Research Article

Synthesis of Monodisperse Iron Oxide Nanoparticles without Surfactants

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Monodisperse iron oxide nanoparticles could be successfully synthesized with two kinds of precipitants through a precipitation method. As-prepared nanoparticles in the size around 10 nm with regular spherical-like shape were achieved by adjusting pH values. NaOH and NH₃·H₂O were used as two precipitants for comparison. The average size of nanoparticles with NH₃·H₂O precipitant got smaller and represented better dispersibility, while nanoparticles with NaOH precipitant represented better magnetic property. This work provided a simple method without using any organic solvents, organic metal salts, or surfactants which could easily obtain monodisperse nanoparticles with tunable morphology.

1. Introduction

In the last decade, iron oxide nanoparticles (mostly Fe₃O₄) have proved to be very promising, and they were widely used for magnetic separation, drug delivery, cancer hyperthermia, magnetic resonance imaging (MRI), targeted cancer therapy, multiparametric detection [1–9], and so forth. In these respects, iron oxide nanoparticles must be monodisperse, highly crystalline, and water-soluble, which could provide reproducible quality, high magnetization values, and good biocompatibility under biological conditions [10, 11]. Some approaches have been developed to synthesize iron oxide nanoparticles and other related metal oxide nanoparticles, such as polylols, microemulsions, sonochemical synthesis, and chemical coprecipitation [12–15]. Kajbafvala et al. [16] synthesized sword-like ZnO nanowires by a fast and template-free microwave-assisted method. Guardia et al. [17] reported a highly reproducible route to synthesize iron oxide nanoparticles. The results showed that the size of yields iron oxide nanocubes was in the range of 14–35 nm and the nanocubes had very high specific absorption rates exploitable for tumor hyperthermia. Kajbafvala et al. [18] studied two different chemical solution methods to synthesize zinc oxide nanostructures via microwave irradiation method. The as-prepared spherical zinc oxide nanoparticles had better photocatalytic performance. Abdulwahab et al. [19] used pivalate clusters to synthesize monodispersed iron cobalt oxide and iron manganese oxide nanoparticles. The effects of the reaction time, temperature, and precursor concentration on the stoichiometry were studied. Park et al. [20] synthesized monodisperse iron oxide nanoparticles with a continuous size spectrum of 6–13 nm. The synthetic procedure was highly reproducible. Peng and Sun [21] reported a facile solution-phase synthesis of monodisperse hollow Fe₃O₄ nanoparticles by controlling oxidation of amorphous core-shell Fe–Fe₃O₄ nanoparticles. Although these nano oxides could be prepared successfully, the aggregation of the particles existed obviously. On account of the high surface energy, naked iron oxide nanoparticles tended to aggregate and flocculate which might reduce the use of iron oxide nanoparticles. Hence, how to stabilize the nanoparticles in the biological medium was very important. The stability of suspensions in water was generally
ensured by the nanoparticles surface charges. To this end, numerous strategies were bringing a suitable biocompatible coating to solve this problem. A number of stabilizers have been used to synthesise monodisperse nanoparticles including polymer stabilizers [22, 23] and organic materials [24]. Nicolás et al. [25] prepared iron oxide nanoparticles and stabilized the particles by modifying the stabilization mechanism with biomolecules. Kovalenko et al. [26] used various oleic acid salts as stabilizers for the size- and shape-controlled synthesis of iron oxide nanocrystals. The results showed the general applicability of oleic acid salts as stabilizers in well-controlled nanocrystals synthesis. Besides, another way was able to optimize the synthesis process. Faiyas et al. [27] improved the coprecipitation procedure and studied the exact dependence of pH value on synthesis of Fe₃O₄ nanoparticles. The results showed the pH value played a major role in the observed phase formation of nanoparticles.

As we know, the zeta potential was a very important parameter for nanoparticles or colloidal system because the value gave an indication of the potential stability of the colloidal system. And the pH value of the colloidal system was one of the most important factors that affected its zeta potential. Figure 1 showed the schematic representation of zeta potential. So, choosing an appropriate pH range for a stable system was of great significance [28]. Based on our previous research work on the inorganic nanoparticles [29–32], in this paper, coprecipitation method was used to synthesize the iron oxide nanoparticles. PH value was chosen as an optimized parameter to create a stable system. In addition, the effects of the two different precipitants were also studied.

2. Experimental

2.1. Materials. Ferrous chloride tetrahydrate (FeCl₂·4H₂O, Beijing Yili fine chemicals Co. Ltd.), sodium hydroxide (NaOH, Beijing Chemical Co. Ltd.), ammonium hydroxide (NH₃·H₂O, Beijing Yili fine chemicals Co. Ltd.), and hydrochloric acid (HCl, Beijing Yili fine chemicals Co. Ltd.) were used without further purification.

2.2. Synthesis of Iron Oxide Nanoparticles. Deionized water was used for preparation of 0.25 M FeCl₂·4H₂O solution, 5.4 M NaOH solution, 1.34 M NH₃·H₂O solution, and 0.1 M HCl solution. In the experimental procedure, 0.25 M FeCl₂·4H₂O solution was mixed with 5.4 M NaOH solution and 1.34 M NH₃·H₂O solution, respectively. The resulting mixture solution was magnetically stirred and heated up to 90°C while kept under nitrogen. The duration time lasted for 1.5 h. Meanwhile, the pH value was adjusted by dropwise addition of 0.1 M HCl solution. The colour of the resulting slurry changed from reseda to black. Then, the slurry was washed repeatedly with deionized water and the suspension of iron oxide nanoparticles was obtained. Figure 2 showed the schematic representation of the synthesis process.

