Solvothermal routes to capped oxide and chalcogenide nanoparticles*

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Abstract: We review our recent contributions to the use of solvothermal methods for the preparation of different oxide and chalcogenide nanoparticles. We have prepared sub 10-nm γ-Fe_2O_3, $ZnFe_2O_4$, and $CoFe_2O_4$ particles by the decomposition of the corresponding cupferron complexes in the presence of *n*-octylamine or *n*-dodecylamine in solvothermal toluene. Similarly, dodecanethiol-capped chalcogenide nanoparticles of CdSe have been prepared by reacting cadmium stearates with H_2Se under solvothermal conditions. The H_2Se is generated in situ by the reduction of Se by tetralin. Using this latter technique, we have also been able to prepare PbSe and PbI_2 in toluene under solvothermal conditions, albeit in bulk (rather than nanocrystalline) form. In the preparation of PbI_2, HI is prepared by the in situ reduction of I_2 by tetralin.

INTRODUCTION

There is a great deal of interest in the synthesis of transition-metal oxide nanoparticles because of their potential applications in catalysis [1], high-performance ceramics [2], magnetic storage [3], solar energy conversion [4], and ferrofluids [5]. Superparamagnetic transition-metal oxide nanoparticles, usually comprising a single magnetic domain, are particularly interesting in their many biomedical applications, which include magnetic cell sorting [6], drug targeting experiments, and gene transfection [7], and in hyperthermic cancer therapy [8].

By the same token, the optical properties of semiconductor chalcogenide nanoparticles are also a fascinating area of study [9], with rapidly emerging applications as luminescent probes in biology [10], and in polymer-quantum dot light-emitting diode (LED) devices [11], to name a few.

In both classes of materials, viz. oxide and chalcogenide nanoparticles, the size of the particles has direct bearing on their properties. In preparative techniques, therefore, the ability to control size is crucial. A few rules of thumb come into play in the preparation of nanoparticles. The first is to avoid excessively high temperatures because these would lead to sintering. The second is to cap particles at the desired size to prevent further growth and to provide stability through the coordinative saturation of dangling bonds on the particle surface. In addition, the separation of the nucleation and growth in the preparation is advisable as this results in narrower size distributions.

The use of a suitable capping agent such as a long-chain amine, a long-chain thiol, trioctylphosphine oxide (TOPO), etc. has the added advantage that these can make the particles soluble in different solvents. Solubility enables size-selective separation and the formation of superlattice assemblies [12].

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The direct oxidation of metals is usually exothermic and results in sintering. As a result, it is usually contraindicated for the preparation of oxides in nanoparticulate form. While many oxide materials can be prepared by hydrolysis in aqueous solution, it is difficult to incorporate a long-chain organic capping agent under these conditions. The many routes for preparation of oxide nanoparticles that have emerged recently are sensitive to these issues. Chemseddine and Moritz [13] have demonstrated the synthesis of monodisperse anatase TiO_2 (anatase) nanoparticles of different sizes and crystal habits, by decomposing titanium alkoxides. Colvin and coworkers [14] have prepared soluble TOPO-capped anatase TiO_2 nanoparticles, using the metathetic reaction between titanium alkoxide and titanium halide. Another interesting nonhydrolytic single precursor approach involves decomposition of metal cupferron complexes to the corresponding metal oxide in trioctylamine at 550 K [15]. Cupferron is N-nitroso N-phenyl hydroxylamine, and it can be complexed with a number of transition-metal ions, making this an important general route to oxide nanoparticles.

In the same vein, many synthetic approaches are available for the preparation of transition-metal chalcogenide nanoparticles. Bawendi and coworkers [16] have demonstrated the preparation of monodisperse CdE (E = S, Se, Te) nanoparticles of different sizes using organometallic precursors and TOPO as solvent and capping agent. Green and O'Brien have reviewed the use of single source precursor to prepare quantum dot nanoparticles [17]. The use of ethylene diamine as a solvent is an effective route to several binary and ternary chalcogenides of different sizes, ranging from the submicron to the nano [18].

