Characterization and synthesis of Fe₃O₄@C nanoparticles by in-situ solid-phase method

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Abstract

Fe₃O₄@C nanoparticles were successfully synthesized by an in situ solid-phase method using FeSO₄, FeS₂, and PVP K30 as the starting materials under the nitrogen atmosphere. In addition, the mechanism of the synthetic of Fe₃O₄@C nanoparticles was studied through in situ characterizations. The results showed that the pyrolysis of PVP K30 participated in the solid-phase reaction and resulted in the formation of carbon shells and a reduction in particle size. The structure of the Fe₃O₄@C nanoparticles was core–shell with the average particle size of ~30 nm and the thickness of the carbon shell of ~2 nm. Besides, the Raman spectrum revealed that the carbon shell mostly existed in the form of amorphous carbon. The surface area and the pore volume of the Fe₃O₄@C nanoparticles were estimated to be 37.74 m² g⁻¹ and 0.227 cm³ g⁻¹. Magnetization hysteresis curve exhibited the values of coercivity and remanence and saturation magnetization are found to be approximately 0.16 kOe, 12.8 emu g⁻¹, and 77 emu g⁻¹, respectively.

1. Introduction

Magnetite nanoparticles (MNPs) have been widely applied in multiple areas such as bio-medicine [1], magnetic separation and magnetic fluid [2, 3], nuclear-magnetic–resonance imaging [4], wastewater treatment [5–7] and battery anode [8] due to their ultra-fine particle size (less than 100 nm), reverse spine structure, and superparamagnetic properties. But single-phase materials have certain defects in their applications, such as easily oxidized and agglomeration [9, 10]. Recently, to solve the defects in the application of MNPs, the design of composite materials has become the focus of today’s research. For example, TiO₂ was used to composite Fe₃O₄ nanoparticles to form a core–shell structure for enhancing the photocatalytic performance [11, 12]. Glutathione-coated Fe₃O₄ nanoparticles were performed to improve the application in the photo-Fenton system [13], a novel composite of g-C₃N₄/Fe₂O₃/Fe₃O₄ was used to effectively degrade Orange II via effective visible-light Fenton system [14].

However, compared to the above-mentioned metal oxide and polymer shells, carbon shells possess much higher chemical and thermal stability in practical applications. Besides, Carbon-based materials are complementary to magnetite because of their conjugated π-electron effect, high porosity, and large specific surface area [15]. In general, the methods of manufacturing carbon composite magnetite nanoparticles primarily comprised co-precipitation [16], hydrothermal [17, 18], layer-by-layer assembly [19], etc. Although the composite materials obtained by these processes have good properties, the industrial application of these materials is hampered by high production costs and complicated preparation procedures.

Compared to the methods mentioned above, the solid-phase method is a more economical and environmentally friendly way because of the uncomplicated process route and solvent-free. Peng Wang et al [20]...
employed carbothermal reduction method to manufacture Fe₃O₄@C nanoparticles using α-Fe₂O₃ nanoparticles and acetylene black as raw materials. Kan Wang et al [21] firstly calcined α-Fe₂O₃ nanoparticles in an acetylene atmosphere to obtain γ-Fe₂O₃@C nanoparticles, then calcined γ-Fe₂O₃@C nanoparticles in an N₂/H₂ (5% H₂) atmosphere to acquire Fe₃O₄@C nanoparticles. However, these methods generally contain a two-step reaction, where the precursor usually synthesized by the hydrothermal or solvothermal method [22, 23], which is still difficult to achieve large-scale industrial production. In previous study, Ren et al [24] put forward a new solid-phase reduction process to synthesis pure Fe₃O₄ nanoparticles with a relatively large particle size of ∼50 nm and a low surface area of 10.6 m² g⁻¹, which exhibits a certain room for improvement. Herein, we proposed a method for in situ synthesis of Fe₃O₄@C nanoparticles by solid-phase reaction using FeSO₄, FeS₂, and PVP K30 as raw materials for the prospect of industrialization production and enhancing the properties of the nanoparticles. The optimum process conditions were determined using analytical reagents as the raw materials and the mechanism of synthesizing Fe₃O₄@C nanoparticles was investigated by sampling and analysis at different reaction temperature. The properties of Fe₃O₄@C nanoparticles were characterized by XRD, XPS, FT-IR, Raman spectrum, VSM, SEM, TEM, and BET method. Besides, the Fe₃O₄@C nanoparticles were applied to the removal of the methylene blue (MB) by Fenton reaction for the perspective of a potential application for the treatment of dye wastewater.

