



# Perovskite CsPbBr<sub>3</sub> Quantum Dots Prepared Using Discarded Lead–Acid Battery Recycled Waste

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**Abstract:** Perovskite CsPbBr<sub>3</sub> quantum dot (CsPbBr<sub>3</sub>-QD) recovery was performed using lead scrap from lead storage batteries. The perovskite CsPbBr<sub>3</sub>-QD characteristics were analyzed using different PbO/recycled PbO<sub>2</sub> ratios. Scanning electron microscopy (SEM) was used to observe the film surface morphology and cross-section. High-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) were used to observe the perovskite CsPbBr<sub>3</sub>-QDs' structural characteristics. A photoluminescence (PL) measurement system was used to analyze the optical properties. The results show that lead scrap from lead–acid batteries as a material for perovskite CsPbBr<sub>3</sub>-QD production can be successfully synthesized. This saves material and also proves that recycling is valuable. The proposed approach is helpful for future material shortages and materials not easily accessible. Although the efficiency is not very high, this process will be purified using recycled lead in the future to achieve higher quantum yield.

Keywords: quantum dots; CsPbBr<sub>3</sub>; perovskite; recycled waste lead

## 1. Introduction

Organometallic halide perovskite material has special optical and electrical properties due to its unique properties [1–4]. The diffusion speed of the carrier current is fast, and the diffusion distance is long. The high absorption coefficient has very good absorption in the entire visible light region, and the perovskite material characteristics allow it to fully absorb sunlight during operation and reduce energy loss in the photoelectric conversion process [5–8]. Perovskite material has a low exciton binding energy, therefore can be excited by light. Organic/inorganic hybrid perovskites,

such as MAPbX<sub>3</sub> (MA = CH<sub>3</sub>NH<sub>3</sub>; X = Cl, Br, I), have attracted widespread attention due to their outstanding performance in solar cells, light-emitting diodes, and optoelectronic devices [9–17]. It is worth noting that MAPbI<sub>3</sub> has been widely used in the field of solar cells. The power conversion efficiency (PCE) of a perovskite solar cell is up to 23.7% in 2019 [18]. Furthermore, due to band gap tunability (400–800 nm) and narrow emission band of approximately 20 nm, the organic/inorganic hybrid perovskites are considered emission components for phosphor-converted white light-emitting diode (PC-WLED) and electroluminescent (EL) devices in wide-gamut color displays [15,19–21]. Compared to organic/inorganic hybrid perovskites, fully inorganic perovskite quantum dots such as  $CsPbX_3$  (X = Cl, Br, I) exhibit higher stability and provide excellent thermoelectric performance [22–24]. The QD atom arrangement is quite tight and can be used to emit light with different wavelengths using QDs with different sizes due to the quantum confinement effect. QDs are superior to traditional organic dye molecules, because of their brightness, good light stability, and reproducible properties. Therefore, QDs are highly valued in the material chemistry and bio-semiconductor fields [25,26]. This study considers the price of commercial perovskite QDs and the environmental protection problem in preparing perovskite CsPbBr<sub>3</sub>-QDs at room temperature using waste lead (PbO<sub>2</sub>) from lead-acid batteries and pure PbO as the Pb-source material. The material and optoelectronic properties of perovskite CsPbBr<sub>3</sub>-QDs with different ratios of PbO/recycled PbO<sub>2</sub> are analyzed and discussed.

#### 2. Materials and Methods

We used scrap lead batteries in this work (standard batteries, 12V). The battery top cover was removed. The acidic electrolyte was poured out and carefully collected. The inner battery wall was rinsed with water several times. Concentrated sulfuric acid (~2.2 M) is contained in the electrolyte and care must be taken to wear protective gloves, safety glasses, and a lab coat during this process. After dismantling the battery, lead source materials (i.e., Pb and PbO<sub>2</sub>) were washed several times with dilute HCl (35%, Echo Chemical Co., Ltd., Miaoli, Taiwan) and DI water. The resulting anode and cathode were naturally dried under atmospheric conditions. The collected materials were ground into a powder using a mortar and pestle as the recycled PbO<sub>2</sub> and ready for the next synthesis.

