins at a temperature higher than 200 °C, and is nearly completed around 400 °C. The final weight loss when the temperature is higher than 590 °C may be a response to decomposition of the residual carbon. There is no obvious weight loss between 400 and 590 °C. This is because on one hand the carbon will further decompose with increasing temperature, and on the other hand the Fe_3O_4 will transfer to Fe_2O_3 by surface oxidation and the weight will increase [16]. The last weight loss from 590 °C may be a response to decomposition of the residual carbon. Therefore, the Fe_3O_4 content is directly read from the TGA curve to be about 81.6 wt %.

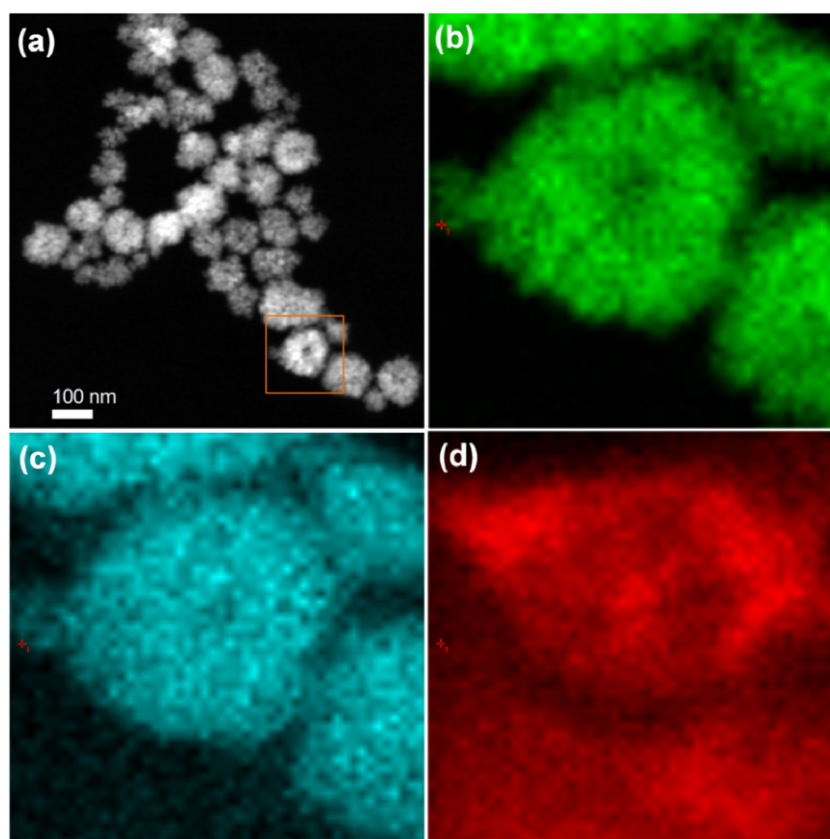


Figure 2. (a) HAADF-STEM image of the FCNPs. (b)–(d) STEM-EDS maps depict the distribution of the constituting elements, the images correspond to (b) the Fe K-edge, (c) the O K-edge and (d) the C K-edge signals, respectively.

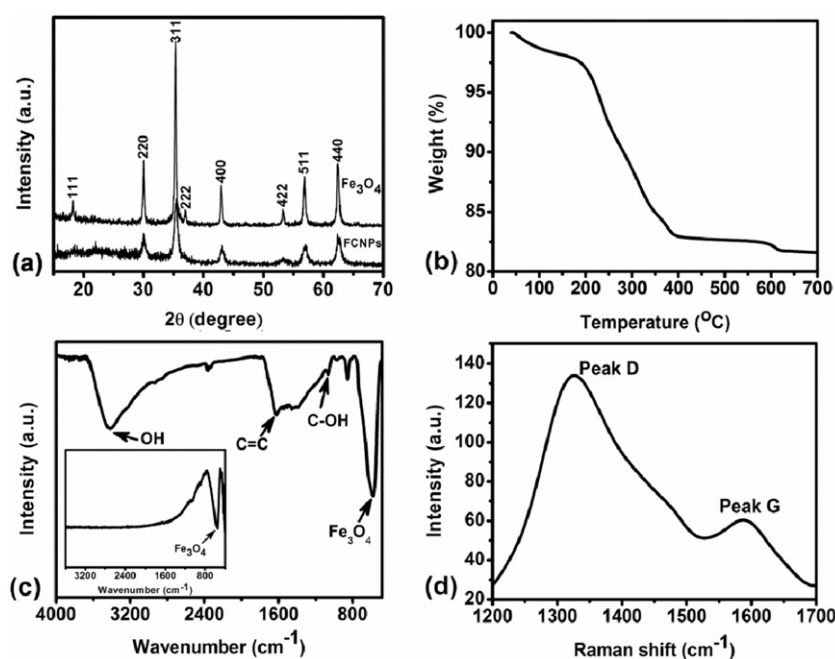


Figure 3. (a) XRD patterns of FCNPs and pure Fe₃O₄ particles. (b) TGA curve, (c) FT-IR spectra and (d) Raman spectrum of FCNPs. Inset in (c): FT-IR spectra of pure Fe₃O₄ particles.

