Temperature-Dependent Photoluminescence of ZnCuInS/ZnSe/ZnS Quantum Dots

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ABSTRACT: Colloidal ZnCuInS/ZnSe/ZnS core/shell/shell quantum dots (QDs) with average particle sizes of 2.3, 2.7, and 3.3 nm were prepared in a noncoordinating solvent. The size-dependent optical band gap and photoluminescence (PL) band shift due to the quantum confinement effect were observed. Because the PL band showed a large Stokes shifts over 400 meV, the origin of the PL band was related to the electronic transition via defect levels. A time-resolved PL measurement indicated that the PL lifetime of the QDs was a characteristic feature of three dominating transitions from the conduction band to surface defect level, from the conduction band to an acceptor level, and from the donor level to an acceptor level. It was investigated as a function of temperature in the range from 50 to 373 K to understand the radiative and nonradiative relaxation processes and fitted with two empirical expressions, from which the Huang–Rhys factor and the phonon energy were calculated. According to the fitting data, the size-dependent parameters were analyzed including the Huang–Rhys factor, the average phonon energy, and the excitonic-acoustic-phonon coupling coefficient. The temperature coefficient was about $-2.32 \times 10^{-4}$ eV/K. The results showed that, in the temperature range from 50 to 373 K, the variations of the energy band gap and the photoluminescence line broadening were predominantly due to an optical transition from the band edge to the defect-related level and the coupling of the carriers to acoustic phonon, respectively.

1. INTRODUCTION

Principal interest in semiconductor nanocrystals or quantum dots (QDs) lies in their unique optical properties which are determined by quantum confinement. Since the physical dimensions of quantum dots are comparable to the de Broglie wavelength of the charge carriers in semiconductors, the energy states of electrons and holes are quantized. The emission wavelength of the charge carriers in semiconductors, the energy states of electrons and holes are quantized. The emission wavelength can be tuned by varying the crystal size. The temperature-dependent PL spectroscopy is used to study the radiative and the nonradiative relaxation processes as well as the exciton–phonon coupling in colloidal QDs. In general, the temperature dependence of the PL emission energy from excitons in QDs should follow that of the band gap in the bulk semiconductors. The change in the PL intensity as a function of temperature can often reflect the decrease of the temperature-dependent nonradiative recombination or the evolution of the PL mechanism. Therefore, it is important and necessary to investigate the temperature-dependent optical properties of ZnCuInS/ZnSe/ZnS core/shell QDs.

It is also known that the band gap of bulk semiconductors varies with temperature. There are a few studies on the temperature dependence of semiconductor nanocrystals, such as CdSe, CdSe/ZnS, ZnSe, InP/ZnS, and PbSe. We report in this paper a study on the temperature dependence of...
the band gap in ZnCuInS/ZnSe/ZnS QDs. The energy band gap was recorded as a function of temperature and was fitted with empirical expressions to derive the Huang–Rhys factor and the average phonon energy involved in the variation. Also the PL line width as a function of temperature was fitted to the fundamental equation describing the temperature dependence of the 1S exciton in semiconductors.\(^28\) Moreover, the size dependent parameters were calculated from the fitting data including the Huang–Rhys factor, the average phonon energy and the carrier-acoustic phonon coupling coefficient. The temperature coefficient was about \(-2.32 \times 10^{-4}\) eV/K which is close to quantum dots with the band edge emission (e.g., \(-2.97 \times 10^{-4}\) eV/K for CdSe QDs\(^27\)).

2. EXPERIMENTAL SECTION

2.1. Chemicals. Indium(III) iodide (InI\(_3\), 99.99%) and selenium powder (Se, 100 mesh) were purchased from Alfa Aesar. Copper(I) iodide (CuI, 98%), dichlorodiphenyltrichloroethane (DDT, 98%), tributylphosphine (TBP, 95%), diethyldithiocarbamic acid zinc (DECZn, 98%), oleyl amine (OAm, 80–90%), and zinc oxide (ZnO, 99.99%) were obtained from Aladdin. Acetone, methanol, hexane, and toluene were purchased from Aldrich. All chemicals were used directly without further treatment.

