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Surface Passivation of CdSe Quantum Dots in All Inorganic Amorphous Solid by Forming Cd_{1-x}Zn_xSe Shell

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CdSe quantum dots (QDs) doped glasses have been widely investigated for optical filters, LED color converter and other optical emitters. Unlike CdSe QDs in solution, it is difficult to passivate the surface defects of CdSe QDs in glass matrix, which strongly suppress its intrinsic emission. In this study, surface passivation of CdSe quantum dots (QDs) by Cd_{1-x}Zn_xSe shell in silicate glass was reported. An increase in the Se/Cd ratio can lead to the partial passivation of the surface states and appearance of the intrinsic emission of CdSe QDs. Optimizing the heat-treatment condition promotes the incorporation of Zn into CdSe QDs and results in the quenching of the defect emission. Formation of CdSe/Cd_{1-x}Zn_xSe core/graded shell QDs is evidenced by the experimental results of TEM and Raman spectroscopy. Realization of the surface passivation and intrinsic emission of II-VI QDs may facilitate the wide applications of QDs doped all inorganic amorphous materials.

Due to the quantum confinement effect, size tunable optical properties of semiconductor nanocrystals (quantum dots, QDs) have great potentials for light harvesting, spectral conversion, information display, and light sources¹⁻³. For example, emission wavelength of II-VI QDs (CdS, CdSe, CdTe) and IV-VI QDs (PbS, PbSe, PbTe) can span over the visible and near-infrared spectral range, respectively, by controlling the size of the nanocrystals⁴⁻⁶. So far, II-VI QDs such as Zn chalcogenide, Cd chalcogenide binary compounds (ZnS, CdS, CdSe, CdTe, *etc.*)⁷⁻¹⁰, ternary compounds (CdS_xSe_{1-x}, Zn_xCd_{1-x}Se, *etc.*)¹¹⁻¹⁴ or even quaternary compounds (Zn_xCd_{1-x}S_ySe_{1-y}, *etc.*)¹⁵, have attracted special attention due to their wide bandgap and large exciton binding energy, which results in efficient excitonic emission at room temperature. Most of the II-VI QDs showed efficient intrinsic emission with high quantum efficiency upon surface passivation¹⁶⁻¹⁹.

Incorporation of QDs into inorganic glasses can combine the unique properties of QDs with the good chemical, mechanical and thermal properties of glasses, and facilitate the wide applications of QDs. The inert nature of the glass matrix guarantees the photo-chemical and thermal stability of QDs embedded inside²⁰⁻²², prevents the agglomeration of QDs and provides access to device fabrication⁶. In fact, II-VI QDs doped glasses have been widely used in optical filters^{23,24} and recent studies have shown their great potentials in luminescent devices, such as LED color converters and other optical emitters^{25,26}.

However, the main problem of glasses containing II-VI QDs is that when these QDs were doped into glasses, defects on the interface between QDs and glass matrices almost quenched the excitonic emission and in most cases, strong defect emissions were observed^{19,21,22}. Generally, the defect emissions are considered as a result of the surface states located in the band gap of the nanocrystals, which act as trapping states for the photo-generated charges²⁷. These surface trapping states are originated from the dangling bonds of some of the surface atoms²⁸. Moreover, the traps also affect the electron-hole pair resonances, which then affect the nonlinear optical properties of II-VI QDs in glasses²⁹. Thus, it is important to passivate the surface of II-VI QDs. The emission influenced by the surface characteristics of QDs and surface reconstruction of chemically synthesized CdSe QDs have been

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Sample	SiO ₂	Na ₂ O	Al ₂ O ₃	ZnO	ZnSe	CdO	ZnSe/CdO molar ratio
C1	50	20	2	27.8	0.2	0.4	0.5
C2				27.6	0.4	0.4	1
C3				24	4	0.4	10
C4				24	4	0.2	20

Table 1. The glass compositions (in mol. %) and the corresponding ratios of ZnSe/CdO.

systematically investigated^{27,30–32}. However, unlike the surface passivation in colloidal chemistry^{16–19}, it is difficult to passivate the surface defects of the QDs in inorganic glasses. Previous studies on glasses with II–VI QDs mainly focused on the formation, size control, spatial distribution and luminescent wavelength of the QDs^{25,33,34}, but investigations on surface passivation of QDs in glass matrix, which can effectively enhance the luminescence efficiency, have not been carried out yet.

On the other hand, ternary II–VI QDs can provide possibilities of the modification of luminescence^{12–14}. Zheng *et al.* have shown that the quantum efficiency of Zn_{1–x}Cd_xSe alloyed QDs was related to Cd mole fraction *x* and reached the maximum of ~50% when *x* = 0.6¹². Sonawane *et al.* reported that the proper amount of Zn doping into Zn_{1–x}Cd_xSe nanocrystals resulted in minimal photoluminescence (PL) quenching and hence assuring the least defect density¹³. Also, the graded core-shell structure^{14,35,36}, such as Zn_xCd_{1–x}Se/ Zn_yCd_{1–y}Se (*x* < *y*) core-shell structure, can be a better alternative than the binary-binary core-shell structure due to the minimized lattice mismatch and smooth variation in bandgap and lattice parameters. Such a variation reduces the strain and interfacial defects thereby increasing the radiative recombination of exciton and hence the PL efficiency¹⁵.

