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Sonochemical Synthesis and Shape Change of Colloidal CdSe Nanocrystals by High-Intensity Ultrasound

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In this article, we have developed the synthesis of CdSe nanocrystals by the introduction of high-intensity ultrasound combined with an anionic surfactant (sodium dodecyl sulfate, SDS). We can control the shape of the nanocrystal by using surfactants. In addition, due to the cavitation effect created by the introduction of high-intensity ultrasound (120W, 40kHz) into the reaction system, a homogeneous environment with high temperature and high pressure was generated. Consequently, the structure of CdSe nanoparticles produced in the bottom of the flask was changed from zinc blende (cubic) to wurtzite (hexagonal) as a result of higher strength ultrasonic waves. The formation of wurzite phase favored the process of self-assembly for particular shapes. At medium concentrations of SDS (0.2M), one-dimensional CdSe nanorods with different aspect ratios were observed. When using low concentrations of surfactant (0.1M), two-dimensional square-like crystals were observed due to all growth crystal faces having roughly the same surface energy.

Keywords: nanocrystal, high-intensity ultrasound, cavitation effect, self-assembly, nanorod

1. Introduction

Due to the progress of nanotechnology in recent years, the particle size and shape of semiconductor materials can be tailored to prepare quantum dots with special optoelectronic properties for use in a variety of applications including biomedicals,[1] light emitting diodes,[2] lasers,[3] and photovoltaics.[4]

Many works on the synthesis of CdSe nanocrystals have been reported, including routes such as the single molecule precursor route, the solvothermal route, the sonochemical route, the microwave irradiation route, the organometallic precursor route. However, several reported studies used high toxicity, high reactivity dimethyl cadmium as the precursor and hazardous, expensive trioctylphosphine (TOP) or trioctylphosphine oxide (TOPO) as the coordinating solvent.

Herein, we have developed a cheaper and greener Non-TOP-Based route for the synthesis of CdSe nanocrystals by the introduction of high-intensity ultrasound combined with an anionic surfactant (sodium dodecyl sulfate,

SDS). It has been stated that high-strength ultrasonic waves can affect the crystal structure and morphology of nanoparticles.[5] On the other hand, the development of colloidal methods for the preparation of nanocrystals has opened interesting opportunities in nanoscience. When nanocrystal surface dynamically absorbs a layer of surfactants, the surfactant allows us to control the nanocrystal growth. Through this approach, the as-prepared particles can be arranged into hollow sphere, porous sphere, rod, and tube shapes, etc.[6]

2. Experimental :

Chemicals : Sodium dodecyl sulfate (SDS, 100 %, J. T. Baker), sodium sulfite (Na_2SO_3, 95.0 %, SHOWA), selenium powder (Se, 99.5 %, Panreac), and cadmium chloride hemi(pentahydrate) ($CdCl_2 \cdot 2.5\ H_2O$, 79.5 % ~ 81.0 %, Panreac) were used without further purification.

Preparation of sodium selenosulfate (Na_2SeSO_3) : A solution of selenium (0.2368 g, 0.4 M) and sodium sulfite (1.5126 g, 1.2 M) dissolved in 10 ml deionic water was heated at 95℃ for 1 h under vigorous stirring.

Synthesis of cadmium selenide (CdSe) nanoparticles : SDS (2.1628 g, 0.2 M) and $CdCl_2 \cdot 2.5H_2O$ (0.20475 g, 0.03 M) were dissolved in 30 ml deionic water in a 50 ml round-bottomed flask. The mixed solution was sonicated for 30 mins under high-intensity ultrasound (40 kHz, 120 W/cm^2). 3 ml of Na_2SeSO_3 aqueous solution was then quickly dropped into the flask. The solution was sonicated for 6 h at room temperature under a nitrogen atmosphere.

3. Results and Discussion :

An illustration for the as-prepared CdSe solution by the introduction of high-intensity ultrasound accompanied with the SDS surfactant is shown in Figure 1. As seen in the figure, three layers with different colors are observed by virtue of the intensity of the associated shock waves from ultrasound being varied with their irradiation radii.