Despite this seeming abundance of methods for the preparation of nanoparticles, the challenge remains for the synthetic chemist to develop new techniques that are environment friendly and economically viable. One of the common features of the many synthetic techniques is the use of expensive and often toxic solvents such as TOPO or trioctylamine. It has occurred to us that ideally one should be able to use a simple and inexpensive solvent such as toluene. The limitation with toluene is that it is low-boiling, and cannot be used under reflux for the preparation of crystalline particles as the temperature would be too low. We overcome this problem of the low boiling point of toluene by using it in a sealed autoclave (bomb) under the autogenous pressure developed on heating. By this simple method, we are able to work with toluene as the solvent at temperatures as high as 573 K. This provides a very appropriate alternative to solvents such as TOPO. In this article, we review our recent solvothermal synthesis of amine-capped transition-metal oxide nanoparticles using cupferron complexes as precursors. We have been able to replace the expensive and toxic amine solvent used by Alivisatos and coworkers [15] by toluene. The preparation of capped sub-10 nm γ-Fe_2O_3 and $CoFe_2O_4$ particles by solvothermal methods, and their magnetic study has been reported by us previously [19].

Soluble 3-nm thiol-capped CdSe nanoparticles have been prepared from cadmium stearate under similar solvothermal conditions. This work has been reported by us elsewhere [20]. The use of stearates instead of toxic and flammable organometallic precursors is worthy of note.

We also report for the first time, the solvothermal preparation of lead selenide PbSe and lead iodide PbI_2 phases, prepared from the stearates in toluene, with H_2Se or HI being generated in situ by the reduction of Se or I_2 by tetralin. In this, we follow some old work by Mitchell and Morgan [21] involving the preparation of binary chalcogenides in hot nujol using the aromatization of sitosterol by Se to generate H_2Se in situ.

OXIDE NANOPARTICLES

The preparation of amine-capped γ-Fe_2O_3, $CoFe_2O_4$, and $ZnFe_2O_4$ was achieved by the solvothermal decomposition of the corresponding metal cupferron complexes in the presence of n-octylamine (or n-dodecylamine) at elevated temperature in a teflon gasketted SS316 stainless steel autoclave. Toluene was used as solvent with 70 % filling. $ZnFe_2O_4$ nanoparticles could, for example, be prepared by taking 0.6 g (1.8 mmol) of Zn-cupferron complex, 1.7 g (3.6 mmol) Fe-cupferron complex, and 6.1 cm^3 of dodecylamine in 48 cm^3 of toluene. The autoclave was placed in an air oven that was

heated to 503 K. The reaction was carried out for 1 h, after which the autoclave was removed and allowed to cool to the room temperature. The resulting solution was brown and viscous with some suspended particles, which could be precipitated by increasing the solvent polarity (adding a polar solvent such as 2-propanol). The collection could be facilitated by placing the material taken in a beaker on a magnet. The particles were washed with 2-propanol and diethyl ether. The other oxide nanoparticles were prepared in a similar fashion.

Figure 1 displays a transmission electron micrograph of *n*-dodecylamine-capped $ZnFe_2O_4$ nanoparticles prepared by solvothermal decomposition of metal cupferron complexes. The mean diameter of the nanoparticles is 7.4 nm with a standard deviation of 0.9 nm. This is in keeping with the Scherrer broadening of the powder X-ray diffraction (XRD) patterns. The correspondence in the particle sizes obtained from the two techniques suggests that the nanoparticles are nearly single-crystalline. Rietveld refinements were performed on the powder XRD patterns using the cubic spinel structure as a model. The Rietveld fits confirm the assignment of crystal structure. The refined cell parameter was $a = 8.50(1)$ Å. The stoichiometry of the spinel oxide could also be established by X-ray photoelectron spectroscopy and energy-dispersive analysis of X-rays (SEM/EDAX). The presence of capping agent could confirmed by using Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis in air.

Transition-metal oxide nanoparticles are often magnetic, being derived from bulk ferrimagnetic spinels (in the case of $CoFe_2O_4$ or $ZnFe_2O_4$). Because of their small size, they usually cannot support more than a single magnetic domain and hence display the phenomenon of superparamagnetism. One of the characteristics of a superparamagnet is that the magnetization (apart from showing no hysteresis) shows a scaling behavior. In the superparamagnetic regime, plots of *M* vs. *H/T* collapse on to a single trace. Figure 2 displays this for 7-nm $CoFe_2O_4$ nanoparticles. In the upper panel (a) are traces of the magnetization as a function of the scaled field (*H/T*) at temperatures of 150, 200, 250, and 300 K. These correspond to a superparamagnetic regime, and the traces are collapsed. In the lower panel (b), *M* vs. *H/T* is displayed at the temperatures of 100 and 50 K. This is now the blocked regime (where domains have made an appearance), and the traces display hysteresis.
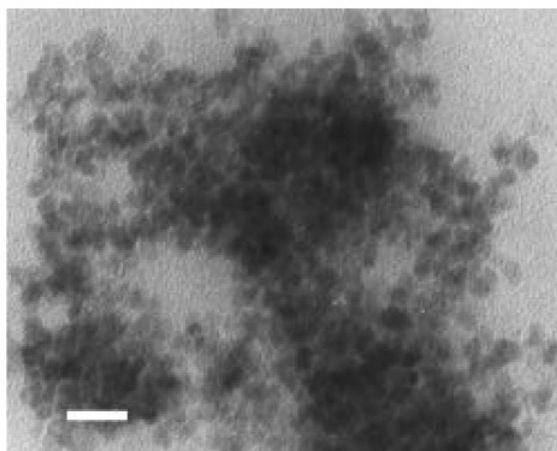

