Influence of Annealing Temperature on Structural Properties and Stability of CsPbBr$_3$/TiO$_2$ Core/Shell

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Abstract. Although all-inorganic CsPbBr$_3$ perovskites quantum dots exhibit an excellent photophysical properties, which could be applied in various applications, they still suffer from poor structural stability owing to environment factors. Therefore, TiO$_2$ was coated on the CsPbBr$_3$ QDs as a protecting shell to enhance their stability. Moreover, anatase phase of TiO$_2$ shell was obtained by annealing at more than 300$^\circ$C due to its most effective electron extraction properties among other crystalline forms of TiO$_2$. However, the CsPbBr$_3$ QDs can be degraded under high temperature. Herein, the annealing temperatures ranging from 300-500$^\circ$C were optimized to obtain the anatase TiO$_2$ shell and good crystallinity of CsPbBr$_3$ QDs core. The morphology and optical properties of CsPbBr$_3$ QDs, CsPbBr$_3$/TiO$_2$ and CsPbBr$_3$/TiO$_2$ were studied by using transmission electron microscope (TEM), photoluminescence (PL) measurement and UV-Visible spectroscopy, respectively. Finally, the CsPbBr$_3$/TiO$_2$ annealed at the optimum temperature was compared with the bare CsPbBr$_3$ QDs to prove the enhancement of their structural stability under ambient air by using X-ray diffraction (XRD).

1. Introduction

CsPbBr$_3$ quantum dots (QDs) are one of perovskite materials that have been reported with the excellent optical properties such as adjustable band gap, long diffusion lengths, ambipolar charge transport, and high carrier mobility [1]. CsPbBr$_3$ QDs with a green emission centered at 510-518 nm presented a high photoluminescence quantum yield (PL QY) of 90-95% and high color purity with a narrow full width at half maximum (FWHM) of 16-27 nm [2]. Although their excellent properties led to the success achieved in various fields, they still suffered from the environment factors such as water and heat because of their inherent ionic nature on polar solvents and the direct decomposition under high temperature. For the enhancement of their stability, CsPbBr$_3$ QDs have been reported with an excellent water stability for 12 weeks maintaining 75% of initial PL intensity when they were encapsulated with TiO$_2$ as a protecting shell; furthermore, it was proved that there was charge carrier transfer from CsPbBr$_3$ QDs core to TiO$_2$ shell in photovoltaic application [3, 4]. TiO$_2$ is widely used as an electron transport layer (ETL) in photovoltaic devices such as perovskite solar cells because it can absorb light at wavelength of ultraviolet region. It can transport electrons generated from perovskite layer to prevent charge recombination and serve as the block layer to hinder direct contact between the holes and fluorine-doped tin oxide (FTO). Anatase phase of TiO$_2$, in particular, exhibited the most effective
electron extraction properties among other crystalline forms of TiO\textsubscript{2} due to the closest conduction band minimum (CBM) to the lowest unoccupied molecular orbital (LUMO) of CsPbBr\textsubscript{3} QDs, that these anatase TiO\textsubscript{2} layers could easily create a quasi-ohmic contact, providing the effective electron transport pathways and enhancing electron extraction [5]. Moreover, TiO\textsubscript{2} appeared a high chemical and thermal stability under stressed condition so it has been attracted more attention to stabilize the perovskite materials. In order to obtain the anatase phase of TiO\textsubscript{2}, the annealing temperature was required in the range of 300 to 500°C before rutile phase of TiO\textsubscript{2} formed and grown at higher temperature. Meanwhile, the high temperature can affect the degradation of CsPbBr\textsubscript{3} QDs, although thermogravimetric analysis (TGA) has shown the weight loss of the CsPbBr\textsubscript{3} QDs only about 5% between 30 and 500°C [3]. In this study, the effects of this heat treatment on the structure of CsPbBr\textsubscript{3}/TiO\textsubscript{2} core/shell were investigated. The annealing temperatures of 300, 400 and 500°C were optimized in order to obtain the highest purity and crystallinity of anatase phase of TiO\textsubscript{2} shell while maintain the good structure of CsPbBr\textsubscript{3} core. Morphology, structural and optical properties were investigated using TEM, XRD pattern, PL emission spectra and absorption value, respectively. The stability of CsPbBr\textsubscript{3}/TiO\textsubscript{2} annealed at the optimum temperature was tested under ambient air to prove the enhancement of their stability.

2. Experimental

The experimental includes the preparation of CsPbBr\textsubscript{3} QDs, encapsulation of CsPbBr\textsubscript{3} QDs with TiO\textsubscript{2} at various annealing temperatures, stability testing in ambient air and characterizations of the samples.