2.2. Precursor Solution. All of the following solutions were made under N\(_2\) protection.

\textit{CuI/OAm Solution.} A total of 85.7 mg of CuI (0.45 mmol) and 10 mL of OAm were loaded into a flask. The suspension was sonicated until all the solid was dissolved to form a light yellow-green solution.

\textit{InI\(_3\)/OAm Solution.} A total of 226.0 mg of InI\(_3\) (0.45 mmol) and 10 mL of OAm were loaded into a flask. The suspension was sonicated until a light yellow solution was obtained.

\textit{DECZn/TBP/ODE Solution.} A total of 181.0 mg of DECZn (0.5 mmol), 6 mL of TBP, and 24 mL of ODE were loaded into a vial. The suspension was heated to 343 K for 1–1.5 h to form a light milk-like liquid.

\textit{Se/TBP Solution.} A total of 78.0 mg of Se and 10 mL of TBP were mixed in a glovebox under vigorously stirring until the powder was dissolved.

\textit{ZnO/OA/ODE Solution.} A total of 100.3 mg of ZnO and 2073 mg of OA were loaded into a 25 mL three-necked flask. Then, the mixture was heated to 473 K until a colorless solution was achieved. After the solution was cooled to room temperature, 10 mL of ODE was added into the flask.

2.3. Synthesis of ZnCuInS/ZnSe/ZnS QDs. The ZnCuInS alloyed core and ZnSe/ZnS double shell (ZCIS/ZnS) QDs were synthesized with an approach modified from the method reported by Uehara et al.\(^29\) and Tan et al.\(^30\) In the typical procedure of 3.3 nm ZnCuInS/ZnSe/ZnS QDs, 20 mL of ODE was loaded into a 100 mL three-necked flask and was degassed under N\(_2\) for 10 min. A total of 2 mL of CuI/OAm (45 mM), 2 mL of InI\(_3\)/OAm, and 6 mL of DECZn/TBP/ODE were loaded into the flask under N\(_2\). The mixture was heated to 343 K for 30 min and then was heated to 483 K for 50 min. The color of solution varied from colorless to red which meant the formation and growth of ZnCuInS core. Then, 2 mL of Se/TBP and 2 mL of ZnO/OA/ODE solution were added drop by drop into the solution of ZnCuInS core to grow a ZnSe shell. Ten min later, 3 mL of DECZn/TBP/ODE were added into the flask for the growth of a ZnS shell. Then, the temperature was maintained at 423 K for 2 h. The solution was cooled to room temperature to collect the products after the purification. The growth temperature of core can be maintained at 473 and 453 K to achieve the particle size of 2.7 and 2.3 nm, respectively.
The hexane solution of QDs was extracted one time with twice volume of methanol. Then the QDs were redispersed in hexane and were precipitated by twice volume of methanol and equal volume acetone to hexane. The purified ZnCuInS/ZnSe/ZnS QDs were finally dispersed in toluene for characterizations.

2.4. Characterizations. Optical Measurements. Absorption spectra were measured on a Perkin-Elmer Lambda 950 UV–vis spectrophotometer. Photoluminescence (PL) spectra were measured on a Perkin-Elmer luminescence LS50B spectrophotometer. The QDs were dissolved into toluene.

Transmission Electron Microscopy (TEM). TEM studies were performed using a TECNAI F30ST TEM operated at 300 kV. Samples for TEM study were prepared by placing a 4 μL of toluene solution of QDs on ultrathin carbon-film-coated copper grids and let it dry.

Time-Resolved Photoluminescence (TRPL). Time-correlated single-photon counting (TCSPC) measurements were performed on a fluorescence spectrometer (mini-τ, Edinburgh Photonics) equipped with an EPL405 laser diode. The maximum repetition rate of the EPL405 laser diode is 10 MHz, corresponding to the 100-ns separation. However, when measured the decay curve, 5-μs separation was employed to avoid the PL accumulation.

3. RESULTS AND DISCUSSION

Figure 1 displays the optical absorption and PL spectra recorded at 300 K for the ZnCuInS/ZnSe/ZnS QDs with different sizes. The insets in Figure 1 show typical TEM images of those ZnCuInS/ZnSe/ZnS particles. The Stokes shifts as determined from Figure 1 are 398.6, 436.7, and 498.8 meV for 3.3, 2.7, and 2.3 nm ZnCuInS/ZnSe/ZnS QDs, respectively. The Stokes shift was around 398.6. Such large Stokes shifts indicate that the emission should be ascribed to the defect-related recombination.

