Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2014, Article ID 740856, 5 pages
http://dx.doi.org/10.1155/2014/740856

Research Article

Synthesis of Monodisperse Iron Oxide Nanoparticles without Surfactants

Xiao-Chen Yang,[1] Yun-Long Shang,[1] Yin-Hua Li,[1] Jing Zhai,[2] Neil R. Foster,[1] Yong-Xia Li,[3] Dan Zou,[3] and Yuan Pu[1]

[1] *School of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China*
[2] *China Coal Research Institute, Beijing 100013, China*
[3] *Hunan Boyun-Dongfang Powder Metallurgy Co., Ltd., Changsha, Hunan 410205, China*

Correspondence should be addressed to Yuan Pu; puyuan@mail.buct.edu.cn

Received 6 August 2014; Accepted 8 October 2014; Published 22 December 2014

Academic Editor: Amir Kajbafvala

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 $NH_3{\cdot}H_2O$ were used as two precipitants for comparison. The average size of nanoparticles with $NH_3{\cdot}H_2O$ 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 Fe_3O_4) 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 polyols, 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 Fe_3O_4 nanoparticles by controlling oxidation of amorphous core-shell Fe-Fe_3O_4 nanoparticles. Although these nanooxides 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 Fe_3O_4 nanoparticles elaborately. All the results showed that 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.

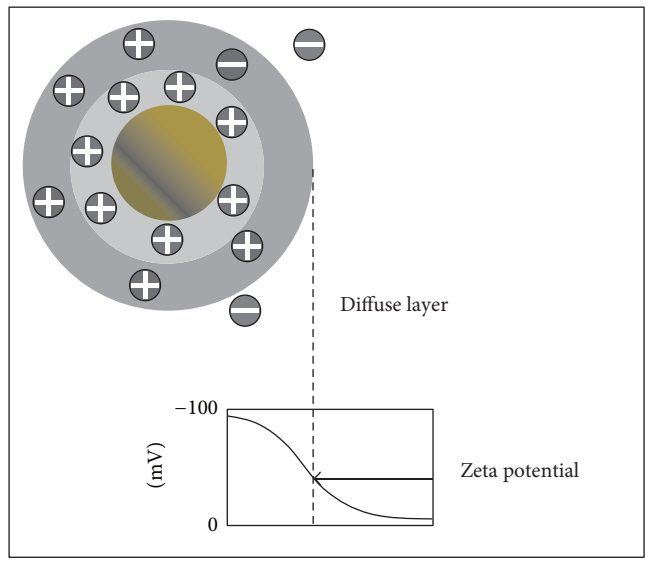


Figure 1: Schematic representation of zeta potential.

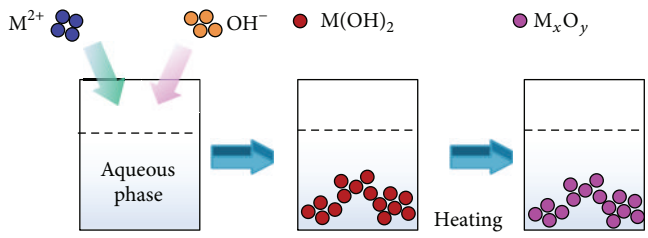


Figure 2: Schematic representation of synthesis.

2. Experimental

2.1. Materials. Ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$, Beijing Yili fine chemicals Co. Ltd.), sodium hydroxide (NaOH, Beijing Chemical Co. Ltd.), ammonium hydroxide ($NH_3{\cdot}H_2O$, 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 $FeCl_2{\cdot}4H_2O$ solution, 5.4 M NaOH solution, 1.34 M $NH_3{\cdot}H_2O$ solution, and 0.1 M HCl solution. In the experimental procedure, 0.25 M $FeCl_2{\cdot}4H_2O$ solution was mixed with 5.4 M NaOH solution and 1.34 M $NH_3{\cdot}H_2O$ 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.

