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A low temperature synthesis of ZnS nanorods

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The effects of the reaction conditions on the preparation of zinc sulfide nanorods from zinc acetate and elemental sulfur in hexadecylamine and octylamine have been studied. The results show a relationship between the reaction temperature and both the morphology and the phase of the final product.

1. Introduction

Control of nanomaterials morphology is paramount in defining their final properties. One challenge in the preparation of anisotropic nanomaterials is producing materials with a narrow size distribution and good redisperseability. Methods for the preparation of CdS, CdSe and CdTe nanorods are now well established [1, 2]. However, there are relatively few examples of the preparation of zinc chalcogenides as anisotropic nanomaterials.

ZnS is an important material for photonics. It has potential uses in a variety of applications including: electroluminescent devices, optical coatings, transistors, transducers and solar cells [3–6]. One-dimensional (1D) nanostructures of ZnS are particularly attractive because they are potential candidates for electronic and optoelectronic nanodevices [7, 8]. ZnS nanoparticles have been reported in the literature [9, 10] and in recent years, progress has been made in the preparation of 1D ZnS nanomaterials such as wires [11–13], rods [14, 15], tubes [16, 17], nanosaws [18] and nanobelts [19] through a wide range of techniques. These include liquid crystal templates [16], an evaporation technique [20], annealing in NaCl flux [21] and micelle methods [22].

Here we report the low-temperature (140°C) growth of ZnS nanorods in a mixture of hexadecylamine and octylamine.

2. Experimental

In a typical procedure 100 g HDA was degassed at 120°C for 1 hr, and then heated under nitrogen to 140°C or 180°C. Two separate dropping funnels containing solutions of sulfur (1 g, 0.32 mol) in octylamine (30 ml) and zinc acetate dihydrate (3.18 g,

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0.32 mol) in octylamine (30 ml) were used to control the addition of the precursors. 1 ml of the zinc stock solution was added followed by 1 ml of the sulfur stock solution under vigorous stirring and the mixture was kept at 140°C for 30 mins. The rest of the stock solutions were then added simultaneously at the same temperature over a period of 20 mins. After complete addition the solution was stirred for a further 2 hrs. Then the solution was cooled to 80°C and the ZnS nanorods were precipitated by the addition of excess ethanol and washed three times with acetone to remove unreacted residuals.

Characterization: X-ray powder diffraction studies were conducted on a Bruker D8 AXS diffractometer using monochromated Cu-K_α radiation. TEM analyses were carried out on a Philips CM200, 200KV DX4EDS. Samples were dissolved in toluene and filtered and a drop of the nanorod solution was then placed on a TEM grid and allowed to dry.

3. Results and discussions

A sequential addition method was employed in which separate solutions of the reagents are slowly added to an initial reaction mixture containing a small amount of the starting materials. Experiments were conducted at two temperatures and in each case the product was isolated as an off-white powder that could readily be dispersed in organic solvents.

The phase of the material (figure 1) prepared depended on the reaction temperature. Powder XRD of the materials prepared at low temperatures (140°C) showed the zinc

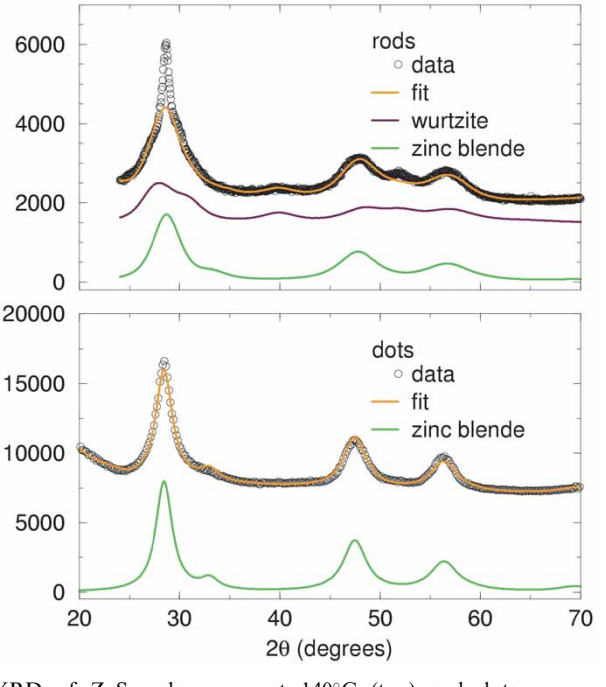

Figure 1. Powder-XRD of ZnS rods grown at 140°C (top) and dots grown at 180°C (bottom). Fitted wurtzite and zinc blende fits are also shown.