FT-IR (figure 3(c)) was employed to examine the surface groups of the as-synthesized FCNPs. The broad band between 3600 and 3100 cm⁻¹ results from the stretching vibrations of

hydroxyl groups [38]. The band at 1069 cm⁻¹ corresponds to the C–OH stretching and O–H bending vibrations [22]. The peak at 1620 cm⁻¹ is attributed to C=C vibrations,

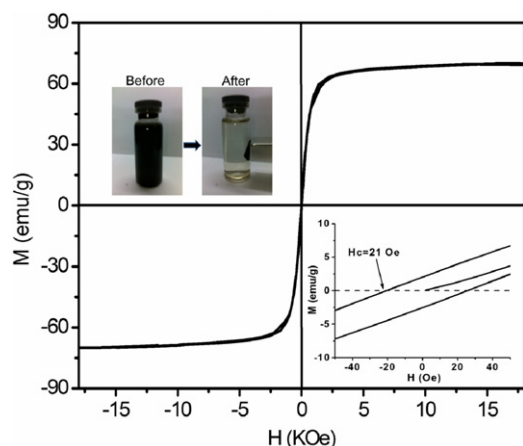


Figure 4. Magnetic behaviors of FCNPs at 300 K. Left inset: separation of the obtained product from the aqueous solution under external magnetic field. Right inset: the magnified field from -50 to 50 Oe.

which reflects the carbonization of glucose [39, 40]. It is indicated that there is a carbonaceous coating and hydroxyl groups on the surface of FCNPs, which provide excellent dispersibility in aqueous solution. The inset in figure 3(c) is the FT-IR spectrum of pure Fe_3O_4 particles. The band at 576 cm^{-1} is attributed to the Fe–O bond vibration of Fe_3O_4 [41]. The carbon and hydroxyl groups of FCNPs might enhance the affinity of other species such as heavy metals, polypeptides, proteins, drugs, TiO_2 and SiO_2 for the particles. Combined with the magnetic properties, this will render the FCNPs ideal candidates for various applications. In order to investigate the properties and type of carbon species, Raman spectroscopy was used (figure 3(d)). The two peaks around 1328 and 1588 cm^{-1} can be clearly seen. The peak at 1328 cm^{-1} (peak D) corresponds to the disordered structure of a carbonaceous solid, which is related to the presence of amorphous carbon [42]. The weak peak at about 1588 cm^{-1} is peak G. Both the vibrational peaks are broad, which indicates the poor crystallinity of FCNPs [43]. The disordered D band is much stronger than the ordered G band with a large I_D/I_G ratio of 1.78, indicating a substantial coating of amorphous carbon on the surface of FCNPs.

Magnetic properties of FCNPs were investigated using a VSM at 300 K between -18 and 18 kOe . Figure 4 shows the room temperature magnetic hysteresis loops of FCNPs and it exhibits typical ferromagnetic behavior. The saturation magnetization of the FCNPs is about 70.1 emu g^{-1} , which implies that the FCNPs possess a stronger response to an external magnet. Given that the Fe_3O_4 content is $81.6\text{ wt\%}$, it exhibits a saturation magnetization $M_s = 85.9\text{ emu g}^{-1}$. This is slightly smaller than the corresponding bulk Fe_3O_4 (92.8 emu g^{-1}) [8], which could be due to the amorphous carbon shell at the interface providing a smaller magnetic moment per unit mass as opposed to that of the ferromagnetic cores [44]. However, the value of M_s is higher than previous reports [16, 17], which may be due to the smaller thickness of the amorphous carbon shell or the formation of a nanocrystal cluster structure by aggregation of primary nanoparticles