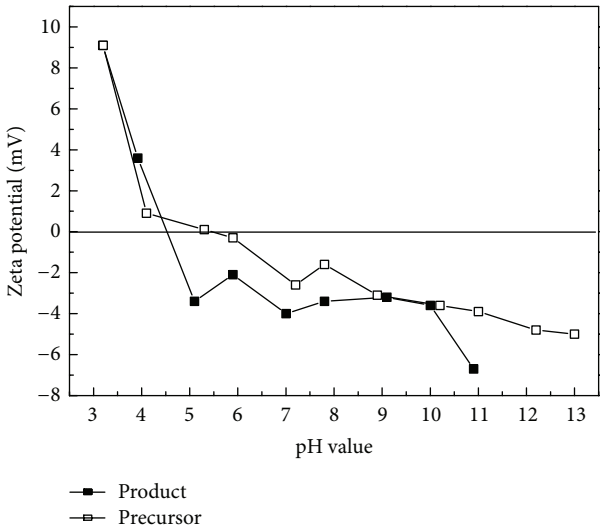
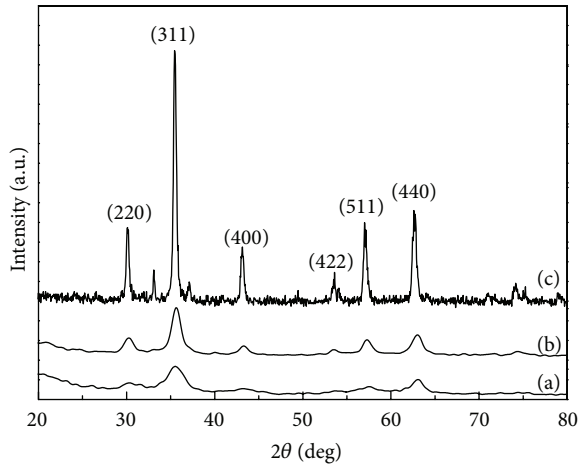


Figure 3: Zeta potentials of precursor and product.



(a) NH_4OH
(b) NaOH
(c) 30 nm product

Figure 4: XRD patterns of Fe_3O_4 with different precipitants.

3.2. Compositions and Morphology. The XRD patterns of iron oxide nanoparticles synthesized with NaOH and $NH_3{\cdot}H_2O$ as precipitants were shown in Figure 4. Figure 4(c) was the pattern of 30 nm Fe_3O_4 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 Fe_3O_4 (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

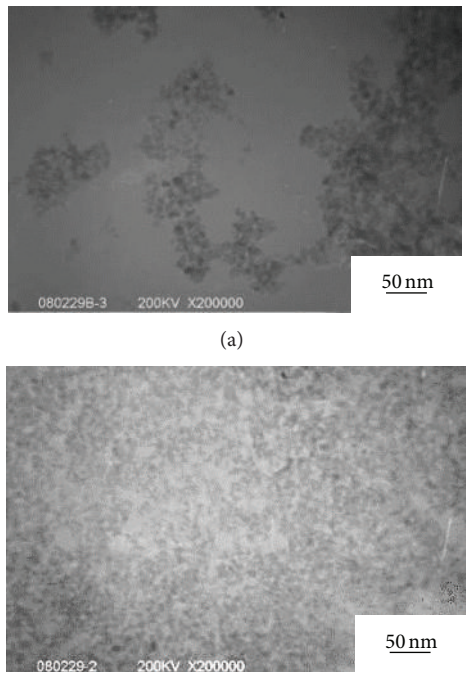


Figure 5: TEM images of Fe_3O_4 with different precipitants.

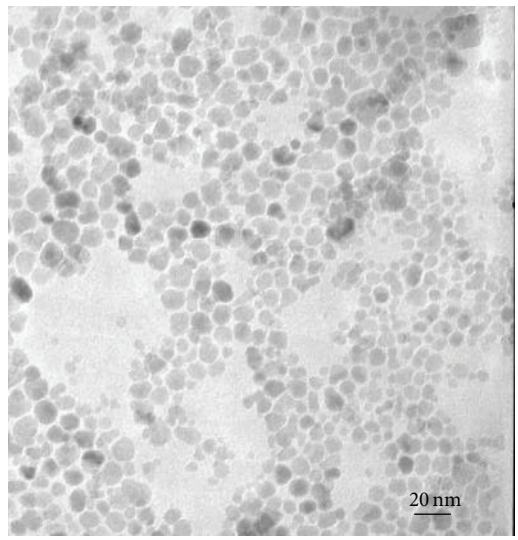


Figure 6: TEM images of Fe_3O_4 with $NH_3{\cdot}H_2O$.

