

Preparation of α -Fe₂O₃ Nanoparticles by Sol-Gel Process with Inorganic Iron Salt

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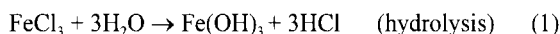
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A simple new method for the preparation of α -Fe₂O₃ nanoparticles by sol-gel process using ethylene oxide and FeCl₃ as starting materials is reported. The size and morphology of α -Fe₂O₃ nanoparticles can be controlled by changing the initial concentration of FeCl₃ and amount of ethanol.

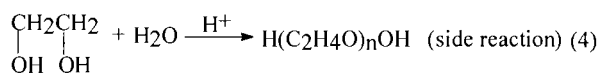
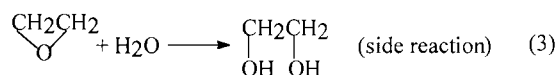
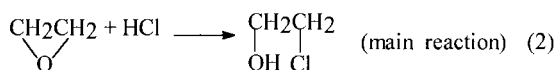
It is well known that α -Fe₂O₃ (hematite) nanoparticles are particularly appealing for experimental and theoretical investigations in view of their technological applications. Actually, they have been widely used as red pigments, catalysts in dehydrogenation reactions, anticorrosive agents,¹ and starting materials in the synthesis of magnetic ferrites. Their applications in nonlinear optics² and gas sensors³ have also been investigated recently.

For the above reasons, considerable efforts have been made in the synthesis techniques of iron oxide nanoparticles, such as forced hydrolysis,⁴ hydrothermal reactions,⁵ microemulsion technique,⁶ sol-gel processes,^{2,7} and so on. Among them, the sol-gel and forced hydrolysis methods are widely used to prepare high yield α -Fe₂O₃ nanoparticles. However, the commonly used precursors of the sol-gel method, i.e., metal alkoxides, are more expensive and less easily available than inorganic metal salts. The starting materials of forced hydrolysis usually are inorganic metal salts and alkalis. However, the desired metal hydroxide or oxide nanoparticles will be contaminated by metal salts, which is one of the products of the hydrolysis process. Unfortunately, when a solvent, such as water, is used to clean the product, the aggregation of the metal hydroxide or metal oxide nanoparticles also takes place at the same time.

In this letter, a simple forced hydrolysis method via sol-gel process was successfully employed to synthesize α -Fe₂O₃ nanoparticles without the contamination and aggregation mentioned above. α -Fe₂O₃ nanoparticles were prepared by using ethylene oxide (EO) and FeCl₃ as starting materials. EO was selected as one of the starting materials because it can actively react with HCl, one of the hydrolysis product of FeCl₃. The main principle of the formation of α -Fe₂O₃ nanoparticles is described as follows. There is a hydrolysis equilibrium in the aqueous FeCl₃ solution:



If EO is dropped in, reactions will take place as follows:



In the last three reactions, EO plays an important role not only in reaction with HCl, which leads to speed the hydrolysis of the FeCl₃, but also in the formation and polymerization of CH₂CH₂(OH)₂. The by-product, H(C₂H₄O)_nOH (PEG), will have an effect on preventing the Fe(OH)₃ nanoparticles from agglomerating, just as other surfactants do. Therefore uniform Fe₂O₃ nanoparticles may be obtained after aging and heating.

The starting materials used included Analytical Reagents of FeCl₃, EO and C₂H₅OH (EtOH). Aqueous solution of FeCl₃ and mixture of EO and EtOH were put into the ice bath and cooled respectively. Then mixture of EO and EtOH was dropped slowly into the aqueous solution of FeCl₃. It can be observed that red-brown sol formed first and high elastic gel later. The gels were heating at 200 °C to drive out the by-products and at 300 °C to form Fe₂O₃ nanoparticles. The size and morphology of Fe₂O₃ nanoparticles can be controlled by varying the initial concentration of FeCl₃ and amount of EtOH. All prepared samples were indexed as pure α -Fe₂O₃ because the distance values calculated from the electron diffraction patterns in TEM views⁸ are all in agreement with those in JCPDS No. 33-664, which is the standard XRD data of α -Fe₂O₃. We found that the molar ratio of EO and Cl⁻ (mol_{EO:Cl⁻}) should not be less than 1.5 for preparing α -Fe₂O₃ nanoparticles with good morphology and crystallinity.

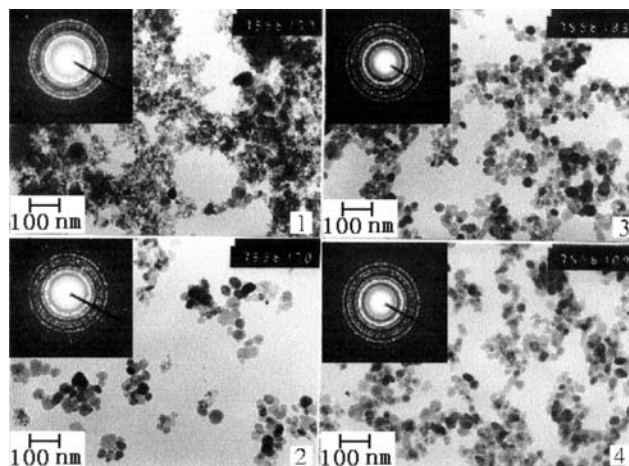


Figure 1. TEM view of α -Fe₂O₃ nanoparticles prepared with different initial concentrations of FeCl₃ (mol_{EO:Cl⁻}:2.5, V_{EtOH}:15%). Sample 1: 0.1 M, Sample 2: 0.3 M, Sample 3: 1 M, Sample 4: 2 M.