Recycled PbO<sub>2</sub> prepared from a part of the recycled lead–acid battery was mixed with pure PbO (90%, Echo Chemical Co., Ltd., Miaoli, Taiwan). The perovskite QD solution was prepared according to different proportions (in this step we used 100%, 80%, 50%, 20%, and 0% for comparison), and 0.25 mmol Cs<sub>2</sub>CO<sub>3</sub> (99.999%, Echo Chemical Co., Ltd., Miaoli, Taiwan) and 2.5 mL of oleic acid (99%, Echo Chemical Co., Ltd., Miaoli, Taiwan) were added together into a 20 mL glass vial. The mixture was magnetically stirred on a hot plate at 160 °C for 60 min to obtain a clear solution. The glass vial was placed in an oven heated to 120 °C to remove moisture for 30 min, then 2.5 mL of toluene was added to dilute the Cs and Pb precursor solutions to 0.1 M. Next, 1.0 mL of the Cs and Pb precursor solution was decanted into 15 mL of toluene (99%, Echo Chemical Co., Ltd., Miaoli, Taiwan) for 15 min with vigorous stirring while adding 0.05 mmol of Br precursor solution, which was synthesized by tetrabutylammonium bromide (TOAB) (90%, Echo Chemical Co., Ltd., Miaoli, Taiwan), 0.25 mL of oleic acid, and 1.0 mL of toluene. An 8 mL portion of toluene was formed. Figure 1 shows the technical procedure for CsPbBr<sub>3</sub>-QD preparation using recovered waste lead from discarded lead–acid batteries. The deployment ratio is summarized in Table 1.



(e) Collected PbO<sub>2</sub> powder (f) CsPbBr<sub>3</sub>-QDs with different ratios

Figure 1. Technical procedure for CsPbBr<sub>3</sub>-QD preparation using recovered waste lead from discarded lead-acid batteries. (a) Discarded lead-acid battery, (b) Electrode inside battery, (c) Recycled electrodes (PbO<sub>2</sub> anode and Pb cathode), (d) Grinding PbO<sub>2</sub>, (e) Collected PbO<sub>2</sub> powder, and (f) CsPbBr<sub>3</sub>-QDs with different ratios under UV-365 nm laser excitation (left to right: PbO/recycled PbO<sub>2</sub> ratio = 100%, 80%, 5%, 20%, and 0%).

PbO/Recycled PbO <sub>2</sub> Ratio	Cs <sub>2</sub> CO <sub>3</sub>	PbO	Recycled PbO <sub>2</sub>
100%	81.45 mg	0 mg	113.60 mg
80%	81.45 m g	22.32 mg	89.28 mg
50%	81.45 mg	55.80 mg	55.80 mg
20%	81.45 mg	89.28 mg	22.32 mg
0%	81.45 mg	113.60 mg	0 mg

#### 3. Results and Discussion

Figure 2 shows the X-ray diffraction (XRD) patterns of CsPbBr<sub>3</sub>-QD films that were deposited onto glass substrates with different PbO/recycled PbO2 ratios. According to a study reports of references [27–29], the primary difference between the cubic and orthorhombic crystal structure of  $CsPbBr_3$  is a diffraction peak of ~30°. It was illustrated that the two dominant diffraction peaks of the synthesized pure CsPbBr<sub>3</sub>-QD (PbO(100%):PbO<sub>2</sub>(0%)) films, namely, (110) at  $2\theta = 15.193^{\circ}$  and (220) at  $2\theta = 30.739^{\circ}$ , demonstrated the cubic perovskite crystal structure. In this work, the structure was similar to those reported in Reference 24. In addition, the few waste lead CsPbBr<sub>3</sub>-QD (PbO(80%):PbO<sub>2</sub>(20%), PbO(50%):PbO<sub>2</sub>(50%), and PbO(20%):PbO<sub>2</sub>(80%)) films showed weak peaks so that the quantum dots had poor crystallinity and grain aggregation. On the other hand, the waste lead CsPbBr<sub>3</sub>-QD (PbO(0%):PbO<sub>2</sub>(100%)) films displayed the three dominant peaks, which were (100) at  $2\theta = 15.179^\circ$ , (110) at  $2\theta = 21.443^{\circ}$ , and (200) at  $2\theta = 30.674^{\circ}$ , respectively. It was observed that the (100) diffraction peak intensity was very strong, indicating that CsPbBr<sub>3</sub>-QDs are high crystallinity along the (100) orientation. The secondary diffraction peak of the (200) plane suggested crystalline perfection. Meantime, the clear splitting of the (100) and (200) diffraction peaks further indicated that the synthesized waste lead CsPbBr<sub>3</sub>-QD films may be of the room-temperature orthorhombic phase [30].

