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A facile method to synthesize high-quality ZnS(Se) quantum dots for photoluminescence

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ABSTRACT

Colloidal zinc sulfide (ZnS) quantum dots are synthesized by a solvothermal route from $Zn(Ac)_2{\cdot}2H_2O$, sulfur powder and oleylamine at 120–240 °C. Microstructural, morphological, and optical properties of the as-synthesized ZnS quantum dots are characterized by X-ray diffraction analysis, transmission electron microscopy, UV–vis absorption spectroscopy, and photoluminescence spectroscopy. Results indicate that the obtained ZnS quantum dots distribute uniformly, the particle size is in the range between 1.7 nm and 3.1 nm, and the band gap decreases from 4.16 eV to 3.90 eV with an increase of the particle size. The size-dependent photoluminescence exhibits a strongly broadened peak accompanied by a pronounced blue-shift. It is also found that the size of the ZnS nanocrystals can be effectively controlled by adjusting synthesis temperature. It is shown that the present method is also applicable to synthesize other binary II–VI semiconductor materials, such as ZnSe quantum dots.

1. Introduction

Semiconductor nanocrystals, also termed quantum dots (QDs), have been attracting a great deal of attention in recent years due to their technical applications, such as biomedical labeling, light-emitting diodes, photocatalysis, solar cells, lasers, and sensors [1–6]. Therefore, II–VI semiconductors, such as CdSe, CdTe and their alloys, have been intensively studied in the form of size-, shape- and stoichiometry-controlled during the past decade [7–9]. However, in view of recent environmental regulation, the intrinsic toxicity of cadmium brings a doubt on the future applicability of the cadmium compounds despite of their great optical and electrical properties. Thus, several Cd-free alternative materials have been proposed including III–V semiconductor nanocrystals and transition-metal-doped ZnS and ZnSe QDs [10–12].

ZnS, as a kind of broad-band semiconductor material, has a wide band gap of 3.68 eV for the cubic blende phase and 3.91 eV for the hexagonal wurtzite phase at room temperature, respectively [13]. As a nontoxic semiconductor material, it shows strong photocatalysis ability and is widely used in light-emitting and microcircuit devices. ZnS layer can inhibit a recombination of the excited electron at the electrode/electrolyte interface and it can be also used as a passivation layer for CdS or CdSe to enhance the performance of the photoelectrode [14,15]. Especially, the energy conversion efficiency of TiO_2/MPTMS/CdSe cell can increase from 1.80% to 2.29% due to the introduction of the ZnS passivation layer [16]. It has been also shown that the ZnS layer cannot only improve the optical properties, but also protect below layers from corrosion by the liquid electrolyte. It has been demonstrated that the properties of the ZnS nanocrystal depend on the size and morphology largely.

Many methods have been developed to obtain uniform II–VI nanocrystals, including vapor deposition process [17], hydrothermal synthesis [18], solvothermal synthesis [19] and sol–gel method [20]. In particular, there are very recent works reporting the synthesis of CdSe and ZnTe nanocrystals in solid templates by using glass as a matrix [21,22], in which the fusion is carried out at a high temperature. As reported in Ref. [23], a reliable synthesis route for high-quality colloidal NCs of the controlled size and shape can be used to synthesize most binary and some ternary semiconductors, but not much attention has been paid to the blende-type ZnS QDs. Furthermore, ZnS crystalline colloidal arrays were synthesized by using thioacetamide and zinc–nitrilotriacetate [24]. Zinc blende ZnS nanowires were synthesized by using a hexagonal liquid crystal as template [25]. Mesostructured wurtzite ZnS–nanowires were synthesized by using a mild-solution reaction with different amines [26]. Tiny wurtzite ZnS nanoparticles were synthesized at 150 °C by a solution chemistry approach [27], and a ligand-controlled synthesis at elevated temperatures higher than 150 °C was also developed [28,29]. In addition, highly luminescent $CuInS_2$/ZnS core/shell nanocrystals were synthesized in octadecene, dimethylformamide and toluene [30]. However, all these synthesis methods are either complicated or high cost, or due to toxic precursors. Herein, we present a synthesis method for the intrinsic ZnS semiconductor QDs and characterize the morphology, absorption, and

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photoluminescence properties. To the best of our knowledge, the ZnS QDs synthesized from oleylamine has been little reported so far. Our method for synthesis of the ZnS QDs is simple and low-cost. Besides, the as-synthesized nanoparticles are uniform and the particle size can be controlled by adjusting reaction temperature. It is found that the synthesis route is versatile to the large-scale production and suitable for preparing other binary or ternary semiconductor materials.

