

Study on the Preparation of Nanometer α -Fe₂O₃ by Sonochemical Hydrolysis Method

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Abstract. The size- and shape –controlled α -Fe₂O₃ nanoparticles has been successfully prepared via a sonochemical method in FeSO₄- NH₄HCO₃ complex solution. The influence of ultrasound field to the dimension, appearance and agglomeration of the product were discussed. The obtained samples were examined by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), thermogravimetry and differential thermal analyses (TG-DTA) techniques. The results revealed that the phase of ferric oxide powders mainly consisted of spherical α -Fe₂O₃. The α -Fe₂O₃ particles were relatively uniform in size and the average size of particles is 50nm. The influence of the synthesis conditions on the size and size distribution of Fe₂O₃ nanoparticles was determined.

1. Introduction

Recent advances in nanostructured materials have been led by the development of new synthetic methods that provide control over size, morphology, and nano/microstructure^[1]. Ultrasound is a mechanism wave with a frequency range of 10kHz-106kHz and a speed of 1500m/s. The technology of ultrasound was becoming one of the top investigation domains of chemistry and engineering and was used widely in some fields such as biochemistry, organic synthesis, polymer chemistry, analytical chemistry, electrochemistry, environment chemistry, pesticide and food^[2-6]. Recently, the sono-chemistry method has always become a new technology for the special physical and chemical condition from the sound cavitation provide an important way to preparing the nanometer materials^[7].

Hematite (α -Fe₂O₃) is one of the most studied nanocrystals due to its wide range of applications, such as in catalysts, pigments, magnetic materials, gas sensors, and lithium ion batteries^[8-13]. Inspired by its excellent characteristics, much effort has been made to fabricate the nanostructured α -Fe₂O₃ with different sizes and shapes because of its strong size- and shape-dependent properties. Presently, the methods of preparing ferric oxide is air-oxidation gel-sol method, forced-hydrolyze method, colloid chemistry, micro-latex method^[14-16]. There are a few literatures to report preparing nano-sized materials with ultrasound, the new experiment not only develops the apply domains of ultrasound, but also

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settle some difficult problem in the source of preparing nano-sized materials.

2. Experimental

2.1 Experimental Method

The seven water ferrous sulfate solution was refined and diluted into a certain concentration solution, then a certain concentration of ammonium bicarbonate as the precipitation agent was added to the solution with appropriate of speed drops. The solution pH value was adjusted by phosphoric acid. The air was injected into the solution with blower, and then the oxidation reaction began to carry out in the solution with the ultrasonic effect. The solid-liquid separation was operated at the end of the reaction via washing, drying and calcination, the Fe_2O_3 nano-particles achieved. The technological process was shown in Fig. 1.

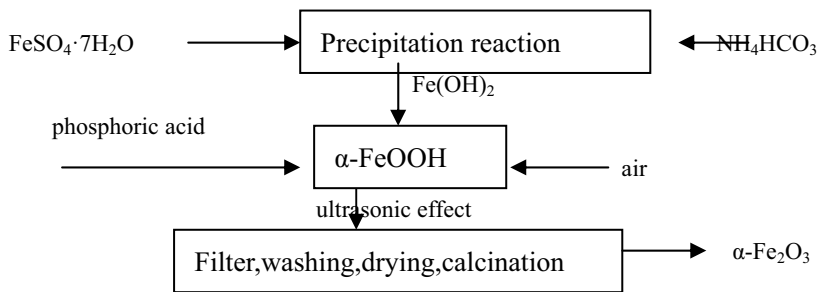


Fig 1. The technological process of preparing $\alpha\text{-Fe}_2\text{O}_3$ nano-particles

2.2 Characterization

The thermal decomposition of $\alpha\text{-FeOOH}$ was characterized by CRY-2(P) differential thermal analyzer with Al_2O_3 as reference, heating rate was $10^\circ\text{C}/\text{min}$, static air; $\alpha\text{-Fe}_2\text{O}_3$ crystalline structure was characterized with Hitachi D/MAX - 3C automatic X-ray diffraction instrument with $\text{Cu K}\alpha$ operated at 40 kV and 30 mA at a scanning speed of $4^\circ/\text{min}$ and a scanning angle (2θ) in the range $10^\circ\text{--}85^\circ$. Particle size and morphology of $\alpha\text{-Fe}_2\text{O}_3$ was observed with Hitachi H - 600 type transmission electron microscopy (TEM).

