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Full Length Article

Quantum confinement luminescence of trigonal cesium lead bromide quantum dots

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ABSTRACT

Cesium lead halides are novel and superior optoelectronic materials. Unlike the cases of the widely investigated cubic $CsPbXr_3$ (X = Cl, Br, or I) nanocrystals, people know little about the optical properties of the "zero-dimensional perovskite" Cs_4PbX_6 nanocrystals. We study the photoluminescence properties of the Cs_4PbBr_6 quantum dots (QDs) with sizes of only a few nanometers. They exhibit stable wavelength-tunable (from 340 to 378 nm) luminescence stemming from quasi-self-trapped excitons. The spectral characterizations in conjunction with first-principles calculations reveal there is remarkable quantum confinement effect in the Cs_4PbBr_6 QDs. The large exciton binding energy obtained from both calculation and experiment explains why the trigonal Cs_4PbX_6 QDs have strong exciton-related absorption and emission at room temperature. This family of wide-gap trigonal cesium lead halide QDs with intrinsic near-UV luminescence have potential applications in short-wavelength photonic nanodevices.

1. Introduction

The lead halide perovskites have emerged as outstanding materials for photovoltaic and luminescence applications owing to excellent optical properties [1–10]. Their have virtues of low cost, facile synthesis, high quantum yields, and wavelength-tunable narrow emission bands, which render them rather competent in optoelectronic applications [11–15]. Recently, people pay great attention to the optical properties of the "zero-dimensional perovskite" Cs_4PbX_6 (X = Cl, Br, or I) nanocrystals (NCs) [16–21]. It had long been observed that bulk Cs_4PbX_6 (especially Cs_4PbBr_6) crystals have near-UV luminescence at low temperature but not at room temperature [22–27]. Bulk Cs_4PbBr_6 exhibited distinct optical properties other than that of bulk $CsPbBr_3$, owing to the difference between their crystal structures. In cubic $CsPbBr_3$, each pair of adjacent $PbBr_6^{4-}$ octahedra share a common Br^- anion, resulting in formation of an interconnected network of octahedra [28]. As a result, the p orbitals of the Br^- ion overlap the s and p orbitals of the two nearest Pb^{2+} ions, and this leads to strong orbital hybridization [23]. It results in substantial reduction of the bandgap of $CsPbBr_3$ (~2.15 eV) [18] relative to that of a single $PbBr_6^{4-}$ cluster (~4 eV) [23-25]. But in trigonal Cs_4PbBr_6, all the $PbBr_6^{4-}$ octahedra are separated from each other by intermediate Cs ions [22,23,25,29], and this prevents the 6s and 6p states of Pb^{2+} from forming extended quantum states, leading to formation of localized states which are approximately confined in the isolated octahedra [23,26]. As a result, the optical bandgap of Cs_4PbBr_6 is close to that of the free $PbBr_6^{4-}$cluster, and Cs_4PbBr_6 could exhibit molecule-like excitonic absorption band [24,30,31]. $CsPbBr_3$ has direct band gap and strong room-temperature luminescence arising from delocalized Wannier excitons [11,27,32]. In contrast, bulk Cs_4PbBr_6 has indirect band gap and low-temperature luminescence originating from localized Frenkel excitons [23,27,32]. The previous studies also indicated that bulk Cs_4PbBr_6 has luminescence properties similar to that of $PbBr6^{4-}$ clusters and lead-doped cesium bromides because the $PbBr_6^{4-}$ octahedra are their common luminescence centers [23–25,27,33]. Compared with the case of bulk materials, the studies of the Cs_4PbX_6 NCs is still in its infancy and the existing conclusions concerning them are under debate, especially about whether they have room-temperature luminescence and about how their optical properties differ from that of the corresponding bulk materials [21]. Our recent study revealed that the Cs_4PbCl_6 NCs have near-UV luminescence at room temperature [20]. Is such luminescence an intrinsic characteristic of this family of trigonal cesium lead halide NCs? Herein, we study the photoluminescence (PL) properties of the small Cs_4PbBr_6 quantum dots (QDs) with sizes down to 1.8 nm. They exhibit stable wavelength-tunable near-UV luminescence at room temperature originating from quantum confinement effect. Their unique electronic and luminescence properties are investigated by using the experiments and the first-principles calculations.