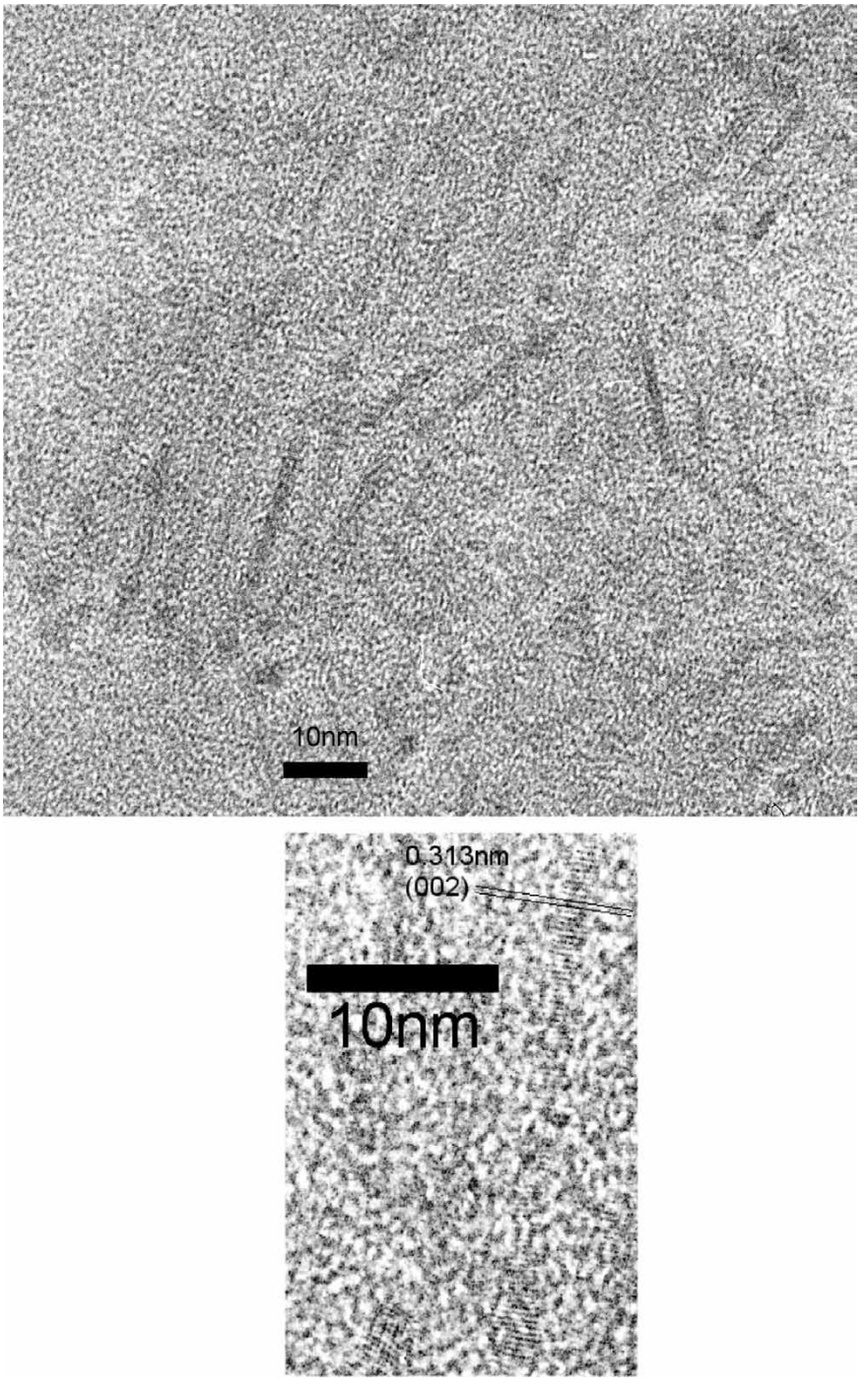

Figure 2. TEM image of ZnS nanorods grown at 140°C (top) and HRTEM of a single ZnS nanorod (bottom).

