

Supporting information

Perovskite Quantum Dot Solar Cells Fabricated from Recycled Lead-Acid Battery Waste

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Experimental section:

Lead iodide (PbI₂, 99.999%, Sigma-Aldrich), Cesium carbonate (Cs₂CO₃, 99%, Sigma-Aldrich), octadecene (ODE, 90%, Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), oleylamine (OLA, Sigma-Aldrich, 70%), hexane (anhydrous, 95%, Sigma-Aldrich), hexane (anhydrous, ≥99%, Sigma-Aldrich), methyl acetate (MeOAc, anhydrous, 99.5%, Sigma-Aldrich), chlorobenzene (CB, anhydrous, 99.8%, Sigma-Aldrich), PCBM (>99.9, Sigma-Aldrich), PTB7 (1-Materials), and tin(IV) oxide (SnO₂, 15% in H₂O colloidal dispersion, Alfa Aesar) were used as received without further purification unless mentioned. Glass/ITO and PET/ITO were purchased from the Zhuhai Kaivo Optoelectronic Technology Co. Ltd.

PbI₂ powder synthesis from spent car lead acid batteries:

A spent lead acid battery was dismantled, and then the acid electrolyte that contains concentrated sulfuric acid was diluted with water and poured out. The electrodes were further rinsed with water

several times and air-dried. The anode and cathode materials were mixed for preparing lead paste, which contains PbSO_4 , PbO_2 , and PbO components. To understand the composition of lead paste, ethylenediaminetetraacetic acid (EDTA) complexometric titration was employed for analyzing the content of chemical components.¹ A certain amount of the spent lead paste was first added to acetic acid (CH_3COOH) to dissolve PbO and then the mixture was filtrated. The filter liquor was titrated by EDTA to determine the content of PbO . Then, the filter residue from this step was then dissolved in ammonium acetate ($\text{CH}_3\text{COONH}_4$) to determine the content of PbSO_4 . At last, the filter residue was reduced by excess hydrogen peroxide solution and then back-titrated with standard liquid of potassium permanganate to determine the content of PbO_2 in the lead paste.

Afterwards, we introduced a facile one-pot solution process to extract Pb source by mixing lead paste (5g) with excess Na_2SO_3 (1g), dilute acetic acid (Ac, 80ml, 0.4mmol /ml) and ammonium acetate (NH_4Ac , 0.5g). Subsequently, the mixture was stirred at 35 °C for 24 h to form lead acetate. After sufficient reaction, the mixture was filtered to obtain clear lead acetate solution. Then excess hydroiodic acid (HI) was added slowly to the lead acetate solution under stirring, and the formation of yellow PbI_2 precipitate can be observed. The yellow solids were collected and dried in vacuum at 60 °C overnight.

CsPbI₃ quantum dot synthesis:

Two three-neck flasks were prepared to synthesize two batches of R-CsPbI₃ and C-CsPbI₃ quantum dots. For each batch of CsPbI₃ QDs, all conditions were the identical except PbI_2 source. 0.5 g of PbI_2 for each kind of PbI_2 powder, 2.5 ml of oleic acid (OA), and 25 ml of octadecene (ODE) were loaded in 100 ml three-neck flask and vacuum pumped under continuous stirring at 100 °C for 1 h. Then, 2.5 ml of oleylamine (OLA) was injected into the flask. After PbI_2 completely dissolved, the temperature was increased to 160 °C under a N_2 flow protection. 4 mL Cs-oleate (0.0625 M) precursor was swiftly injected into the reaction mixture, and the solution was quenched by ice bath. The crude CsPbI₃ QDs solution was evenly divided into 3 centrifugation tubes and then methyl acetate was added into tubes with the volume ratio of 1:3 (QD solution: methyl acetate). Subsequently, QD precipitate was extracted by centrifugation at the speed of 8000 rpm for 3 min. All QD precipitate in 3 tubes was dispersed with 3 ml hexane and then precipitated by adding 4.5 ml methyl acetate and centrifuged again at 8000 rpm

for 3 min. Finally, the extracted QDs were dissolved in hexane for characterizations and device fabrication.

Device fabrication and characterizations:

Two batches of CsPbI₃ QD devices were fabricated using the same conditions except CsPbI₃ QDs, R-CsPbI₃ and C-CsPbI₃ QDs. The SnO₂ nanoparticle solution with a diluted weight concentration of 2.5% was spin-coated onto pre-patterned ITO glass substrates and annealed at 150 °C for 10 min in ambient condition. Then the SnO₂ film was treated with O₂ plasma for 2 min before the following layers would be deposited. The as-synthesized CsPbI₃ solution with a concentration of 50 mg/ml was spin-coated on the SnO₂ layer atop of ITP glass at 1000 RPM for 30 s, treated with pure anhydrous MeOAc for 20 s. This procedure was repeated 4 times to deposit thick film as absorber layer. PTB7 solution (10 mg/mL in chlorobenzene) was spin-coated on top QD films at 2000 rpm as HTLs. Finally, 100 nm Au electrode were prepared by thermal evaporation. The devices were masked with a black metal aperture to define an active area of 0.072 cm². QD solar cell devices were tested on a Newport AAA solar simulator (94023A-U) with xenon lamp at room temperature using Keithley 2400 (*I-V*) digital source meter. The intensity of the solar simulator was calibrated to 100 mW/cm² AM 1.5 G by a standard silicon cell with a KG-5 filter. *J-V* scans were measured from forward bias to reverse bias step and from reverse bias to forward (-1.3 V → 1.3 V, step 0.0125 V, scan rate: 0.1 V/s). For the light intensity dependence measurement, neutral density filters were used with optical densities ranging from 0.1 to 1 with 0.2 increments. EIS measurements were performed on a Zahner IM6 electrochemical workstation.

