Wenyan Liu,[†] Yu Zhang,^{*,†,‡} Weiwei Zhai,[‡] Yinghui Wang,[‡] Tieqiang Zhang,[‡] Pengfei Gu,[†] Hairong Chu,[§] Hanzhuang Zhang,[‡] Tian Cui,[‡] Yiding Wang,[†] Jun Zhao,^{||,⊥} and William W. Yu^{*,†,||,⊥}

[†]State Key Laboratory on Integrated Optoelectronics, and College of Electronic Science and Engineering, Jilin University, Changchun 130012, China

[‡]State Key Laboratory of Superhard Materials, and College of Physics, Jilin University, Changchun 130012, China

[§]Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130025, China

Department of Chemistry and Physics, Louisiana State University, Shreveport, Louisiana 71115, United States

¹College of Material Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

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



Article

pubs.acs.org/JPCC

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 -2.32×10^{-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.¹ The emission efficiencies of QDs are generally much higher than those of their bulk counterparts and, most importantly, the emission wavelength can be tuned by varying the crystal size.^{2–5} These properties and their resistance to photobleaching make QDs attractive for applications such as biomedical tags,^{6–8} hybrid light-emitting diodes,^{9,10} solar cells,¹¹ photorefractive devices,¹² and potential laser development.¹³ Recently the I–III–VI QDs have been gaining increased attention.

The synthesis and optical properties of colloidal $CuInS_2$ – ZnS alloyed quantum dots (ZCIS QDs) have been recently reported.¹⁴ 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.¹⁵⁻¹⁹ 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.^{15,17,20–27} We report in this paper a study on the temperature dependence of

 Received:
 March 11, 2013

 Revised:
 July 26, 2013

 Published:
 July 29, 2013



Figure 1. UV–vis and PL spectra of ZnCuInS/ZnSe/ZnS QDs recorded at room temperature for three different sizes: 3.3 (a), 2.7 (b), and 2.3 nm (c). Insets: TEM photographs of the QDs. The bottom left (d) shows the schematic diagrams of inter- and intraband structures of QDs including the surface-related radiative recombination from the CB level to the ES level, the recombination a quantized conduction-band state to a localized intragap state from the CB level to the EA level, and the DAP recombination from the ED level to the EA level.

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 -2.32×10^{-4} eV/K which is close to quantum dots with the band edge emission (e.g., -2.97×10^{-4} eV/K for CdSe QDs²⁷).

2. EXPERIMENTAL SECTION

2.1. Chemicals. Indium(III) iodide (InI₃, 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.

Cul/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.

 Inl_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.

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.

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.

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/ ZnSe/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 N₂ for 10 min. A total of 2 mL of CuI/ OAm (45 mM), 2 mL of InI₃/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.



Figure 2. PL decay curves of ZnCuInS/ZnSe/ZnS QDs and the fitting parameters (table); the evolution of the emission with time with the particle sizes of 3.3 (b), 2.7 (c), and 2.3 nm (d).

Purification. 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.^{3,31,32} 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 4μ L 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- μ s 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 400–500 meV. This value is too large to be attributed to a direct excitonic recombination because the Stokes shift is at most 100 meV for excitonic recombination.³³ 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^{35,36}

$$h\nu = E_{\rm g} - E_{\rm A} - E_{\rm D} + \frac{e^2}{4\pi\varepsilon r} \tag{1}$$

where $h\nu$ and $E_{\rm g}$ are the DAP recombination energy and bulk energy band gap, respectively, $E_{\rm D}$ and $E_{\rm A}$ are the respective ionization energies of the donor and acceptor levels, and ε is the electric permittivity. According to eq 1, the energy shift associated with Coulomb interaction was calculated to be only \sim 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),³⁷ 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 QDs³⁸), and therefore, the size-dependent increase in energy of the conduction band should be greater than that of the valence band. The sizedependent 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 3. PL spectra of ZnCuInS/ZnSe/ZnS QDs with the particle sizes of 3.3 (a), 2.7 (b), and 2.3 nm (c) at different temperatures from 50 to 373 K.



