Preparation and Characterization of \(\alpha\)-Fe\(_2\)O\(_3\) from Iron Mud by Hydrothermal Synthesis

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Abstract. As a solid waste, the synthesis of \(\alpha\)-Fe\(_2\)O\(_3\) from iron sludge remains a challenge. In this experiment, \(\alpha\)-Fe\(_2\)O\(_3\) nanocrystals were successfully synthesized by hydrothermal method using iron sludge as iron source, and the effects of reaction time and pH on the experimental results were studied. The synthesized products were characterized by X-ray diffraction, SEM, FT-IR and VSM analysis. The results show that the optimum synthesis time and pH are 6 h and 6 respectively. Under these conditions, the size of nanocrystalline \(\alpha\)-Fe\(_2\)O\(_3\) is about 80 nm. According to the hysteresis loop, the powder synthesized is a weak magnetic material, which has broad application prospects in high frequency electromagnetic materials.

1. Introduction

The \(\alpha\)-Fe\(_2\)O\(_3\) is an important inorganic material, which attracts much attention because of its wide application and unique properties. It is mainly used in catalysts, magnetic materials, pigments, gas sensors, lithium batteries [1]. At the same time, it has potential applications in optics, thermology, electronics, acoustics and other fields. According to different composition and microstructure, \(\alpha\)-Fe\(_2\)O\(_3\) will show different properties, so its application fields are different. For example, the gas sensitivity of spherical film is higher than that of ellipsoid, and the catalytic performance of rod-like film is better than that of spherical film. Moreover, \(\alpha\)-Fe\(_2\)O\(_3\) has high stability, low cost and non-toxicity and is widely used for the degradation of pollutants in water. Nowadays, besides nanospheres, nanotubes, nanorods, nanoribbons, nanowires and nanocubes are also prepared [2].

In the past few decades, the preparation technology of \(\alpha\)-Fe\(_2\)O\(_3\) nanocrystals has been relatively mature, including sol-gel [3], hydrothermal [4], co precipitation [5], template [6] and forced hydrolysis [7]. Among them, the requirement of hydrothermal synthesis for equipment is relatively simple. Water is used as the medium in the reaction process. Using the closed-loop environment provided by the reactor, nanoparticles with uniform morphology and size were prepared in a high temperature and high pressure environment at an appropriate temperature. And the product has good dispersion, so this method is the most commonly used preparation method of \(\alpha\)-Fe\(_2\)O\(_3\) nanocrystals.

The raw material of this experiment is iron sludge from steel plants. Hydrothermal synthesis method is used to synthesize \(\alpha\)-Fe\(_2\)O\(_3\) nanocrystals. As solid industrial waste, iron sludge must occupy a large amount of land. Improper disposal of solid waste will have a very negative impact. At present, iron mud is mainly used in the preparation of pigments, ferrosilicon alloys, sintering raw materials and sponge iron. The preparation of sinter for internal use is the most common. However, through analysis and detection, it is found that the iron oxide content in iron mud is as high as 98%, which is the ideal solid waste material for preparing \(\alpha\)-Fe\(_2\)O\(_3\) nanocrystals. At present, there are few reports on the...
synthesis of $\alpha$-Fe$_2$O$_3$ nanocrystals from solid waste. The preparation of nano-sized $\alpha$-Fe$_2$O$_3$ from iron sludge has not been reported. It can improve the economic value of solid waste treatment.

2. Materials and Methods

2.1. Materials
The iron sludge from steel plants is roasted at 600°C for 4 h, so that all iron in the sludge exists in the form of Fe$^{3+}$. After cooling at room temperature, iron sludge is dissolved in 2M HCl solution, and FeCl$_3$·6H$_2$O is precipitated after evaporation, concentration, cooling and crystallization. The crystal is dried and reserved.

2.2. The Preparation of $\alpha$-Fe$_2$O$_3$ Nanocrystals
In order to study the effect of reaction time on the experiment, four groups of comparative experiments were carried out. 8g FeCl$_3$·6H$_2$O was dissolved in 20ml deionized water respectively. NaOH solution was used to adjust the pH to 9. After 10 minutes of electromagnetic stirring, it is placed in the reactor. Heat preservation for 2 h, 4 h, 6 h and 8 h in an oven at 150°C. The powder was collected after cooling at room temperature, washed repeatedly with deionized water, and dried for 6 h at 80°C.

In order to study the effect of pH on the experiment, according to the above experimental methods, the pH was adjusted to 3, 5, 7, 9 respectively, and kept in oven for 6 hours. Other conditions and processes were the same.

3. Characterization
The crystal structure of the powders was characterized by X-ray diffraction (XRD) under the radiation of Cu Kα ($\lambda$=0.15418 nm). Fourier transform infrared spectroscopy (FTIR, Nicolet IS10) was used to study the infrared spectra of the powders. The spectra ranged from 400 cm$^{-1}$ to 4000 cm$^{-1}$. The morphological characteristics of the powders were characterized by Hitachi S4800 scanning electron microscopy. The magnetic properties of the product were characterized by vibrating sample magnetometer (VSM Versalab).

