



ZnSe based semiconductor core-shell structures: From preparation to application

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ABSTRACT

Inorganic core-shell semiconductor materials have attracted increasing interest in recent years because of the unique structure, stable chemical properties and high performance in devices. With special properties such as a direct band-gap and excellent photoelectrical characteristics, ZnSe based semiconductor core-shell structures are promising materials for applications in such fields as photocatalysts, light-emitting diodes, solar cells, photodetectors, biomedical science and so on. However, few reviews on ZnSe based semiconductor core-shell structures have been reported so far. Therefore this manuscript mainly focuses on the research activities on ZnSe based semiconductor core-shell composites including various preparation methods and the applications of these core-shell structures, especially in photocatalysts, light emitting, solar cells and photodetectors. The possibilities and limitations of studies on ZnSe based semiconductor core-shell composites are also highlighted.

1. Introduction

It is well known that core-shell structure consists of a central particle (core) and a cladding shell, which usually has new properties that the single component material does not have. The shell not only adjusts the surface properties of the core, but also changes the surface charge density, functional groups, reactivity, biocompatibility, stability and dispersibility of these composite structures [1]. Therefore the catalytic activity, biomedical, optical, electrical and super-hydrophobic properties of the core material can be improved or changed. Semiconductor core-shell structure is one of the most important core-shell structures.

ZnSe has a wide direct band gap (2.7 eV) and a large exciton binding energy (21 meV) at room temperature. During the last two decades, ZnSe has been widely used in windows, lenses, output couplers, beam expanders, biomedical labels, optically controlled switching and photodetectors [2,3] for its low absorbance of infrared region and high photosensitivity. In recent years, ZnSe based semiconductor core-shell structure has been widely studied as well. In ZnSe based semiconductor core-shell structures, ZnSe can serve as either core material or shell material. From now on, a variety of ZnSe based semiconductor core-shell structures were prepared by different methods and the applications of these structures were investigated widely. Most of these ZnSe based core-shell structures are type-II core-shell heterostructures which have a staggered band alignment such as (ZnSe/CdS)/CdS [4], ZnSe/CdS/ZnSe [5], and ZnSe/CdS (or CdS/ZnSe) [6–8]. There are a few type-I and reverse-type-I core-shell heterostructures based on ZnSe

which is known as CdSe/ZnSe [9], ZnSe/CdSe [10] and ZnSe/ZnS [11]. It was found that ZnSe based semiconductor core-shell structures have improved optical [12], photoelectrochemical [13] and photoelectric properties. Therefore, such core-shell structures can be used in biological applications including cell imaging [11], light-emitting diodes (LEDs) [14], photocatalysts [15,16] and solar cells [17].

Here, a selection of recent work related to ZnSe based semiconductor core-shell structures is reviewed, with particular focus on the preparations and applications. The preparation methods of ZnSe based semiconductor core-shell structures will be presented firstly. Then, the main applications of these core-shell structures will be discussed. This review will be concluded with an outlook of possibilities and limitations in this area.

2. Preparation of ZnSe based semiconductor core-shell structures

In the past few years, several methods including physical and chemical methods have been developed to prepare core-shell structures. Traditionally, ZnSe based core-shell structures can be prepared by hydrothermal method, hot injection, and thermal evaporation.

2.1. Hydrothermal method

Water-soluble blue-emitting ZnSe/ZnS core-shell quantum dots (QDs) were synthesized via a one-step hydrothermal method with thiol ligand N-acetyl-L-cysteine (NAC) as the stabilizer [18]. From the

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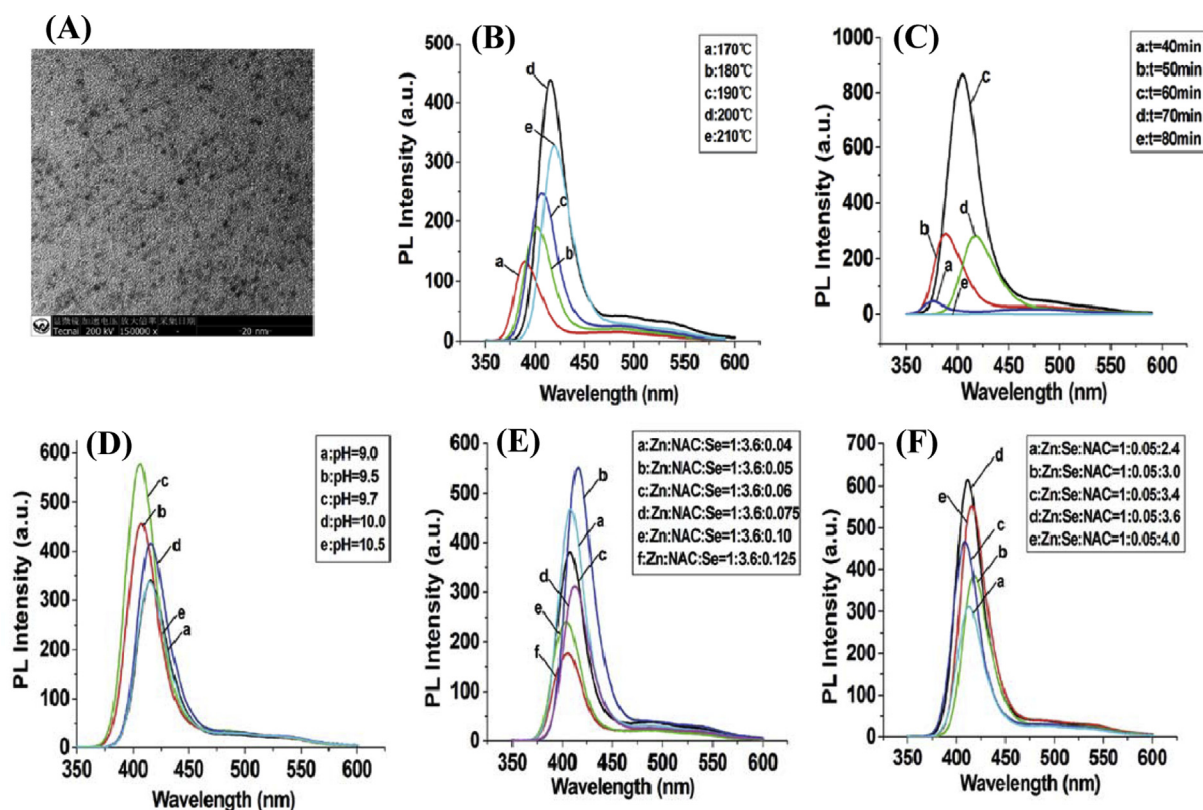


