Photoluminescence Investigation of Carrier Localization in Colloidal PbS and PbS/MnS Quantum Dots

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ABSTRACT: The existence of surface organic capping ligands on quantum dots (QDs) has limited the potential in QDs emission properties and energy band gap structure alteration as well as the carrier localization. This drawback can be addressed via depositing a thin layer of a semiconductor material on the surface of QDs. Herein, we report on the comparative study for photoluminescent (PL) properties of PbS and PbS/MnS QDs. The carrier localization effect due to the alteration of energy band gap structure and carrier recombination mechanism in the QDs were investigated via PL measurements in a temperature range of 10–300 K with the variation of the excitation power from 10 to 200 mW. For PbS QDs, the gradient of integrated PL intensity (IPL) as a function of excitation power density graph was less than unity. When the MnS shell layer was deposited onto the PbS core, the PL emission exhibited a blue shift, showing dominant carrier recombination. It was also found that the full width half-maximum showed a gradual broadening with the increasing temperature, affirming the electron–phonon interaction.

1. INTRODUCTION

Colloidal PbS quantum dots (QDs) have attracted interest due to their unique electronic structure and optical properties in the near-infrared (NIR) region. They have been widely used in biological markers, photovoltaic solar cells, and optoelectronic devices. Fundamentally, QDs are semiconductor crystals with a size in the nanometer scale length with physical dimensions smaller than the exciton Bohr radius that lead to the quantum confinement effect. The movement of charge carriers (e.g., electrons and holes) in QDs is confined in a three-dimensional system, which eventually leads to a discrete near-infrared absorption and emission process.

It is worth mentioning that energy relaxation and recombination in QDs are strongly dependent on the surface passivation condition such as high surface-to-volume ratio. The highly dynamic region of the surface of QDs provides an active adsorption site for other chemical species such as ligands and ionic solvents that eventually alter the properties of QDs. This phenomenon indirectly induces the formation of surface trap states in the energy band gap structure of QDs and facilitates the nonradiative transition between the electronic states. To eliminate the surface trap states as well as dangling bond defects on the surface of QDs, an effective method involving formation of a core–shell heterostructure was introduced by depositing a layer of a wide-band-gap semiconductor material (shell) around the photoactive core QDs (core), aiming to tune the surface defects to the outer region of the shell. These core–shell QDs introduce new physicochemical properties and multifunctional characteristics, making them attractive in both theoretical and experimental research by controlling their surface nature and subsequently tuning and improving their optical properties.

Among all of the core–shell systems, type-I band alignment is the most attractive structure targeted by researchers. The common examples include CdSe/ZnS and PbS/CdS. In these systems, the core is passivated with a shell of another semiconductor material of a wider band gap that comprises a lower-energy band state in the valence band and a higher-energy band state in the conduction band as compared to the band structure of the core level. Both charge carriers (electrons and holes) are confined inside the nanostructure regime, allowing spatially direct exciton recombination. Thus, the emission energy in the type-I system is determined by the energy band gap of the core material. A previous study reported that the implementation of a wide-band-gap shell material on a narrow-band-gap core material could increase the charge-carrier confinement in the core region as observed by...
organometallic methods. In this approach, the precursor of exchange approach is an alternative solution to synthesize well-properties are still being widely investigated. The cation Therefore, the design and controllable synthesis strategy of the structural features and the mechanism remains challenging. properties. However, understanding the relationship between conductor in the MnS layer in this system prevents aggregation of MnS. The embedded PbS semi-potential energy well of MnS. The embedded PbS semi-shell QD system is PbS/MnS. In this system, charge carriers were concentrated in the PbS core and sandwiched in the large shell QD system is PbS/MnS. In this system, charge carriers and sedimentation of QDs and targeting of the optical processes involved in these nanostructures. Despite a large number of synthesis and experimental works dealing with the study of the fundamental properties of type-I core–shell QDs, there is still limited attention on the investigation of carrier localization inside the QDs, by analyzing the dependence of integrated PL intensity (IPL) on the excitation power density (Pex). On another note, it has been reported that nonradiative recombination is dominant in PbS QD system as proved by the superlinear relation in the gradient analysis of the plot IPL versus Pex at room temperature. In the high-temperature regime, the thermal activation energy of the nonradiative decay channel was favorable and led to the thermal quenching process.