Figure 4. Temperature-dependent peak energy for ZnCuInS/ZnSe/ZnS QDs with three different particle sizes (top) and the fitting parameters (bottom). Left column is the fitting results (solid lines) according to eq 3 (a), right column is the fitting results (solid lines) according to eq 4 (b).

Figure 1d. With the decrease of crystal size, the energies of the CB levels increase as a result of the quantum confining 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, which can be an internal defect. 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

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right)$$
(2)

where A_1 , A_2 , and A_3 are fractional contributions of PL decay lifetime of τ_1 , τ_2 , and τ_3 , respectively. The fitted results are

summarized in Figure 2 (bottom), with τ_1 of about 20 to 40 ns, τ_2 from 100 to 160 ns, and τ_3 from 300 to 460 ns. According to the previous studies, the shorter lifetime (τ_1) with a time of tens of nanoseconds may be due to the surface-related radiative recombination (IDS emission).^{39,40} The medium one (τ_2) can be attributed to the recombination a quantized conductionband state to a localized intragap state.^{40,41} The longer time (τ_3) can be attributed to the DAP recombination.^{39,42,43} 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,⁴⁴ with the assumption that the Stokes shift is independent of temperature

The Journal of Physical Chemistry C

$$E_{g}(R, T) = E_{g}(R, 0) - \frac{\alpha(R)T^{2}}{T + \beta(R)}$$
(3)

where $E_{\sigma}(R, 0)$ 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 literature¹⁵ that $\beta(R)$ is of the order of the Debye temperature (θ_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 ZnČuInS/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 CuInS₂ (temperature coefficient $dE/dT \approx -2.0 \times 10^{-4}$ eV K⁻¹, Debye temperature 264 K³⁴), while the value of $E_{\sigma}(R, 0)$ differs significantly from that of bulk ZnS (3.67 eV) and CuInS₂ (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 equation⁴⁷ theoretically, since the parameters used in the equation are related to an intrinsic interaction within semiconductors, namely, the electron-phonon coupling,

$$E_{\rm g}(R, T) = E_{\rm g}(R, 0) - 2S \left\langle \hbar \omega \right\rangle \left[\exp \left(\frac{\langle \hbar \omega \rangle}{k_{\rm B} T} - 1 \right) \right]^{-1}$$
(4)

where S is the Huang–Rhys factor, $\langle \hbar \omega \rangle$ is the average phonon energy, and $k_{\rm B}$ 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 $E_{\sigma}(R, 0)$ 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 CuInS₂, but are in accordance with the reported longitudinal acoustic (LA) phonon energies. The average of phonon energies is close to the bulk CuInS₂ 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}





Figure 5. Temperature-dependent fwhm of the PL spectra for ZnCuInS/ZnSe/ZnS QDs with three different sizes (top) and the fitting parameters (bottom). Solid lines are the fitting results according to eq 5.

$$\Gamma(T) = \Gamma_{\rm inh} + \sigma T + \Gamma_{\rm LO} \left[\exp\left(\frac{E_{\rm LO}}{k_{\rm B}T}\right) - 1 \right]^{-1}$$
(5)

where $\Gamma_{\rm inh}$ 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, σ is the carriersacoustic phonon coupling coefficient, $\Gamma_{\rm LO}$ represents the strength of carriers-LO-phonon coupling, and $E_{\rm LO}$ is the LOphonon energy. The fitting results are tabulated in Figure 5 (bottom). The values obtained from the fitting for $\Gamma_{\rm inh}$ and $\Gamma_{\rm LO}$ are in accordance with the data from the study of CuInS₂ films.⁴⁹ The values of the fitting for $E_{\rm LO}$ agree with the values of bulk CuInS₂ ($E_{\rm LO} = 36 \text{ meV}^{50}$) 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 $k_{\rm B}T$ are shown in Figure 6. The PL intensity of the QDs decreases rapidly when temperature increases. The solid lines are the fitted curves using eq 6⁵¹

$$I_{\rm PL} = \frac{I_0}{1 + A \, \exp\left(-\frac{E_{\rm a}}{k_{\rm B}T}\right) + B \, \exp\left(-\frac{E_{\rm b}}{k_{\rm B}T}\right)} \tag{6}$$