Fig. 1. (A) is TEM image of ZnSe/ZnS core-shell QDs; (B), (C), (D), (E) and (F) are PL spectra of NAC-capped ZnSe/ZnS core-shell QDs prepared at different reaction temperature, reacting time, pH values, HSe⁻/Zn²⁺ values and NAC/Zn²⁺ values, respectively. Reproduced from Ref. [18]. Copyright © The Royal Society of Chemistry (2014).

photoluminescence (PL) characterization, it was found that the quantum yields (QY) of the as-prepared QDs can be greatly influenced by reaction temperature, reaction time, pH value of precursor solution and molar ratio of reactants. Fig. 1B–F show the PL spectra of the as-prepared QDs with different reaction temperatures, reaction times, pH values of precursor solution and molar ratios of HSe⁻/Zn²⁺ and NAC/Zn²⁺, respectively. As can be seen, increase of reaction temperature or time can both lead to red-shift of emission peak due to the increased diameter of QDs. Higher reaction temperature (> 200 °C) or longer reaction time (> 60 min) resulted in lower QY because of the decomposition of stabilizer NAC. While lower reaction temperature (< 170 °C) or shorter reaction time (< 60 min) led to lower QY as well because of the low growth rate of QDs at lower temperature and more surface defects caused by high surface-to-volume ratio of smaller QDs with shorter reaction time. The weakly alkaline reaction environment and relatively lower Se content in reactants were profitable for the formation of high quality QDs as shown in Fig. 1D and E. Proper molar ratio of NAC and Zn²⁺ is needed to obtain high QY because NAC served as both stabilizer and sulfur provider. However when the concentration of NAC further increased, Zn²⁺ ions were capped by excess NAC molecule, interfering with their reaction with HSe⁻ to form ZnSe core and thus decreasing the PL QY (Fig. 1F). Therefore the optimum reaction conditions were proposed: molar ratio of Zn²⁺: HSe⁻: NAC is 1.0: 0.05: 3.6, PH is 9.7, reaction time is 60 min and reaction temperature is 200 °C, respectively. The PL QY is up to 39% under the optimum reaction conditions.

ZnSe/CdSe core-shell microspheres formed by ZnSe core and CdSe shell were prepared by using the as-prepared ZnSe microspheres as the template under the hydrothermal condition [19]. Firstly, powders of ZnSe nanocrystals were obtained by hydrothermal method. Then the as-prepared ZnSe nanocrystals were converted to ZnSe/CdSe core-shell microspheres by introducing Cd²⁺ under hydrothermal condition.

Fig. 2 shows the SEM images of the as-prepared ZnSe microspheres and ZnSe/CdSe core-shell spheres obtained with mole ratio of ZnSe to Cd(NO₃)₂ of 1:1, 1:0.25, 1:0.5, 1:0.75, respectively. It was found that when the mole ratio of ZnSe to Cd(NO₃)₂ is 1:1, solid spheres composed by nano-units of ZnSe and CdSe can be obtained as indicated in Fig. 2A. While when the molar ratio of ZnSe to Cd(NO₃)₂ is greater than 1:1 (1:0.25, 1:0.5 and 1:0.75), many hollow shells were obtained as shown in Fig. 2B, C and D. The thickness of CdSe shell and the particle size of the building nano-unit increased as the amount of Cd(NO₃)₂ increasing. The core-shell product cannot be synthesized when the molar ratio of ZnSe to Cd(NO₃)₂ is less than 1:1.

2.2. Hot injection

Hot injection method is usually used to form QDs. Mn and Cu co-doped ZnSe/ZnS core-shell QDs were prepared through a versatile microwave-assisted hot-injection method in aqueous solution by the group of Jie Zhang [20]. In a typical procedure, Se precursor (NaHSe solution) was prepared by Se and NaBH₄. Reaction mixture of ZnSO₄·7H₂O, stabilizer (thioglycolic acid, TGA) and Se precursor was heated to reflux at 100 °C for 24 h under nitrogen flow with a condenser attached by microwave irradiation to form ZnSe QDs. In order to form ZnS shell, Na₂S solution was injected into the as-prepared ZnSe QDs solution. To prepare Mn and Cu co-doped ZnSe/ZnS QDs, mixture of ZnSO₄·7H₂O, TGA, MnCl₂ and Se precursor was heated to form Mn:ZnSe QDs. Then CuCl₂ solution was injected into the boiled Mn:ZnSe QDs to form Cu,Mn:ZnSe QDs. Finally, ZnS shell stock solution was added. It was found that microwave irradiation may accelerate the growth of ZnSe QDs and when capped with ZnS layer, ZnSe QDs can achieve better optical performance as shown in Fig. 3A. Fig. 3B indicates that when the shell of ZnS was capped on ZnSe QD, the PL intensity was greatly enhanced and a blue-shift of band-gap emission

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