2. Materials and methods

2.1. Materials

Ferrous sulfate heptahydrate (FeSO₄·7H₂O, AR, 99.0%, Beijing Hawk Science and Technology Co., Ltd), pyrite (FeS₂, AR, 99.0%, Beijing Hawk Science and Technology Co., Ltd) and PVP K30 ((C₆H₉NO)n, AR, 98.0%, Shanghai Yuanye Biotechnology Co., Ltd) are deployed directly without any additional purifications.

2.2. Preparation of Fe₃O₄@C nanoparticles

The specific preparation steps are as follows: Firstly, Ferrous sulfate heptahydrate was dried at 453 K for 6 h to obtain FeSO₄·H₂O. Secondly, the FeSO₄·H₂O, FeS₂, and PVP K30 were mixed at different mass ratios, and the formed mixture was ground for 30 min for mixing homogeneity. Subsequently, the mixture was set in a tube furnace at a given heating program (reaction temperature: 500 °C, heating rate: 10 °C min⁻¹). Finally, the product after calcining was cooled down to ambient temperature under nitrogen protection and washed by DI water and ethanol and then dried under vacuum at 80 °C till constant weight.

2.3. Characterization techniques

The XRD (Empyrean, PANalytical) with a Cu Kα radiation (λ = 0.154 18 nm) is employed to characterize the phase compositions and crystal structures of the products. The FT-IR spectra (Avatar370, Thermo Nicolet, Germany) is applied to determine the surface functional groups of the products. The SEM (SIGMA500, ZEISS) is used to measure the shape and the size of the products, and the TEM (FEI Talos F200x, USA) is employed to obtain the lattice of the products. The XPS (XSAM800, Kratos, Britain) is applied to investigate the surface elemental composition of the sample, the structure of the compound, and the chemical state of the surface elements of the sample. The surface area and corresponding pore structure of the products were determined by the use of the standard BET method (77 K, NOVA1000e analyzer).

3. Results and discussion

3.1. XRD analysis

Figure 1 exhibited the XRD patterns of the products manufactured at a different adjunction of PVP K30 when the mass ratio of FeSO₄/FeS₂ was 10/1, the calcination temperature was 500 °C, and the reaction time was 30 min. When the amount of PVP K30 was 1.0 wt.% and 2.5 wt.%, except for the diffraction peaks of magnetite (JCPDS 00-019-0629) [25], no other impurity peaks were found, indicating that pure magnetite had been composed. As the proportion of PVP K30 reached 5.0 wt.% and 7.5 wt.%, the characteristic peaks of Fe₇S₈ (JCPDS 00-025-0411) were observed. However, according to the crystallite sizes measured by Debye–Schererrer’s equation (D = Kγ/Bcosθ), where D is the average thickness of the crystal grain perpendicular to the crystal plane direction, K is the Scherrer constant, γ is the x-ray wavelength, B is the half-height width of the measured diffraction peak of the sample, and θ is the Bragg diffraction angle) [26] in the light of the strongest diffraction peak (311) displayed in table 1, at the proportion of PVP K30 was 5.0 wt.%, the crystallite size of the products were significantly reduced, from 30.5 nm to 20.7 nm. Furthermore, the SEM images showed in figure 2 confirmed this tendency. As the proportion of PVP K30 increased from 1.0 wt.% to 7.5 wt.%, the primary
Particle sizes decreased from ∼50 nm to ∼30 nm. Figure 2 also demonstrated that a higher proportion of PVP K30 led to severe agglomeration. Thus, based on the purpose of improving the properties of the particles, chose 5 wt.% as the optimum proportion.