Figure 1 shows the bright field TEM micrographs of α -Fe₂O₃ nanoparticles prepared with different initial concentrations of FeCl₃ (C_{FeCl₃}). It can be seen that the α -Fe₂O₃ nanoparticles prepared with C_{FeCl₃} value of 0.1 M (Sample 1) did not show very good morphology and indicated aggregation

of the particles. However, small and uniform α -Fe₂O₃ nanoparticles formed when C_{FeCl_3} was not less than 0.3 M. This can be demonstrated by the theory of colloidal chemistry. It is well known that there are two stages in the crystallization of the particles from the sol, i.e., nucleation stage and nucleus growth stage.⁹ When C_{FeCl_3} was less than 0.3 M, the nucleus growth rate (V_2) is restricted and collosol formed; V_2 increased with increasing C_{FeCl_3} and this condition was suitable for the growth of particles. When the concentrations increase further (samples 2-4, from 0.3 M to 2 M), the nucleation rate (V_1) is much larger than V_2 and a large number of fine Fe(OH)₃ particles formed. It can be seen that sols easily transformed into gels under this condition because of the connection of large quantity of fine particles. When C_{FeCl_3} was up to 2 M, gel formed in three minutes. So it can be found that, when sols easily form gels, the higher the initial concentrations of FeCl₃, the more uniform the morphology of the particles, and the smaller the average particle size of the particles. Therefore the particle size decreases with the decreasing gelation time and uniform particles about 20-40 nm can be prepared with high concentrations of FeCl₃. However, the possibility of formation of gels by polymerization of ethylene glycol will also increase with increasing C_{FeCl_3} because the molar ratio of H₂O and Fe³⁺ may be low enough for the polymerization of ethylene glycol with FeCl₃ as a catalyst.

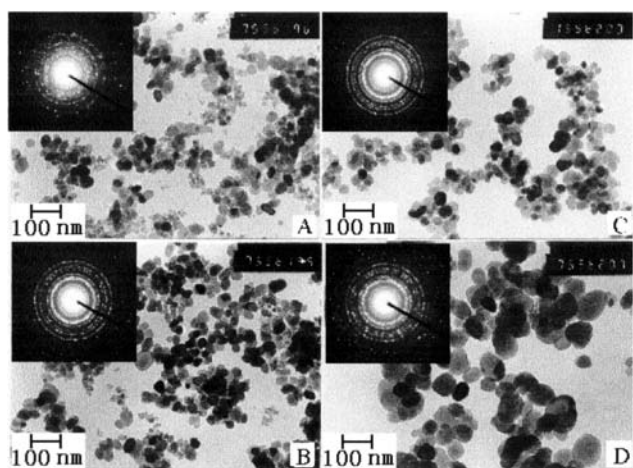


Figure 2. TEM view of α -Fe₂O₃ nanoparticles prepared with different volume percentage of EtOH in the mixture of the starting materials (C_{FeCl_3} : 0.5 M, $\text{mol}_{\text{EtOH}}/\text{Cl}^-$: 2.25). Sample 1: 0.1 M, Sample 2: 0.3 M, Sample 3: 1 M, Sample 4: 2 M

The effect of EtOH on the formation of uniform α -Fe₂O₃ nanoparticles with different sizes has also been investigated. Figure 2 shows the TEM view of α -Fe₂O₃ nanoparticles prepared with different volume percentage of EtOH (V_{EtOH}) in the mixture of starting materials. It can be seen that when the sols formed gels easily, the uniformity of the particles increases

with the increasing V_{EtOH} , i.e., from 25% (Sample A) to 45% (Sample C) (about 20-40 nm). However, when sols did not form gels in a very long time, the size of the α -Fe₂O₃ nanoparticles prepared with 55% EtOH (Sample D) (about 50-60 nm) was much larger than those prepared with lower V_{EtOH} . We once estimated that EtOH may behave as a stabilizer for the colloidal particles to avoid aggregation because of its hydrophobicity and smaller particles would be obtained with its increasing V_{EtOH} . However, the experimental results were contrary to the estimation. The reasons should be investigated furthermore.

α -Fe₂O₃ nanoparticles were prepared by sol-gel process using ethylene oxide and FeCl₃ as starting materials. The molar ratio of EO and Cl⁻ should not be less than 1.5 for the formation of uniform α -Fe₂O₃ nanoparticles with good morphology. Gel will be formed more quickly with the increasing FeCl₃ concentrations because the formation and connection of a large number of Fe(OH)₃ fine particles. The size of the particles can also be controlled by varying the EtOH volume percentage. This preparation method is very useful to produce α -Fe₂O₃ nanoparticles with low cost of starting materials. It is also very easy to prepare α -Fe₂O₃ thin films during the sol-gel process. The thin films are expected to have potential applications in the area of nonlinear optics. However, the contamination of carbon in α -Fe₂O₃ nanoparticles can not be avoided if the samples are calcinated at 500 °C or higher because the residual organic compounds of the side reaction can not be completely driven out. The particle size became larger and the morphology of some particles changed from sphere to ellipsoid after the samples were heated at 700 °C for three hours.

References and Notes

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