Figure 1 also shows that the PL and the absorption for ZnCuInS/ZnSe/ZnS QDs are size-dependent. Both the PL and absorption peaks are blue-shifted as the diameter of the QDs decreases. The energies of deeply trapped states are more or less independent of the particle size;34 therefore, the weak size dependency of DAP recombination comes from the change in the Coulomb interaction with changing DAP separation, according to the equation:

\[ \nu = E_g - E_A - E_D + \frac{e^2}{4\pi\varepsilon r} \]  

where \( \nu \) and \( E_g \) are the DAP recombination energy and bulk energy band gap, respectively, \( E_D \) and \( E_A \) are the respective ionization energies of the donor and acceptor levels, and \( \varepsilon \) is the electric permittivity. According to eq 1, the energy shift associated with Coulomb interaction was calculated to be only \( \approx 20.3 \) meV when the ZnCuInS QD size was reduced from 3.3 to 2.4 nm.30 The large size-dependent shift of the emission energy (242 meV), which corresponds to approximately the size-dependent shift of the optical band gap (334 meV), indicates that the emission is related to the quantum confined level. The strong size-dependent PL band for the QDs could not be mainly attributed to a donor–acceptor pair (DAP) recombination. In ZnCuInS/ZnSe/ZnS QDs, the effective mass of an electron is generally smaller than that of a hole (they are respectively 0.16 and 1.30 for CuInS2 QDs), and therefore, the size-dependent increase in energy of the conduction band should be greater than that of the valence band. The size-dependent shift of emission (242 meV) reaches up to 72.5% of that in the optical band gap (334 meV). Thus the transition from the conduction band to a defect-related level might be one of the important electronic transitions responsible for the emission. Schematic diagrams of inter- and intraband structures for the present ZnCuInS/ZnSe/ZnS QDs are presented in Figure 2.
With the decrease of crystal size, the energies of the CB levels increase as a result of the quantum confinement effect; the defect levels are lightly dependent on the crystal size. The time-resolved PL of ZnCuInS/ZnSe/ZnS QDs is shown in Figure 2. The PL lifetimes were 296.7, 263.9, and 223.7 ns for 3.3, 2.7, and 2.3 nm ZnCuInS/ZnSe/ZnS samples, respectively. The long emission lifetime and the large "global" Stokes shift between the PL band and the band-edge absorption feature, coupled with the observation of a pronounced size-dependence of emission wavelength, are not completely consistent with either strictly band-edge recombination or recombination between two localized states. Instead, they indicate that the radiative recombination in these NCs involves a transition from a quantized conduction-band state to a localized intragap state. The PL decays are not single-exponential, indicating the existence of several emission recombination in the QDs. Based on the nonlinear least-squares analysis, the decay traces of the samples were fitted with a triexponential function

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right)$$

where $A_1$, $A_2$, and $A_3$ are fractional contributions of PL decay lifetime of $\tau_1$, $\tau_2$, and $\tau_3$, respectively. The fitted results are summarized in Figure 2 (bottom), with $\tau_1$ of about 20 to 40 ns, $\tau_2$ from 100 to 160 ns, and $\tau_3$ from 300 to 460 ns. According to the previous studies, the shorter lifetime ($\tau_1$) with a time of tens of nanoseconds may be due to the surface-related radiative recombination (IDS emission). The medium one ($\tau_2$) can be attributed to the recombination a quantized conduction-band state to a localized intragap state. The longer time ($\tau_3$) can be attributed to the DAP recombination. The evolution of the emission with time after the excitation is shown in Figure 2. The emission spectra show red shift probably from the high energy conduction band-related recombination with short lifetime to low energy DAP recombination with long lifetime.