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 $1/k_{\rm B}T$ (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_S , In_{Cu} can be acceptors or donors, resulting in recombination of a donor–acceptor pair and the conduction band-acceptor 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 temperaturedependent 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 50-373 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 50-373 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.

AUTHOR INFORMATION

Corresponding Author

*E-mail: yuzhang@jlu.edu.cn (Y.Z.); wyu6000@gmail.com (W.W.Y.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National 863 Program (2011AA050509), the National Natural Science Foundation of China (61106039, 61225018, and 51272084), the National Postdoctoral Foundation (2011049015), Hongkong Scholar Program (XJ2012022), the Shandong Natural Science Foundation (ZR2012FZ007), and the Jilin Province Youth Foundation (201101025).

REFERENCES

(1) Prasad, P. N. *Nanophotonics*; John Wiley & Sons: New York, 2004.

(2) Alivisatos, A. P. Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science* **1996**, *271*, 933–937.

(3) Yu, W. W.; Wang, Y. A.; Peng, X. Formation and Stability of Size-, Shape-, and Structure-Controlled CdTe Nanocrystals: Ligand Effects on Monomers and Nanocrystals. *Chem. Mater.* **2003**, *15*, 4300–4308.

(4) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. *Chem. Mater.* **2003**, *15*, 2854–2860.

(5) Yu, W. W.; Falkner, J. C.; Shih, B. S.; Colvin, V. L. Preparation and Characterization of Monodisperse PbSe Semiconductor Nanocrystals in a Noncoordinating Solvent. *Chem. Mater.* **2004**, *16*, 3318– 3322.

(6) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. Semiconductor Nanocrystals as Fluorescent Biological Labels. *Science* **1998**, *281*, 2013–2016.

(7) Yu, W. W.; Chang, E.; Falkner, J. C.; Zhang, J. Y.; Al-Somali, A. M.; Sayes, C. M.; Johns, J.; Drezek, R.; Colvin, V. L. Forming Biocompatible and Non-Aggregated Nanocrystals in Water Using Amphiphilic Polymers. J. Am. Chem. Soc. **2007**, *129*, 2871–2879.

(8) Yu, W. W. Semiconductor Quantum Dots: Synthesis and Water-Solubilization for Biomedical Applications. *Expert Opin. Biol. Ther.* **2008**, *8*, 1571–1581.

(9) Tessler, N.; Medvedev, V.; Kazes, M.; Kan, S.; Banin, U. Efficient Near-Infrared Polymer Nanocrystal Light-Emitting Diodes. *Science* **2002**, 295, 1506–1508.

(10) Zhang, Y.; Xie, C.; Su, H. P.; Liu, J.; Pickering, S.; Wang, Y. Q.; Yu, W. W.; Wang, J. K.; Wang, Y. D.; Hahm, J.; Dellas, N.; Mohney, S. E.; Xu, J. Employing Heavy Metal-Free Colloidal Quantum Dots in Solution-Processed White Light-Emitting Diodes. *Nano Lett.* **2011**, *11*, 329–332.

(11) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. Hybrid Nanorod-Polymer Solar Cells. *Science* 2002, 295, 2425–2427.

(12) Winiarz, J. G.; Zhang, L.; Lal, M.; Friend, C. S.; Prasad, P. N. Observation of the Photorefractive Effect in a Hybrid Organic-Inorganic Nanocomposite. *J. Am. Chem. Soc.* **1999**, *121*, 5287–5295.

