Exciton radiative recombination in spherical CdS/CdSe/CdS quantum-well nanostructures

Jianfeng Xu and Min Xiao
Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701

David Battaglia and Xiaogang Peng
Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701

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Photoluminescence (PL) and lifetimes of colloidal CdS/CdSe/CdS (core/well/shell) quantum-well (QW) nanostructures are investigated for different well thicknesses in the temperature range of 77–300 K. When the temperature increases, the PL intensity decreases continuously and PL peak shifts to lower energy side. The PL lifetimes for the 1–3 monolayer (ML) CdSe QWs increase with temperature and radiative recombination dominates the decay processes. The radiative lifetimes basically increase linearly with temperature, which indicates the existence of free two-dimensional excitons. For the 4 ML CdSe QW sample, the lifetime does not increase with temperature, showing more nonradiative processes due to more defect formation within the thicker QWs. © 2005 American Institute of Physics. [DOI: 10.1063/1.2001731]

The optical properties of planar two-dimensional (2D) semiconductor quantum wells (QWs) and zero-dimensional (0D) colloidal CdSe quantum dots (QDs) have been studied extensively and their emission recombination processes are well understood. Recently, a new spherical QW nanostructure, which includes one or more monolayers (ML) of CdSe (1.75 eV bulk bandgap) between a CdS (2.7 eV bulk bandgap) core and an outer CdS shell, has been synthesized. The CdS core is only 3.7 nm in diameter and the outside shell layer of CdS is 4 ML. The PL spectra are excited by the 514.5 nm line of a cw Argon ion laser and detected by a liquid-nitrogen-cooled charged coupled device camera. A frequency-doubled (400 nm), mode-locked (~1 ps) Ti:sapphire pulse laser and a time-correlated photon-counting system were used for the PL decay measurements. Each sample for PL and PL decay measurements was prepared by spin-coating a clean fused silica coverslip with a solution of QWs in toluene followed by a 1 wt. % PMMA solution. The samples were mounted inside a micro-objective cryostat with a controllable temperature between 77 K and room temperature.

In this letter, we report our detailed optical studies of such unique spherical CdS/CdSe/CdS QW nanostructures, especially the temperature dependence of photoluminescence (PL) and lifetime of QWs with different thicknesses. The exciton lifetime measurements can help us to understand and determine different radiative and nonradiative recombination processes, which are very important for the potential applications of such colloidal QW nanostructures in optoelectronic devices and biophotonic labeling.

The QW structure is formed by growing low bandgap CdSe layers between a high band gap CdS core and an outside shell. This CdS/CdSe/CdS QW system, with a well thickness between 1 and 4 CdSe ML (1 ML ~ 0.35 nm), was synthesized by a modified successive ion layer adsorption and reaction method and the PL as well as Raman spectra were measured. The CdSe layers have the wurtzite crystal structure, the same as that of CdS core and outside shell. Their QYs were measured by comparing the emission spectra against that of a laser dye having known QY. For all the samples used in the experiments, the CdS core diameter is 3.7 nm and the outside shell layer of CdS is 4 ML. The PL spectra were excited by the 514.5 nm line of a cw Argon ion laser and detected by a liquid-nitrogen-cooled charged coupled device camera. A frequency-doubled (400 nm), mode-locked (~1 ps) Ti:sapphire pulse laser and a time-correlated photon-counting system were used for the PL decay measurements. Each sample for PL and PL decay measurements was prepared by spin-coating a clean fused silica coverslip with a solution of QWs in toluene followed by a 1 wt. % PMMA solution. The samples were mounted inside a micro-objective cryostat with a controllable temperature between 77 K and room temperature.

Figure 1(a) presents the PL spectra of CdSe QWs with thicknesses from 1 to 4 ML at room temperature. The PL peak position is strongly dependent on the thickness of the QWs and is shifted from 2.23 eV for the 1 ML CdSe QW to 1.93 eV for the 4 ML CdSe QW. In addition, the PL spectra...
of the QW structures are broader in comparison to CdSe QDs, which is mainly due to fluctuations of the well thickness and structural variations of the interfaces between CdSe and the surrounding CdS barriers. The inset of Fig. 1(a) shows the schematic drawing of the QW core/well/shell nanostructure. Figure 1(b) displays the dependences of PL peak position and PL QY on the thickness of the QWs. With increasing CdSe QW thickness, the PL QY increases to a maximum value at around 2 ML and then decreases.

Figure 2 shows the PL intensity and peak position for the 2 ML CdSe QWs as a function of temperature. On decreasing the temperature from 300 to 77 K, the intensity of the PL spectrum increases gradually, indicating a higher radiative decay rate at low temperature. The PL peak shifts to the low energy side with increasing temperature, which reflects band gap change of QWs as PL comes from the electronic transition from bottom of the conduction band to the top of valence band. The variation of the band gap with temperature can be attributed to the effects of lattice dilation and electron-lattice interaction.