$NH_3{\cdot}H_2O$ 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 $NH_3{\cdot}H_2O$ 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

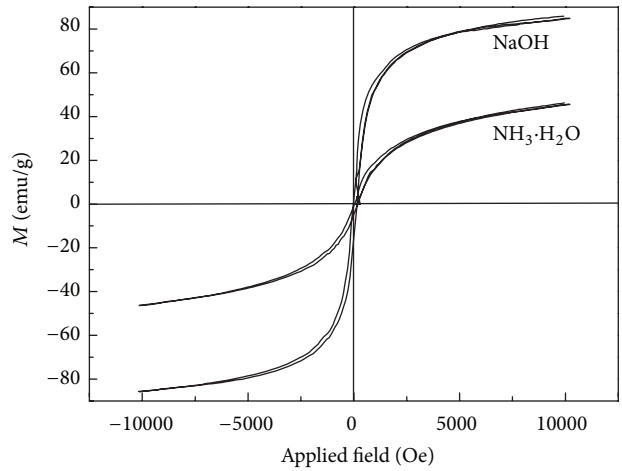


Figure 7: Hysteresis loops of iron oxide nanoparticles.

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_3O_4 could be adjusted. The difference between $NH_3{\cdot}H_2O$ and NaOH was that $NH_3{\cdot}H_2O$ 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 $NH_3{\cdot}H_2O$ 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 $NH_3{\cdot}H_2O$ as precipitants were 83.7 $emug^{-1}$ and 44.7 $emug^{-1}$, 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 $NH_3{\cdot}H_2O$ showed better dispersion.

4. Conclusion

Monodisperse iron oxide nanoparticles with NaOH and $NH_3{\cdot}H_2O$ 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 $NH_3{\cdot}H_2O$ 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.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (no. 21306005) and State "863" Plans (no. 2013AA032001).

References

[1] A.-H. Lu, E. L. Salabas, and F. Schüth, "Magnetic nanoparticles: synthesis, protection, functionalization, and application," *Angewandte Chemie International Edition*, vol. 46, no. 8, pp. 1222–1244, 2007.

[2] M. Shao, F. Ning, J. Zhao, M. Wei, D. G. Evans, and X. Duan, "Preparation of Fe_3O_4@SiO_2@layered double hydroxide core-shell microspheres for magnetic separation of proteins," *Journal of the American Chemical Society*, vol. 134, no. 2, pp. 1071–1077, 2012.

[3] M. I. Majeed, Q. Lu, W. Yan et al., "Highly water-soluble magnetic iron oxide (Fe_3O_4) nanoparticles for drug delivery: enhanced *in vitro* therapeutic efficacy of doxorubicin and MION conjugates," *Journal of Materials Chemistry B*, vol. 1, no. 22, pp. 2874–2884, 2013.

[4] K. H. Bae, M. Park, M. J. Do et al., "Chitosan oligosaccharide-stabilized ferrimagnetic iron oxide nanocubes for magnetically modulated cancer hyperthermia," *ACS Nano*, vol. 6, no. 6, pp. 5266–5273, 2012.

[5] L. Xiao, J. Li, D. F. Brougham et al., "Water-soluble superparamagnetic magnetite nanoparticles with biocompatible coating for enhanced magnetic resonance imaging," *ACS Nano*, vol. 5, no. 8, pp. 6315–6324, 2011.