![Figure 1. XRD patterns of the products manufactured at a different proportion of PVP K30.](image1)

![Figure 2. SEM images of the Fe₃O₄@C nanoparticles synthesized at different proportion of PVP K30: (a) 1.0 wt%, (b) 2.5 wt%, (c) 5.0 wt%, (d) 7.5 wt%.](image2)

| Content         | Products |
|-----------------|----------|
| Adjunction/wt.% | 1.0      |
| Average diameter/nm | 30.5  |
|                 | 2.5      |
|                 | 25.8     |
|                 | 5.0      |
|                 | 20.7     |
|                 | 7.5      |
|                 | 20.6     |
Due to the proportion of PVP K30 in the amount of 5 wt.% caused impurity peak in the XRD patterns, adjust the mass ratio of FeSO4/FeS2 to obtain pure products was of significance. Figure 3 displayed the XRD patterns of the products manufactured at mass ratios of FeSO4/FeS2 when the amount of PVP K30 was 5 wt.%, the calcination temperature was 500 °C, and reaction time was 30 min. As shown in figure 2, the characteristic peaks observed at $2\theta = 30.1^\circ, 35.2^\circ, 43.1^\circ, 53.7^\circ, 57.0^\circ, \text{and } 62.5^\circ$ were attributed to the ($220$), ($311$), ($222$), ($400$), ($422$), ($511$), and ($440$) crystal planes of the PDF standard card (JCPDS 00-019-0629) of magnetite as the mass ratio of FeSO4/FeS2 increased from 10/1 to 19/1. Furthermore, the XRD patterns verified that magnetite nanoparticles were successfully synthesized at the mass ratio of raw materials was above 10:1. Table 2 exhibited the calculated average crystallite size of magnetite nanoparticles synthesized by the solid-phase reduction method under different ratios of raw materials.

| FeSO4/FeS2/wt.% | 10  | 11  | 13  | 15  | 17  | 19  |
|-----------------|-----|-----|-----|-----|-----|-----|
| Average diameter/nm | 20.7| 20.8| 20.7| 20.6| 22.1| 22.9|

3.2. FT-IR analysis

Figure 5 showed the FT-IR spectrum of the product manufactured when the proportion of PVP K30 was 5 wt.%, the mass ratio of FeSO4/FeS2 was 15/1, calcination temperature was 500 °C, and the reaction time was 30 min. As depicted in figure 3, the peak observed at a wavenumber of $\sim$3400 cm$^{-1}$ was attributed to the stretching vibration of the $\text{–OH}$ band from the adsorbed water on the particle surface [28]. The sharp peak at a wavenumber of 1636 cm$^{-1}$ was corresponding to the stretching vibration of $\text{C–O}$ in amide bond [29], which was derived from the decomposition of PVP K30. The peak of the $\text{SO}_4^{2–}$ stretching vibration could be seen at a wavenumber of $\sim$1123 cm$^{-1}$, which may be corresponding to the residual ferrous sulfate [30]. Besides, the peak found at a wavenumber of $\sim$565 cm$^{-1}$ can be assigned to the stretching vibration of the $\text{Fe}^{3+}$–$\text{O}$ [31], suggesting that the Fe$_3$O$_4$@C nanoparticles were successfully synthesized.

3.3. Raman spectroscopy analysis

The Raman spectroscopy of the product manufactured when the proportion of PVP K30 was 5 wt.%, the mass ratio of FeSO4/FeS2 was 15/1, calcination temperature was 500 °C, and the reaction time was 30 min was...
displayed in figure 6. The peaks observed at wavenumbers of 1580 cm$^{-1}$ and 1350 cm$^{-1}$ were corresponding to the G band (Graphite) and D band (disordered) of the carbon-carbon bonds, respectively [32, 33], and the peak found at 1180 cm$^{-1}$ was belong to the disordered graphitic lattice (A$_{1g}$ symmetry) [34]. Besides, the observed diffraction peak at about 670 cm$^{-1}$ was indexed to the A$_{1g}$ mode of magnetite [35]. Therefore, the Raman spectroscopy further demonstrated that Fe$_3$O$_4$@C nanoparticles were obtained successfully.

3.4. TEM analysis
The TEM images and the SAED pattern of the Fe$_3$O$_4$@C nanoparticles synthesized when the proportion of PVP K30 was 5 wt.%, the mass ratio of FeSO$_4$/FeS$_2$ was 15/1, calcination temperature was 500 °C, and the reaction time was 30 min were illustrated in figure 7. As shown in figures 7(a) and (b), the morphology of the Fe$_3$O$_4$@C nanoparticles synthesized at different mass ratio of FeSO$_4$/FeS$_2$: (a) 11:1, (b) 13:1, (c) 15:1, (d) 17:1.
Figure 6. The Raman spectroscopy of the Fe$_3$O$_4$@C nanoparticles.