In this paper, we present a comparative study for temperature and power dependence of PL analysis in PbS and PbS/MnS QDs. The dominant carrier recombination mechanism based on the integrated PL intensity versus power density graph was presented. A series of experimental and analyzed results were consistently supported with the postulated carrier recombination mechanism that occurred in the as-synthesized type-I PbS/MnS QD system under the controlled temperature system. Our results presented the quenching of PL intensity for the PbS/MnS QD sample in the high-temperature regime, which can be attributed to the transition of carrier excitation into the nonradiative recombination centers. A prominent blue shift of dominant PL peaks at ~21 meV for PbS/MnS QDs was also observed when the temperature was increased from 10 to 300 K. These results further proved the enhancement of the electron–phonon coupling and confinement-induced mixing among discrete and continuum states in the PbS/MnS QD system.

2. EXPERIMENTAL SECTION

2.1. Materials. Lead (II) acetate trihydrate (Pb(CH3CO2)2, 99.99%, R&M Chemicals), sodium sulfide (Na2S·9H2O, 99.99%, R&M Chemicals), manganese (II) acetate salt (Mn(CH3CO2)·4H2O, 98.5%, R&M Chemicals), thioglycerol (TGL) (C3H8O2S, 95%, Sigma-Aldrich), di-thioglycerol (DTG) (HOCH2CH(SH)CH2SH, 95%, Sigma-Aldrich), triethylamine (C8H15N, 99.5%, Chemiz), and deionized water.

2.2. Sample Synthesis. In this experiment, all chemicals were used without any further purification. The synthesis was started with the preparation of PbS QDs in aqueous solution, which followed the procedure as reported by Zaini et al.23 Briefly, the sample preparation utilized lead (II) acetate to extract Pb2+ as a lead precursor and sodium sulfide to extract S2− as a sulfide precursor. TGL and DTG were used as capping ligands. For the preparation of 30 mL of Pb2+ solution, 0.189 g (0.0166 M) of Pb(C2H3O2)2 was dissolved in deionized water at room temperature. Afterward, the reaction flask was degassed by flowing nitrogen gas inside the flask. Triethylamine was added dropwise to adjust the pH until it reached pH 10−11. Next, 0.259 mL of TGL was added followed by 0.099 mL of DTG into a three-neck flask containing the Pb2+ precursor. The S2− precursor was prepared by adding 0.120 g (0.1 M) of Na2S·9H2O to 5 mL of deionized water. The Pb2+ and S2− precursors were mixed with the molar ratio of Pb2+ and S2− precursors fixed to 1 and 0.3, respectively. After the precursors were introduced into the system accompanied by continuous stirring at 400 rpm, the solution changed from colorless to dark brown immediately, indicating the formation of PbS QDs. For the fabrication of PbS/MnS core–shell QDs, the Mn2+ precursor was added to the PbS solution under the flow of nitrogen (N2) gas. The Mn2+ precursor was prepared by dissolving 0.017 g of manganese (II) acetate salt in 0.6 mL of deionized water. Then, the solution was rapidly mixed with 7.0 mL of the PbS core QDs and stirred for 30 min to produce PbS/MnS core–shell QDs. The samples were then stored in a chemical refrigerator at a low controlled temperature of 4 °C, to avoid oxidation and aggregation before the characterization process. The schematic diagram of the preparation of QDs is presented in Figure 1.