Figure 3 shows top and cross-sectional scanning electron microscopy (SEM) (GeminiSEM, ZEISS, Oberkochen, Germany) images of CsPbBr<sub>3</sub>-QDs coated onto indium tin oxide (ITO) glass substrates. It can be clearly seen that there are a large quantity of flakes on the surface of the ITO glass substrate, and each grain size is around 200 nm. Each of them is constructed by the recovered lead perovskite CsPbBr<sub>3</sub>-QD clusters. This means that the recycled lead perovskite CsPbBr<sub>3</sub>-QDs can effectively form

a thin film. In Figure 3b, it can be seen that the interface is clear and flat. A continuous QD film was formed by stacking CsPbBr<sub>3</sub> flakes. The thickness of the recycled lead perovskite CsPbBr<sub>3</sub>-QDs layered using QD-flake stacking is around 100 nm.



**Figure 2.** X-ray diffraction (XRD) patterns of CsPbBr<sub>3</sub>-QD films with different PbO/recycled PbO<sub>2</sub> ratios.



**Figure 3.** (a) Top and (b) cross-sectional scanning electron microscopy (SEM) images of CsPbBr<sub>3</sub>-QDs on ITO glass substrate.

Since the recycled lead perovskite CsPbBr<sub>3</sub>-QD particle size is very small, it must be clearly examined using high-resolution transmission electron microscopy (HRTEM) to observe the lattice structure of the quantum dots, as well as the quantum dot distribution and particle size. The sample preparation must go through a drying step before examining the quantum dots owing to the inability to observe the QD distribution in the colloidal solution. Therefore, the distribution image is observed using HRTEM, obtained by immersing a copper mesh into the recovered lead perovskite CsPbBr<sub>3</sub>-QD solution and then drying it by heating. Figure 4 displays the microstructural images observed by TEM (JEM2100F, JEOL, Tokyo, Japan) for CsPbBr<sub>3</sub>-QD films with different PbO/recycled PbO<sub>2</sub> ratios. As shown in Figure 4a, it can be seen that the QD feature clearly presented a nearly cubic shape and good monodispersion in the pure CsPbBr<sub>3</sub>-QD (PbO(100%):PbO<sub>2</sub>(0%)) film. However, as the PbO<sub>2</sub> content is increased, the QD feature clearly appears in these waste lead CsPbBr<sub>3</sub>-QD films, as is shown in Figure 4b–e. The average CsPbBr<sub>3</sub>-QD particle size is evaluated at approximately 10–15 nm. Figure 4f exhibits the high-resolution TEM (HRTEM) image of the waste lead CsPbBr<sub>3</sub>-QD  $(PbO(0\%):PbO_2(100\%))$  film. The grain with the clear lattice feature can be observed in this image, indicating that it is crystalline. Based on our calculation, the d-spacing value of this lattice arrangement is 2.91 Å, which is indexed to the (200) plane. Except for the HRTEM image, the selected area electron diffraction (SAED) pattern also can be used to confirm the crystal phase. Figure 4g,h

shows the SAED images of waste lead CsPbBr<sub>3</sub>-QD (PbO(50%):PbO<sub>2</sub>(50%) and PbO(0%):PbO<sub>2</sub>(100%)) films, respectively. In Figure 4g, the electron diffraction pattern is indistinct, revealing that the CsPbBr<sub>3</sub>-QD (PbO(50%):PbO<sub>2</sub>(50%)) film is almost amorphous. On the other hand, the CsPbBr<sub>3</sub>-QD (PbO(0%):PbO<sub>2</sub>(100%)) film possesses the clearer electron diffraction pattern. The diffraction rings shown in Figure 4h are determined to be (100) and (200) planes. The TEM observations are in good agreement with the XRD results.



