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Hydrolysis and amine-capping in a glycol solvent as a route to soluble maghemite γ-Fe_2O_3 nanoparticles

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The preparation of capped metal oxide nanoparticles through the hydrolysis of metal salts is made arduous by the difficulty of dissolving long organic chain capping agents in water; by performing the reaction in propylene glycol under reflux, instead of water, we are able to hydrolyse $FeCl_3$ in the presence of *n*-octylamine to obtain (repeatedly) soluble, monodisperse ~5 nm γ-Fe_2O_3 particles that display a tendency to aggregate into superlattices.

There are a number of reasons for the resurgence of interest in nanoparticles of inorganic solids. On the one hand, new and powerful tools, both theoretical and experimental, have become available that permit an understanding of these fascinating materials. On the other hand, recent and novel applications such as luminescent probes,[1] and in high density magnetic storage devices[2] are being found. Perhaps most important is the finding that these materials, particularly when capped, behave almost like molecules in terms of their solubility,[3,4] and the manner in which they can be crystallized into superlattices.[4,5] In addition, there is the possibility of covalently modifying nanoparticle surfaces, in very much the same manner as one might a molecule.[6]

Noble metal salts are easily reduced in organic solvents in the presence of surfactants or capping agents using what has now become a standard method.[3] Capped noble metal nanoparticles can be dissolved and reprecipitated repeatedly, yielding a convenient method for size selection. In a similar vein, capped nanoparticles of semiconductor chalcogenides,[7] can be size-selected[8] to an extent that yields crystalline superlattices.[9]

The situation is different with transition metal oxides. Despite their exhibiting the widest spectrum of properties of any single class of materials,[10] the number of techniques available for preparing them as capped nanoparticles are few. Early transition metals such as Ti form alkoxides that can be decomposed (neat as well as in organic solvents) to the oxide under suitable conditions to yield capped nanoparticles.[11,12] There is an early report of soluble iron oxide particles forming superlattices.[13] Certain carbonyls can be decomposed in organic media to yield soluble oxide nanoparticles.[14] Surfactant-as-reactant approaches to oxide (and other) nanoparticles have been pursued by Pileni.[15] Recently, a very general route to metal oxide nanoparticles was reported by Alivisatos and coworkers,[16] involving the decomposition of metal cupferron complexes in an amine solvent. This route has now been extended to the use of solvothermal conditions to perform the decomposition.[17] The aggregation of nanoparticles prepared by the cupferron route has been studied.[18] While these amine-capped nanoparticles are initially soluble, it is quite difficult to redissolve them following precipitation using a non-polar solvent.

In general, routes to transition metal oxide nanoparticles, and in particular, magnetic oxides of transition metals such as iron, involve hydrolysis in water. The problem associated with hydrolysis, is that it is nearly impossible to dissolve a suitable surfactant in water, so that the nanoparticles obtained are difficult to cap and to take into an organic phase. In this communication, we present two advances that we feel could be important. The first is that we demonstrate that hydrolysis in the presence of a capping agent can be performed by using a glycol (1,2-propanediol) under reflux. The capping agent is *n*-octylamine. The second is the finding that the nanoparticles so formed are soluble in a non-polar solvent from which they can be precipitated by using a polar non-solvent such as 2-propanol. Crucially, this dissolution/reprecipitation can be carried out many times, permitting for example, size-selective precipitation.[8] The solvent is toluene, taken with a few weight percent of the capping agent. Redissolution does not seem to be possible without the addition of small amounts of *n*-octylamine, the capping agent. This suggests that the capping agent is not very strongly bound to the nanoparticle surface.†

The upper panel of Fig. 1 displays a TEM image of an aggregate of the γ-Fe_2O_3 nanoparticles. The tendency to form a close packed lattice is clearly seen. A histogram of the particle

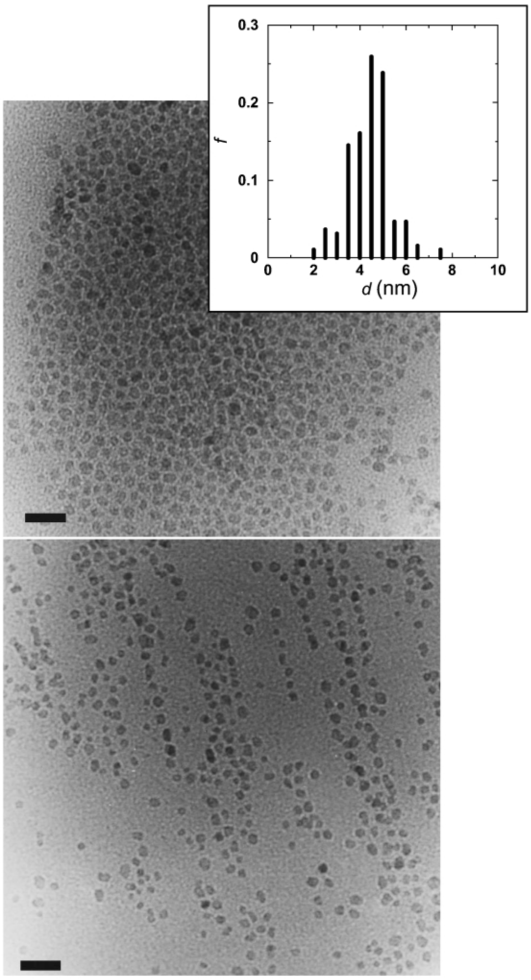

Fig. 1 TEM images of a closed-packed aggregate of γ-Fe_2O_3 nanoparticles (upper panel) and of a more dilute region showing aligned arrays (lower). The bars correspond to 20 nm. The inset is a histogram of the particle sizes.