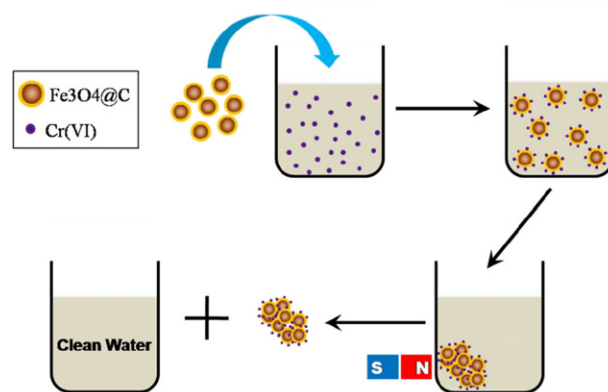


Figure 5. FCNPs used as a facile tool for removal of Cr (VI) from wastewater.

of different sizes. Ge *et al* [26] showed that nanocrystal clusters would have a much stronger response to an external field than a single nanodot. Luna *et al* [45] stated that the saturation magnetization values are larger for the bigger sizes at room temperature. The right inset of figure 4 indicates that the coercivity (H_c) of the FCNPs is much lower than that at a field of 21 Oe (defined as the magnitude of field necessary to obtain $M = 0$). The size of the nanocrystals is one of the critical parameters for the magnetic properties of magnetic particles [45–48]. Herzer [46] presented the grain size dependence of the magnetic properties of various nanocrystallized alloys and pointed out that the coercivity is well reflected for grain sizes below 50 nm . Iida *et al* [48] showed that Fe_3O_4 nanoparticles have much lower coercivity (8.8 – 9.8 Oe) for a diameter of approximately 9 nm , and high coercivity (66.0 – 97.5 Oe) for a diameter of about 37 nm . Herein, the low coercivity (H_c) of FCNPs we observed may be due to the size effect. The photographs in the left inset of figure 4 demonstrate that the FCNPs dispersed in aqueous solution can be harvested and separated by a magnetic field. The process takes about 10 s .

3.2. Possible mechanism of formation of FCNPs

Figure 6 shows the FE-SEM images of the nanoparticles prepared using various initial amounts of glucose. These nanoparticles have different particle sizes, corresponding to the different amounts of glucose: no glucose/ca. 360 nm (figure 6(a)), $0.25\text{ mmol/ca. }200\text{ nm}$ (figure 6(b)), $0.5\text{ mmol/ca. }80\text{ nm}$ (figure 6(c)) and $1.0\text{ mmol}/<50\text{ nm}$ (figure 6(d)), respectively. Regarding the formation process of nanoparticles with hollow interiors, Ostwald ripening should be the underlying mechanism [49–51]. The EG acted both as a high boiling point solvent and a reducing agent. The urea provided a basic medium and also served as an accessory reducing agent. Particles from figure 6(a) were synthesized without glucose, which indicated that the EG works as a reducing agent. So, at the initial stage, Fe(III) is partly reduced to Fe(II) by EG and then transformed into $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$ in the basic environment [30, 51]. Then, the

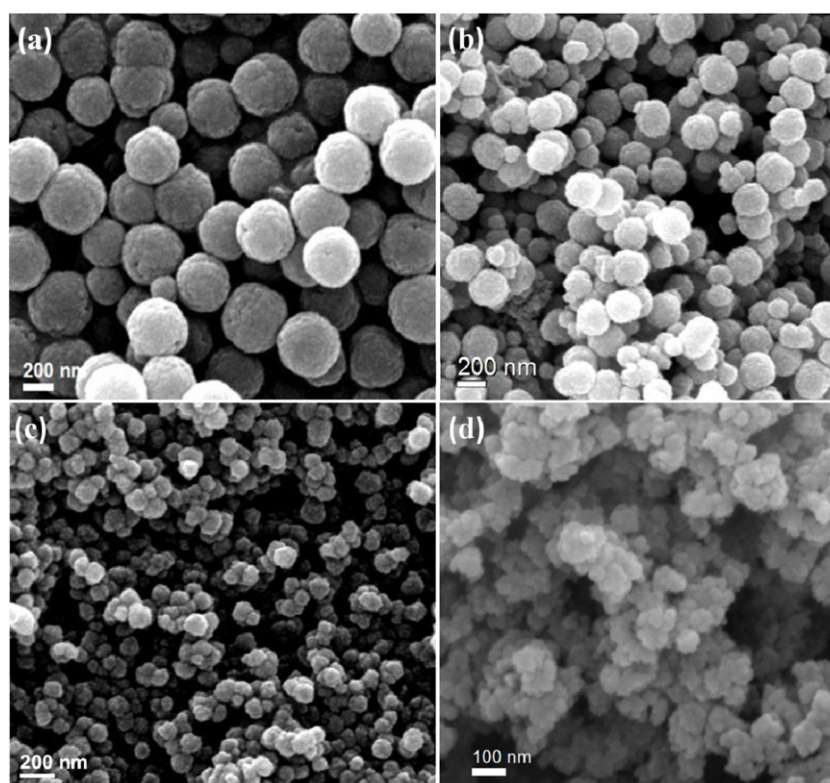
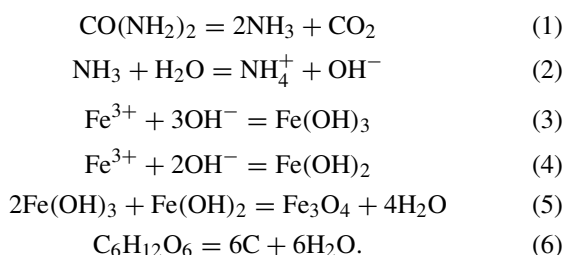