2.3. Characterization. The magnetic nanoparticles were characterized by several techniques including XRD, TEM, VSM, and zeta potential. The compositions of the samples were characterized by using an XRD (XRD-6000) with Cu Kα radiation (λ = 1.5406 Å), employing a scanning rate of 5 min⁻¹ in the 2θ ranging from 20° to 80°. The morphology of the nanoparticles was recorded by using a TEM (JEOL-1200). Magnetic measurements were carried out at room temperature using VSM (homemade) with a maximum magnetic field of 15 kOe. And surface charge measurements were performed with a Beckman Coulter Delsa 440SX zeta potential analyzer.

3. Results and Discussion

3.1. Characterization of Zeta Potentials. On the base of the pH value, the electrokinetics of the particles was measured as zeta potentials. As a function of zeta potentials, Figure 3 showed the surface properties of the iron oxide nanoparticles. The particle isoelectric point (IEP) of the precursor and the product was found around pH 4.5 and pH 6, respectively. As we know, nanoparticles with zeta potentials at IEP were aggregated easily. So, it was necessary to keep pH away from IEP strictly. In order to obtain smaller particles, the pH value of precursor should be adjusted around 3 or 13, while it was noted that the pH values of slurry below 5 and above 11 were better to get smaller particles.
3.2. Compositions and Morphology. The XRD patterns of iron oxide nanoparticles synthesized with NaOH and NH₃·H₂O as precipitants were shown in Figure 4. Figure 4(c) was the pattern of 30 nm Fe₃O₄ for comparison. It was noted that the two products revealed a cubic spinel structure of magnetite which had characteristic peaks matching well pure spinel ferrite Fe₃O₄ (JCPDS file number 10-0319). It was clear that the reflection peaks of Figures 4(a) and 4(b) became more broadened than those of Figure 4(c), which revealed that the average size got smaller. It was also observed that the full-width at half-maximum (FWTH) of the characteristic peaks in Figure 4(a) broadened compared with the corresponding peaks in Figure 4(b), which suggested that the crystallinity was better.

Figures 5(a) and 5(b) showed the TEM images of the morphology of iron oxide nanoparticles with NaOH and NH₃·H₂O as precipitants, respectively. It was clear that, in Figure 5(a), the particles were aggregate. In contrast, the particles in Figure 5(b) had better dispersion. It was observed that both of the particles in Figures 5(a) and 5(b) were composed of spherical-like crystals with a mean size of 10 nm. Figure 6 showed the TEM image of the morphology of iron oxide nanoparticles with NH₃·H₂O as precipitant. It was found clearly that the particles had good dispersion. In the precipitation synthesis process, precipitant played a key role in the formation of nanostructure of iron oxide nanoparticles. In the system, the precipitant mainly acted as a pH buffer...
and reacted with water to provide a supply of OH\(^-\) anions; that is, the supply of OH\(^-\) could be a main driving force for the structure of particles. It caused a competition between the precipitation and shape-controlled nanostructures reactions, in which the nucleation and thus the growth of Fe\(_2\)O\(_4\) could be adjusted. The difference between NH\(_3\)-H\(_2\)O and NaOH was that NH\(_3\)-H\(_2\)O was weak base which could provide a slow and constant supply of OH\(^-\), while NaOH could not [33]. So, the size of nanoparticles synthesized with NH\(_3\)-H\(_2\)O as precipitant was smaller which was in accordance with the XRD test results, while the nanoparticles synthesized with NaOH were aggregate.

3.3. Magnetic Properties. The magnetization curves were shown in Figure 7. Both of the two iron oxide nanoparticles synthesized with different precipitants displayed relatively high saturation magnetization. The magnetic values of two kinds of particles with NaOH and NH\(_3\)-H\(_2\)O as precipitants were 83.7 emu\(g^{-1}\) and 44.7 emu\(g^{-1}\), respectively. Apparently, the iron oxide nanoparticles precipitated by NaOH had relatively higher magnetic values. According to the results of XRD and TEM, the monodisperse iron oxide nanoparticles precipitated by NH\(_3\)-H\(_2\)O showed better dispersion.

4. Conclusion

Monodisperse iron oxide nanoparticles with NaOH and NH\(_3\)-H\(_2\)O as precipitants have been successfully prepared through precipitation method. The morphology and magnetic properties of iron oxide nanoparticles were found to be related to the kinds of precipitants. Typical spinel structures of nanoparticles which had a size of about 10 nm were obtained. In addition, the pH values of the precursor and the product were found. Besides, the size of iron oxide nanoparticles with NH\(_3\)-H\(_2\)O as precipitant got smaller than the other one. And the magnetic property of iron oxide nanoparticles with NaOH as precipitant was much better. The as-synthesized iron oxide nanoparticles were to be expected to be in magnetic, biomedicine, and surface modification.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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