Figure 7. The TEM images of the Fe$_3$O$_4$@C nanoparticles (a), (b), the HRTEM image of the Fe$_3$O$_4$@C nanoparticles (c), and the SAED pattern of the Fe$_3$O$_4$@C nanoparticles (d).
nanoparticles was spherical and the primary particle size was ~30 nm. The HRTEM image showed in figure 7(c) exhibited clear lattice fringes with an interlayer spacing of 0.26 nm, which closely matched the d-spacing of (311) plane in cubic Fe3O4 and the thickness of the carbon shell was ~2 nm. The SAED pattern revealed in figure 7(d) further verified the polycrystalline feature of the Fe3O4@C nanoparticles, where the diffraction rings could be ascribed to the (220), (311), (400), (511), and (440) planes of Fe3O4.

3.5. Specific surface area analysis
Figure 8 demonstrated the nitrogen adsorption-desorption isotherm and pore size distribution of the Fe3O4@C nanoparticles. From figure 8, the Nitrogen adsorption-desorption process of the Fe3O4@C nanoparticles had a hysteresis loop within a relative pressure of 0.5–1.0, which was corresponding to the type IV in the classification of the International Union of Pure and Applied Chemistry, and had a hysteresis loop of H3, indicating that the Fe3O4@C nanoparticles should belong to mesoporous materials. The surface area calculated by the BET method was 37.74 m² g⁻¹ and the average pore diameters and pore volume were estimated by the BJH method to be 3.78 nm and 0.227 cm³ g⁻¹, respectively.

3.6. Magnetic properties
To compare the magnetic property between the Fe3O4@C nanoparticles and Fe3O4 nanoparticles, pure Fe3O4 nanoparticles were synthesized by the solid-phase method with the mass ratio of FeSO4/FeS2 was 8/1, the reaction temperature of 500 °C and reaction time of 30 min. The magnetic property comparison of the Fe3O4@C nanoparticles and Fe3O4 nanoparticles determined by VSM was displayed in figure 9. From figure 9, it could be seen that saturation magnetization (Ms) of the Fe3O4@C nanoparticles was 77 emu g⁻¹ where the Ms of the pure Fe3O4 nanoparticles was 89 emu g⁻¹. The lower Ms of the as-synthesized Fe3O4@C nanoparticles might due to the lower proportional to the amount of weight for the same magnetic material [36]. Also, the remnant magnetization and the coercivity value of the Fe3O4@C nanoparticles was found to be 12.8 emu g⁻¹ and 0.16 kOe, respectively, which was lower than the pure Fe3O4 nanoparticles because of the size effect [37, 38]. Therefore, the as-synthesized Fe3O4@C nanoparticles possessed a strong magnetization, small coercivity, and low magnetic remanence that could be applied in multiple areas such as magnetic storage, catalyst, and wastewater treatment.

3.7. The mechanism of the synthetic of Fe3O4@C nanoparticles
Given the results of XRD, Raman spectroscopy, FT-IR, TEM, and XPS results above, it was proved that Fe3O4@C nanoparticles with better properties were successfully manufactured. Besides, the formation process of the Fe3O4@C nanoparticles was investigated by in situ XRD analysis, TG-DSC analysis, and in situ FT-IR analysis.

3.7.1. In-situ XRD and TG-DSC analysis
Figures 10(a) and (b) exhibited the in situ XRD patterns of the reaction process and the TG-DSC result of the solid-phase reaction process. The primary components of raw materials depicted in figure 10(a) were FeSO4·H2O (JCPDS 01-074-1332) and FeS2 (JCPDS 01-071-2219). The dehydration of the binding water of
FeSO₄·H₂O had been completed at the calcination temperature of 350 °C and then transforms to α-FeSO₄ (JCPDS 01-073-1057) [39]. When the calcination temperature reached 450 °C, the phase of α-FeSO₄ changed to β-FeSO₄ (JCPDS 00-033-0682) [40] where this transformation process could be seen at the calcination temperature was 400 °C. The phase of magnetite (JCPDS 00-019-0629) appeared when the calcination temperature was 500 °C and no impurities peaks were found, indicated that the initial temperature of the solid-phase reaction is above 450 °C. With the extension of reaction time, the phase of magnetite remained unchanged, suggesting that the Fe₃O₄ nanoparticles were manufactured. The TG-DSC curves showed in figure 10(b) further confirmed that the initial reaction temperature was about 450 °C and the terminating reaction temperature was about 530 °C. The first two weight-loss stages in the temperature range from 30 °C–300 °C were fundamentally the loss of absorbed water and binding water of the raw materials. Then the next weightlessness step that occurred from 300 °C–530 °C was principally a process where the ferrous sulfate, pyrite, and PVP K30 forms magnetite through solid-phase reaction. Also, the weight-loss of this stage was about 43.31% and was slightly larger than the theoretical value, which might be caused by the decomposition of PVP K30. Huang et al [41] systematically studied the thermodynamics of the solid-phase reaction of FeSO₄ and FeS₂, results showed that at the temperature of 450 °C, the main product was comprised of Fe₂O₃, Fe₃O₄, FeS₂, and FeSO₄, indicating that the main reaction formulas to synthesize Fe₃O₄ were the reactions as followed:

\[
8\text{FeSO}_4 + \text{FeS}_2 \xrightarrow{N_t} 3\text{Fe}_3\text{O}_4 + 10\text{SO}_2 \uparrow \quad (1) \\
2\text{FeSO}_4 \xrightarrow{N_t} \text{Fe}_2\text{O}_3 + \text{SO}_2 \uparrow + \text{SO}_3 \uparrow \quad (2)
\]
However, in this study, there was no phase of Fe$_3$O$_4$ was detected in the solid-phase reaction process, indicating that after adding PVP K30, the kernel of the solid-phase reaction was the reaction of $\beta$-FeSO$_4$, FeS$_2$, and PVP K30. Also, the SEM images of the nanoparticles synthesized by adding different carbon resources exhibited in figure S1 (available online at stacks.iop.org/MRX/8/025016/mmedia) further determined that the PVP 30 played an important role in reducing the particle size. As displayed in figure S1, except for PVP K30, the other different carbon resources showed a limited effect on the particle sizes. Meanwhile, the TG-DTG curves of the pure PVP K30 (the heating rate was 10 °C min$^{-1}$ and the protection atmosphere was N$_2$) showed in figure S2 suggesting that the starting temperature for carbonization of PVP K30 was about 375 °C and the ending temperature was about 475 °C, which was lower than the starting temperature of the reaction of FeSO$_4$, FeS$_2$, and PVP K30, revealing that the formation of carbon-shell was before the core solid-phase reaction. Thus, one of the reasons that adding PVP K30 can reduce the particle size in the solid-phase method may due to the coating of the carbon-shell reduce the agglomeration effect between particles.

3.7.2. In-situ FT-IR analysis

Figure 11 depicted the in situ FT-IR spectra of the reaction process. The broad peak discovered at a wavenumber of $\sim$3300 cm$^{-1}$ discovered at each reaction stage was corresponding to the stretching vibration of the hydroxyl group [28]. Meanwhile, the stretching vibration of C=O and C-N at wavenumbers of $\sim$1630 cm$^{-1}$ and 1492 cm$^{-1}$ also appeared and the intensity gradually decreased as the reaction progresses [29, 42]. When the reaction temperature was below 400 °C, the peak observed at $\sim$840 cm$^{-1}$ was assigned to the stretching vibration of the functional groups of PVP K30 of the C-C ring [43, 44]. When the reaction temperature rose to 500 °C, the intensity of the peaks that were corresponding to the C-N and C-C ring gradually decreased, suggesting that the PVP K30 had participated in the solid-phase reaction. Figure 10 suggested that the C-N and C-C ring were the main functional groups involved in the reaction of $\beta$-FeSO$_4$, FeS$_2$, and PVP K30, and the core functional group in the carbon-shell was the C=O in amide bond.

