Synthesis and Characterization of Pyramidal CdSe Nanoparticles

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We synthesized pyramidal CdSe nanoparticles by using $CdCl_2$ as the cadmium precursor. TEM and HRTEM image showed that the nanoparticles are aggregations of many small nanocrystals.

During the past decade, there has been considerable interest in semiconductors of nanometer dimensions.[1] Especially, controlling the shape of II-VI semiconductor crystals remains an important goal of modern materials engineering, with most of the investigations on CdS or CdSe nanocrystals. One means of achieving shape control is colloidal self-assembly. Another is by the use of static template to enhance the growth rate of one crystallographic face over another, just like the growth of InAs on GaAs[2] and Ge on Si.[3] Recently, there are many demonstrated cases of nanocrystals which have interesting shape. Pileni's group synthesized flat triangular CdS nanocrystals using reverse micelles method.[4] Alivisatos' group yielded rod-, arrow-, teardrop-, tetrapod-shaped CdSe.[5] And new mechanisms for the formation of complex nanostructures, called "oriented attachment" and "contact epitaxy",[6] have been proposed. But the pyramidal particles were obtained most in III-V semiconductor using molecular beam epitaxy. Here we demonstrate that pyramidal shape CdSe nanoparticles were fabricated in colloid solution.

Since Murray et al. reported the synthesis of high quality cadmium chalcogenides nanocrystals using dimethyl cadmium as the cadmium precursor,[7] the synthesis of CdSe nanocrystals using this precursor has been well developed.[5,7] But because of the disadvantage of $Cd(CH_3)_2$, some other alternative precursor were used,[8] for example, Peng et al. used CdO as the cadmium precursor. Here we used $CdCl_2$ as the cadmium precursor. All the following procedures were carried out under the protection of Ar. 0.8 g sample of Se powder (99.95%) was dissolved in 30 g of tributylphosphine (TBP), after which 7.9 g cadmium chloride was added. The mixture was ultrasonicated for twenty minutes. 12 g of 99% tri-n-octylphosphine (TOPO, Merck) was heated to 200 °C for 30 min. Then the mixture was injected intermittently. The reaction flask was heated gradually until the temperature reached 240–250 °C. Keeping the temperature for a period of time, the reaction solution was removed from the heat and allowed to cool. Addition of anhydrous methanol to the solution resulted in the reversible flocculation of the nanocrystals. The flocculation was separated from the supernatant by centrifugation. The flocculation was redispersed in anhydrous toluene, flocculated by adding anhydrous methanol, and centrifuged again. This procedure was repeated several times.

The transmission electron microscopy (TEM)[9] micrograph (Figure 1) showes that most of the particles are characterized by an angular shape, with each side of equal size, approximately 70 nm. From the high-resolution transmission electron microscopy (HRTEM) micrograph (Figure 2), it is seen that the nanoparticle shows many lattice directions, which means the CdSe nanoparticle is not a large single crystal, but composed of small nanocrystals. The size of the nanocrystal is about 8–9 nm. It is also seen the edge is thinner than the inside, indicating the CdSe nanoparticle is not of flat triangular shape. So we presume the nanoparticles are pyramidal shape. Atomic force microscopy (AFM) was employed to investigate the real shape of the CdSe nanoparticle. Figure 3 shows that the nanoparticle is indeed of pyramidal shape (some typical pyramidal nanoparticles pointed by the arrowhead), which is consistent with the conjecture. Considering each face is formed under the same condition, it is concluded that the nanoparticle is just like the simulation of pyramidal shape particle (Figure 2). Calculated from formula,[9] the height of the pyramidal nanoparticle is about 57 nm.

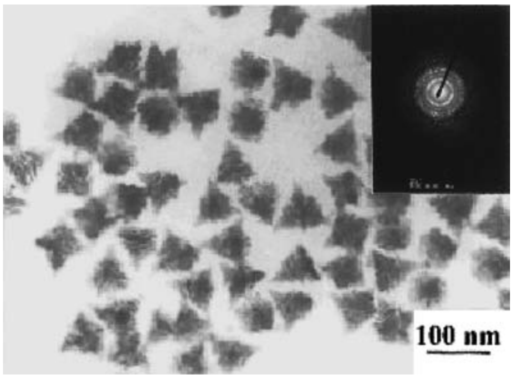

Figure 1. TEM micrograph and electron diffraction pattern of as-synthesized CdSe nanoparticles.