2.1. Preparation of CsPbBr\textsubscript{3} QDs

16 mg of cesium carbonate (Cs\textsubscript{2}CO\textsubscript{3}), 76 mg of lead acetate trihydrate (Pb(CH\textsubscript{3}COO)\textsubscript{2}.3H\textsubscript{2}O), 5.00 mL of octadecene (ODE), 0.45 mL of oleic acid (OA) and 1.00 mL of oleylamine (OLM) were mixed in a three-neck flask, stirred at 250 rpm and heated under vacuum at 130°C for 1.40 h. Then, the solution was heated under argon flow at 170°C for 15 min. 72 µL of benzoyl bromide (C\textsubscript{6}H\textsubscript{4}COBr) was swiftly injected to form yellow colloidal solution of CsPbBr\textsubscript{3} QDs. The solution was immediately cooled down in an ice-water bath to room temperature (25°C). The CsPbBr\textsubscript{3} QDs solution was collected by using 5 mL of toluene and poured into the centrifuge tube. Afterwards, it was centrifuged at 4,000 rpm for 10 min and the supernatant was discarded to remove the ligands. Then the QDs in precipitates were re-dispersed in 5 mL of toluene. The centrifugation and re-dispersion process was repeated 1 time. The CsPbBr\textsubscript{3} QDs were collected in toluene for further use.

2.2. Preparation of CsPbBr\textsubscript{3}/TiO\textsubscript{2}

20 µL of titanium tetraisopropoxide (TTIP) in 1 mL of toluene was dropped into 10 mL of CsPbBr\textsubscript{3} QDs in toluene (1 mg/mL) and the solution was stirred for 3 h under 40%RH at room temperature. The solution was centrifuged at 5,000 rpm for 5 min to separate the CsPbBr\textsubscript{3}/TiO\textsubscript{x}, which were dried under vacuum for 1 h. Next, the CsPbBr\textsubscript{3}/TiO\textsubscript{x} were annealed under nitrogen flow at 300, 400 and 500°C for 1 h with heating rate of 5°C/min to transform amorphous TiO\textsubscript{2} shell to anatase TiO\textsubscript{2} shell.

2.3. Stability testing of CsPbBr\textsubscript{3}/TiO\textsubscript{2}

The bare CsPbBr\textsubscript{3} QDs and CsPbBr\textsubscript{3}/TiO\textsubscript{2} were stored under ambient air (40%RH, 25°C). The samples were characterized by XRD at day 0, 2, 5 and 11 to investigate their structural stability.

2.4. Characterizations of structural and optical properties

The Fourier Transform Infrared spectrophotometer (FT-IR, FT/IR-4100, JASCO Co.) was employed to investigate the ligand removal of QDs during the process. The morphology of CsPbBr\textsubscript{3} QDs was observed by transmission electron microscope (TEM-2000FX, JEOL). The crystallinity of CsPbBr\textsubscript{3} QDs core and the anatase TiO\textsubscript{2} shell were determined by X-ray diffraction (RINT2100, Rigaku Co., Ltd) with CuK\textsubscript{α} radiation source in the range of 10-60°. The optical properties were studied by using a UV-Visible spectrophotometer (V-650, JASCO Co.) at the wavelength range of 300-700 nm. Steady state PL spectra were obtained with a spectrometer (FP-6000, JASCO Co.) with excitation at 330 nm.
3. Results and discussion

Li group reported that the structure of CsPbBr$_3$ QDs started to decompose at around 500°C. However, the nucleation and growth of anatase phase was initiated at high temperature. Therefore, CsPbBr$_3$/TiO$_2$ annealed at 400°C was the most suitable representative of the annealed sample in this study. The sample before annealing, named CsPbBr$_3$/TiO$_x$, and the sample after annealing at 400°C, named CsPbBr$_3$/TiO$_2$, were investigated to study the effects of heat treatment on morphology and optical properties. Afterwards, the samples annealed at various temperatures were performed to study the influence of annealing temperature on their structural properties.

The CsPbBr$_3$ QDs were obtained by hot-injection method improved from M. Imran et al. [6] that was based on the dissolution of Cs$^+$ and Pb$^{2+}$ cations in fatty acids and used benzoyl halides as halide precursors. It was possible to precisely tune the composition of the final QDs. Furthermore, the QDs had a high phase purity and a high level of particle-morphology control. In order to control the growth of CsPbBr$_3$ QDs in solution via this method, the long carbon chain organic ligands including of oleic acid (OA) and oleylamine (OLM) have been applied to surround the QDs as a stabilizing shell. However, these ligands have prevented charge transfer as an insulating shell in optoelectronic devices as well as hinder the encapsulation of TiO$_2$ around QDs surface. Therefore, the ligands were inspected by FT-IR measurements on CsPbBr$_3$ QDs, CsPbBr$_3$/TiO$_x$ before annealing and CsPbBr$_3$/TiO$_2$ annealed at 400°C.