In this work, silicate glasses containing ZnSe and CdO were prepared through the melting-quenching method, and CdSe QDs were precipitated after thermal treatment. The incorporation of Zn ions into CdSe QDs and its influence on the surface passivation of CdSe QDs in glasses were studied. Efficient intrinsic emission from CdSe QDs doped glasses was realized, and effects of Se/Cd proportions and heat-treatment condition on the optical properties were investigated.

Method

Sample preparation. Glasses with nominal compositions of 50SiO₂–20Na₂O–2Al₂O₃–(28–*x*–*y*)ZnO–*x*ZnSe–*y*CdO (in mol%) were prepared through the conventional melt-quenching method. Glasses with four different ZnSe/CdO ratios were prepared (Table 1). Chemical powders with purity of ≥99.9% were weighed, thoroughly mixed, and then melted in alumina crucibles at 1350 °C for 40 min under an ambient atmosphere. The glass melts were then poured onto a preheated brass mould and pressed with another one for quenching. Glasses thus obtained were annealed in a furnace at 350 °C for 2 h to reduce the thermal stress and then cut into small species with the size of about 10 mm × 10 mm × 2 mm for heat-treatments. The as-prepared (AP) glasses were heat-treated under various temperatures or durations to precipitate QDs in the glass matrix. Either one-step or two-step heat-treatment was employed. All the heat-treated glass specimens were optically polished for further characterization.

Structural characterization. To verify the crystallization of the heat-treated samples, X-ray diffraction (XRD) patterns of the glass specimens were recorded using D8 Advance diffractometer (Voltage 40 kV, current 40 mA, Cu Kα) with a scanning rate of 1°/min and a step width of 0.02°. The XRD patterns were collected within the range of 20° < 2θ < 60° (instrumental error ±0.05°). Raman spectra were recorded in the back (180°) scattering configuration using a Renishaw inVia laser confocal Raman spectrometer and a 488 nm laser of 10 mW is employed as the excitation source. The resolution in the frequency of the Raman spectrometer is ±0.5 cm^{–1}. The structure and distribution of the QDs in glass were characterized using a high-resolution transmission electron microscope (HR-TEM, JEM-2200FS, JEOL, Japan) with an image Cs-corrector and an Ω-filter. The specimens for TEM analysis were prepared through the standard disc grinding, dimple grinding and ion milling. To reduce the charge accumulation on the surface and enhance the electrical conductivity of the samples, both sides of these TEM specimens were coated with carbon.

Spectroscopic measurement. The absorption spectra of the AP glass and the heat-treated glasses were measured by SHIMADZU UV-3600 spectrophotometer. The PL spectra of all specimens were recorded with a combination of 365 nm UV-LED, mechanical chopper, 0.25 m monochromator, photomultiplier tube, and lock-in amplifier. All the optical measurements were carried out at room temperature.

Results and Discussions

Effects of ZnSe/CdO ratio on the optical properties of CdSe nanocrystals. Formation of semiconductor nanocrystals in glasses is based on the phase decomposition of oversaturated solid solution^{4,37}. In glasses, formation of chalcogenide QDs, such as CdS, CdSe, PbS and PbSe QDs, is mainly dependent on the oversaturation of chalcogens, instead of chalcogenide compounds⁴. Changes in the ZnSe/CdO ratio can modulate the oversaturation of Se in the glasses, and affect the growth and optical properties of semiconductor nanocrystals (Fig. 1). When the ZnSe/CdO molar ratio increased from 0.5 to 20, the absorption edges of the AP C1, C2, C3 and C4 specimens were found at 344 nm, 360 nm, 380 nm, and 371 nm (Fig. 1a), respectively. A shift in the absorption edges should be related to the formation of some chemical bonds, radicals or even some tiny clusters^{38,39}. When C1 specimen was heat-treated at 530 °C for 10 h, the absorption edge showed a further red-shift to 375 nm. For C2 and C3 specimens, absorption shoulders appeared at 420 nm and 470 nm, respectively, when heat-treated at