2.3. Sample Characterization. Customized photoluminescence (PL) spectroscopy was used in optical measurements. A 532 nm green diode-pumped solid-state laser was used as an excitation source in near-infrared (NIR) wavelength detection. The spectroscopy setup was equipped with a double monochromator, a lock-in amplifier, a chopper, an InGaAs detector, and a temperature controller. In detail, the emitted PL signal was collected by a lens and then focused onto the entrance slit of the monochromator. During the measurement, all of the samples were drop-cast on the glass substrate. The integration time was set as 1 s, and the scanning range was...
fixed from 800 to 1600 nm. For temperature dependence measurements, the samples were placed in the cryostat and the temperature was controlled in the range of 10−300 K. The transmission electron microscope (TEM) equipped with energy-dispersive X-ray (EDX) (FEI Technai-G2 20S-TWINTEM-EDX) was used in the structural characterization of the as-synthesized QDs. The sample was prepared by the drop-casting method onto a carbon-coated Cu grid. The size distribution and particle size of QDs for the sample were analyzed from the HRTEM image obtained.

3. Results and Discussion

This research work focused on the PL emission of colloidal PbS and PbS/MnS core−shell QDs in an aqueous solution under the existence of thiol-based ligands (TGL and DTG). Figure 2 represents the HRTEM image of the colloidal PbS QDs with an average diameter of 6.00 ± 1.00 nm. It can be seen that the PbS QDs are clearly prevented from binding together due to protection from thiol ligands. Thiol-based organic ligands were selected because of their excessive functional groups that consisted of sulfur atoms and hydrogen atoms. These compounds enable hydrogen bond formation between the ligands and the surface of QDs. The thiol ligands are also used to prevent the coalescence of PbS/MnS QDs via passivating the active surface of QDs. Specifically, the repulsive interaction between the ligands and the QDs eventually stabilizes the compound via either electrostatic interactions or van der Waals forces. The MnS shell was formed on the surface of QDs via the method involving the cation exchange between Mn2+ and Pb2+. This method was selected because the operating temperature is relatively low, which indirectly minimized the Ostwald ripening process and resulted in the homogeneous QD size distribution.

Figure 2.

Figure 2. HRTEM image of PbS QDs with lattice spacing (white arrow).

Figure 3.

Figure 3. Magnified HRTEM image of colloidal PbS/MnS QDs in aqueous solution. The white arrows show the lattice spacing of PbS and MnS.

Figure 4.

Figure 4. EDX spectrum of PbS/MnS core−shell QDs.

The EDX peak at a dispersion energy of 5.9 keV can be indexed to the element Mn. The EDX spectrum shows that the PbS/MnS QDs have a higher surface-to-volume ratio, and the elemental ratio of compounds is significantly affected by the number of surface atoms. The presence of Pb and S peaks resulted from the PbS QDs, while the Cu peak can be assigned to the copper grid. The ratio of atomic percentage between Pb and S was 0.5. The atomic percentage for the elements Mn, S, and Pb was 0.13, 66.12, and 33.75%, respectively. The high atomic percentage of the element S could have originated from the presence of organic capping ligands TGL and DTG that are attached on the surface of the QDs via hydrogen bonding. It is noteworthy that the compounds TGL and DTG consisted of sulfur atoms in the functional groups. The EDX peak at a dispersion energy of 5.9 keV can be indexed to the element Mn.

Figure 5.

Figure 5 shows the normalized PL intensity of PbS and PbS/MnS QDs measured at a temperature of 10 K. For PbS QDs, the PL peak was detected at an emission energy of ~1.01 eV, which is comparable to a previous work reported by Turyanska et al. (Eg = 1.0 eV). For PbS/MnS QDs, the PL peak was blue-shifted with respect to the individual emission energy to EpbS/MnS of ~1.05 eV. A similar result was reported by Zhao et al. on PbS/CdS with a significant blue shift of PL peaks after...
cation exchange. The results suggested the shrinking of PbS core size due to the replacement of the lead ion with the cadmium ion during the formation of the CdS shell, and in our case, the blue shift of the PL peak energy of PbS/MnS was due to the confinement effect induced by the MnS shell present. A prominent blue shift of dominant PL peaks in PbS/MnS QDs was also observed when the temperature was increased from 10 to 300 K, as shown in Figure 6a. These results further proved the enhancement of the electron−phonon coupling and confinement-induced mixing among discrete and continuum states in the PbS/MnS QD system. It is also proved that the presence of the MnS shell and the structural properties of QDs have influenced the optical line width and the emission energy. This claim can be seen from the broadening of PL line width that affirmed the compositional disorder within the nonuniformity of the prepared QDs matrix, which is probably due to less uniformity of the size of QDs.