2. Materials and methods

Zinc acetate dihydrate ($Zn(Ac)_2{\cdot}2H_2O$), sulfur (S) powder, selenium powder, hexane, and ethanol were purchased from China National Medicines Corporation Ltd. Oleylamine (OLA; 90%) was purchased from Jingchun Reagent Co. Ltd., Shanghai. All the chemicals used in our experiment were received from commercial products without any further purification and they are analytical grade reagents.

A flask was used as reaction vessel in our experiment. Firstly, 0.439 g (2 mmol) of $Zn(Ac)_2{\cdot}2H_2O$, and 10 mL of oleylamine were mixed together in the flask at room temperature, and then the mixed solution was heated to 80 °C with a magnetic stirring and maintained for 30 min until the Zn salt was completely dissolved in the solvent. Thus, the transparent solution was obtained. Secondly, 0.064 g (2 mmol) of S powder was dissolved in the previous solution. The resulting mixture was then heated to 120–240 °C and maintained for 30 min with vigorous magnetic stirring to form a dispersive mixture. It was noted that the color of the mixed solution changed from colorless to pale yellow and then to dark yellow with the addition of the S powder. After the flask was cooled to room temperature, the products were slowly precipitated with the addition of the anhydrous ethanol. The mixture was centrifuged and the supernatant was decanted. Then the sediment was dispersed in hexane. The process of the dispersion and centrifugation was repeated for 3 times with hexane and ethanol to remove the rest precursor. Finally, the ZnS QDs were dispersed in hexane for characteristic analysis without any size-selective precipitation. For the synthesis of the ZnSe QDs, the above procedure is exactly followed with the exception of 2 mmol Se powder replacing S powder.

X-ray diffraction (XRD) analysis was employed to characterize the crystallinity of the as-synthesized nanoparticles by a D/max 2400 X Series X-ray diffractometer. The X-ray radiation source, obtained at 40 kV, 100 mA, was Cu Kα, and the scanning speed was 10° min^{-1} at a step of 0.02°. A transmission electron microscopy (a JEOL 2010F TEM operating at 300 KeV) was used to characterize the morphological properties of the ZnS nanoparticles. The UV–vis absorption spectra of the ZnS nanocrystals in hexane were obtained by a JASCO V-570 UV/VIS/NIR Spectrometer in the range of 250–800 nm. The photoluminescence spectra of the ZnS nanocrystals were measured at room temperature by a Fluoromax-4 spectrometer.

3. Results and discussion

As reported in Ref. [31], the nanometer-sized scale of the QDs can confine electrons in a small box and quantize the energy band possessed by bulk materials into discrete energy states. That is to say, the band gap of the semiconducting materials can be tunable to a desired energy through changing the particle size due to the quantization effect and this variability of the band gap can tune its absorption and emission spectra. For a material, its Bohr excitonic radius, R_B, can be given by the following equation [32]:

$$R_B = \varepsilon_\infty \left(\frac{1}{\mu_e} + \frac{1}{\mu_h}\right) a_B \quad (1)$$

where ε_∞ is the high-frequency dielectric constant, μ_e is the electron effective mass, μ_h is the hole effective mass, a_B is the Bohr radius of hydrogen atom, which is 0.105 nm. Taking the ZnS bulk values of $\varepsilon_\infty = 5.7$, $\mu_e = 0.34$, $\mu_h = 0.58$, thus, the Bohr radius of the ZnS nanocrystals can be calculated by Eq. (1) and its value is 2.79 nm. Generally, if the diameter of the nanocrystals is less than its Bohr excitonic radius, there will be quantum confinement effect for the nanocrystal materials, and the band gap shifts toward higher energies, also named "blue-shift". Compared to the bulk materials, there are many new different features for the QDs, such as generating multiple electron–hole pairs per photo as shown in Fig. 1(b), and Fig. 1(a) shows the situation of generating single electron–hole pair per photo.