[6] M. Mahmoudi, S. Sant, B. Wang, S. Laurent, and T. Sen, "Superparamagnetic iron oxide nanoparticles (SPIONs): development, surface modification and applications in chemotherapy," *Advanced Drug Delivery Reviews*, vol. 63, no. 1-2, pp. 24–46, 2011.

[7] S. Laurent, S. Dutz, U. O. Häfeli, and M. Mahmoudi, "Magnetic fluid hyperthermia: focus on superparamagnetic iron oxide nanoparticles," *Advances in Colloid and Interface Science*, vol. 166, no. 1-2, pp. 8–23, 2011.

[8] C. de Montferrand, L. Hu, I. Milosevic et al., "Iron oxide nanoparticles with sizes, shapes and compositions resulting in different magnetization signatures as potential labels for multiparametric detection," *Acta Biomaterialia*, vol. 9, no. 4, pp. 6150–6157, 2013.

[9] F. M. Kievit and M. Q. Zhang, "Surface engineering of iron oxide nanoparticles for targeted cancer therapy," *Accounts of Chemical Research*, vol. 44, no. 10, pp. 853–862, 2011.

[10] X. Yang, W. Jiang, L. Liu et al., "One-step hydrothermal synthesis of highly water-soluble secondary structural Fe_3O_4 nanoparticles," *Journal of Magnetism and Magnetic Materials*, vol. 324, no. 14, pp. 2249–2257, 2012.

[11] J. Q. Wan, W. Cai, X. X. Meng, and E. Liu, "Monodisperse water-soluble magnetite nanoparticles prepared by polyol process for high-performance magnetic resonance imaging," *Chemical Communications*, no. 47, pp. 5004–5006, 2007.

[12] C. M. Cheng, F. J. Xu, and H. C. Gu, "Facile synthesis and morphology evolution of magnetic iron oxide nanoparticles in different polyol processes," *New Journal of Chemistry*, vol. 35, no. 5, pp. 1072–1079, 2011.

[13] C. Okoli, M. Sanchez-Dominguez, M. Boutonnet et al., "Comparison and functionalization study of microemulsion-prepared magnetic iron oxide nanoparticles," *Langmuir*, vol. 28, no. 22, pp. 8479–8485, 2012.

[14] M. Nazrul Islam, L. Van Phong, J.-R. Jeong, and C. Kim, "A facile route to sonochemical synthesis of magnetic iron oxide (Fe_3O_4) nanoparticles," *Thin Solid Films*, vol. 519, no. 23, pp. 8277–8279, 2011.

[15] J. S. Basuki, A. Jacquemin, L. Esser, Y. Li, C. Boyer, and T. P. Davis, "A block copolymer-stabilized co-precipitation approach to magnetic iron oxide nanoparticles for potential use as MRI contrast agents," *Polymer Chemistry*, vol. 5, no. 7, pp. 2611–2620, 2014.

[16] A. Kajbafvala, M. R. Shayegh, M. Mazloumi et al., "Nanostructure sword-like ZnO wires: rapid synthesis and characterization through a microwave-assisted route," *Journal of Alloys and Compounds*, vol. 469, no. 1-2, pp. 293–297, 2009.

[17] P. Guardia, A. Riedinger, S. Nitti et al., "One pot synthesis of monodisperse water soluble iron oxide nanocrystals with high values of the specific absorption rate," *Journal of Materials Chemistry B*, vol. 2, no. 28, pp. 4426–4434, 2014.

[18] A. Kajbafvala, H. Ghorbani, A. Paravar, J. P. Samberg, E. Kajbafvala, and S. K. Sadrnezhaad, "Effects of morphology on photocatalytic performance of Zinc oxide nanostructures synthesized by rapid microwave irradiation methods," *Superlattices and Microstructures*, vol. 51, no. 4, pp. 512–522, 2012.

[19] K. O. Abdulwahab, M. A. Malik, P. O'Brien et al., "A one-pot synthesis of monodispersed iron cobalt oxide and iron manganese oxide nanoparticles from bimetallic pivalate clusters," *Chemistry of Materials*, vol. 26, no. 2, pp. 999–1013, 2014.