4. Results and Discussion

4.1. Results
In order to determine whether to synthesize $\alpha$-Fe$_2$O$_3$ and to test the purity and crystallinity of the synthesized products, the synthesis of $\alpha$-Fe$_2$O$_3$ nanoparticles at different reaction time was analyzed by XRD. Figure 1 shows the XRD results. The spatial group of these rhombic powders is R-3c, the lattice constant is $a$=5.0356, $c$=13.7489. Meanwhile, the peaks at (012), (104), (110), (113), (024), (116), (214) and (300) are similar to those of rhombohedrite (PDF code: 00-033-0664). From the XRD diagram, it can be seen that the intensity of the peak increases gradually with the prolongation of the reaction time. The intensity of the XRD peak obtained at 6 h and 8 h of the reaction time does not change significantly. No other peaks are observed, indicating that the synthesized sample is $\alpha$-Fe$_2$O$_3$. 

XRD analysis shows that α-Fe₂O₃ was successfully synthesized. In order to prove the uniform morphology of the nanocrystals, the products were analyzed by electron microscopy. Figure 2 shows the SEM diagrams of different reaction time, in which a–d is the SEM diagrams of reaction time of 2–6 h respectively. Figure 2a clearly shows that there is no fixed morphology of α-Fe₂O₃. Because the reaction time is too short, the crystal does not begin to nucleate and grow. Figure 2b shows that spherical particles have begun to form at 4h, because some of them are still growing, leading to particles sticking together. Figure 2c shows spherical particles with uniform morphology and good dispersion. The size of spherical particles is about 80 nm. At the same time, there is no obvious difference between Figure 2d and Figure 2c, which indicates that the nucleation is complete at 6 h.
The samples obtained under different pH conditions were analyzed by SEM. The results are shown in Figure 3. Figure 3a–3d shows the SEM diagram of reaction conditions at pH 3–9. Figure 3a can clearly see spherical particles with good dispersion, but the particle size is about 2μm, so α-Fe₂O₃ nanocrystals cannot be synthesized at pH 3. In Figure 3b, it can be observed that the particle size is about 80 nm, but the dispersion is not good. Figure 3c and Figure 3d have successfully synthesized α-Fe₂O₃ nanocrystals with good dispersion and size of about 80 nm. It can be concluded that nanocrystals of α-Fe₂O₃ nanocrystals can be successfully synthesized when the pH is 7 and the holding time is 6 hours at 150°C.

![SEM of synthesis of α-Fe₂O₃ at different pH](image)

Figure 3. SEM of synthesis of α-Fe₂O₃ at different pH

4.2. Characterization

In order to further verify the synthesis of α-Fe₂O₃ at pH 7, 150°C. for 6 h, the powder synthesized under this condition was tested by FTIR. Figure 4a shows FTIR spectra of α-Fe₂O₃ in the range of 4000 cm⁻¹-400 cm⁻¹. Four peaks can be observed. The characteristic absorption bands at 471 cm⁻¹ and 540 cm⁻¹ are related to the Fe-O of α-Fe₂O₃. In addition, the characteristic peaks at 1627 cm⁻¹ and 3406 cm⁻¹ are correlated with the O-H bending frequency of water-absorbing molecules [8]. Therefore, α-Fe₂O₃ has been successfully synthesized under this condition.

At 300K, the hysteresis loop of α-Fe₂O₃ prepared by hydrothermal synthesis is shown in Figure 4b. It can be seen that the hysteresis loop is narrow and long, the coercivity is 383.04 Oe, the remanence is 0.0299 emu/g, and the hysteresis phenomenon is not obvious. This material is easy to magnetize and demagnetize. It is the main material used to manufacture transformers, relays, motors and various high frequency electromagnetic components.
5. Conclusion

α-Fe₂O₃ nanoparticles were synthesized from iron sludge by hydrothermal method, which can effectively recover iron sludge with high added value and realize harmless, reduction and resource utilization of waste. α-Fe₂O₃ nanoparticles with good dispersion were successfully synthesized at pH 7, 150 °C for 6 h. Compared with the traditional experimental conditions, the reaction time was shortened and the ferromagnetic behavior of the nanocrystals was weak. It has broad application prospects in high frequency electromagnetic materials.

6. Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Nos. 51874039) and Major Science and Technology Program for Water Pollution Control and Treatment (2017ZX07402001).

7. Reference

[1] Jianmin M, Jiabiao L, Xiaochuan D, Xiaodi L and Wenjun Z 2010 J. Phys. Chem. C 114 10671–6.
[2] Xiaohe L, Guanzhou Q, Aiguo Y, Zhong W and Xingguo L 2007 Journal of Alloys and Compounds 433 216–20.
[3] L.E. Mathevulaa, L.L. Notoa, B.M. Mothudia, M. Chithambob and M.S. Dhlaminia 2017 Journal of Luminescence 192 879–87.
[4] M.Y. Nassar, I.S. Ahmed and H.S. Hendy 2018 Journal of Molecular Liquids 271 844–56.
[5] H. Mansour, R. Bargougui, C. Autret-Lambert, A. Gadri and S. Ammar 2018 Journal of Physics and Chemistry of Solids 114 1–7.
[6] L.S. Valladares, L. Leon, S.M.E. Suarez, A.G.B. Dominguez, T. Mitrelias, S. Holmes, N.O. Moreno, J.A. Aguiar and C.H.W. Barnes, 2016 Materials Chemistry and Physics 169 21–7.
[7] J. Stajdohar, M. Ristic’ and S. Music’ 2012 Journal of Alloys and Compounds 532 41–8.
[8] H. Bazrafshan, Z.A. Tesieh, S. Dabirnia, R.S. Toubia, H. Manghabati, B. Nasernejad 2017 Powder Technology 308 266–72.