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2. Experimental

2.1. Synthesis of Cs_4PbBr_6 QDs

We synthesized the colloidal Cs_4PbBr_6 QDs by using the solvothermal synthesis method. Firstly, we synthesized Cs-oleate by using the oil bath method. 0.407 g Cs_2CO_3, 20 mL octadecene (ODE), and 1.25 mL oleic acid were added into a 50-mL 3-neck flask and the mixture was degassed under argon gas flow at 120 °C for 1 h. Then it was heated at 150 °C under argon gas flow until Cs_2CO_3 reacted completely with oleic acid to produce a uniform solution containing Cs-oleate. 5 mL oleylamine (for improving conversion of $CsPbBr_3$ into Cs_4PbBr_6 such that the product contained pure Cs_4PbBr_6 QDs [4,34]), 0.0345 g $PbBr_2$, and 0.25 mL oleic acid were added into a beaker, and then 0.2 mL as-prepared Cs-oleate solution was injected into it. The mixed solution underwent ultrasonic treatment for 5 min. Subsequently, the solution was transferred into a special container, which was then sealed in a stainless-steel autoclave. The autoclave was heated at 160 °C in a drying oven for 40 min or 1 h to obtain the Cs_4PbBr_6 QDs. The crude solution was washed with the same volume of ethyl acetate and then underwent centrifugation for 2 min. The precipitate was collected and dispersed in hexane.

2.2. Characterization

PL spectra, PL excitation (PLE) spectra, and time-resolved PL spectra were measured at room temperature by using a fluorolog3-TCSPC spectrofluorometer (HORIBA JOBIN YVON) with a Xe lamp and pulsed-laser diodes as light sources. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) were conducted by using a Tecnai G2 T20 transmission electron microscope (FEI) operating at 200 kV. UV–Vis absorption spectra were recorded by using a UV–Vis spectrophotometer (HITACHI U-3900). X-ray diffraction (XRD) spectroscopy was performed by using a Smartlab (3) X-ray diffractometer. The X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5000 VersaProbe spectrometer equipped with a monochromatic Al Ka source.

3. Results and discussion

The TEM observation (Fig. 1(a)) reveals that the Cs_4PbBr_6 QDs synthesized at 160 °C with reaction time of 1 h are nearly spherical, they have a most probable diameter of 8.2 nm. The high-resolution TEM image of a typical particle (inset of Fig. 1(a)) shows clear lattice fringe, indicating high crystallinity of the particle, and the lattice spacing (0.311 nm) is consistent with that of the (2 1 4) planes of trigonal

Cs_4PbBr_6. Fig. 1(b) shows the selected-area electron diffraction (SAED) pattern of the QDs, which matches well that of trigonal Cs_4PbBr_6 [35]. The PL measurement shows that these Cs_4PbBr_6 QDs have stable near-UV luminescence at room temperature. This result is surprising considering that bulk Cs_4PbBr_6 has luminescence only at low temperature [22,25]. The main reason is that the luminescence efficiency of a quantum dot can be much higher than that of corresponding bulk material due to spatial confinement of the carriers and excitons [36]. In the Cs_4PbBr_6 QDs, the excitons are trapped by the isolated $PbBr_6^{4-}$ octahedra (Fig. 1(c)), hence the Cs_4PbBr_6 QDs are expected to have luminescence properties quite different from that of the cubic $CsPbBr_3$ NCs. Fig. 1(d) shows the PL, PLE, and UV–Vis absorption spectra of the Cs_4PbBr_6 QDs in hexane. The PL spectrum contains a single near-UV band centered at around 378 nm, being very close to that (375 nm) of bulk Cs_4PbBr_6 [22,27]. Its full width at half maximum (FWHM) is 0.54 eV. The PLE spectrum of the Cs_4PbBr_6 QDs comprises a sharp exciton absorption line at around 315 nm, which is close to that of bulk Cs_4PbBr_6 (310 nm) [22,27]. Their UV–Vis absorption spectrum comprises an exciton absorption line at around 317 nm and an absorption band edge at 306 nm. The exciton binding energy is calculated to be 0.14 eV, which is consistent with the general conclusion that the exciton binding energy of a large-bandgap material is usually big [37]. It explains why the Cs_4PbBr_6 QDs have strong exciton absorption at room temperature. The similarity between the light absorption and emission spectra of the current Cs_4PbBr_6 QDs and those of bulk Cs_4PbBr_6 suggests that the luminescence of these QDs arises also from localized Frenkel excitons. The linewidth (0.54 eV) of the PL spectrum of the Cs_4PbBr_6 QDs (Fig. 1(d)) is significantly larger than that (0.18 eV) of bulk Cs_4PbBr_6 measured at 4.2 K [25]. This is on the one hand ascribed to the enhanced phonon broadening at higher temperature, on the other hand, the considerable deviation among the energy gaps of the Cs_4PbBr_6 QDs of different sizes due to the quantum confinement effect also contributes to the spectral broadening. The Cs_4PbBr_6 QDs have a very large Stokes shift of 0.66 eV, as obtained from the PL and PLE spectra, which is close to the bulk value of 0.79 eV [25]. In contrast, the Stokes shift of the $CsPbBr_3$ NCs is only around 0.04 eV. This is because the electronic states in the Cs_4PbBr_6 QD are strongly localized [26], and when the electronic transition occurs between such two states, there will be strong lattice relaxation, which leads to large Stokes shift between the absorbed and emitted photons [20,38,39].