Figure 3 shows the temperature-dependent photoluminescence spectra of ZnCuInS/ZnSe/ZnS QDs at 50–373 K. A red-shift as well as a broadening of the emission peak is observed with increasing temperature and a blue-shift with decreasing temperature. Figure 4a shows the band gap as a function of temperature for ZnCuInS/ZnSe/ZnS QDs with different particle sizes. The band gap values in this work were calculated from the peak position obtained from the PL spectra. The data could be well fitted using the traditional phenomenological equation introduced by Varshni for the temperature dependence of the band gap, with the assumption that the Stokes shift is independent of temperature.
\[ E_g(R, T) = E_g(R, 0) - \frac{\alpha(R)T^2}{T + \beta(R)} \]  \hspace{1cm} (3)

where \( E_g(R, 0) \) represents the band gap of ZnCuInS/ZnSe/ZnS QDs (sum of PL peak energy and the Stokes shift observed at room temperature) at 0 K, and \( \alpha(R) \) and \( \beta(R) \) are constants for the QDs with a certain size. It is known from the literature \(^{15} \) that \( \beta(R) \) is of the order of the Debye temperature (\( \theta_D \)) of the semiconductor obtained at 0 K. This equation takes into account both the change in lattice parameter and the temperature dependence of the electron–lattice interaction. It should be noted that eq 3 was originally derived for the infinite crystal, yet it has been used for bulk semiconductors as well as quantum dots. \(^{15,24} \) The values of \( E_g(R, 0), \alpha(R), \) and \( \beta(R) \) obtained from these fittings for ZnCuInS/ZnSe/ZnS samples with different sizes are tabulated in Figure 4 (bottom left). The values of \( \alpha(R) \) and \( \beta(R) \) agree with those reported for bulk CuInS \(_2\) (temperature coefficient \( dE/dT \approx -2.0 \times 10^{-4} \text{ eV K}^{-1} \), Debye temperature 264 K \(^{34} \)), while the value of \( E_g(R, 0) \) differs significantly from that of bulk ZnS (3.67 eV) and CuInS \(_2\) (1.55 eV) \(^{14,45} \) owing to the quantum confinement effect.

The data in Figure 4a could also be fitted to another expression, \(^{46} \) which improves upon the Varshni equation \(^{47} \) theoretically, since the parameters used in the equation are related to an intrinsic interaction within semiconductors, namely, the electron-phonon coupling.

\[ E_g(R, T) = E_g(R, 0) - 2S \left( \frac{\hbar \omega}{k_B T} \right) \left( \exp \left( \frac{\hbar \omega}{k_B T} \right) - 1 \right)^{-1} \]  \hspace{1cm} (4)

where \( S \) is the Huang–Rhys factor, \( \langle \hbar \omega \rangle \) is the average phonon energy, and \( k_B \) is the Boltzmann constant. The fitting results are shown as Figure 4b and tabulated there (bottom right). The fitting values of \( S \) signify that the electron–phonon coupling increases as the diameter of the nanocrystal decreases and are consistent with the data as shown in Figure 1. The values of \( E_g(R, 0) \) obtained from the fittings to eqs 3 and 4 are the same. Unfortunately the error involved in the determination of the phonon energy is relatively large. Yet we have ascertained that the values of \( \langle \hbar \omega \rangle \) in the range of 9–10 meV are incompatible with the data. This shows that the average phonon energies are much smaller than the longitudinal optical (LO) and the transverse optical (TO) phonon energies of bulk CuInS\(_2\), but are in accordance with the reported longitudinal acoustic (LA) phonon energies. The average of phonon energies is close to the bulk CuInS\(_2\) which is 8.3 meV. \(^{48} \) Consequently, the reduction of the energy gap with increasing temperature (Figure 4) is most likely caused by the coupling of the carriers to acoustic phonon modes.

Figure 5 shows the full width at half-maximum (fwhm) of the emission spectra of ZnCuInS/ZnSe/ZnS QDs with different particle sizes as a function of temperature. In order to gain a deeper insight into the carrier-phonon scattering processes involved in the line broadening, we fitted the experimental data to the expression given in eq 5. This equation describes the temperature dependence of the excitonic peak broadening in bulk semiconductors and has been used for QDs. \(^{17,24} \) The total line width can be described as the sum of three terms, an inhomogeneous broadening term, and two other terms representing homogeneous broadening due to acoustic and optical phonon–exciton interactions, respectively. \(^{17,28} \)