(13) Klimov, V. I.; Mikhailovsky, A. A.; Xu, S.; Malko, A.; Hollingsworth, J. A.; Leatherdale, C. A.; Eisler, H. J.; Bawendi, M. G. Optical Gain and Stimulated Emission in Nanocrystal Quantum Dots. *Science* **2000**, 290, 314–317.

(14) Nakamura, H.; Kato, W.; Uehara, M.; Nose, K.; Omata, T.; Otsuka-Yao-Matsuo, S.; Miyazaki, M.; Maeda, H. Tunable Photoluminescence Wavelength of Chalcopyrite CuInS₂-Based Semiconductor Nanocrystals Synthesized in a Colloidal System. *Chem. Mater.* **2006**, *18*, 3330–3335.

(15) Valerini, D.; Cretí, A.; Lomascolo, M.; Manna, L.; Cingolani, R.; Anni, M. Temperature Dependence of the Photoluminescence Properties of Colloidal CdSe/ZnS Core/Shell Quantum Dots Embedded in a Polystyrene Matrix. Phys. Rev. B 2005, 71, 235409-235414.

(16) Morello, G.; De Giorgi, M.; Kudera, Manna, S.; Cingolani, L. R.; Anni, M. Temperature and Size Dependence of Nonradiative Relaxation and Exciton-Phonon Coupling in Colloidal CdTe Quantum Dots. J. Phys. Chem. C 2007, 111, 5846–5849.

(17) Al Salman, A.; Tortschanoff, A.; Mohamed, M. B.; Tonti, D.; van Mourik, F.; Chergui, M. Temperature Effects on the Spectral Properties of Colloidal CdSe Nanodots, Nanorods, and Tetrapods. *Appl. Phys. Lett.* **2007**, *90*, 093104–093106.

(18) Wuister, S. F.; van Houselt, A.; de Mello Doneg, C.; Vanmaekelbergh, D.; Meijerink, A. Temperature Antiquenching of the Luminescence from Capped CdSe Quantum Dots. *Angew. Chem., Int. Ed.* **2004**, *43*, 3029–3033.

(19) Jing, P. T.; Zheng, J. J.; Ikezawa, M.; Liu, X. Y.; Lv, S. Z.; Kong, X. G.; Zhao, J. L.; Masumoto, Y. Temperature-Dependent Photoluminescence of CdSe-Core CdS/CdZnS/ZnS-Multishell Quantum Dots. J. Phys. Chem. C 2009, 113, 13545–13550.

(20) Dai, Q. Q.; Zhang, Y.; Wang, Y. N.; Hu, M. Z.; Zou, B.; Wang, Y. D.; Yu, W. W. Size-Dependent Temperature Effects on PbSe Nanocrystals. *Langmuir* **2010**, *26*, 11435–11440.

(21) Zhang, Y.; Dai, Q. Q.; Li, X.; Zou, B.; Wang, Y. D.; Yu, W. W. Beneficial Effect of Tributylphosphine to the Photoluminescence of PbSe and PbSe/CdSe Nanocrystals. *J. Nanopart Res.* **2011**, *13*, 3721–3729.

(22) Zhang, Y.; Dai, Q. Q.; Li, X.; Cui, Q.; Gu, Z.; Zou, B.; Wang, Y. D.; Yu, W. W. Formation of PbSe/CdSe Core/Shell Nanocrystals for Stable Near-Infrared High Photoluminescence Emission. *Nanoscale Res. Lett.* **2010**, *5*, 1279–1283.

(23) Joshi, A.; Narsingi, K. Y.; Manasreh, M. O.; Davis, E. A.; Weaver, B. D. Temperature Dependence of the Band Gap of Colloidal CdSe/ ZnS Core/Shell Nanocrystals Embedded into an Ultraviolet Curable Resin. *Appl. Phys. Lett.* **2006**, *89*, 131907–131909.

(24) Suyver, J. F.; Wuister, S. F.; Kelly, J. J.; Meijerink, A. Luminescence of Nanocrystalline ZnSe:Mn²⁺. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5445–5448.