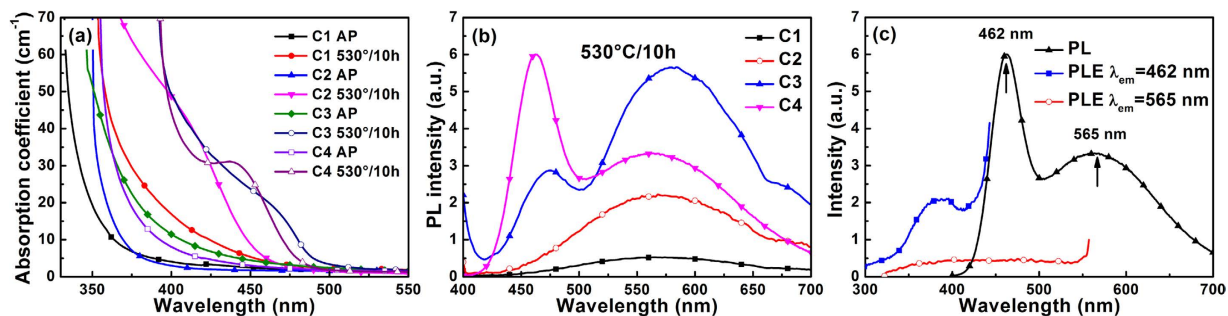


Figure 1. (a) Absorption and (b) photoluminescence spectra of the as-prepared and heat-treated glasses with the compositions of C1, C2, C3, and C4, (c) photoluminescence and excitation spectra of C4 specimen heat-treated at 530 °C for 10 h.

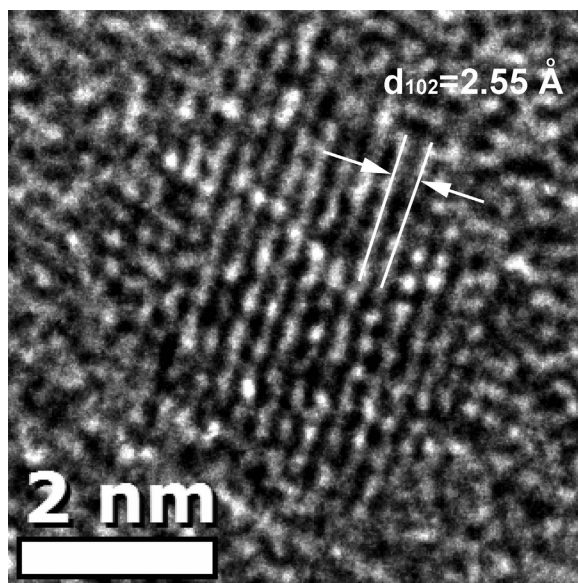


Figure 2. HR-TEM image of one nanocrystal formed in C4 specimen heat-treated at 530 °C for 10 h.

530 °C for 10 h. This phenomenon was closely related to the increase in the concentration of ZnSe in the glasses, which increase the degree of oversaturation of Se in the glass and promote the formation of nanocrystals in the glasses upon thermal treatment. However, for C4 specimen with reduced amount of CdO, the absorption peak appeared at 441 nm, much shorter than that observed in C3 specimen when heat-treated at the same condition. This indicated that in addition to Se, concentration of Cd also has a strong effect on the formation of nanocrystals in the glasses.

Previously, Weyl proposed that Se and Cd were present in the melts as ZnSe and CdO, and should be predominant in the quenched glass⁴⁰. At lower temperature, CdSe is more stable than ZnSe and CdO⁴⁰. During the heat-treatment at temperature of 500–700 °C, ZnSe and CdO dissociate and diffusion of Se and Cd through the glass lead to the formation of CdSe nanocrystals, which was confirmed by the X-ray absorption spectroscopy^{41,42}. Based on the Gibbs-Helmholtz equation and the Kirchhoff's law of thermochemistry⁴³, it was found that the chemical reaction (1) will occur spontaneously during the cooling process and lead to the formation of CdSe nanocrystals upon heat-treatment at low temperatures (Detailed calculation process can be found in the Electronic Supplementary Information).



Therefore, it can be expected that semiconductor nanocrystals formed upon heat-treatment at 530 °C for 10 h were CdSe QDs, which was confirmed by the TEM image (Fig. 2). The diameter of the nanocrystal formed in the C4 specimen heat-treated at 530 °C for 10 h was found to be 4.2 nm, comparable to 4.1 nm calculated from the first excitonic absorption peak (441 nm) using the empirical equation⁴⁴. The interplanar distance was found to be 2.55 Å, consistent with the (102) lattice plane distance of CdSe crystals (JCPDS No.: 77–2307). Therefore, nanocrystals formed in glasses upon heat-treatment at 530 °C for 10 h were CdSe QDs. Formation of CdSe QDs was