Fig. 2 shows exclusive XRD patterns of the ZnS QDs synthesized at different synthesis temperatures, which indicate a highly crystalline characteristic of the as-synthesized product. It can be

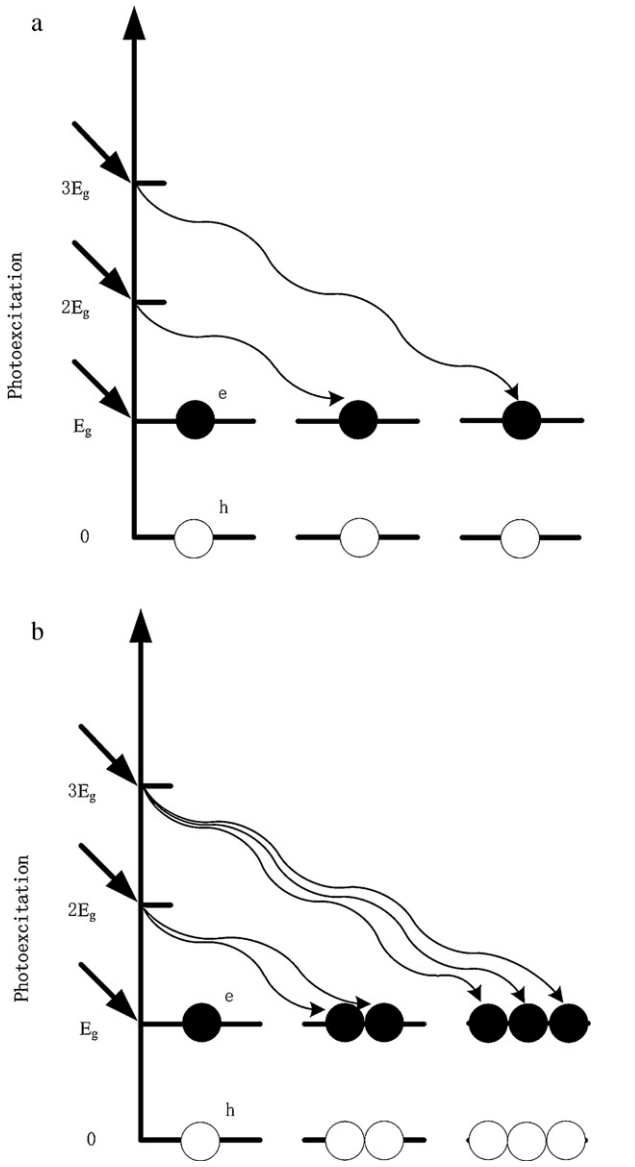

Fig. 1. Schematic diagram of photoexcitation without (a) and with (b) multiple exciton generation.

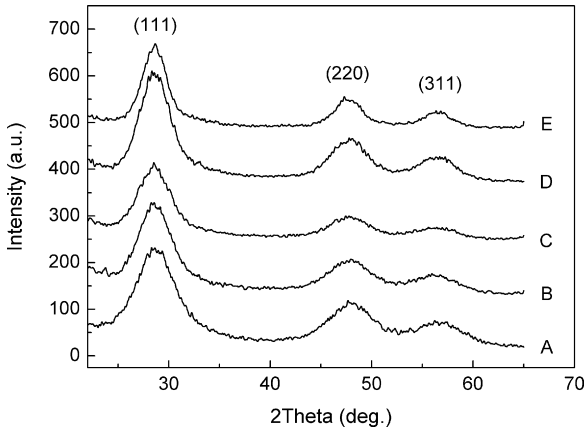

Fig. 2. XRD patterns of the ZnS QDs synthesized at (A): 120 °C; (B): 150 °C; (C): 180 °C; (D): 210 °C; and (E): 240 °C.