\[ \Gamma(T) = \Gamma_{inh} + \sigma T + \Gamma_{LO} \left( \exp \left( \frac{E_{LO}}{k_B T} \right) - 1 \right)^{-1} \]  \hspace{1cm} (5)

where \( \Gamma_{inh} \) is the inhomogeneous line width that is temperature-independent and is due to the fluctuations in size, shape, composition, and so forth, of the nanocrystals, \( \sigma \) is the carriers-acoustic phonon coupling coefficient, \( \Gamma_{LO} \) represents the strength of carriers-LO-phonon coupling, and \( E_{LO} \) is the LO-phonon energy. The fitting results are tabulated in Figure 5 (bottom). The values obtained from the fitting for \( \Gamma_{inh} \) and \( \Gamma_{LO} \) are in accordance with the data from the study of CuInS\(_2\) films. \(^{49} \) The values of the fitting for \( E_{LO} \) agree with the values of bulk CuInS\(_2\) (\( E_{LO} = 36 \text{ meV}^{66} \)) obtained from Raman spectra. The numerical values (in Figure 5, bottom) show that a dominant contribution to the line broadening in ZnCuInS/ZnSe/ZnS QDs still comes from the coupling of carriers to the acoustic phonons modes.

In order to investigate the nonradiative relaxation processes in QDs, we analyzed the temperature dependence of the integrated PL intensity. The PL intensities of ZnCuInS/ZnSe/ZnS QDs with different diameters as a function of inverse \( k_B T \) are shown in Figure 6. The PL intensity of the QDs decreases rapidly with temperature increases. The solid lines are the fitted curves using eq 6 \(^{51} \)

\[ I_{PL}(T) = \frac{I_0}{1 + A \exp \left( \frac{E_a}{k_B T} \right) + B \exp \left( \frac{E_b}{k_B T} \right)} \]  \hspace{1cm} (6)

where \( I_{PL}(T) \) is the integrated PL intensity at temperature \( T \), \( I_0 \) is the 0 K integrated PL intensity, \( E_a \) and \( E_b \) are the thermal activation energy, and \( A \) and \( B \) represent the ratios of the radiative lifetime in QDs to the capture time from emitting centers by nonradiative recombination centers. The parameters \( E_a, E_b, A, \) and \( B \) for the samples of ZnCuInS/ZnSe/ZnS QDs are summarized in Figure 6 (bottom). The nonradiative
Figure 6. Integrated PL intensities of ZnCuInS/ZnSe/ZnS QDs with different particle sizes as a function of $1/k_B T$ (top) and the fitting parameters (bottom). Solid lines are the fitting results according to eq 6.

relaxation process with a small activation energy (40–50 meV) results in a decrease in the PL intensity. It is known that many defects such as $V_{Cu}$, $V_{Se}$, In$_{Cu}$ can be acceptors or donors, resulting in recombination of a donor–acceptor pair and the conduction band-transition in the luminescence process in ZnCuInS/ZnSe/ZnS QDs. Therefore, the PL of ZnCuInS/ZnSe/ZnS QDs probably comes from several kinds of the recombinations including the surface-related radiative recombination, the recombination a quantized conduction-band state to a localized intragap state and the DAP recombination.

4. CONCLUSION

In summary, we have studied the size- and temperature-dependent spectra of ZnCuInS/ZnSe/ZnS core/shell/shell QDs. The PL spectra were recorded for several ZnCuInS/ZnSe/ZnS QDs with different diameters. The Stokes shift obtained by taking the difference between the positions of the absorption and emission peaks was found to increase with the increased QD size. The energy band gap of QDs with different diameters was investigated as a function of temperature in the range $300–373$ K and fitted with two empirical expressions, from which the Huang–Rhys factor and the average phonon energy were achieved. The electron–phonon coupling was found to be stronger for QDs with smaller diameters. The FWHM of the PL peak was also investigated and analyzed as a function of temperature. In the temperature range $300–373$ K, we found that the variation of both the energy band gap and the PL peak broadening for ZnCuInS/ZnSe/ZnS QDs was most likely caused by the coupling of the carrier to acoustic phonon. The three dominating recombination mechanisms probably exist including the surface-related radiative recombination, the recombination a quantized conduction-band state to a localized intragap state and the DAP recombination.

REFERENCES