3. Results and Discussion

3.1 Sample Characterization

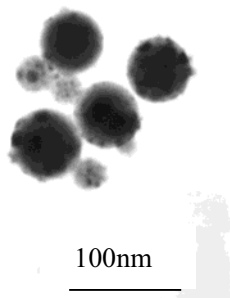


Fig 2 the TEM photograph of $\alpha\text{-Fe}_2\text{O}_3$

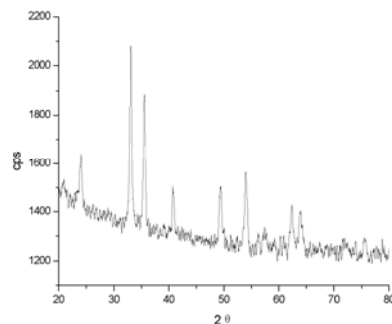


Fig 3 XRD pattern of $\alpha\text{-Fe}_2\text{O}_3$ calcined for 2h on 700°C

The TEM photograph of α -Fe₂O₃ obtained by α -FeOOH calcined for 2 hours on 700°C is shown in Fig.2, The photograph illustrates that particles size of products is uniformity, and the average particle size is 50nm around according to statistical measurement. The XRD pattern of α -Fe₂O₃ which has been obtained by α -FeOOH calcined for 2 hours on 700°C is shown in Fig. 3 .The peaks of XRD is agreement with the standard pattern of α -Fe₂O₃.According to the scherrer equation, the average particle size of 42.3 nm is calculated.

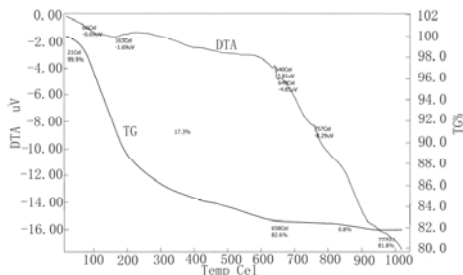


Fig.4 TG-DTA curve of α -FeOOH

The diagram of DTA analysis about the middle product α -FeOOH in 0-1000°C is agreed with the analysis above. A wider decalescence apix in 163-650°C shows in Fig.4, it is the course of removing the dissociating water in 63-640°C and the dehydration of crystal water in α -FeOOH and series of crystal styles transformation above 640°C. The suitable calcinations temperature of preparing nanometer ferric oxide is around 757°C.

The sample weight loss 17.3% in 21-650°C according to the TG curve, means the surface adsorption water and crystal water lose almost. The weight loss is only 0.8% between 650-999°C. As a result, so iron oxide crystal type exists transformation only after 650°C.

3.2 Ultrasonic Effect on the Preparation of Iron Oxide

The reaction time under the action of ultrasonic has important effect on the production, the product are prepared with 60 minutes, 90 minutes or 120 minutes reaction time while other conditions remain unchanged. Then the FeOOH powder are calcined in 700 °C for 2 hours, finally the TEM graph of product respectively as shown in Fig. 5, Fig. 6 and Fig. 7.