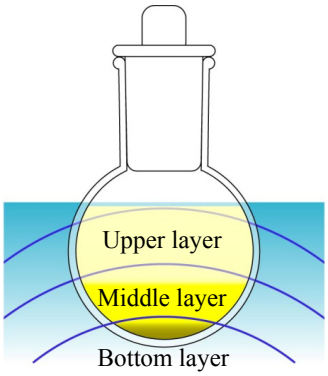

Figure (1) : An illustration for the effect of the instensity of ultrasound on the crystal structure of the reaction product.

Fluorescence spectroscopy analyses were taken to investigate the different characteristics of the three layers, as shown in Figure 2. It is apparent that the particles in the bottom part have two emission peaks compared to those of another two layers. Since it has been indicated that emission peaks of photoluminescence (PL) for CdSe nanocrystals are in relation to the particle size, shape, and crystal structure,[7] it is obvious that the particle composition in the bottom layer is different with that of other layer.

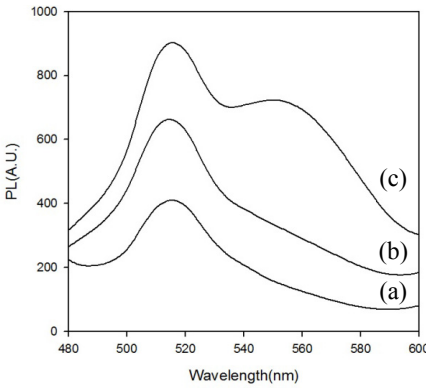

Figure (2) : PL spectra of (a) upper layer, (b) middle layer, and (c) bottom layer of the as-prepared solution.

Since it has been reported that zinc blende CdSe crystal could be obtained from the combination of low-intensity ultrasound (18 kHz, 6 W/cm^2) with the SDS surfactant,[8] the yield of wurtzite phase may be due to the phase transition of zinc blende resulting from the physical effects of high-intensity ultrasound.[9] In

our case, we used an ultrasound facility with intensity (40 kHz, 120 W/cm^2) higher than normal case to manipulate the sonochemical synthesis; therefore, a phase transition from zinc blende to wurtzite might occur.

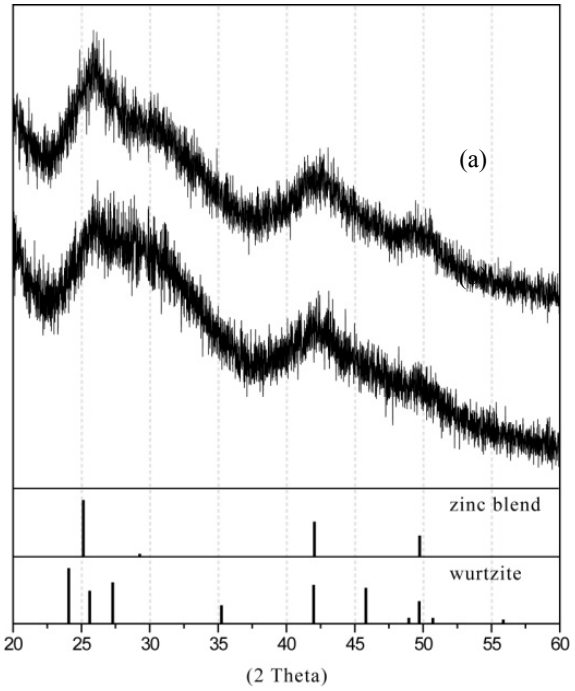

Figure (3) : XRD patterns of (a) upper or middle layer, and (b) bottom layer of the as-prepared sample.