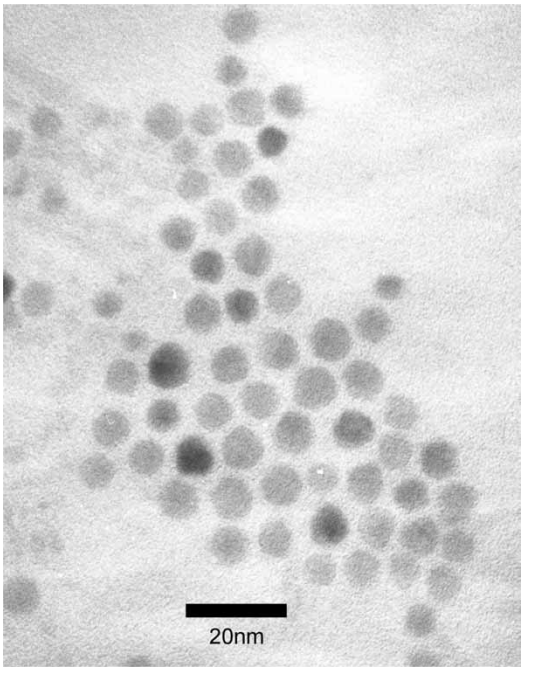

Figure 3. TEM image of ZnS dots grown at 180°C.

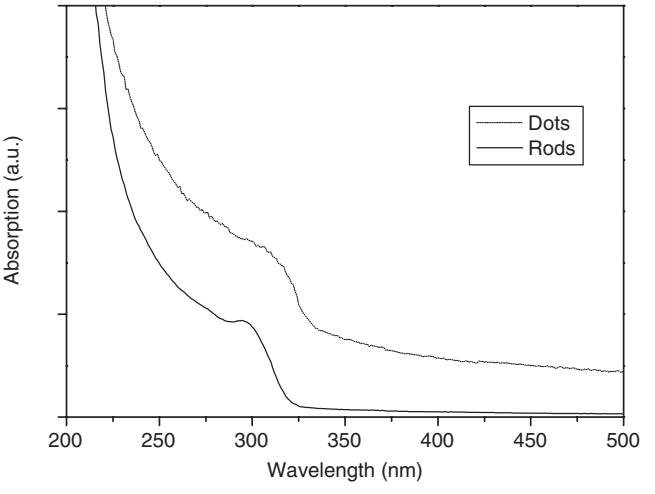

Figure 4. UV–Vis spectra of ZnS nanorods grown at 140°C (solid line) and ZnS dots grown at 180°C (dashed line).

sulfide to be a mixture of wurtzite and zinc blende, whereas at the high temperature (180°C) it was found that the cubic phase, or possibly polytypical material, dominated. The cubic and hexagonal systems have quite similar XRD pattens, especially for the nanodispersed forms. However, the presence of a peak at 38° and the absence of a peak

at 53° strongly suggests the cubic assignment to be correct. The data were subjected to a Reitveld refinement in order to assess the phase composition of the materials. It was found that the rods were consistent with a mixture of a hexagonal and a cubic phase, the missmatch in the fit being attributed to either a large number of cubic dislocations or orientation of the rods in the powder holder. The particles were found to consist of a pure cubic phase. The most stable form of zinc sulfide is the cubic (zinc blende) phase; it is therefore no surprising that the cubic phase is dominant at the higher temperatures. However, previous studies of bulk zinc sulfide have shown that the phase of the material is particularly dependent on the reaction conditions, with the hexagonal phase being dominant at temperatures much lower than would be expected from a purely thermodynamic approach [23]. Furthermore, recent work with cadmium sulfide has shown similarly that a change in the phase of nanomaterials can depend on the reaction rate even when a similar synthetic method is employed [24].

TEM images of the ZnS nanorods grown at 140°C show the formation of straight nanorods (figure 2). The average diameter of the rods is 1.9 ± 0.2 nm and they are 23 ± 3 nm in length, giving an average aspect ratio of aproximately 1:13. A high-resolution TEM image of a single nanorod is given in figure 2 (bottom) and confirms the crystallinity by indicating well-resolved {002} lattice planes. The experimental lattice spacing, 0.31 nm, is consistent with the 0.311 nm spacing expected from X-ray diffraction data. The morphology of the zinc sulfide grown at 180°C is close to spherical (figure 3). The average diameters of the dots are 7.5 ± 1 nm.

The UV–Vis spectra of the nanorods grown at 140°C (solid line) and nanodots grown at 180°C (dotted line) are shown in figure 4. The nanorod UV–Vis spectra show the band edge onset at 300 nm. In contrast, the dots have a near bulk band edge at 320 nm. Irradiation at 250–300 nm in hexane did not give any noticable photoluminescence which could be attributed to ZnS.

This new route may open the way to the creation of other nanostructures (e.g. tetrapods, etc.) and avoid the use of high temperatures generally used for the cubic–hexagonal phase transformation. Currently, studies are being carried out to investigate the systematic control of the nanorod aspect ratio.

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