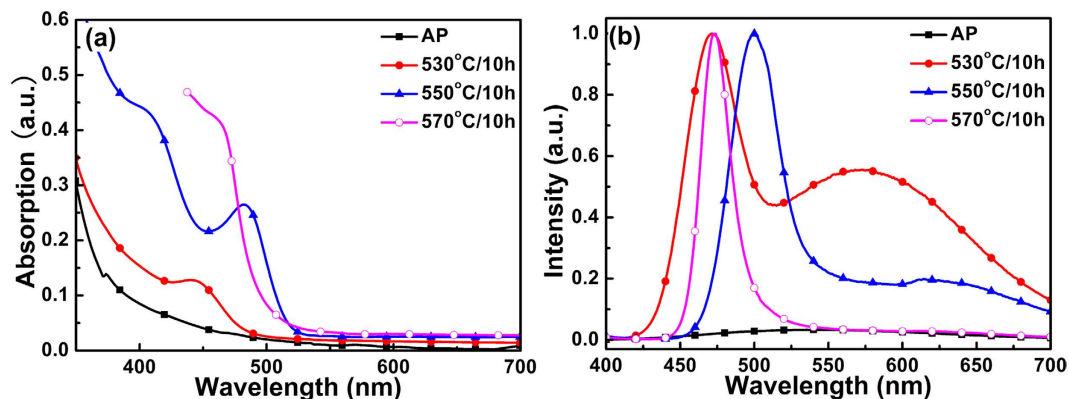


Figure 3. (a) Absorption and (b) photoluminescence spectra of the as-prepared and heat-treated C4 specimens.

also observed in borosilicate glass when heat-treated at low temperatures⁴⁵. Figure 1b shows the PL spectra of C1, C2, C3 and C4 specimens heat-treated at 530 °C for 10 h. For C1 and C2 specimens with a ZnSe/CdO ratio of 0.5 and 1, broad band emissions from 450 nm to 700 nm were observed. These broad band emissions may come from Se related radicals or clusters, surface defects of small CdSe or $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ nanocrystals^{25,46}. This broad band emission was also observed in C3 and C4 specimens. However, in addition to the broad band emissions, narrow band emissions located at 474 nm and 462 nm were observed in C3 and C4 specimens, respectively. The excitation spectra (Fig. 1c) monitored at 462 nm and 565 nm of the heat-treated C4 specimen showed that the narrow band emission and the broad band emission have different origins. Compared to the absorption spectra in Fig. 1a, the narrow band emission in the blue region can be ascribed to the intrinsic emission of CdSe QDs formed in the glasses, and the broad band emission can be assigned to the defect emission.

Apparently, excess Se had a strong effect on the emission properties of CdSe QDs formed in the glasses, and the ratio of intrinsic emission and defect emission increased as the ratio of ZnSe/CdO increased (Fig. 1b). Due to the relatively smaller effective mass of electron compared to hole ($m_e^- : m_h^+ = 1:5$)⁴⁷, the electron has the larger possibility to move to the surface of the nanocrystals and trapped by the surface defects, rather than staying inside of the CdSe QD³⁰. Thus, excess Se may help to modify the surface of the QDs and decrease the defect emission. For chemically synthesized CdSe QDs, it was also reported that a large excess of the selenium precursor was necessary to achieve a high PL quantum yield value and a narrow emission profile²⁷. Similar phenomena were also found in some other chemically synthesized CdSe QDs or $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ QDs and they contributed this “PL bright point” to surface structure reconstruction^{12–14,48–51}. Due to the large intensity ratio between intrinsic emission and defect emission, defects of CdSe QDs formed in C4 specimen were probably partially passivated. Therefore, C4 specimens with ZnSe/CdO ratio of 20 were used for the following study.

Surface passivation of CdSe QDs by $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ shell. It has been reported that Zn can be incorporated into CdSe QDs⁴⁵ and CdS QDs⁵² during high temperature heat-treatment. In our previous work, it was further found that ZnSe nanocrystals can be precipitated in silicate glass with a similar composition when heat-treated at temperatures higher than 630 °C³⁹. Since the concentration of Cd was much smaller than that of Zn and Se in the C4 specimens, Cd will be depleted much faster than Se and Zn during the growth of CdSe QDs. Under this condition, excess Se and Zn may participate in the successive growth of CdSe QDs with further increase in heat-treatment temperature. Figure 3a shows the changes of absorption spectra of C4 specimens with the increase in heat-treatment temperature. Absorption peaks firstly red-shifted from 441 nm to 482 nm, and then blue-shifted to 462 nm, when the heat-treatment temperature increased from 530 °C to 550 °C and 570 °C, respectively (Fig. 3a). Intrinsic emission of nanocrystals formed in these heat-treated glasses showed similar changes (Fig. 3b). The peak wavelength of the intrinsic emission bands firstly red-shifted from 471 nm to 500 nm and blue-shifted to 472 nm, and the full width at half maximum (FWHM) of the intrinsic emission bands decreased from 32 nm to 32 nm and 18 nm when the heat-treatment temperature increased from 530 °C to 550 °C and 570 °C, respectively. Generally, absorption and emission of QDs red-shift with the increase in heat-treatment temperature due to the growth of nanocrystals⁴⁶. The blue-shift in absorption and intrinsic emission peaks indicated that effective bandgap energies of the nanocrystals increased. Either size reduction of CdSe QDs or incorporation of Zn into CdSe QDs can lead to the increase in bandgap energies. In the case of size reduction of CdSe QDs, the defect emission band cannot be quenched due to the lack of surface passivation. In the case of Zn incorporation into CdSe QDs, when homogeneous $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ QDs are formed, defect emission can also be observed due to the unpassivated surface⁴⁵. It should also be pointed out that the defect emission bands decreased in intensity relative to the intrinsic one as the heat-treatment temperature increased, and it was almost completely quenched in C4 specimen heat-treated at 570 °C for 10 h (Fig. 3b), indicating that surface defects of nanocrystals were further passivated when heat-treated at 570 °C. Probably, Zn started to be incorporated into the CdSe QDs and formed a $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ shell when the heat-treatment temperature increased to 550 °C or above.