3.7.3. XPS analysis

Figure 12 exhibited the XPS spectra of the Fe$_3$O$_4$@C nanoparticles synthesized when the proportion of PVP K30 was 5 wt.%, the mass ratio of FeSO$_4$/FeS$_2$ was 15/1, calcination temperature was 500 °C, and the reaction time was 30 min. Compared to the full XPS spectra of the raw materials displayed in figure S3(a), as the solid-phase reaction processed, the S2p and S2s peaks disappeared and the intensity of the N1s peak decreased, which suggested that the solid-phase reaction went thoroughly and the PVP K30 participated in the reaction. Figure 12(b) gave the deconvolution of the C1s peak of the as-synthesized Fe$_3$O$_4$@C nanoparticles, the peaks acquired at a binding energy of 288.0 eV, 286.0 eV, and 284.6 eV were attributed to the C=O, C-N, and C-C, indicating that the surface of the Fe$_3$O$_4$@C nanoparticles possessed the decomposition products of the PVP K30 [29, 45]. Figure 12(c) displayed the Fe2p$_{3/2}$ and Fe2p$_{1/2}$ peaks of the Fe$_3$O$_4$@C nanoparticles, the peaks with binding energies of 725.4 eV and 712.3 eV were corresponding to the Fe2p$_{3/2}$-Fe(III) and Fe2p$_{1/2}$-Fe(III) and the peaks with the binding energy of 723.5 eV and 710.3 eV were the characteristic peaks of Fe2p$_{3/2}$-Fe(II) and

$$16\text{Fe}_3\text{O}_4 + \text{FeS}_2 \xrightarrow{N_2} 11\text{Fe}_3\text{O}_4 + 2\text{SO}_3$$

Figure 11. The in situ FT-IR spectra of the reaction process.
Fe\textsubscript{2}p\textsubscript{1/2}–Fe(II) of the magnetite [46]. Besides, the intensity ratio of Fe(III)/Fe(II) was 1.93, which was in accord with the stoichiometric magnetite. Figure 12(d) showed the O1s peaks of the Fe\textsubscript{3}O\textsubscript{4}@C nanoparticles, where the peak of O1s could be deconvoluted into three peaks. The peak at a binding energy of 530.9 eV could be assigned to the O\textsuperscript{2−} bonded with Fe and the peak at a binding energy of 532.8 eV was attributed to the C=O bonds [47]. Besides, the peak at the binding energy of 531.2 eV was corresponding to the –OH [48]. Concerning the O1s peak of the raw materials displayed in figure S3(d) (supplementary materials), the deconvoluted peak at 531.3 eV was assigned to SO\textsubscript{4}\textsuperscript{2−} and the deconvoluted peak at 532.9 corresponded to the C=O bands [49]. The N1s core-level spectra of the raw materials and the Fe\textsubscript{3}O\textsubscript{4}@C nanoparticles were shown in figures S3(e) and 12(e), the peak observed at a binding energy of 400 eV was assigned to the C–N bond [45], and the intensity decrease of the C–N

Figure 12. The XPS spectra of the Fe\textsubscript{3}O\textsubscript{4}@C nanoparticles. (a) wide-scan, (b) C1s, (c) Fe2p, (d) O1s, (e) N1s.
The Fe₃O₄@C nanoparticles were successfully manufactured using FeSO₄, FeS₂, and PVP K30 as raw materials. The average particle size of the Fe₃O₄@C nanoparticles is ~30 nm and the thickness of the carbon shell is ~2 nm. The surface area obtained by the BET method is ~37.44 m² g⁻¹. FT-IR and Raman analysis confirmed the product manufactured by the in situ solid-phase reaction was the Fe₃O₄@C nanoparticles. Besides, the saturation magnetization value of the Fe₃O₄@C nanoparticles was approximately 77 emu g⁻¹ at room temperature. At the same time, the formation process of the Fe₃O₄@C nanoparticles was researched by employing sampling and analysis at different reaction temperatures. The in situ XRD analysis and TG-DSC curves revealed that the starting temperature of the solid-phase reaction was 450 °C, and the kernel of the solid-phase reaction was the reaction of Fe₂FeSO₄, FeS₂, and PVP K30. The in situ FT-IR spectra analysis demonstrated that partial C=N bond and C–C ring bond disappeared when the temperature was above 450 °C, which proved that the C–N bond and C–C ring were the main functional groups involved in the reaction of Fe₂FeSO₄, FeS₂, and PVP K30, and the core functional group in the carbon-shell was the C=O in amide bond. Also, the comparison of the XPS spectra denoted that the Fe₃O₄@C nanoparticles had been manufactured successfully. These results affirmed that the adjunction of PVP K30 could not only facilitate the manufacture of the Fe₃O₄@C nanoparticles using in situ solid-phase reaction but also played an important role in regulating the particle size to a smaller degree.

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