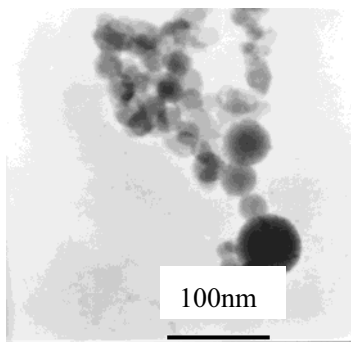


Fig 5 TEM photograph of α -Fe₂O₃ with 60 min

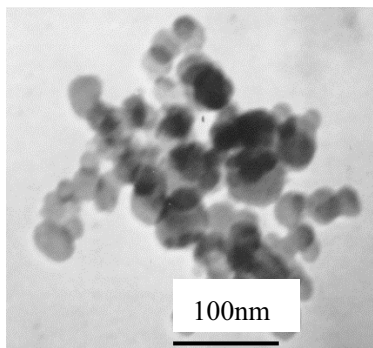


Fig 6 TEM photograph of α -Fe₂O₃ with 90 min

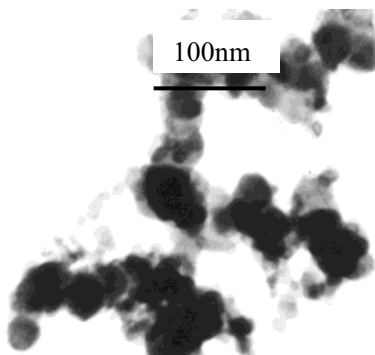


Fig 7 TEM photograph of α -Fe₂O₃ with 90 min

The TEM photographs show that particle diameter produce different degree of reunion at the same time with the extension of ultrasonic reaction time after the reaction tend to be more fully, and the time longer, the more serious of the reunion phenomenon. The appropriate reaction time, the proper frequency of ultrasonic cavitation effect of ultrasound generated by high temperature and high pressure make the generation of Fe(OH)₂ quickly via the oxygen oxidation process, then make Fe(OH)₂ particles generate tiny crystal nucleus of scattered. But following the reaction times extend further the grain grows due to the solute to the nucleation surface diffusion and chemical reaction. Ultrasound both only has the dispersion effect, also the energized effect, such as particle surface can increase, particle reunion phenomenon more serious, which is not conducive to obtain monodisperse ultrafine particles. Therefore, choosing the proper reaction time, ultrasonic can use to prepare superior performance of iron oxide nanoparticles.

When the other conditions are fixed, the different effects of the action of ultrasonic waves (frequency of 40 KHz) and mechanical mixing (stirring speed $r = 800$ r/min) are studied. Results show that iron oxide particles dispersion with the effect of ultrasonic system of mixing are better than mechanical agitation system, and the time of generate the precursor of α -FeOOH time significantly shortened. Under the condition of the two reaction, after washing, drying, and under 700 °C calcination 2 hours, α -Fe₂O₃ particles finally are got.

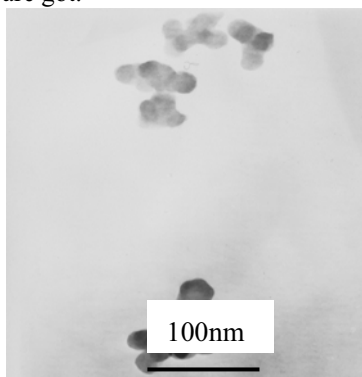


Fig 8 TEM photograph of α -Fe₂O₃ under ultrasound

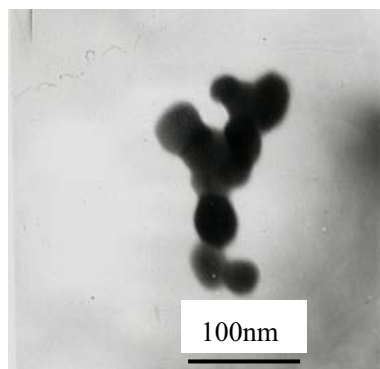


Fig 9. TEM photograph of α -Fe₂O₃ under agitation

TEM photographs of the product prepared respectively by ultrasonic and (1 hour) or mechanical stirring (5 hours) are shown in Fig. 8 and Fig. 9. The results show that the α -Fe₂O₃ particles are sphere, small particle size without agglomeration under the action of ultrasonic wave. But α -Fe₂O₃ particles are bigger with apparent agglomeration in Fig. 9.

This is maybe because during the Fe (OH)₂ oxidation process, the oxygen transfer is control step, the role of ultrasound accelerates the transfer rate of oxygen, then oxidation reaction is fully, and ultrasonic cavitation effect produces a powerful shock waves and micro jet, so the power impacts in the liquid-solid interface, prevent effectively the crystal nucleus growing up. At the same time the generated particles surface and the intermolecular interaction force between the water molecules are damaged and weaken, thus further to prevent particles together. The experiments find it is advisable ultrasonic reaction time with 1 hour during the preparation of α -FeOOH. While, the response time of the preparation of α -FeOOH is 5 hours under the influence of mechanical agitation. The ultrasonic wave can greatly shorten the reaction time.

4. Conclusion

The nanometer iron oxide powde are prepared under ultrasonic action Using industrial waste seven water ferrous sulfate and industrial grade ammonium bicarbonate as raw materials. Using industrial waste seven water ferrous sulfate as raw material to the preparation of nanometer iron oxide, industrial waste utilization is significance. The results show that the generated iron oxide nanoparticles is spherical with average particle diameter of 50 nm, size is uniform and good dispersibility. Compared with mechanical mixing reaction, the reaction time with ultrasonic application reduce four times in the preparation of nanometer iron oxide powder reaction process. The ultrasonic wave in the process of the formation of iron oxide nanoparticles mechanism to be further explored.

Acknowledgment

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