In order to verify this proposition, C4 specimens were subjected to two-step heat-treatment. The specimens were firstly heat-treated at 550 °C for 10 h (the specimens then named as C4-0, hereafter), then heat-treated at 570 °C for 2 h (C4-2), 5 h (C4-5) or 10 h (C4-10), respectively. Upon the first step heat-treatment at 550 °C for 10 h, Cd should be largely depleted in the glass matrix due to the formation of semiconductor nanocrystals.

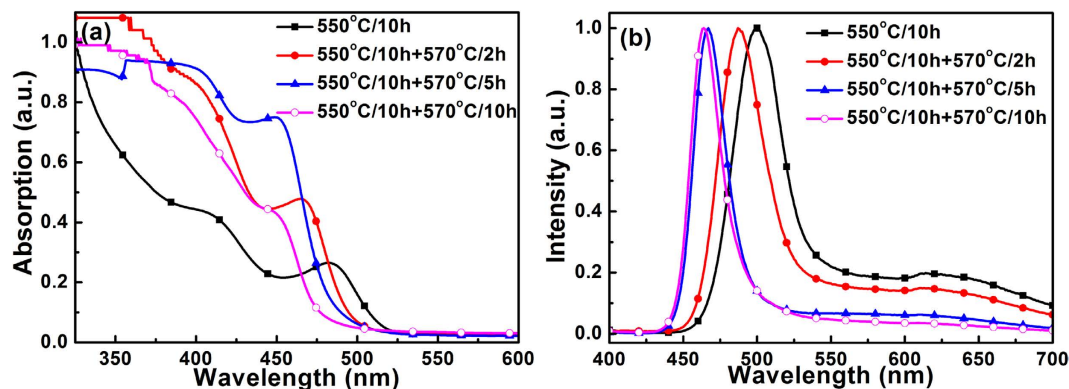


Figure 4. (a) Absorption and (b) photoluminescence spectra of C4-0, C4-2, C4-5 and C4-10 specimens.

If the incorporation of Zn into the CdSe QDs was mainly responsible for the blue-shift in the absorption and emission spectra (Fig. 3), the second step heat-treatment at 570 °C can be considered as the incorporation of Zn into the nanocrystals formed during heat-treatment at 550 °C for 10 h. In this case, more Zn can be incorporated into the nanocrystals and lead to more obvious blue-shift in absorption and emission spectra compared to that observe in C4 specimen directly heat-treated at 570 °C for 10 h. It was found that with the increase in the duration of the second step heat-treatment, the first excitonic absorption peaks shifted from 482 nm (C4) to 467 nm (C4-2), 454 nm (C4-5) and 453 nm (C4-10), respectively (Fig. 4a). The peak wavelength of the intrinsic emission band also shifted from 500 nm (C4) to 488 nm (C4-2), 467 nm (C4-5) and 464 nm (C4-10), respectively (Fig. 4b). Again, the defect emission was quenched during the second-step heat-treatment. These results confirmed that blue-shift in the absorption and emission spectra of semiconductor nanocrystals in C4 specimens was induced by the Zn incorporation.

Structural and compositional changes of nanocrystals formed in C4 specimens were further analyzed using high resolution TEM, X-ray diffraction and resonant Raman scattering spectroscopy. As shown in Fig. 5a, when the C4 specimens were heat-treated at temperatures lower than 550 °C for 10 h, no diffraction peaks can be observed in the patterns, mainly due to the small size and low volume fraction of the nanocrystals. When the specimens were subjected to the second step heat-treatment at 570 °C, diffraction peaks corresponding to the hexagonal crystal (PDF#15–0105 for ZnSe and PDF#77–2307 for CdSe) started to occur and grow in intensity. Careful observation showed that these peaks located between the diffraction peaks of CdSe and ZnSe, closer to the diffraction peaks of ZnSe. This indicated that $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ QDs were formed in the glasses. Using the 2θ angles of the (110) diffraction peaks, interplanar distances of 110 crystal plane were found to be 2.017 Å and 2.012 Å for $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ QDs in C4-5 and C4-10 specimens. Assuming a linear dependence of the lattice constant on the x , compositions of the $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ crystalline phases were calculated to be $\text{Cd}_{0.13}\text{Zn}_{0.87}\text{Se}$ and $\text{Cd}_{0.1}\text{Zn}_{0.9}\text{Se}$ for C4-5 and C4-10 specimens, respectively.