Fig. 1 TEM image of *n*-dodecylamine-capped 7-nm Zn Fe$_2$O$_4$ nanoparticles. The bar corresponds to 20 nm.
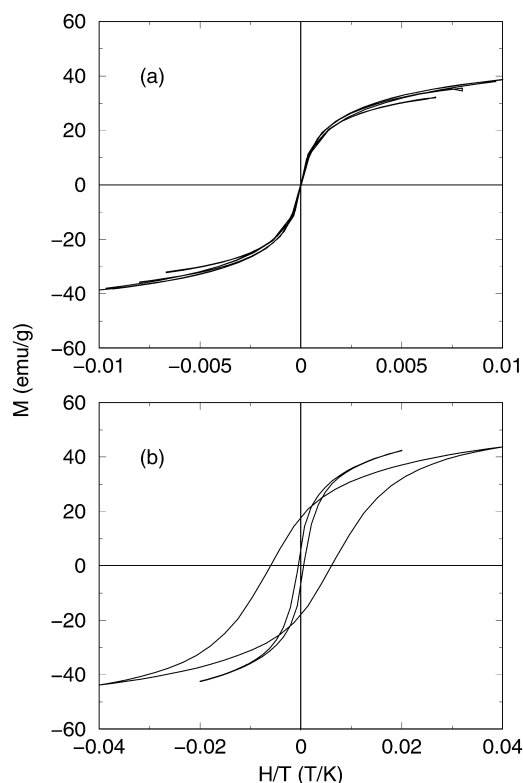
Fig. 2 (a) *M* vs. *H/T* in the superparamagnetic regime for 7-nm $CoFe_2O_4$ nanoparticles. The temperatures at which the data were acquired were 150, 200, 250, and 300 K. (b) *M* vs. *H/T* in the blocked regime at the temperatures 50 and 100 K.

CHALCOGENIDES AND HALIDES

For the synthesis of chalcogenide phases, the starting materials of choice were the metal stearates. These are soluble in hot toluene, and in comparison with other metal sources (such as dimethyl cadmium) are inexpensive and relatively safe. In a typical preparation of metal chalcogenide or halide, the metal stearate is taken in toluene with selenium or iodine and a small amount of tetralin. This is sealed in a stainless steel autoclave and then placed in a preheated air oven held at the required temperature. After the reaction is over, the autoclave is taken out and allowed to cool to room temperature, following which the product is collected.

Cadmium stearate was prepared by reacting $Cd(OH)_2$ with molten stearic acid at 363 K. The product was recrystallized from toluene. For the preparation of CdSe nanoparticles, 1.36 g (2 mmol) of $[Cd(St)_2]$, 0.158 g of selenium (2 mmol), 0.2 g of tetralin (1.5 mmol), and 0.1 g (0.5 mmol) of dodecanethiol as capping agent was taken in 50 cm^3 of toluene (which is 70 % filling in the autoclave). The autoclave was then placed in an oven preheated to 523 K where it was held for 5 h. The dark red solution obtained from the reaction precipitated CdSe nanoparticles when the solvent polarity was increased by adding the polar nonsolvent 2-propanol. Lead stearate was prepared by adding hot aqueous solution of the metal salt to hot sodium stearate solution (prepared from stearic acid and sodium hydroxide solution). Lead stearate was immediately precipitated. After washing with copious quantities of hot water and, subsequently, with ether to remove excess stearic acid, it was characterized by XRD and IR spectroscopy.
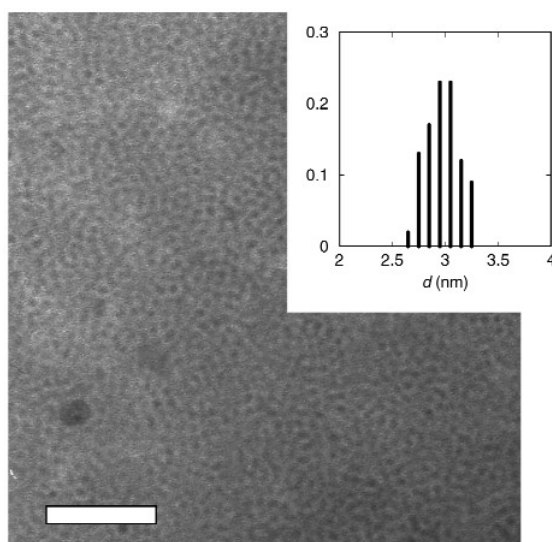
Fig. 3 TEM image of 3-nm CdSe nanoparticles showing a tendency to close packing in the plane. The bar corresponds to 50 nm. The inset is a histogram of particle size. Reproduced from ref. [20] with permission from the Royal Society of Chemistry.

