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Formation of CdS/$Cd_{1-x}Zn_xS$ sandwich-structured quantum dots with high quantum efficiency in silicate glasses

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ABSTRACT

CdS/$Cd_{1-x}Zn_xS$ sandwich-structured quantum dots (QDs) were precipitated in silicate glasses with high quantum efficiency up to 53%. The QDs were composed by a CdS core with a $Cd_{1-x}Zn_xS$ shell of about 1–3 nm in thickness through heat-treatment at 550 °C for 10 h. With the increased heat-treatment temperature, the intensity ratio between the intrinsic emission and the defects emission increased and the Stokes shift decreased from 84 to 4 meV, which was caused by both the increased size and passivated surface defects of the QDs.

1. Introduction

Semiconductor quantum dots (QDs) made of cadmium chalcogenide, which possess wide bandgap and large excitonic binding energy, show great advantages in the photoluminescence of visible spectral range and have been widely investigated for photoelectric applications [1,2]. For the application of cadmium chalcogenide QDs in the luminescent devices, it is important to passivate the surface defects on the QDs to realize the intrinsic emission with high quantum efficiency. The QDs prepared in solution are easily coated by an inorganic shell or modified by some organic ligand on their surfaces. After modification, especially forming the core-shell structure, the quantum efficiency can be increased to exceeding 90% [3], making them attractive materials in biological labeling [4]. However, the poor thermal stability, chemical stability and mechanical stability of the QDs in solution limited the device manufacturing.

As a stable solid material, inorganic glass can be a good choice to act as the matrix instead of solution. Embedding QDs into glass matrix can prevent the QDs from agglomeration and secure the stability. II-VI QDs doped glasses have been used in optical filters [5,6], but the use in luminescent devices is still a problem mainly due to the low quantum efficiency. In 2015, Han et al. [7] combined a commercial blue light-emitting diode (LED) with CdSe or CdS QDs doped glasses to make white LED with the quantum efficiency of 3%, which was caused by complete defects emission from CdSe or CdS QDs under the excitation of blue light. Recently, quantum efficiency of the white LED made from glasses containing core/shell structured CdSe/CdS QDs has been increased to 20% by realizing the intrinsic emission [8]. However, the defects emission still existed and it is difficult to adjust the defects emission intensity to achieve a higher quantum efficiency [8]. In this work, partial surface passivation of CdS QDs was realized by forming $Cd_{1-x}Zn_xS$ shell in silicate glasses though thermal treatment, and as a result, quantum efficiency up to 53% was achieved from these CdS/$Cd_{1-x}Zn_xS$ sandwich-structured QDs with the gradually passivated defects emission.

2. Experimental details

Glass with nominal composition (mol%) of 65SiO_2-25Na_2O-10CaO with additional 0.8ZnS and 0.8CdO was prepared using conventional melt-quenching method. Batch of about 50 g raw materials were weighted and mixed thoroughly for 10 h. The mixed raw materials were melted in an alumina crucible at 1350 °C for 40 min under the ambient atmosphere. Then the melt was poured onto a preheated brass mould for quenching in air and annealed in a furnace at 350 °C to remove the residual thermal stress. Glass thus obtained was cut into small pieces of $10 \times 10 \times 2$ mm^3 for heat-treatment at various temperatures. All the as-prepared (named as S0) and heat-treated glass specimens were polished for further characterization. The specimens were named as S1, S2, S3, and S4 for the ones heat-treated at 530, 550, 570, and 590 °C for 10 h, respectively.

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X-ray diffraction (XRD, D8 Advance, Bruker) patterns of the glass specimens were recorded to illustrate the structural changes during the heat-treatment process. Cu-Kα radiation with a scanning rate of 1°/min was used for the measurement with a resolution of 0.02°. The XRD patterns were collected within the range of $20° < 2\theta < 60°$ (instrumental error $\pm 0.05°$). The microstructure and distribution of the quantum dots in glasses were characterized by using high-resolution transmission electron microscope (HR-TEM, JEM-2100F, JEOL) with an image Cs-corrector and an Ω-filter. The absorption spectra of the as-prepared glass and the heat-treated glasses were collected by an UV/Vis/NIR spectrophotometer (UV-3600, Shimadzu). The photoluminescence spectra were recorded using time-resolved fluorescence spectrometer (FL3-22, Jobin-Yvon) under the excitation wavelength of 325 nm with a 340 nm optical filter. The photoluminescence quantum efficiency of the heat-treated specimens excited at 365 nm was examined by a quantum efficiency measurement system (QE-2000, Otsuka Electronics Co. Ltd.). The emission and the excitation source were collected by an integrated sphere during the measurement of quantum efficiency.

3. Results and discussion

It has been shown that precipitation of chalcogenide nanocrystals (NCs) was strongly dependent on the oversaturation of chalcogen element in glasses [9,10]. In our previous work, ZnSe and ZnS nanocrystals have been successfully precipitated in the silicate glasses by increasing the doping concentration of Se and S in the glasses [9]. In this work, ZnS and CdO were introduced into the glass instead of CdS, in order to simultaneously precipitate CdS and ZnS (or $Cd_{1-x}Zn_xS$) nanocrystals in the glasses. Compared to previous report [11], current doping concentration of ZnS in the glass was high enough to guarantee the oversaturation of S.