Figure 6. FE-SEM images of the nanoparticles prepared under various initial amounts of glucose: (a) 0 mmol, (b) 0.25 mmol, (c) 0.5 mmol and (d) 1.0 mmol.

hydroxides were transformed into Fe_3O_4 nucleates under hydrothermal treatment [52]. The large number of small Fe_3O_4 crystallites that nucleate with high surface energy had a great tendency to aggregate rapidly [53]. The amorphous carbon adsorbed on the surface of the Fe_3O_4 nanocrystal due to the carbonization of glucose, however, prevented their further aggregation. An oriented-attachment process dominated, forming the observed near-spherical particles. The main possible chemical reactions in our experiment to fabricate FCNPs are proposed as follows:



From the tunable particle sizes shown in figure 6, there is no doubt that the amount of glucose plays a significant role in controlling the size of the FCNPs in our experiments. Firstly, the glucose is the carbon source. Secondly, the aggregation of Fe_3O_4 nanocrystal and the adsorption of amorphous carbon occurred simultaneously. In other words, there are two possible competing reactions. The adsorption of carbon onto the surfaces of Fe_3O_4 nanocrystals prevents their further aggregation. The more carbon formed and adsorbed, the slower the aggregation process, leading to

smaller nanoparticles. Thirdly, the glucose can also decrease the interfacial tension between the crystallizing phase and the surrounding solution and provide a high nucleation frequency of the Fe_3O_4 product, leading to small grain size [16].

3.3. Adsorption removal of Cr(VI)

As discussed above, the carbon shell and hydroxyl groups on the surface would enhance the affinity between the FCNPs and other species. Herein we investigated the removal of the heavy metal Cr(VI) by adsorption using FCNPs. After stirring for 2 h, the FCNPs were separated by a magnetic field. The scheme of the removal experiment is illustrated in figure 5. The concentration of Cr(VI) ions decreased from 500 to $48.9 \mu\text{g l}^{-1}$. The removal efficiency is 90.22 wt% Cr(VI), achieving a lower level than the US Environmental Protection Agency (EPA) regulation that the maximum contaminant level of total chromium in drinking water is $100 \mu\text{g l}^{-1}$ [54]. The adsorption ability of FCNPs is possibly due to the nature of the carbon shell and surface hydroxyl functional group [55]. It is known that the reaction time always plays an important role in the adsorption of Cr(VI). The time chosen here (2 h) is because the equilibrium between adsorption and desorption has been reached [2]. There is a negligible influence on the percentage of Cr(VI) removed with further increase in time.

4. Conclusion

In summary, FCNPs have been successfully prepared by a facile one-step solvothermal method. The FCNPs are

aggregated into primary nanocrystals with a size of 10–12 nm. Fe₃O₄ nanocrystals can be easily encapsulated in a carbon shell and the particle size of FCNPs can be tuned simply by changing the initial amount of glucose. This is a simple, effective, low-cost and green approach. It is found that the FCNPs show several outstanding properties, such as a hollow interior, excellent absorption ability, abundant surface hydroxyls and a quick response to an external magnetic field, which render them ideal candidates for various applications. In our experiments, the FCNPs presented a high adsorption removal rate of heavy metals Cr(VI) from aqueous solution. An Ostwald ripening process and possible competing reactions, i.e. the aggregation of Fe₃O₄ nanocrystal and the adsorption of amorphous carbon, were considered the plausible mechanism for the formation and size control of the FCNPs. Owing to their unique properties, we believe that these FCNPs will be of interest in future applications.

Acknowledgments

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