FT-IR spectra (figure 1) showed that the sample exhibited characteristic modes of oleyl groups corresponding to the OA and OLM as follows: peaks at 2,924 cm$^{-1}$ and 2,854 cm$^{-1}$ correlating with the asymmetric and symmetric CH stretching mode in both OA and OLM, respectively, and peaks at 1,462 cm$^{-1}$ and 1,376 cm$^{-1}$ correlating with the CH$_2$ and CH$_3$ bending in OLM, respectively [7]. After coating the CsPbBr$_3$ with amorphous TiO$_x$, the intensity of the ligand absorption band decreased significantly compared to CsPbBr$_3$ QDs because the ligands surrounding QDs were probably replaced with TiO$_x$ and discarded by centrifugation. However, the ligands removal possibly caused an agglomeration of CsPbBr$_3$/TiO$_x$ due to the strong ionic nature between the uncapped QDs of neighboring particles [8] as well as between the oxide of titanium. After annealing at high temperature, all ligands were removed due to the decomposition of their structure under an elevated temperature. Moreover, the peaks from 800 to 600 cm$^{-1}$ were occurred due to the presence of Ti-O bond [9] from the anatase TiO$_2$ shell.

![Figure 1. FT-IR spectra of CsPbBr$_3$ QDs, CsPbBr$_3$/TiO$_x$ and CsPbBr$_3$/TiO$_2$ (400°C).](image)

The TEM image showed that bare CsPbBr$_3$ QDs had the average size-particle of 11±1 nm with a cubic shape.
The CsPbBr$_3$ QDs were coated with TiO$_2$ by using titanium tetraisopropoxide (TTIP) under 40%RH at ambient temperature. This titanium alkoxide (Ti(OR)$_n$) was hydrolysed when there was a presence of water in an ambient air and subsequently condensed to form an amorphous oxide (TiO$_x$.nH$_2$O) that covered on the surface of agglomerated CsPbBr$_3$ QDs core as seen as a gray shadow area in TEM figure 2a). After annealing the sample, the particles had a larger size of 160-170 nm with a polycrystalline structure (Figure 2c). Besides the chemical bond interaction between -Ti-O-Ti- network and QDs, the change in morphology of coatings could be attributed to the densification mechanisms activated during the heat treatment leading to grain growth and increase in the particle agglomeration.

**Figure 2b.** TEM images of (a) bare CsPbBr$_3$ QDs, (b) CsPbBr$_3$/TiO$_x$ and (c) CsPbBr$_3$/TiO$_2$ (400°C).

PL emission spectra (figure 3a) showed that the bare CsPbBr$_3$ QDs exhibited a sharp green emission peak at wavelength of 515 nm (2.41 eV) with a full width at half maximum (FWHM) of 18.09 nm when excited at 330 nm (3.76 eV). After coating CsPbBr$_3$ QDs with titanium precursor, the color changed from green solution of CsPbBr$_3$ QDs to yellow solution of CsPbBr$_3$/TiO$_x$ because the emission peak slightly shifts to 518 nm (2.39 eV) with a FWHM of 16.95 nm. The PL intensity of the sample after annealing was very low but the sample still absorbed radiation and has a UV-Vis absorption spectrum. This red-shift of PL emission peak corresponded to the QDs agglomeration. PL quenching of CsPbBr$_3$ QDs after coating TiO$_2$ were possibly attributed to the delocalization of the electron wave function from
CsPbBr$_3$ core into TiO$_2$ shell [4] since the CBM of TiO$_2$ was lower and closer to the LUMO of CsPbBr$_3$ QDs, which provided the effective electron transport pathways. For the absorption spectrum (figure 3b), CsPbBr$_3$ QDs, CsPbBr$_3$/TiO, and CsPbBr$_3$/TiO$_2$ had the excitonic peak at 508 nm, 509 nm and 523 nm, respectively. When compare in term of the intensity, CsPbBr$_3$/TiO$_x$ and CsPbBr$_3$/TiO$_2$ possessed a strong absorption into the UV region (< 350 nm) due to the UV absorption of TiO$_2$ shell.

![Figure 3](image.png)

**Figure 3.** (a) PL emission spectra and (b) UV-Visible absorption of CsPbBr$_3$ QDs, CsPbBr$_3$/TiO$_x$, and CsPbBr$_3$/TiO$_2$ (400°C). The excitation wavelength was 330 nm.