To give more supporting evidences concerning the composition and crystal structure of the synthesized QDs, we measured the EDX, XRD, and XPS spectra of the QDs (Fig. 2). The EDX spectrum (Fig. 2(a)) comprises Cs, Pb, and Br signals with atomic ratio of Cs:Pb:Br = 34.4:9.6:56, which is very close to the stoichiometric ratio 4:1:6 of Cs_4PbBr_6. The XRD spectrum (Fig. 2(b)) comprises a series of peaks which agree well with those of Cs_4PbBr_6, and the broadening of the peaks are attributed to the small sizes of the particles. Fig. 2(c) shows the complete XPS spectrum of the sample. It contains clear Cs, Pb, and Br signals. The high-resolution XPS spectra (Fig. 2(d)–(f)) further reveal the fine signals of Cs $3d_{3/2}$, Cs $3d_{5/2}$, Cs $4d_{3/2}$, Cs $4d_{5/2}$, Pb $4f_{5/2}$, Pb $4f_{7/2}$, Br $3d_{5/2}$. Note that the Si and O signals in the full spectrum arise from the silica substrate we used for the measurement of the XPS spectra. The C signal may arise from the residual organics in the sample or from the adsorbed CO_2 molecules. These characterizations definitely demonstrate that the synthesized QDs are well-crystallized Cs_4PbBr_6 QDs.

Our measurement indicated that the light absorption and emission bands of the above sample do not shift with varying excitation wavelength, showing no remarkable quantum confinement effect. We further study the optical properties of the Cs_4PbBr_6 QDs with much smaller sizes synthesized with shorter crystallization time (40 min at 160 °C). The TEM image reveals such QDs are nearly spherical (Fig. 3(a)), and their sizes range from 6.8 nm down to below 1.8 nm, with a most probable size of 3.9 nm.

All the particles have good crystallinity. The inset of Fig. 3(a) shows the high-resolution TEM image of a typical particle, whose lattice spacing (0.308 nm) corresponds to that of the (3 1 2) planes of Cs_4PbBr_6. The SAED pattern (Fig. 3(b)) is characteristic of that of trigonal Cs_4PbBr_6 [35]. Fig. 3(c) shows the PL and PLE spectra of these Cs_4PbBr_6 QDs in hexane at room temperature. The peak of the PL spectrum shifts from 340 to 378 nm with increasing excitation wavelength, exhibiting clear evidence of quantum confinement effect for a collection of nanoparticles with considerable size distribution [40,41]. The PL peak wavelength is plotted as a function of excitation wavelength in Fig. 3(d). We notice that when the excitation wavelength increases, the PL peak wavelength first increases monotonically and then approaches a maximum (~378 nm). The emission bands with shifting peaks are mainly contributed by the smaller QDs in the sample having remarkable quantum confinement effect; in contrast, the emission bands with nearly fixed peaks (at around 378 nm) are mainly contributed by the larger QDs in which the quantum confinement effect is nearly absent. Fig. 3(d) shows also that the peak intensity of the PL spectrum increases first and decreases then with increasing excitation wavelength, reaching a maximum at around 300 nm. This variation

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