(25) Narayanaswamy, A.; Feiner, L. F.; van der Zaag, P. J. Temperature Dependence of the Photoluminescence of InP/ZnS Quantum Dots. J. Phys. Chem. C 2008, 112, 6775–6780.

(26) Dai, Q.; Song, Y.; Li, D.; Chen, H.; Kan, S.; Zou, B.; Wang, Y.; Deng, Y.; Hou, Y.; Yu, S.; Chen, L.; Liu, B.; Zou, G. Temperature Dependence of Band Gap in CdSe Nanocrystals. *Chem. Phys. Lett.* **2007**, 439, 65–68.

(27) Li, S.; Zhang, K.; Yang, J. M.; Lin, L.; Yang, H. Single Quantum Dots as Local Temperature Markers. *Nano Lett.* **2007**, *7*, 3102–3105.

(28) Rudin, S.; Reinecke, T. L.; Segall, B. Temperature-Dependent Exciton Linewidths in Semiconductors. *Phys. Rev. B* **1990**, *42*, 11218–11231.

(29) Uehara, M.; Watanabe, K.; Tajiri, Y.; Nakamra, H.; Maeda, H. Synthesis of CuInS₂ Fluorescent Nanocrystals and Enhancement of Fluorescence by Controlling Crystal Defect. *J. Chem. Phys.* **2008**, *129*, 134709–134714.

(30) Tan, Z. A.; Zhang, Y.; Xie, C.; Su, H. P.; Liu, J.; Zhang, C. F.; Dellas, N.; Mohney, S. E.; Wang, Y. Q.; Wang, J. K.; Xu, J. Near-Band-Edge Electroluminescence from Heavy-Metal-Free Colloidal Quantum Dots. *Adv. Mater.* **2011**, *23*, 3553–3358.

(31) Yu, W. W.; Peng, X. Formation of High-Quality CdS and Other II-VI Semiconductor Nanocrystals in Noncoordinating Solvents: Tunable Reactivity of Monomers. *Angew. Chem., Int. Ed.* **2002**, *41*, 2368–2371.

(32) Zhang, Y.; Dai, Q. Q.; Li, X. B.; Liang, J. Y.; Colvin, V. L.; Wang, Y. D.; Yu, W. W. PbSe/CdSe and PbSe/CdSe/ZnSe Hierarchical Nanocrystals and Their Photoluminescence. *Langmuir* **2011**, *27*, 9583–9587.

(33) Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and Characterization of Nearly Monodisperse CdE (E = Sulfur, Selenium, Tellurium) Semiconductor Nanocrystallites. *J. Am. Chem. Soc.* **1993**, *115*, 8706–8715.

(34) Dijiken, A.; Meulenkamp, E. A.; Vanmaekelbergh, D.; Meijerink, A. Identification of the Transition Responsible for the Visible Emission in ZnO Using Quantum Size Effects. *J. Lumin.* **2000**, *90*, 123–128.

(35) Thomas, D. G.; Gershenzon, M.; Trumbore, F. A. Pair Spectra and "Edge" Emission in Gallium Phosphide. *Phys. Rev.* **1964**, *133*, A269–A279.

(36) Leite, R. C. C.; DiGiovanni, A. E. Frequency Shift with Temperature as Evidence for Donor-Acceptor Pair Recombination in Relatively Pure n-Type GaAs. *Phys. Rev.* **1967**, *153*, 841–843.

(37) Omata, T.; Nose, K.; Otsuka-Yao-Matsuo, S. Size Dependent Optical Band Gap of Ternary I-III-VI₂ Semiconductor Nanocrystals. *J. App. Phys.* **2009**, *105*, 073106–073110.

(38) Rincon, C.; Gonzalez, J. Acoustic Deformation Potentials in $A^{I}B_{III}C_{2}^{VI}$ Chalcopyrite Semiconductors. *Phys. Rev. B* **1989**, *40*, 8552–8554.