The PL analysis was conducted by varying the temperature from 10 to 300 K for both samples of PbS QDs and PbS/MnS QDs. The peak position and the temperature coefficient of the sample can be analyzed using the temperature dependence PL method and calculated using the modified Varshni equation

\[ E_g(T) = E_g(0) + \alpha T^2 / (\beta + T) \]  

where \( E_g(0) \) is the band gap at \( T = 0 \) K, \( \alpha \) represents the band gap energy temperature coefficient, and \( \beta \) is a constant of the order of magnitude of the semiconductor material Debye temperature. For PbS and PbS/MnS QDs samples, a plus sign was used in the second term because the PL peak energy was increased in terms of temperature.

Generally, the PL peak was shifted to a higher energy of ~20 meV and the PL line width was increased to ~170 meV. As can be seen in Figure 6a, the PL peak of PbS QDs was blue-shifted to ~19.9 meV, and it is approximately linear for \( T > 80 \) K. The energy shift at \( T > 80 \) K was calculated and can be described by a temperature coefficient of \( \alpha_{\text{PbS}} = 0.1 \) meV/K. This value is smaller than that of the bulk PbS (\( \alpha = 0.52 \) meV/K), but it is comparable to that in the reported studies of thiol-capped PbS QDs (\( \alpha = 0.3 \)meV/K) and PbS QDs in glass (\( \alpha = 0.2 \) meV/K). For the PbS/MnS QD sample, the value of \( \alpha_{\text{PbS/MnS}} \) becomes significantly smaller than that for PbS QDs, which is 0.05 meV/K. This result is expected due to the negative value of \( \alpha \) in MnS bulk (\( \alpha_{\text{MnS}} = -2 \) meV/K).

Emission energy shifts in the samples can be due to the following factors: (i) electron−phonon coupling, (ii) thermal expansion of the crystal lattice, and (iii) strain because of thermal expansion mismatch. When the temperature changed, the temperature coefficient, \( \alpha \), could be altered by the strong quantum confinement in the individual QD system whereby the value of \( \alpha \) was dominated by lattice dilation and interband electron−phonon coupling in the specific band structure of QDs. This claim was proved by the smaller value of \( \alpha \) in PbS/MnS QDs than that in PbS QDs because of the negative value of \( \alpha \) recorded in MnS bulk (\( \alpha_{\text{MnS}} = -2 \) meV/K). Besides, the value of \( \alpha \) in QDs could be modified by the changes in the Coulomb energy, exciton−phonon scattering, and confinement energy. On another note, the emission energy shift on PbS/MnS QDs also can be caused by the temperature-dependent strain experienced by the PbS core because of the thermal expansion coefficients. This mechanism could lead to a blue shift or red shift in the emission energy that strongly depends on the type of materials.

The effects of temperature on PbS QDs and PbS/MnS QDs are further studied by investigating the full width half-maximum (FWHM) obtained from a Gaussian fit of the PL spectra as a function of temperature. The FWHM of the PL signal for both samples PbS QDs and PbS/MnS QDs increased significantly when the temperature increased. Based on Figure
The FWHM of PbS/MnS QDs broadens monotonously from ∼160 to ∼200 meV when the temperature is set at 10 and 300 K, respectively. Szendrei et al. mentioned that the decrease of the FWHM with decreasing temperature is due to suppression of the phonon-coupled quenching of the excitons. Also, monotonous line width broadening of PbS/MnS QDs is due to scattering of the exciton by optical and acoustic phonons. From our measurement, we expect the gain width of FWHM with the increasing temperature, and consequently, the FWHM follows the trend. The number of lattice vibrations (phonons) is reduced at low temperature, thus resulting in the narrow FWHM in the PL peak. There are several factors affecting the PL line width, which include (i) inhomogeneous particle size distribution and spectral diffusion of charge trapping in the defect state and (ii) thermal activation of PbS nanoparticles at T ∼ 150 K. This thermal activation is also observed in this study. For PbS QDs, inhomogeneous broadening that occurs at T < 50 K is due to fluctuation in QD sizes, and the PL curve is broad at ∼20 K as a result of multi-peak overlapping from QDs of different sizes. In the high-temperature regime, it is speculated that the PL line width is controlled by an intrinsic scattering process due to carrier interaction with phonons. The schematic illustration of electron–phonon coupling in PbS QDs and PbS/MnS QDs is depicted in Figure 7.