The as-prepared glass was pale yellow and changed into orange upon heat-treatment, indicating the precipitation of chalcogenide nanocrystals in the glasses. As indicated by the arrows in Fig. 1, several broad diffraction peaks appeared on the XRD patterns of the heat-treated glasses. However, these diffraction peaks were relatively weak and broad, indicating the small average size and low volume fraction of nanocrystals formed in the heat-treated glasses. Compared to the diffraction patterns of bulk CdS crystal (JCPDS No.: 77-2306) and bulk ZnS crystal (JCPDS No.: 75-1547), nanocrystals formed in the heat-treated glasses have hexagonal structure with a space group of P63mc. Diffraction angles of the nanocrystals formed in the glasses showed that lattice constants of

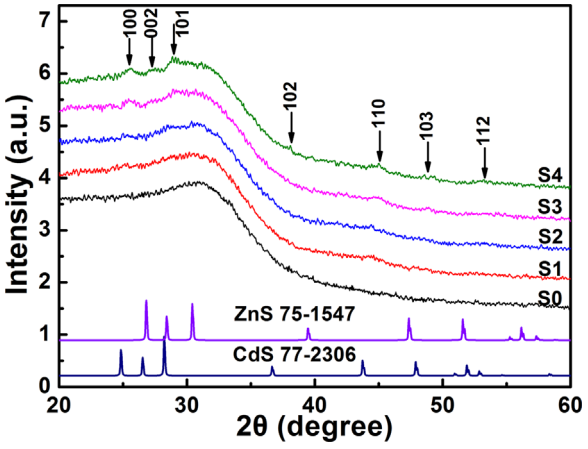

Fig. 1. XRD patterns of the as-prepared and heat-treated specimens at various temperatures for 10 h.

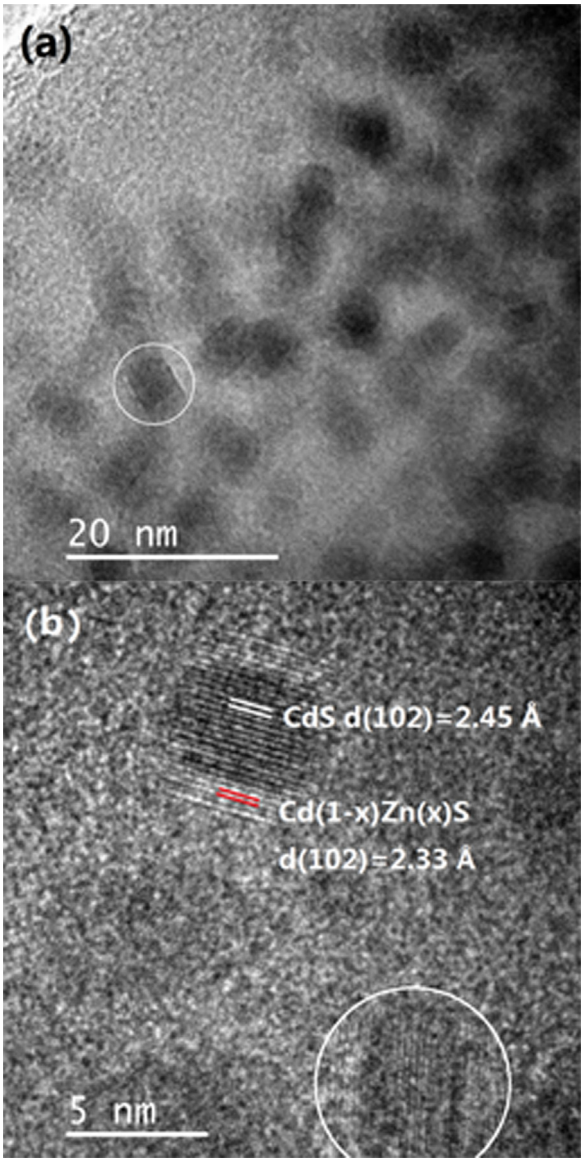

Fig. 2. HR-TEM image of (a) overall distribution and (b) several CdS/$Cd_{1-x}Zn_xS$ sandwich-structured nanocrystals formed in the specimen heat-treated at 550 °C for 10 h (S2).

nanocrystals were larger than that of ZnS and smaller than that of CdS. Considering the composition of glass and many previous works [12,13], $Cd_{1-x}Zn_xS$ ternary nanocrystals were probably formed in the glasses.

To illustrate the structure and size of the nanocrystals, glass heat-treated at 550 °C for 10 h (S2) was examined by TEM (Fig. 2). Almost all nanocrystals were oval-shaped or rectangular with a size of 6–8 nm (Fig. 2a). Most of the nanocrystals (QDs) have a dark central core surrounded by a relatively brighter shell, as indicated by the white circle. Careful observation showed that the interplanar distance was 2.45 Å in the core region and 2.33 Å in the shell part (along the direction shown in Fig. 2b). The interplanar distance in the core region was consistent with the lattice constant of (102) plane of CdS crystal (d_{102}=2.45 Å, JCPDS No.: 77-2306). It confirmed that the core region was mainly composed of CdS, but partial incorporation of Zn into the core region cannot be excluded. While, the interplanar distance of the shell region was larger than (102) plane of ZnS crystal (d_{102}=2.28 Å, JCPDS No.: 75-1547), indicating that the shell was mainly composed of $Cd_{1-x}Zn_xS$. Combining the above results obtained from XRD