Synthesis and Characterization of Iron-Oxide (Magnetite) Nanocrystals

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ABSTRACT

Monodispersed iron oxide based nanocrystals of uniform size and shape were prepared using the LSS (liquid-solid-solid) synthetic route. Various morphologies of the iron (II) oxide nanostructures can be achieved by varying the growth parameters (concentration of sodium hydroxide and surfactant). The morphology and structure of the iron oxide nanocrystals were examined using scanning electron (SEM) and transmission electron microscope (TEM). Detailed chemical analysis on the nanocrystals was carried out using X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray (EDX).

INTRODUCTION

Iron oxides are interesting due to their catalytic, magnetic and semiconducting properties. In this work, we have employed the use of liquid-solid-solution (LSS) to synthesized monodispersed iron oxide nanocrystals. In essence, the LSS process (Figure 1) involves the reduction of Fe\(^{2+}\) ions by ethanol at the interfaces of metal oleate (solid), ethanol-oleic acid liquid phase (liquid) and water-ethanol solutions (solution) at the designated temperature. After the aqueous solution of Fe\(^{2+}\) ions, sodium oleate and the mixture of oleic acid and ethanol were added to the vessel in order. Three phases formed in this system: sodium linoleate (solid), the liquid phase of ethanol and linoleic acid (liquid), and the water–ethanol solution containing Fe\(^{2+}\) ions (solution).

A phase transfer process of the noble metal ions occurred spontaneously across the interface of sodium oleate (solid) and the water–ethanol solution (solution) based on ion exchange, which led to the formation of iron oleate and the entering of the sodium ions into the aqueous phases. Then at a designated temperature, the ethanol in the liquid and solution phases reduced the Fe\(^{2+}\) ions at the liquid–solid or solution–solid interfaces. Along with the reduction process, the in-situ generated oleic acid absorbed on the surface of the Fe\(^{2+}\) nanocrystals with the alkyl chains from oleic acid on the outside, through which the produced Fe\(^{2+}\) nanocrystals will gain hydrophobic surfaces. A spontaneous phase-separation process then occurred because of the weight of the metal nanocrystals and the incompatibility between the hydrophobic surfaces and their hydrophilic surroundings, and the noble metal nanocrystals can be easily collected at the bottom of the container (Xun Wang, 2005).
EXPERIMENTAL

All chemicals were used as received without any further purification. De-ionized water was used throughout the experiments. Fe\((\text{SO}_4)_2(\text{NH}_4)_2\cdot6\text{H}_2\text{O}\), oleic acid, linoleic acid, TOP were supplied by Sigma-Aldrich. Firstly, 8 mL of de-ionized water was used to dissolve 0.5 g of NaOH. This solution was mixed by stirring at room temperature at 10 minutes. 5 mL of ethanol was added to the NaOH solution and mixed again for 5 minutes. Subsequently, 5 mL of oleic acid was added to the mixture and mixed for another 5 minutes. Meanwhile, 0.0076 g of iron precursor was weighed and dissolved in 2 mL of de-ionized water. The iron precursor is added finally to the mixture and mixed for a final 5 minutes. A dirty-green precipitate is formed. This precipitate is then transferred to an autoclave. The autoclave will be placed in an oven for 10 hours at 180 °C (Xin Liang, 2006). After heating, the mixture is then centrifuged. The top layer of oleic acid is removed and 30 mL of ethanol is added. The resultant mixture is then centrifuged again.

RESULTS AND DISCUSSIONS

Effect of NaOH concentrations

One of the more important synthetic parameters in influencing the phase transition between magnetite and goethite is the NaOH concentration (Xin Liang, 2006). The Fe\(^{2+}\) concentration, ethanol/water ratio, reaction temperature and oleic acid quantity were kept constant. Figure 2 a, b and c show the SEM images of the sample when 0.25, 0.5 and 0.75 g of NaOH were used in the synthesis respectively. Figure 2a shows a mixture of agglomerated nanocrystals and some nanorods while Figure 2b shows mainly elongated nanocrystals of approximately 50-100 nm in length. On the other hand, 0.75 g of NaOH produces relatively uniform quasi-spherical
nanocrystals of diameter ~ 20-50 nm. As the amount of NaOH used in the synthesis increases, the morphology of the nanocrystals assumes a more spherical in shape.

This trend is explained by Jolivet et. al. in his paper on iron oxide chemistry. When the medium is alkaline, solubility of the intermediate phase is low, and the dissolution-crystallization process is completely hindered so that the transformation can only be continued via a dehydration in situ and local rearrangement, favouring the formation of magnetite which takes the form of nanocrystals (Jean-Pierre Jolivet, 2004).

![Figure 2: SEM image of the produced nanocrystals using (a) 0.25 (b) 0.5 and (c) 0.75 g of NaOH.](image)

**Effect of surfactant variations**

Surfactants are used to reduce the surface tension of water by absorbing water at the liquid-gas interface. The surfactant molecules will wrap around the Fe$^{2+}$ ion during the synthesis process and this results in the produced nanocrystals to be well-dispersed. In our reference sample, the surfactant used is oleic acid while other surfactants namely linoleic acid and Tri-Octyl Phosphate (TOP) were also employed.

Figure 3a and b shows a low-resolution (LR) and a high-resolution (HR) image of the nanocrystals synthesized using TOP surfactant. The hexagonal nanocrystals are largely uniform and are approximately 20 nm in diameter. Figure 3c and d show both LR and HR images of the nanocrystals synthesized using linoleic acid surfactant. This synthesis yields uniform cubic nanocrystals of approximately 20 nm in diameter. The nanocrystals are well-dispersed and highly-crystalline. The measured interplanar spacing is 0.259 nm.
Figure 3: Low and high resolution TEM images using (a-b) TOP and (c-d) linoleic acid as the surfactant.

Figure 4 shows the XRD results of the sample. There are four peaks shown in the diffraction pattern. Through observing the peaks and their respective directions, we found that the content of our results matches with JCPDS card 76-1849. This confirms the as-synthesized nanocrystals is of magnetite structure. EDX was used to identify the elemental composition of our end product. EDX spectra from two samples each produced by different surfactant oleic acid (Figure 5b) and linoleic acid (Figure 5c) were obtained. Despite the change in the surfactants, there is no other impurities found in the samples as can be seen, there are only Fe and O elements detected in both the samples. This shows that the added surfactant serves to disperse the nanocrystals. The Si is detected due to the fact that the samples were dispersed on a silicon substrate.
Figure 4: XRD pattern of the as-synthesized nanocrystals

Figure 5: EDX spectra obtained from the nanocrystals synthesized using (a) oleic acid and (b) linoleic acid as the surfactant
XPS was used to carry out chemical analysis on the synthesized nanocrystals. Figure 6a shows the O1s 530.2 eV which complements the O1s of Fe$_2$O$_3$ (Haiying Xiao, 2007). Figure 6b, the Fe 2p spectrum with peaks at 710.7 eV and 724.5 eV is in good agreement with the formation of Fe$_3$O$_4$ (J. Zarpello, 2007).

CONCLUSIONS

In the report, the uses of the characterization tools have been explored extensively. The reaction parameters have been varied so as to investigate the effects of individual parameters on the final product – the morphology and the uniformity of the produced nanostructures. The results seem to suggest that NaOH does have a significant effect on the morphology of the sample. The use of TOP and linoleic acid, in place of oleic acid, will found improve the dispersivity of the nanocrystals.
REFERENCES