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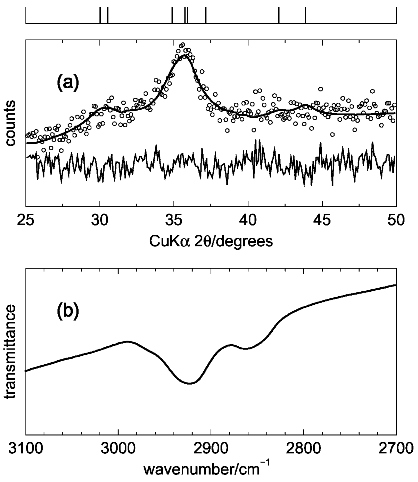

Fig. 2 (a) Rietveld refined X-ray diffraction profile of the γ-Fe_2O_3 nanoparticles. The data are shown as points and the fit and difference as solid lines. The vertical lines at the top indicate expected peak positions. (b) FT-IR spectrum of the nanoparticles in the C–H stretch region.

sizes is shown as an inset. The mean diameter of the particles is found to be 4.4 nm with a standard deviation of 0.9 nm. In the lower panel in this figure is an image of a more dilute region where the particles lined up with the Earth's magnetic field before all the solvent had evaporated and thereby immobilized the particles. This alignment of the magnetic nanoparticles is reminiscent of what is seen in magnetotactic bacteria, the frontal region of the sockeye salmon, and other living systems that use aligned nanomagnets for navigation.[19]

Fig. 2(a) is the Rietveld fitted X-ray diffraction pattern of the nanoparticles, with vertical lines at the top of the figure indicating expected peak positions. The xnd Rietveld program[20] was employed, and cell parameters, scale and profile factors were refined starting from the orthorhombic structure of maghemite γ-Fe_2O_3.[21] Extraction of peak intensities from the Rietveld fit yielded a Scherrer broadening corresponding to 4.5 nm particles. The agreement of particle size from X-ray line broadening and TEM suggests that the nanoparticles are nearly single-crystalline.

Fig. 2(b) shows the FT-IR spectrum of the nanoparticles in the C–H stretch region. The symmetric and asymmetric C–H stretch from the CH_2 groups on the chain are observed at 2921 and 2824 cm^{-1}. These positions suggest that the chains are in largely all-*trans* conformation,[22] *i.e.* sticking out radially from the surfaces of the nanoparticles. Capping is also verified from thermogravimetry in air which shows 8% weight loss starting at 373 K corresponding to physisorbed organics and a further 11% weight loss starting at 473 K corresponding to chemisorbed *n*-octylamine.

In conclusion, we present a simple, one-pot route to capped, soluble, γ-Fe_2O_3 nanoparticles from hydrolysis of an Fe^{III} salt in propylene glycol in the presence of a capping agent. The route is very general and should easily lend itself to the preparation of a host of capped oxide spinel nanoparticles.

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Notes and references

† γ-Fe_2O_3 nanoparticles were prepared under reflux in 50 cm^3 of 1,2-propanediol, starting with 4.0 g (0.015 moles) of $FeCl_3{\cdot}6H_2O$, 3.7 g (0.045 mol) of sodium acetate as the hydrolysing agent, 3 cm^3 of water and 5.5 cm^3 of the capping agent *n*-octylamine. Reflux was carried out in a 250 cm^3 round-bottomed flask that was fitted with a water condenser held at 283 K. After refluxing for 5 h, the material was precipitated with the help of a permanent magnet and the addition of a large volume (~ threefold excess) of 2-propanol. The use of 1,2-propanediol closely follows the procedure of Ammar *et al.*[23] to make $CoFe_2O_4$ nanoparticles. These authors also explain how the total water content (water of crystallization and added water) is calculated so that complete hydrolysis of the metal salt takes place. A small excess of water does not seem to affect the product. There is the possibility that the glycol 'buffers' the free water through hydrogen bonding. After washing with 2-propanol, solid material was collected by centrifugation. The material was washed with ether to remove excess amine and glycol and then dried in air at 50 °C to obtain the crude product. Prior to all measurements, about 1 g of the crude product was redissolved in 50 cm^3 of toluene to which 1 cm^3 of *n*-octylamine had been added. Most of the crude product went into solution within 12 h. From this solution, material could be reprecipitated with 2-propanol and it was this reprecipitated material that was subject to study. XRD studies of the crude product indicate the presence of an insoluble γ-Fe_2O_3 component with a larger particle size.

For microscopy, toluene (with some *n*-octylamine) solutions of the once-reprecipitated samples were evaporated on to carbon-coated Cu grid and examined using a Jeol 3010 FE-TEM with an accelerating voltage of 300 kV. Powders were subject to X-ray diffraction (Siemens D5005, Cu-Kα, 0.5° min^{-1}, 0.1° rebinning) and FT-IR (KBr pellets, Perkin-Elmer FTIR Spectrum 1000).

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