Figure 3 shows the transmission electron microscopy (TEM) image of the CdSe nanoparticles. The inset is a histogram of the particle sizes. The mean diameter of the particles was found to be 3.0 nm with a standard deviation of 0.2 nm, which is about 6 % of the mean. Powder XRD patterns indicate that the nanoparticles are crystallized in the cubic zinc blend structure rather than the usual hexagonal wurtzite structure. Rietveld refinement yields an *a* lattice parameter of 6.01(1) Å. The cubic structure is further supported by simulating the powder XRD pattern using the DIFFaX program [22], which allows hcp and fcc stackings of 3×3 nm of CdSe to be considered. Optical properties of the CdSe nanoparticles are consistent with what would be expected of particles in this size range. FTIR spectra as well as thermogravimetric analysis in air confirm the presence of capping agents. In the EDX analysis, the Cd:Se atomic ratio was found to be 1:1, while that for S:Se:Cd was found to be 1:2:2 (within a 5 % error).

PbSe prepared solvothermally as indicated above results in rather crystalline particles with sizes in the sub-1 μm range, rather than the nanometer range. Figure 4a displays the powder XRD pattern of these particles. The vertical lines are the expected peak positions for the cubic NaCl structure of PbSe. PbI_2 is a layered compound, and the solvothermal preparation results in some turbostratic disorder, evidence for which are the sawtooth profiles observed for some of the reflections in the powder XRD pattern in Fig. 4b. This phase cannot be described as nano either. Both for PbSe and PbI_2, it was not possible to control the growth of the particles through the use of capping agents.
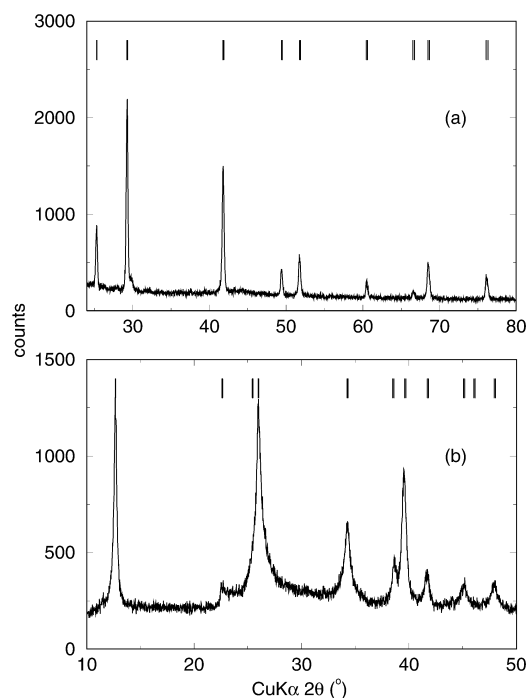
Fig. 4 Powder XRD patterns of solvothermally prepared (a) PbSe and (b) PbI$_2$. The vertical lines within the plots are the expected peak positions for these phases.

CONCLUSION

We have developed novel solvothermal synthetic routes to nanoparticles, which possess the qualities of being environment friendly and inexpensive. In addition, the reactions involve simple precursors. Since the reactants are sealed, an inert atmosphere is not needed, and, at the same time, the risk of exposure to hazardous chemicals is reduced. All these contribute to making the schemes outlined here amenable to scale-up, to prepare large quantities of capped nanoparticles. The schemes also lend themselves to making a variety of materials. For a single material, particles of different sizes can perhaps be obtained. For this, the parameter space of suitable conditions needs to be explored.

ACKNOWLEDGMENTS

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