XRD analysis for the as-prepared particles of the three layers further confirmed our postulation (Figure 3). Particles in the upper and middle layer exhibit the typical cubic zinc-blende crystal structure of CdSe, while those of the bottom layer display a little different pattern, more or less like the combination of zinc blende and wurtzite structure (hexagonal phase), on account of they being a mixture of particles with different crystal phases. In addition, the broad peaks of the XRD patterns indicate that most particles in each layer have poor crystallinity, which is an important characteristics of sonochemical synthesis.[10] Part of the particles in the bottom layer with the zinc blende phase might transfer to the wurtzite structure under the irradiation of extremely high intensity ultrasound. The high pressure and temperature arising from the acoustic cavitation rendered the occurrence of the phase transition, resulting in a mixture of particles with zinc blende or wurtzite phase.[11]

TEM examination for the particles in bottom layer indicates that CdSe nanorods were formed in the as-prepared sample (Figure 4). Moreover, it can be seen that both nanorods are surrounded by finely particles with particle size no more than 5 nm. Since wurtzite CdSe is intrinsically an anisotropic material, and when the overall growth rate is fast, growth is generally faster along c-axis;[12] consequently, nanorods were formed by self-assembly as seen in this case.

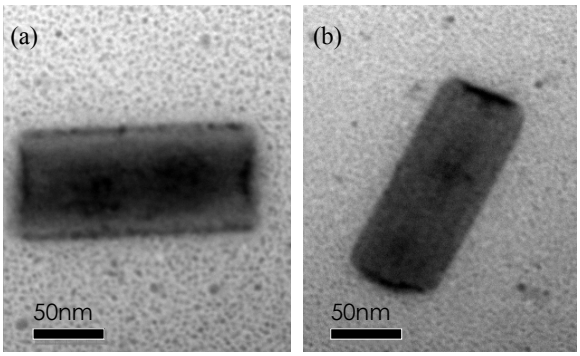

Figure 4. TEM images for the particles in the bottom layer of the reaction solution.

TEM image in Figure 5(a) shows that the process of self-assembly for particular shapes was deeply affected by the intensity of ultrasound. Owing to the high concentration of CdSe particles in the bottom layer of the reaction flask, interparticle collisions occurred by various colliding velocities associated with different intensities of shock waves.[13] Consequently, nanorods with a variety of aspect ratios were formed

To investigate the effect of surfactant concentration on the self-assembly process of CdSe nanoparticles, the preparation reaction was also carried out at a lower surfactant concentration (0.1M). The resultant crystal shapes from the self-assembly process in bottom layer are shown in Figure 5(b). The TEM image in Figure 5(b) clearly shows that a square-like shape was obtained in this case.

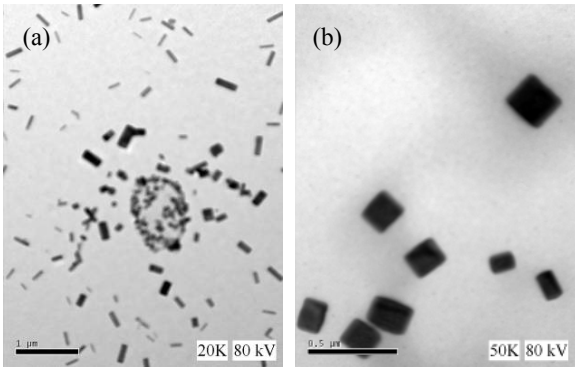

Figure (5) : TEM images of the particles in the bottom layer of the reaction solution. (a) One-dimensional nanorods with various aspect ratios, (b) two-dimensional square-like crystal.

Because the surface energy is varied with the concentrations of surfactant, thus if the concentration of surfactant is too low to cover all of the crystallographic faces, all of the crystallographic faces have roughly the same growth rate, resulting in the formation of two-dimensional square-like nanocrystals.[14]

4. Conclusions :

By means of high-intensity ultrasound, part of the particles in the bottom layer of the reaction flask might transfer their crystal structure from zinc blende to wurtzite phase due to the acoustic cavitation arising from the high-intensity ultrasound. The phase transition was confirmed by PL and XRD. In addition, TEM images confirmed various aspect ratios of one-dimentional nanorods could be obtained because of the intrinsically anisotropic nature of the wurtzite phase. The concentration of anionic surfactant SDS also had much effect on the crystal shape, and hence two-dimensional square-like crystals were observed at low concentration.

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