The effects of encapsulation and annealing temperature on the structure of CsPbBr$_3$ QDs and CsPbBr$_3$/TiO$_2$ were studied by XRD (figure 4a, and 4b). The XRD result confirmed that CsPbBr$_3$ QDs exhibited an orthorhombic phase. For CsPbBr$_3$/TiO$_x$, the XRD pattern was similar to the bare CsPbBr$_3$ QDs phase according to no phase transition in the QDs structure upon encapsulation process. After coating TiO$_2$ and annealing at various temperatures, the XRD patterns confirmed the existence of TiO$_2$ shell at $2\theta = 25.2^\circ$ assigning to the anatase planes of (101) for CsPbBr$_3$/TiO$_2$ at 400°C and 500°C. The largest amount of transformed anatase phase was occurred at 500°C. The peak shapes of CsPbBr$_3$/TiO$_2$ became sharper owing to crystal size growth, in which the crystallinity of CsPbBr$_3$ QDs was improved by 37.2%. In addition, the peak split around $2\theta = 30.5^\circ$ was appeared corresponding to the (040) and (202) inter-reticular planes of Pnma orthorhombic phase. As the annealing temperature was increased, these peaks were slightly broader and the (040) peaks shifted to lower angles, which coincided to a thermal cell expansion and there might be a distortion or a preferred orientation during the process.

Although the grain growth of QDs should increase with an increase of annealing temperature, the sample annealed at 400°C showed a higher peak intensity due to its better crystallinity compared to the sample annealed at 500°C because the addition of larger amount of anatase TiO$_2$, which annealed at 500°C, to the coating probably acted to retard the growth of QDs grains during this heat treatment, as predicted by Zener pinning. When counterbalanced between the quality of CsPbBr$_3$ core and anatase TiO$_2$ shell, annealing CsPbBr$_3$/TiO$_2$ at 400°C improved its crystallinity; meanwhile the amorphous of TiO$_2$ shell was transformed to the excellent charge-transfer crystalline form of anatase phase.
Figure 4. (a) XRD spectra of CsPbBr$_3$ QDs, CsPbBr$_3$/TiO$_x$ and CsPbBr$_3$/TiO$_2$ prepared at various annealing temperatures and (b) XRD spectra of (040) and (202) peaks.

To verify the stability enhancement of CsPbBr$_3$/TiO$_x$ annealed at 400°C with respect to bare CsPbBr$_3$ QDs, XRD measurement was performed to observe the transformation of their structures (figure 5a- and 5b), in which the samples were stored without an aqueous medium under ambient air with 40%RH. The normalized XRD pattern showed that CsPbBr$_3$ QDs had a poor stability when stored under ambient air for a long time because there was a rapid decrease in crystallinity by 19.3% within 5 days. A decrease of (110) peak intensity at 2θ = 15° and a peak splitting were observed. It was possible that the environment factors such as light, oxygen and humidity have destroyed their structure as studied in previous researches [8]. On the other hand, the CsPbBr$_3$/TiO$_x$ annealed at 400°C showed the excellent stability for more than a week under ambient atmosphere. Additionally, the change of material composition due to the degradation was not occurred. It can be explained that TiO$_2$ acted as a protecting shell because of its high thermal and water stability under stressed conditions, and prevented the CsPbBr$_3$ QDs core from contacting with degradation factors [3]; at the same time, the structure of CsPbBr$_3$ QDs still maintained a good crystallinity after heat treatment at 400°C.
Figure 5. (a) XRD spectra of bare CsPbBr$_3$ QDs and (b) XRD spectra of CsPbBr$_3$/TiO$_2$ annealed at 400°C, when stored under ambient air for 11 days.

4. Conclusion
The encapsulation process of CsPbBr$_3$ QDs with TiO$_2$ caused the ligand removal, which was useful for further optoelectrical applications, as well as the change of morphology and optical properties due to the particle agglomeration. Charge extraction capability can be enhanced owing to the suitable energy level of TiO$_2$ shell with respect to the CsPbBr$_3$ QDs. The structure of orthorhombic CsPbBr$_3$ QDs was maintained after coating with TiO$_2$ and annealing at elevated temperature. Furthermore, the heat treatment enhanced the crystallinity of CsPbBr$_3$/TiO$_2$ but distorted their structure and caused the polycrystalline particles at the same time. For annealing at 300°C, 400°C and 500°C, the sample annealed at 400°C exhibited the best crystallinity and appeared the desired anatase phase of TiO$_2$ shell. Moreover, CsPbBr$_3$/TiO$_2$ annealed at 400°C showed the excellent structural stability against the bare CsPbBr$_3$ QDs when stored under ambient atmosphere for 11 days. It has proven that encapsulation with TiO$_2$ shell and annealing at a suitable temperature had a significant influence on both structural property and stability of the CsPbBr$_3$ QDs.

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