(39) Zhong, H. Z.; Zhou, Y.; Ye, M. F.; He, Y. J.; Ye, J. P.; He, C.; Yang, C. H.; Li, Y. F. Controlled Synthesis and Optical Properties of Colloidal Ternary Chalcogenide CuInS₂ Nanocrystals. *Chem. Mater.* **2008**, *20*, 6434–6443.

(40) De Trizio, L.; Prato, M.; Genovese, A.; Casu, A.; Povia, M.; Simonutti, R.; Alcocer, M. J. P.; D'Andrea, C.; Tassone, F.; Manna, L. Strongly Fluorescent Quaternary Cu-In-Zn-S Nanocrystals Prepared from $Cu_{1,x}InS_2$ Nanocrystals by Partial Cation Exchange. *Chem. Mater.* **2012**, *24*, 2400–2406.

(41) Li, L.; Pandey, A.; Werder, D. J.; Khanal, B. P.; Pietryga, J. M.; Klimov, V. I. Efficient Synthesis of Highly Luminescent Copper Indium Sulfide-Based Core/Shell Nanocrystals with Surprisingly Long-Lived Emission. J. Am. Chem. Soc. **2011**, 133, 1176–1179.

(42) Li, L.; Daou, T. J.; Texier, I.; Tran, T. K. C.; Liem, N. Q.; Reiss, P. Highly Luminescent $CuInS_2/ZnS$ Core/Shell Nanocrystals: Cadmium-Free Quantum Dots for In Vivo Imaging. *Chem. Mater.* **2009**, 21, 2422–2429.

(43) Chi, T. T. K.; Le, Q. P.; Nguyen, Q. L.; Li, L.; Reiss, P. Timeresolved Photoluminescence Study of CuInS₂/ZnS Nanocrystals. *Adv. Natl. Sci.: Nanosci. Nanotechnol.* **2010**, *1*, 025007–025011.

(44) Varshni, Y. P. Temperature Dependence of the Energy Gap in Semiconductors. *Physica* **1967**, *34*, 149–154.

(45) Luck, I.; Henrion, W.; Scheer, R.; Doering, T.; Bente, K.; Lewerenz, H. J. Determination of the Optical Bandgap of Solid Solutions out of the $ZnS/CulnS_2$ System by Diffuse Reflection Spectroscopy. *Cryst Res. Technol.* **1996**, *31*, 841–844.

(46) O'Donnell, K. P.; Chen, X. Temperature Dependence of Semiconductor Band Gaps. *Appl. Phys. Lett.* **1991**, *58*, 2924–2926.

(47) Thomas, D. G.; Hopfield, J. J.; Augustyniak, W. M. Kinetics of Radiative Recombination at Randomly Distributed Donors and Acceptors. *Phys. Rev.* **1965**, *140*, A202–A220.

(48) Krustoka, J.; Raudoja, J. Temperature Dependence of Very Deep Emission from an Exciton Bound to an Isoelectronic Defect in Polycrystalline CuInS₂. *Appl. Phys. Lett.* **2006**, *89*, 051905–051907.

(49) Ho, C.; Lo, S.; Chi, P. Electronic Structure and E1 Excitons of CuInS₂ Energy-Related Crystals Studied by Temperature-Dependent Thermoreflectance Spectroscopy. *J. Electrochem. Soc.* 2010, 157, H219–H226.

(50) Alvarez-Garciaa, J.; Rudigierb, E.; Regab, N.; Barconesa, B.; Scheerb, R.; Perez-Rodrigueza, A.; Romano-Rodrigueza, A.; Morantea, J. R. Growth Process Monitoring and Crystalline Quality Assessment of CuInS(Se)₂ Based Solar Cells by Raman Spectroscopy. *Thin Solid Films* **2003**, 431–432, 122–125.

(51) Wu, Y.; Arai, K.; Yao, T. Temperature Dependence of the Photoluminescence of ZnSe/ZnS Quantum-Dot Structures. *Phys. Rev.* B **1996**, *53*, 485–488.