**Figure 4.** TEM images of CsPbBr<sub>3</sub>-QD films with (**a**) PbO(100%):PbO<sub>2</sub>(0%), (**b**) PbO(80%):PbO<sub>2</sub>(20%), (**c**) PbO(50%):PbO<sub>2</sub>(50%), (**d**) PbO(20%):PbO<sub>2</sub>(80%), and (**e**) PbO(0%):PbO<sub>2</sub>(100%) ratios. (**f**) HRTEM image of the CsPbBr<sub>3</sub>-QD (PbO(0%):PbO<sub>2</sub>(100%)) film. SAED images of CsPbBr<sub>3</sub>-QD films with (**g**) PbO(50%):PbO<sub>2</sub>(50%) and (**h**) PbO(0%):PbO<sub>2</sub>(100%) ratios.

To obtain the CsPbBr<sub>3</sub>-QDs' optical properties, the PL spectra for these samples were studied using a fluorescence spectrophotometer system (F-7000, Hitachi, Tokyo, Japan), as shown in Figure 5a. The PL spectral intensity of CsPbBr<sub>3</sub>-QDs decreases as the PbO<sub>2</sub> ratio of waste lead increases. Simultaneously, the PL spectrum shift is usually as a result of the quantum size effect in the nano crystal [31,32]. The pure CsPbBr<sub>3</sub>-QDs (PbO(100%):PbO<sub>2</sub>(0%)) and waste lead CsPbBr<sub>3</sub>-QDs ((PbO(80%):PbO<sub>2</sub>(20%), PbO(50%):PbO<sub>2</sub>(50%), PbO(20%):PbO<sub>2</sub>(80%), and PbO(0%):PbO<sub>2</sub>(100%)) displayed emission peak positions centered at 488.2, 488.2, 489.6, 493.4, and 483.4 nm, with the narrow full width at half maximum (FWHM) values of 41.48, 43.39, 43.76, 40.83, and 38.32 nm from the PL spectrum, respectively. The photoluminescence quantum yield (PLQY) of all the colloidal CsPbBr<sub>3</sub>-QDs was estimated to be 40%, as shown in Figure 5b. The PLQY of the CsPbBr<sub>3</sub>-QDs was lower than that of traditional CsPbBr<sub>3</sub>-QDs, but the materials in this work were synthesized using used waste lead from discarded lead–acid storage batteries. The perovskite CsPbBr<sub>3</sub>-QDs prepared using the recycled process in this work save costs and also promote environmental recycling. Future work will involve purifying the recycled lead perovskite CsPbBr<sub>3</sub>-QDs, increasing the concentration, and promoting PLQY.





### 4. Conclusions

This study successfully used waste recovered lead oxide from storage batteries as the material to make perovskite CsPbBr<sub>3</sub>-QDs with different ratios of PbO/recycled PbO<sub>2</sub>. From the TEM observations, the QD feature clearly appears in these CsPbBr<sub>3</sub>-QD films. The average CsPbBr<sub>3</sub>-QD particle size was confirmed using TEM to be approximately 10–15 nm. Based on XRD and TEM results, the CsPbBr<sub>3</sub>-QD (PbO(0%):PbO<sub>2</sub>(100%)) film has the higher crystal quality. The CsPbBr<sub>3</sub>-QD quantum yield was 40% as measured by PLQY. Compared with the price of pure lead or lead oxide as opposed to recycled lead or lead oxide, the current lead recycling can achieve cost savings. However, waste lead recovered from lead storage batteries will exhibit grain agglomeration in the production process. Therefore,

it is necessary to optimize the concentration and grain size to improve the quantum yield through a well-designed purification process. Moreover, when the  $PbO_2$  mixture is employed and the  $PbO_2$  content increases, and because it is not easy to dissolve  $PbO_2$  in oleic acid, a small number of  $PbO_2$  particles remain in the mixture, resulting in aggregation of the quantum dots. Therefore, the use of acetic acid or sodium hydroxide as a solvent for  $PbO_2$  to improve quantum dot aggregation should be considered in the future.

**Author Contributions:** L.-C.C. carried out the experiments, designed the study, and gave significant suggestions on the writing of the entire manuscript. C.-H.T. conceived the original idea and wrote the manuscript. S.-L.O. and K.-Y.L. helped to analyze and interpret the data, and helped draft the manuscript. J.T., Z.-L.T., and H.-C.K. reviewed and commented on the manuscript. H.-T.C. prepared the samples and carried out all measurements. A.-C.S. provided HRTEM equipment for image observation. All authors approved this manuscript.

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