TEM image of the C4-10 specimen was shown in Fig. 5b. Spherical nanocrystals with a diameter of 5–8 nm were precipitated and distributed homogeneously in the glass. Figure 5c shows HR-TEM image of one nanocrystal formed in the C4-10 specimen. The fast Fourier transformation (inset in Fig. 5c) showed that nanocrystals formed in the glass had a hexagonal structure. It was found that most of the nanocrystals have a dark central core surrounded by a brighter shell (Fig. 5b). This phenomenon was different from that of C4-0 specimen. As shown in Fig. 5(d) and the inset therein, the NCs in C4-0 specimen were formed without obvious bright shell around. Most probably, at the initial stage of Zn incorporation, concentration of Zn in the shell was too low and the shell was too thin to show the contrast between the core and shell in the TEM image. Upon the second step heat-treatment, the shell became thicker and concentration of Zn in the shell increased, and as a result, contrast between the core and shell became more clear and a bright shell can be observed in the TEM image (Fig. 5b and c). Careful observation showed that the interplanar distance in the core region was ~ 1.861 Å (along the direction shown in Fig. 5c), corresponding to the lattice constant (200) plane of CdSe crystals ($d_{200} = 1.8615$ Å, PDF#: 77-2307). While, in the brighter shell, the interplanar distance along the same direction decreased down to 1.826 Å, indicating the incorporation of Zn in the surface layer of CdSe QDs or the formation $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ shell. A shell can change the local environment of QDs' surface, physically separates the surface of the optically active core from its surrounding medium⁵³. Also, the formation of a shell ($\text{Cd}_{1-x}\text{Zn}_x\text{Se}$) with a wider bandgap than the core (CdSe) provides an energy barrier between the core and the shell, which can reduce the number of surface dangling bonds and suppress the charge carriers being trapped by the defects, thereby increase the intrinsic emission of the QDs⁵³.

Resonant Raman scattering spectra of C4 specimens obtained through one-step or two-step heat-treatment were shown in Fig. 6a. For C4 specimen heat-treated at 530 °C, no Raman vibration bands can be observed. While, for specimens heat-treated at higher temperature, one can clearly observe one shoulder near ~ 200 cm^{-1} and one strong peak at 235–250 cm^{-1} with its overtones. Through a careful background correction and Gaussian simulation, the Raman spectra in the range of 150–400 cm^{-1} can be fitted by three Gaussian peaks (P1, P2 and P3) (Fig. 6b). For P3, the peak position shifted from 235.3 cm^{-1} , 242.2 cm^{-1} , 246.0 cm^{-1} to 248.3 cm^{-1} for C4-0, C4-2, C4-5 and C4-10 specimens, respectively (Fig. 6b). The Raman peak P3 located between the longitudinal optical (LO) phonon frequencies of bulk hexagonal CdSe (210 cm^{-1}) and ZnSe (255 cm^{-1}), representing the formation of Zn-Cd-Se ternary crystals^{54,55}. With the increasing ratio of Zn in $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ crystals, the Raman peak shifted

