Distinctive Spectroscopic Characteristics Observed in Colloidal Perovskite CsPbBr₃ Quantum Dot

Received 15 July, 2021; revised 19 July, 2021; accepted 29 July, 2021

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ABSTRACT

Distinctive spectroscopic characteristics are observed in colloidal perovskite CsPbBr₃ quantum dot (QD) dispersed in octane doped with PPO. As the content of CsPbBr₃-QD increases, the emission and the absorption energies decrease due to QD-cluster formed in case of the inter-QD distance smaller than diameter of QD. Spectroscopic evidences supporting QD-cluster are found in the Urbach energy and the carrier lifetime. Unusual absorption lines showing explicit QD dependence are observed in Fourier-transform infrared spectra, which is explained by vibrational modes of bound PPO hybridized with CsPbBr₃-QD.

Keywords: Perovskite, CsPbBr₃, Quantum dot, Time-resolved photoluminescence, Absorption, Fourier-transform infrared spectroscopy

1. Introduction

By virtue of distinguished characteristics in light emission and absorption, the perovskite (Px) structure has abruptly emerged as a new semiconductor system [1]. The application has been widely spreading over all fields of optoelectronic devices, such as solar cells [2, 3], light-emitting devices [4], photodetectors [5], X/γ-ray detectors [6, 7], and THz emitters [8]. In these, the solar cell has rapidly developed in 10 years since Miyasaka [9] first reported the efficiency of 3 % in 2009. By introduction of organic-inorganic hybrid Px (FAPbI₃/MAPbBr₃) and of pseudo-halide anion formate (HCOO⁻), the efficiency jumps up to 24.23 (2019) [2] and 25.6 % (2021) [3], respectively, whose values are superior to that of Si-based solar cell. In particular, all-inorganic CsPbX₃ (X=Cl, Br, I) is drawing attention as new Px candidate that could replace the hybrid Px with drawback like phase decomposition. Nano-crystalline CsPbX₃ exhibits quantum-dot (QD) behavior [10, 11] that shows extremely high photoluminescence quantum yield (PLQY) and photoelectric conversion efficiency (PCE). In addition, it has been known that the wavelength modulation is available in the whole range of visible light (~430–780 nm) by simply substituting halogen element (X). Therefore, a variety of Px-based materials and their photoelectric applications are now under study [10–13].

Figure 1 illustrates some experimental results obtained in previous study [14]. The specimens used were CsPbX₃-QDs dispersed in solvent (octane, C₈H₁₈) with a small amount of fluorescent substance of PPO (2,5-diphenyloxazole, C₁₅H₁₁NO), which was successfully applied to high-sensitivity liquid X-ray scintillator. Figure 1(a) is optical photographs for representative 5 samples synthesized in our laboratory, Figs. 1(b)/1(c) the light emission of each sample under irradiation of UV (365 nm)/X-ray (6 MV), and Figs. 1(d)/1(e) representative photoluminescence/radioluminescence (PL/RL) spectra. Figure 1(f) is a demonstrative X-ray image taken by the CsPbBr₃-QD scintillator. Figures 1(d)/1(e) reveal that each CsPbX₃-QD sample of different component/composition (X) has a unique spectrum, and added PPO

Figure 1. Photographs for emission of colloidal CsPbX₃-QD samples taken under (a) white light, (b) UV (365 nm), and (c) X-ray (6 MV). (d) PL spectra, (e) RL spectra, and (f) schematic diagram of X-ray imaging system and X-ray image obtained by using lab-fabricated CsPbBr₃-QD liquid scintillator.

does not perturb spectral characteristics of QD in the visible light region at all. The details on the lab-fabricated PPO-assisted CsPbBr₃-QD scintillator are described in previous report [14].

In this study, we report some unusual spectroscopic behaviors observed in colloidal CsPbBr₃-QD doped with PPO. The formation of QD-cluster is proposed on the basis of PL and absorption (AB) spectra showing QD dependence. The Urbach energy manipulated from AB spectra and the carrier lifetime identified by time-resolved photoluminescence (TRPL) spectra are discussed as additional data supporting QD-cluster. In Fourier-transform infrared (FTIR) spectroscopy, the

Figure 2. (a) PL spectra and (b) PL peak intensity and energy plotted as a function of QD content.

QD-PPO hybridization is proposed for explanation of distinctive behavior on AB lines growing with the QD content.

2. Experimental details

CsPbBr₃-QD samples used in this study were prepared by the hot-injection synthesis that was introduced by Schmidt *et al.* [15] and Protesescu *et al.* [4] for metal-calcogenide QD and metal-halide Px-QD, respectively. First, for Cs-precursor, cesium-carbonate (Cs₂CO₃) and oleic-acid (OA) were mixed with octadecene (ODE) and reacted by heating in nitrogen atmosphere. PbBr₂ precursor was prepared by mixing PbBr₂/ODE with ligands of OA+OLA(oleylamine). When PbBr₂ was dissolved, the temperature was raised up to 180 °C and Cs-precursor was injected. The mixture was quenched in a cooling reservoir and separated CsPbBr₃-QD powder through centrifugation.