The mechanism of charge-carrier recombination was further explored by analyzing the dependence of integrated PL (IPL) on excitation power density. In Figure 8, the integrated PL intensity of PbS QDs and PbS/MnS QDs across the spectral region ∼0.7–1.55 eV was plotted on a log–log scale. It was observed that the integrated PL intensity increased linearly with the excitation power density. This can be described by eq 2.

\[ I_{\text{PL}} = \eta I_0^m \]  

where \( I_{\text{PL}} \) is the integrated PL intensity, coefficient \( \eta \) is related to the PL efficiency, and \( I_0 \) is the excitation power density. The exponent \( m \) is dependent on the value of the gradient in the IPL graph, and it indicates the carrier recombination mechanism. The results are expected to be close to unity due to the excitonic recombination. The gradient, \( m \), can be categorized into three groups: \( m \sim 1, 1 < m < 2, \) and \( m \sim 2 \). Each group corresponds to the condition of the dominant carrier recombination mechanism where radiative (\( m \sim 1 \)), mixture of radiative and nonradiative (\( 1 < m < 2 \)), and nonradiative dominant (\( m \sim 2 \)).

From Figure 8a,b, the IPL increases linearly with the increasing power density. The slope of the graph was presented in the increasing trend from low temperature to high temperature. Similar behavior can also be seen in other
semiconductor materials. At 10 and 70 K, the gradient of the graph is recorded as 0.64 and 0.66, respectively. The gradient of the plot showed an increasing trend when the temperature was further increased to 70 K. At this low temperature, the electrons and holes are favorable to possess a radiative recombination path due to excitonic recombination resulting from minimal thermal energy available for exciton dissociation.

For the PbS/MnS QD sample, the gradient of the graphs is detected to be <1 and close to unity for the testing temperature. This result indicates that radiative recombination is dominant in the PbS/MnS system. When the temperature was increased to 150 and 220 K, the gradient values were found to be approximately 0.71 and 0.82 at all excitation power densities. These findings further concluded that radiative recombination is dominant over the entire investigated excitation range. When the temperature was increased to 300 K, the slope was increased to 0.99, suggesting that the PL peak might reflect the recombination of excitons from the ground state of the QDs, which indicates the strong confinement of the charge carriers even at room temperature. Papagiorgis et al. also reported a similar result where the slope for their PbS QD solids was ~0.96 when the temperature was set above 200 K and explained by the monomolecular behavior. The schematic illustration of the charge-carrier mechanism with variation of temperature and power excitation is depicted in Figure 9.

4. CONCLUSIONS

In summary, the temperature- and power-dependent PL properties of PbS/MnS core–shell QDs play a vital role in understanding the recombination processes and the nature of carrier escape. The type-I PbS/MnS QDs with a stable emission along the near-IR spectral range were successfully synthesized in aqueous solution. The temperature-dependent PL analysis showed that PL peak energies were blue-shifted at ~21 meV for PbS/MnS due to the presence of the MnS shell, which was related to the quantum confinement effect. When the temperature increased, the FWHM broadening signified the interaction of charge carriers with phonons. The carrier recombination was explored using a PL power-dependent analysis. The radiative recombination was proved to be dominant in the PbS/MnS QD system compared to PbS QDs with the following results: (i) the value of gradient was close to unity (0.99 at 300 K) and (ii) the integrated PL intensity increased with the increasing power density.

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Notes
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