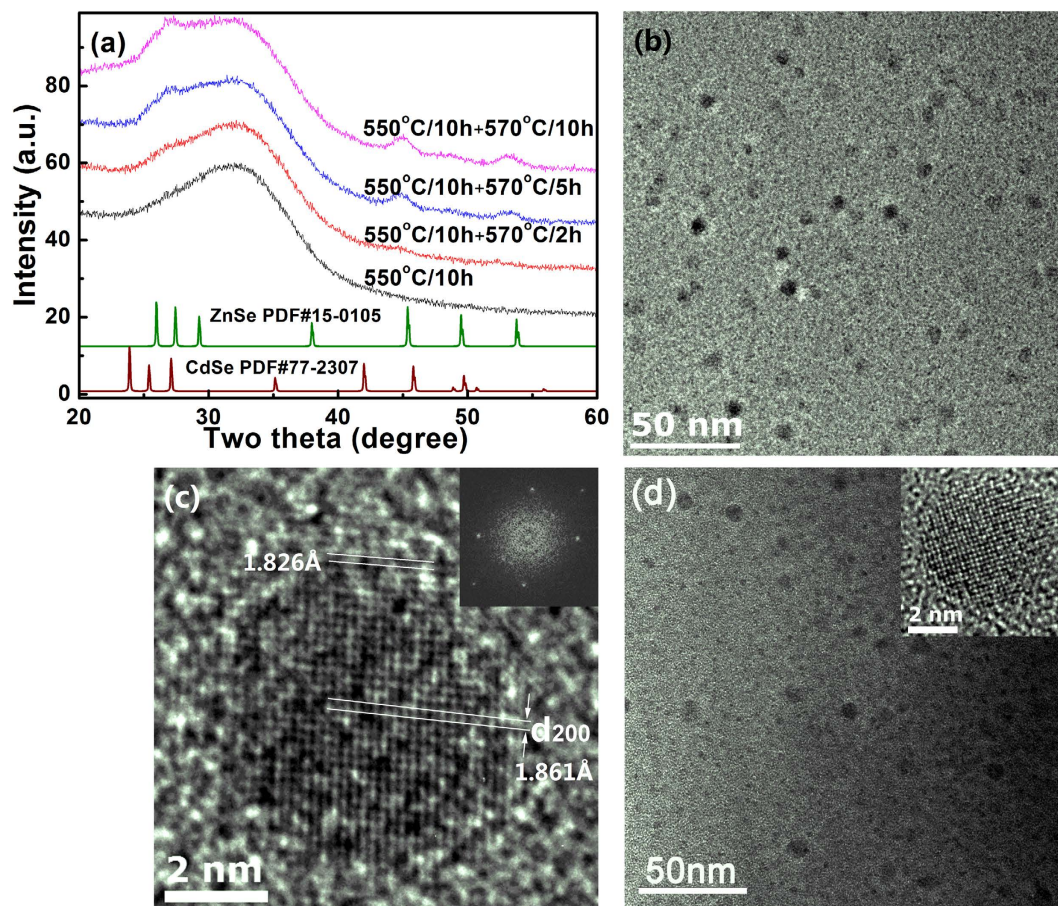


Figure 5. (a) X-ray diffraction patterns of C4-0, C4-2, C4-5 and C4-10 specimens, (b) TEM image of C4-10 specimen and (c) one nanocrystal formed in C4-10 specimen, (d) TEM image of C4-0 specimen. The inset in (c) is the fast Fourier transformation image of the nanocrystal shown in (c), and the inset in (d) shows the HR-TEM image of one nanocrystal formed in C4-0 specimen.

with the phonon frequency getting closer and closer to the standard LO phonon frequency of bulk wurtzite ZnSe (255 cm^{-1}). This phenomena was consistent with the one mode character of the compositional transformation of phonon spectra in ternary $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ bulk crystals^{54,56}, and QDs with compositional of $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ or $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ^{45,52}. Using the compositional dependence of the phonon spectra⁵⁴, it was found that average values of x in $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ crystalline phase formed in C4-0, C4-2, C4-5 and C4-10 specimens were found to be 0.52, 0.71, 0.81, and 0.87, respectively, confirming that more Zn was incorporated into the CdSe QDs with the increase in heat-treatment temperature. For C4-5 and C4-10 specimens, the value of x obtained from the Raman peak were smaller than that calculated from the X-ray diffraction patterns, mainly due to the phonon confinement effect of small nanocrystal, which leading to the red-shift of the Raman peak compared to the bulk crystals⁵⁵. Since the homogeneous $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ phase should exhibit only one main Raman peak, the shoulder (P1) at $\sim 200\text{ cm}^{-1}$ cannot be assigned to the $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ crystalline phase. With the change in the heat-treatment condition, the peak position of the P1 band varied in the range of 192.7 to 198.5 cm^{-1} . This peak position indicated the presence of CdSe QDs in these four specimens^{32,55}. The Raman spectra analysis with the preceding results indicated that CdSe/ $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ QDs were probably formed in C4-2, C4-5 and C4-10 specimens. Similar to the core/shell structured QDs, a broad vibration band was observed between P1 and P3, which can be assigned to the interface phonons⁵⁷. Therefore, core/shell structured CdSe/ $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ QDs were formed in the glasses upon one-step or two-step heat-treatment, which lead to the blue-shift in the absorption and PL spectra, and the quenching of the defect emission.

Although ZnSe nanocrystals cannot be precipitated into this glass composition at temperatures below $630\text{ }^\circ\text{C}$ ³⁹, Zn can incorporate into CdSe QDs and form $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ ternary compounds^{45,52}. Previous studies about $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ alloyed QDs prepared by chemical method deemed the association constant of CdSe is larger than ZnSe¹². The fluorescence intensity gradually increased due to the removal of surface defects after incorporation¹². For a certain glass composition and an enough HT duration, the concentration of Zn in $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ QDs was related to temperature only⁵⁸. When the HT temperature reached the critical temperature, the excess Zn ions began to incorporate into CdSe QDs. With increased HT duration, more Zn ions diffused into CdSe QDs, forming a ternary graded shell with a CdSe core, as shown in Fig. 7.

Previous studies have demonstrated a dot-like nanostructure embedded in a barrier material is expected to have an interface (IF) phonon, which has a characteristic frequency lying between the bulk transverse optical