Several tens of milligrams of QD powder were synthesized in a single batch, and a series of CsPbBr₃-QD samples for each spectroscopy were prepared by dispersing QD powder in octane just before measurement. It was confirmed that CsPbBr₃-QD samples used in this study exhibited excellent PLQY and unique PL spectra, as demonstrated in Fig. 1.

3. Results and discussion

3.1. Red shift in photoluminescence spectra

Figure 2 presents (a) PL spectra and (b) a pair of curves for the intensity and the energy of PL peaks of CsPbBr₃-QDs plotted as a function of QD content. As the QD content increases from 1→10 mg/ml, the intensity monotonically increases, but the energy abruptly decreases from 2.458 to 2.420 eV. It can be easily understood for increase of PL intensity in terms of the number of QDs, but a plausible explanation is required for the anomaly of PL energy.

We have introduced the inter-QD distance as a parameter alternative to the QD content, as denoted on the upper axis of Fig. 2. When the distance between QDs becomes smaller than diameter of QDs, a

Figure 3. (a) AB spectra and (b) optical bandgap and Urbach energy plotted as a function of QD content.

bulk of QDs adhere and entangle each other to form QD-cluster. The sublevel energy of QD-cluster suffers the red shift that is lower than that of individual QD due to the quantum confinement effect [16]. The QD content increases more, the size of QD-cluster becomes bigger, and the red shift becomes larger.

The average inter-QD distance D introduced to justify the red shift of PL energy was simply manipulated by the equation of

$$D = [M/N_A d]^{1/3}, \quad (1)$$

where N_A is the Avogadro number ($6.02 \times 10^{23} \text{ mol}^{-1}$), and M and d the molecular weight of CsPbBr₃ and the QD content, respectively. As the QD content (d) changes from 1→10 mg/ml, the inter-QD distance (D) approaches from 9.8 to 4.6 nm whose values are comparable to or smaller than QD diameter of 8–12 nm. These figures confirm that the inter-QD distance is sufficiently close to form QD-clusters.

3.2. Optical bandgap and Urbach energy in absorption spectra

Experimental results supporting the QD-cluster formation can be seen in the AB spectra. Figure 3 shows (a) AB spectra and (b) a pair of plots for the optical bandgap [$E_g(O)$] and the Urbach energy [$E(U)$] of CsPbBr₃-QD.

$E_g(O)$ was determined from the intercept of the relationship known to Tauc plot as

$$(\alpha E)^n = k[E - E_g(O)], \quad (2)$$

where α is AB coefficient, $n=2$ for the direct allowed transition, and k a proportional constant. As the QD content increases from 1→10 mg/ml, $E_g(O)$ decreases from 2.490 to 2.475 eV whose values are higher than the PL peak energy by 32–55 meV equivalent to 6–12 nm in wavelength. The difference is well known to the Stokes shift that is frequently observed in normal spectroscopy, and decreasing $E_g(O)$ may be the other evidence for the QD-cluster formation.

Figure 4. (a) TRPL spectra and (b) carrier lifetimes for fast and slow decays plotted as a function of QD content.

The Urbach energy $E(U)$ was estimated from the exponential term expressing the spectral abruptness near AB edge as

$$\alpha = \alpha_0 \exp[E/E(U)], \quad (3)$$

where α_0 is the value at $E=0$. $E(U)$ is a parameter corresponding to the linewidth energy of band-tail formed by defects. As shown in Fig. 3, $E(U)$ monotonically decreases with increasing QD content, which indicates surface defects reduced by the QD-cluster formation. In other words, the surface-to-volume ratio (SVR) of QD-cluster formed by a bulk of QDs is smaller than those of individual QDs. Therefore, the surface trap due to dangling bonds becomes decreased, which leads to reduction of $E(U)$.

3.3. Carrier lifetime in time-resolved photoluminescence spectra

We suggest the carrier lifetime as an additional result for QD-cluster. Figure 4 presents (a) TRPL spectra and (b) a couple of plots for the fast/slow decay time taken at PL peaks for CsPbBr₃-QDs, which was analyzed by double-exponential decay function. As the QD content increases, the fast decay exhibits a minor increase in the range of 10–20 ns, but the slow decay experiences a rapid decrease from 150 to 50 ns.

Table I. Summary of 6 AB lines observed in FTIR spectra and suggested origin.