PL lifetime measurements were taken by monitoring the PL peak decay at different temperatures. Curves shown in Fig. 3 are examples of the PL decay profiles from a 2 ML CdSe QW sample. The data can be fitted well with single-exponential functions. The PL signal decays exponentially with a lifetime of 11.9 ns at room temperature. The PL lifetime shortens when the QW sample is cooled down. The exciton lifetimes obtained for different QW samples with different well thicknesses are plotted in Fig. 4 as a function of temperature. For the 1–3 ML QWs, the lifetime increases with temperature, indicating that radiative decay processes dominate, which is in agreement with the higher PL QYs compared to the 4 ML sample shown in Fig. 1(b) as well as 5 ML sample (not shown here). Such temperature dependence of the PL lifetime also shows the characteristic behavior of the 2D excitation and is different from the luminescence dynamics of 0D CdSe QDs. Labeau et al. investigated the luminescence lifetime of CdSe QDs at various temperatures. They found that the luminescence lifetime of CdSe QDs drops with increasing temperature at the range of 2–90 K, then becomes constant at higher temperatures, which is qualitatively consistent with a model of thermal activation of excitons from the dark ground state to higher-lying bright states.

The measured PL lifetime is given by \( \tau_{\text{PL}} = \tau_{\text{rad}} + \tau_{\text{nr}} \), where \( \tau_{\text{rad}} \) and \( \tau_{\text{nr}} \) are the radiative and nonradiative decay lifetimes, respectively. \( \tau_{\text{rad}} = \frac{\tau_{\text{PL}}}{\text{QY}} \), with QY to be the quantum yield. From the PL decay time (\( \tau_{\text{PL}} \)) and the PL QY, the values of \( \tau_{\text{rad}} \) and \( \tau_{\text{nr}} \) for the emission from a 2 ML QW sample are plotted as a function of temperature, as shown in Fig. 5. It is clearly shown that \( \tau_{\text{rad}} \) nearly increases linearly.
with temperature. This is an indication that excitons are free 2D excitons because the theoretical calculation predicts the relation of $\tau_{\text{rad}} \propto T^{-1.0}$ for 2D excitons.\(^9\) On the other hand, $\tau_{\text{nr}}$ is a monotonically decreasing function of measured $T$ below 200 K and becomes nearly a constant at higher temperature. The increasing tendency of the temperature dependence of the PL lifetime is determined mainly by the radiative processes. Radiative decay processes dominate in the 2 ML QW sample at low temperature range ($T<210$ K). At higher temperature ($T>210$ K), the nonradiative decay processes play more important roles. We note that emission lifetime of the 3 ML QW sample increases with temperature below 200 K, then saturates at higher temperature, and the lifetime of the 4 ML QW sample does not increase with temperature. This may be explained by the defects or strains within the QWs. For thicker wells, we expect a significant change in the lattice parameters inside the CdSe layers, which can result in the presence of a greater number of defects as well as a larger lattice strain. It is known that for heteroepitaxially growth thin layers, if the layer is very thin, the layer lattice parameters can change even without defects. However, if the layer becomes to be thicker than certain critical thickness, the lattice will relax with defect formation, and the lattice constant approaches the intrinsic value. These defects induce more nonradiative recombinations, especially at higher temperature. In such case, the QY is lower and PL lifetime is relatively shorter compared to other thinner QW samples. However, further experimental studies and theoretical modeling are necessary to clarify the detailed carrier recombination processes.

Planar semiconductor QWs are promising structures for the development of optoelectronic devices. For example, today the most efficient commercial diode lasers are made of multiple planar QWs. However, the fabrication processes of the planar QWs are complicated and the defects and strains formed within the QWs make PL lifetimes, in general, drop with increasing temperature because of the dominant nonradiative recombinations, which hinder their wide applications.\(^{10–12}\) On the other hand, colloidal QDs have the advantages of high emission QY and easily tunable emission wavelengths. The spherical QW nanostructure studied here combines the promising characteristics of both 2D planar QW and 0D colloidal QD and will have potential applications in nanoscale lasers and light emitting devices.

In summary, we studied the temperature behaviors of the PL and lifetimes of colloidal CdS/CdSe/CdS QW structures with different well thicknesses. The PL lifetime increases with temperature in the 1–3 ML QWs, which shows that the radiative decay processes dominate. The nearly linear increase of radiative lifetime with temperature indicates that the excitons are likely to be free excitons in 2D system. The unique properties for such colloidal QW nanostructures, a new system to the semiconductor nanocrystal family, will greatly promote fundamental understanding of low-dimensional semiconductor nanocrystals, especially for QW systems, and have potential applications in opto-electronic devices and biological labeling.

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