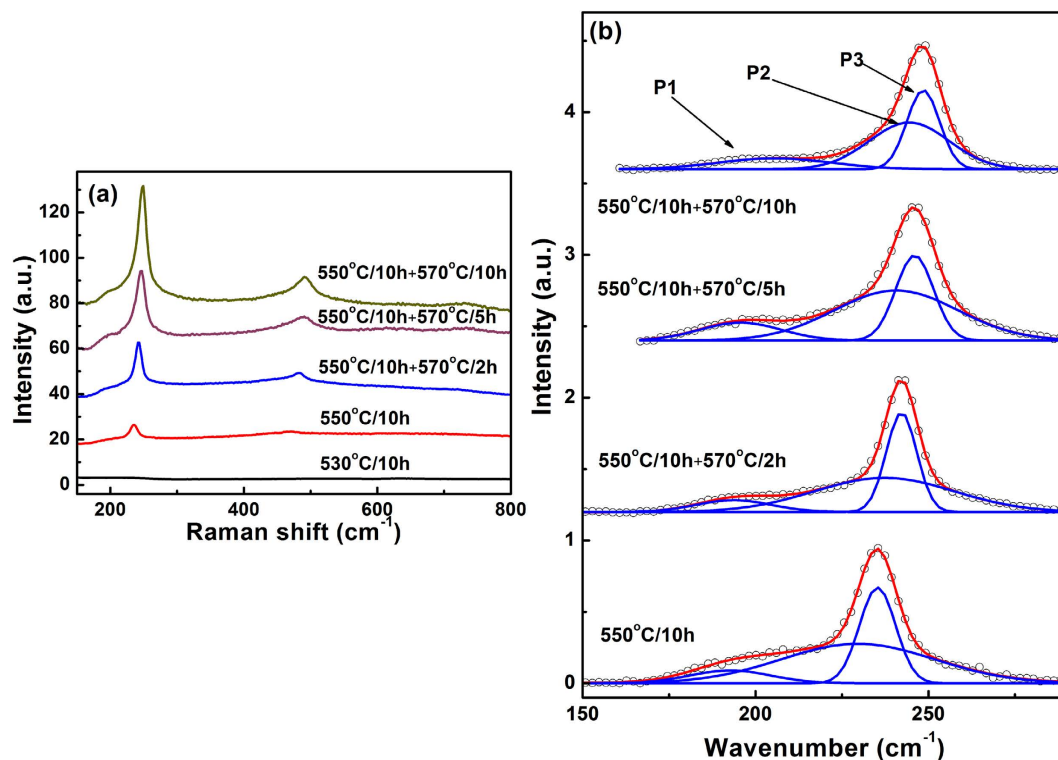


Figure 6. (a) Raman spectra of heat-treated glasses with composition of C4, (b) Gaussian deconvolution of the Raman vibration bands from 150 to 280 cm^{-1} .

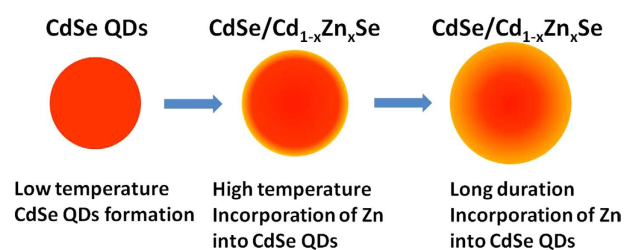


Figure 7. Schematic mechanism of $\text{CdSe/Cd}_{1-x}\text{Zn}_x\text{Se}$ QDs formation in glass.

(TO) and longitudinal optical (LO) phonon frequencies^{58–60}. Rho *et al.* also observed the broad IF phonon vibration band of CdSe/ZnSe core-shell QDs in the Raman spectra and covered the vibration band of the ZnSe shell⁵⁷. Similarly, a broad vibration band was observed between P1 (represents CdSe) and P3 (represents $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$) in $\text{CdSe/Cd}_{1-x}\text{Zn}_x\text{Se}$ core-shell NCs. The interface was more complicated due to the shell was graded. For different percentage of Zn in $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ shell, the characteristic frequency of interface phonon changed, resulting in the tiny shift of P2, which represented the interface phonon vibration.

Conclusion

In summary, effects of glass compositions and heat-treatment schedules on the formation and optical properties of CdSe QDs were investigated. When ZnSe/CdO ratios increased from 0.5 to 20, intensity ratio between the intrinsic emission and defect emission increased for CdSe QDs formed in the glass heat-treated at 530 °C for 10 h. For glass with ZnSe/CdO = 20, the intensity ratio between intrinsic emission and defect emission was further enhanced with the increase in heat-treatment temperature, and pure intrinsic emission was observed in specimen heat-treated at 570 °C for 10 h. TEM and Raman spectroscopy analysis confirmed that CdSe QDs were formed during low-temperature heat-treatment, and Zn was incorporated into the CdSe QDs and formed $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ ternary shell at higher temperature heat-treatment, resulting in the blue shift in the absorption and photoluminescence spectra, and the quenching of defect emission from QDs.

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Author Contributions

M.L.X. accomplished all the experiments in the article and the manuscript writing. C.L. put forward the initial idea, provided experiments guidance and accomplished the manuscript revision. Y.S.X. provided the Raman test assistance. C.G.L., J.H. and X.J.Z. provided the valuable suggestions during this work. Z.Y.Z., J.W., S.X.D. and J.J.H. attended in discussions after all the works were done. All authors have reviewed the manuscript and given approval to the final version of the manuscript.

Additional Information

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