AB Line	QD Dependence	Mode	Suggested Origin
1465 cm ⁻¹	None	C-H Bending	Individual PPO
1378 cm ⁻¹	Weak	C-H Bending	Hybrid QD-PPO
1240 cm ⁻¹	Weak	C-N Stretching	Hybrid QD-PPO
1056 cm ⁻¹	Strong	C-O Stretching	Hybrid QD-PPO
887 cm ⁻¹	Weak	C=C Bending	Hybrid QD-PPO
719 cm ⁻¹	None	C=C Bending	Individual PPO

Figure 5. FTIR spectra of solvent (C₈H₁₈) and colloidal CsPbBr₃-QDs with different QD content.

The fast decay reflects an average lifetime for carriers captured at surface traps such as dangling bonds. As the size of QD-cluster grows larger, the number of surface defects reduces and the average lifetime becomes longer. On the other hand, the slow decay time includes an information on the recombination rate (R) of free electron/hole (n/p) in conduction/valence sublevel. As previously discussed in PL/AB spectra, the red shift of the QD sublevel due to the cluster formation results in enhancement of the recombination rate ($R \sim np$), which makes the carrier lifetime short.

3.4. Bonding modes in Fourier-transform infrared spectra

An interesting behavior was observed in infrared spectroscopy. Figure 5 shows FTIR spectra of colloidal CsPbBr₃-QDs that are basically the same as samples used in this study. It is noted that the QD spectrum displays the net intensity eliminated by the solvent background (topmost) from the raw QD signal via a graphic software. Six AB lines were found in FTIR spectra, and they could be categorized into 2 groups. One is Group-A for 2 outermost AB lines (1465, 719 cm⁻¹) with invariable intensity over all QD spectra, and the other is Group-B that consists of 4 inner AB lines (1378, 1240, 1056, 887 cm⁻¹) showing explicit QD dependence.

Table I is a summary on 6 AB lines observed in FTIR spectra. The bonding modes suggested were retrieved from the Reference Data Book [17]. Considering that PPO spectrum is composed of only 2 Group-A lines invariable for all QD spectra, it is clear that the 2 AB lines (1465/719 cm⁻¹) are attributed to C-H/C=C bending of individual PPO molecules (C₁₅H₁₁NO).

Taking consideration of spectral evolution of Group-B growing with the QD content, Group-B should be strongly correlated with QDs, absolutely opposite to Group-A. Here is an ambiguity in Group-B. Despite that Group-B exhibits explicit dependence on CsPbBr₃-QD, no vibrational mode related with Cs-Pb-Br bonds exists in the whole FTIR spectral range of 4000–400 cm⁻¹. The contradiction of Group-B can be explained by hybridization of QD (CsPbBr₃) and PPO (C₁₅H₁₁NO). The hybridized system was already proved both theoretically and experimentally in previous study [14], and the schematic model of PPO hybridized with QD is sketched in Fig. 6. In this configuration, negatively charged N of PPO and positively charged Pb of QD form ionic bond, so PPO molecule is tightly bound to CsPbBr₃-QD via Pb-N bond. Here, we can suggest exceptional vibrational modes attributed to oxazole radical (C₃HNO=) in PPO bound to heavy QD-molecule/QD-cluster. Four kinds of vibrational modes of C-H, C-N, C-O, and C=C are available in C₃HNO=, and each mode can be corre-

Figure 6. Schematic picture of hybridized QD-PPO ($\text{CsPbBr}_3\text{-C}_{15}\text{H}_{11}\text{NO}$). (This figure is the duplicate of Fig. 2(e) in Ref [14].)

sponded to one of 4 Group-B lines, as listed in Table I. The AB intensity of C-O stretching mode stronger than those of the other modes (C-H, C-N, C=C) may be due to difference in strength of dipole moment.

4. Conclusions

We discussed some unusual spectroscopic characteristics of colloidal CsPbBr_3 -QDs observed in PL, AB, TRPL, and FTIR spectra. The anomaly of PL and AB energies decreased with increase of QD content was explained by QD-cluster formed by a bulk of QDs. The Urbach energy $[E(U)]$ of AB spectra and the carrier lifetime of TRPL spectra were suggested as additional data supporting the QD-cluster formation.

The FTIR spectra exhibited 2 kinds of distinctive characteristics. The former was 2 AB lines (Group-A; $1465, 719\text{ cm}^{-1}$) with invariable intensity over all QD spectra that were due to bending modes of C-H/C=C of individual PPO, and the latter was 4 AB lines (Group-B; $1378, 1240, 1056, 887\text{ cm}^{-1}$) with explicit QD dependence that were attributed to bending/stretching modes of C-H/C-N/C-O/C=C of bound PPO hybridized with QD-molecule/cluster. Though the origin of QD-dependent Group-B lines was identified as PPO bound to QD, we judge that the observation of QD-dependent FTIR lines is a very distinctive result.

Acknowledgements

This work was supported by the National Research Foundation (NRF) of Korea (Grant No. 2021R1F1A1062672, 2019R1I1A1A01048852) and Technology Innovation Program (Grant No. 20013597) funded by the Ministry of Trade, Industry & Energy.

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