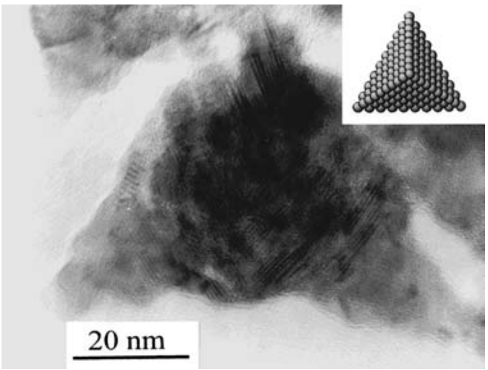

Figure 2. HRTEM micrograph of an as-synthesized CdSe nanoparticles and simulation of a pyramid shape particle.

To investigate the composition of the nanoparticles, energy dispersive spectrometry (EDS) measurement was performed. In

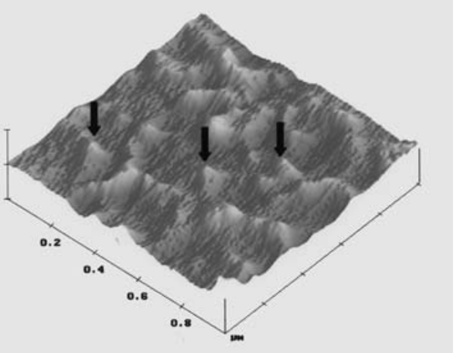

Figure 3. AFM micrograph of as-synthesized CdSe nanoparticles (some typical pyramidal CdSe nanoparticles pointed by arrows).

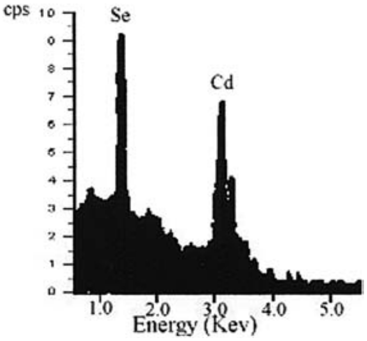

Figure 4. EDS of as-synthesized CdSe nanoparticle.

the EDS spectrum (Figure 4) of the as-synthesized nanoparticles, cadmium and selenium peaks were found. The atomic ratio of Cd and Se is close to 1 : 1, indicating that the pyramid nanoparticles consist of CdSe.

The electron diffraction pattern (Figure 1) shows many diffraction rings. The calculated '*d*' value of the nanoparticles from the electron diffraction ring,[4,10] namely, 3.72, 2.57, 1.98, could be ascribed to the reported hexagonal CdSe corresponding to planes (100), (102), (103). While the third line '*d*' value of 2.13 corresponds to cubic CdSe. It is concluded that the nanoparticles are characterized by a hexagonal structure (wurtzite). However, the presence of a small quantity of cubic (zinc blende) nanoparticles cannot be excluded.

According to the confinement properties of quantum dots, blue shift can be observed in the absorption spectrum,[11] if the particle size is smaller than the bulk Bohr exciton (11.2 nm for CdSe[12]). Thus the absorption spectrum was measured in this study. The absorption spectrum was obtained using an ultraviolet-visible absorption (UV-vis) diode array spectrometer. To offset the diffraction factor, integration ball was used. The onset of the absorption curve is 712 nm, which is the same as that for the bulk CdSe. It means that the size of the nanoparticle is too large for quantum confinement, and beyond the bulk Bohr exciton. And the curve of the nanoparticles is different from that of single nanocrystal CdSe (The single nanocrystals curve comes from the Murry et al.'s report[7]).

This communication demonstrated the formation of pyramidal nanoparticles by using thermal decomposition of precursors. The nanoparticles are composed of small nanocrystals. This is different from Pilein's work.[4] Their nanocrystal is of flat triangular shape, and is single crystal. But ours is pyramidal shape and is the aggregation of small nanocrystals. The discovery that aggregation of nanoparticles yields an ordered crystal is interesting. There are some reported cases,[13] for example, faced colloidal crystal CdSe was formed by slowly evaporating the solvent in a dispersion of CdSe quantum dots.[13] In our case, we think that "oriented attachment" of nanocrystals is not operative here, for it considers the chain connection of two particles, cannot explain why the layer becomes smaller, and forms the pyramidal shape. In the previous paper,[5] it was demonstrated that low monomer concentration results in the formation of a spherical particle shape, while high monomer concentration leads to anisotropic shape. And when the CdSe nanocrystal nucleates in the zinc blende structure instead of the wurtzite structure, a tetrapod is formed. As we have proved that the as-synthesised nanoparticles are characterized by wurtzite and zinc blende structures, we conume that the initial injection formed the small nanocrystals, which are of the zinc blende structure. As a next step, the monomer concentration increased with an additional injection. The particles connection occurred selectively. First formed the tetrapods, and then aggregated to pyramidal shape nanoparticles. But the real microscopic mechanism requires future study.

References and Notes

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