[20] J. Park, E. Lee, N. M. Hwang et al., "One-nanometer-scale size-controlled synthesis of monodisperse magnetic iron oxide nanoparticles," *Angewandte Chemie*, vol. 44, no. 19, pp. 2872–2877, 2005.

[21] S. Peng and S. Sun, "Synthesis and characterization of monodisperse hollow Fe_3O_4 nanoparticles," *Angewandte Chemie*, vol. 46, no. 22, pp. 4155–4158, 2007.

[22] M. D. Shultz, S. Calvin, P. P. Fatouros, S. A. Morrison, and E. E. Carpenter, "Enhanced ferrite nanoparticles as MRI contrast agents," *Journal of Magnetism and Magnetic Materials*, vol. 311, no. 1, pp. 464–468, 2007.

[23] H. Zhang and G. Q. Zhu, "One-step hydrothermal synthesis of magnetic Fe_3O_4 nanoparticles immobilized on polyamide fabric," *Applied Surface Science*, vol. 258, no. 11, pp. 4952–4959, 2012.

[24] S. Mohapatra and P. Pramanik, "Synthesis and stability of functionalized iron oxide nanoparticles using organophosphorus coupling agents," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 339, no. 1–3, pp. 35–42, 2009.

[25] P. Nicolás, M. Saleta, H. Troiani, R. Zysler, V. Lassalle, and M. L. Ferreira, "Preparation of iron oxide nanoparticles stabilized with biomolecules: experimental and mechanistic issues," *Acta Biomaterialia*, vol. 9, no. 1, pp. 4754–4762, 2013.

[26] M. V. Kovalenko, M. I. Bodnarchuk, R. T. Lechner, G. Hesser, F. Schäffler, and W. Heiss, "Fatty acid salts as stabilizers in size- and shape-controlled nanocrystal synthesis: the case of inverse spinel iron oxide," *Journal of the American Chemical Society*, vol. 129, no. 4, pp. 6352–6353, 2007.

[27] A. P. A. Faiyas, E. M. Vinod, J. Joseph, R. Ganesan, and R. K. Pandey, "Dependence of pH and surfactant effect in the synthesis of magnetite (Fe_3O_4) nanoparticles and its properties," *Journal of Magnetism and Magnetic Materials*, vol. 322, no. 4, pp. 400–404, 2010.

[28] R. Xu, "Progress in nanoparticles characterization: sizing and zeta potential measurement," *Particuology*, vol. 6, no. 2, pp. 112–115, 2008.

[29] Y. Pu, X. Tao, X. Zeng, Y. Le, and J. F. Chen, "Synthesis of Co-Cu-Zn doped Fe_3O_4 nanoparticles with tunable morphology and magnetic properties," *Journal of Magnetism and Magnetic Materials*, vol. 322, no. 14, pp. 1985–1990, 2010.

[30] Y. Pu, H. Zou, J.-X. Wang, J. Zhai, N. R. Foster, and J.-F. Chen, "Novel Sr-Zn-Co hexagonal ferrite nano-rods by wood-template chemical solution synthesis," *Materials Letters*, vol. 65, no. 14, pp. 2213–2215, 2011.

[31] Y. Pu, X. Tao, J. Zhai, and J.-F. Chen, "Hydrothermal synthesis and magnetic properties of $Co_{0.2}Cu_{0.03}Fe_{2.77}O_4$ nanoparticles," *Materials Research Bulletin*, vol. 45, no. 5, pp. 616–620, 2010.

[32] Y. Pu, X. Tao, J. Zhai et al., "Synthesis and electromagnetic properties of microwave absorbing material: $Co_x(Cu_{0.5}Zn_{0.5})_{1-x}Fe_2O_4$ ($0<x<1$) nanoparticles," *Materials Science and Engineering B*, vol. 176, no. 2, pp. 163–166, 2011.

[33] Y. Y. Zheng, X. B. Wang, L. Shang et al., "Fabrication of shape controlled Fe_3O_4 nanostructure," *Materials Characterization*, vol. 61, no. 4, pp. 489–492, 2010.