DFT simulation: First-principles calculations based on density functional theory (DFT) were carried out to investigate possible self-purification mechanisms in the CsPbI₃ QD.² The PBEsol exchange-correlation energy functional³ as it is implemented in VASP was used⁴. The projector-augmented wave method (PAW)⁴ was employed to represent the ionic cores and the following electronic state were considered as valence: Cs 5s 5p and 6s; Pb 6p and 5d; I 4d 5s and 5p; Na 3s and 2p; K 3s, 3p and 4s. The energy cutoff was set to be 400 eV. All ground-state geometries were obtained by minimizing the

forces on the atoms below 0.05 eV/Å. Periodic boundary conditions were applied along the three Cartesian directions. A 5-atom unit cell of CsPbI₃ was first relaxed with the Brillouin zone sampled with a 9×9×9 k-mesh of Monkhorst-Park scheme. Then a 3×3×4 slab system representing a CsPbI₃ surface with <001> orientation and Pb-I termination was constructed by adding a 25 Å-thick vacuum layer (to exclude the interactions with system images replicated along the direction perpendicular to the slab surface). The slab was subsequently relaxed with a 1×1×1 Gamma k-point. Subsequently, one Na⁺ ion was inserted at an interstitial position located at different distances from the slab surface and the whole system was relaxed with the same technical parameters as described above. The Na interstitial formation energy is defined as:

$$E_f = E_{CsPbI_3 + Na} - E_{CsPbI_3} - E_{Na}$$

where E_{CsPbI_3} , E_{Na} and $E_{CsPbI_3 + Na}$ are the zero-temperature DFT energies calculated for the CsPbI₃ slab, one Na atom in a bulk fcc crystal, and one Na interstitial in the CsPbI₃ slab, respectively.

Characterizations:

The PL spectra measurements were performed at room temperature using a custom laser PL spectroscopy system (Crystal Laser, Model BLC-050-405). The laser pulse width was 130 fs, and the repetition rate was 100 MHz. The excitation wavelength for both PL and TRPL measurements is 600 nm. SEM measurements were carried out by using an FEI Nova Nano SEM 450. TEM measurements were performed by a JEOL JEM-2010 and JEOL JEM-F200 operated at 200 kV. UV-Vis absorption spectra were obtained using a U-4100 spectrophotometer (Hitachi). FTIR was performed on a Thermo Fisher FTIR6700. XPS measurements were conducted by a VG ESCALAB MK2 system with monochromatized Al K α radiation under a pressure of 5.0×10^{-7} Pa. XRD (Panalytical Empyrean I system, Cu K α radiation with a wavelength of 0.154 nm) and SEM (FEI Nova Nano 450) measurements were used to measure the structures of PbI₂ powder and surface morphology of QD films, respectively. XPS measurements were conducted by a VG ESCALAB MK2 system with monochromatized Al K α radiation under a pressure of 5.0×10^{-7} Pa.

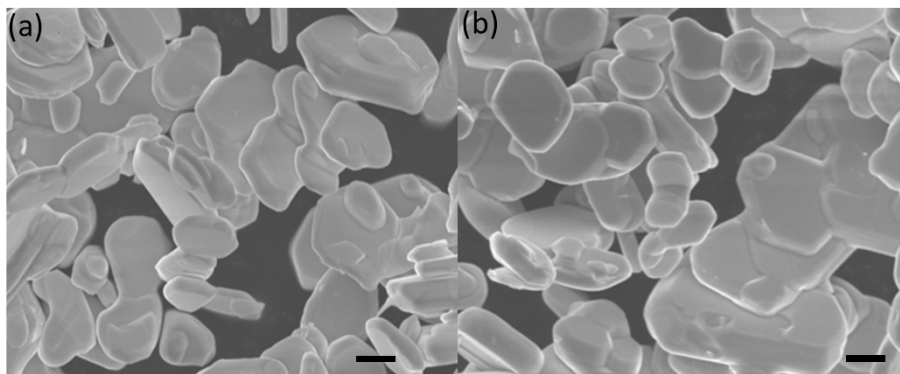


Figure S1. SEM images of (a) C-PbI₂ and (b) R-PbI₂

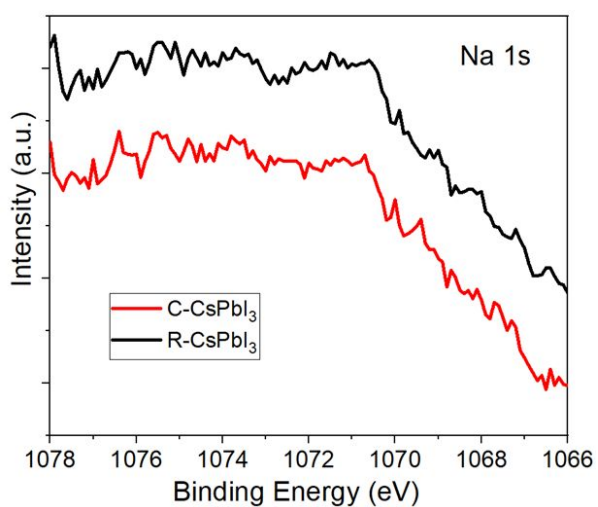


Figure S2. XPS spectra of Na 1 s in R-CsPbI₃ QD film.

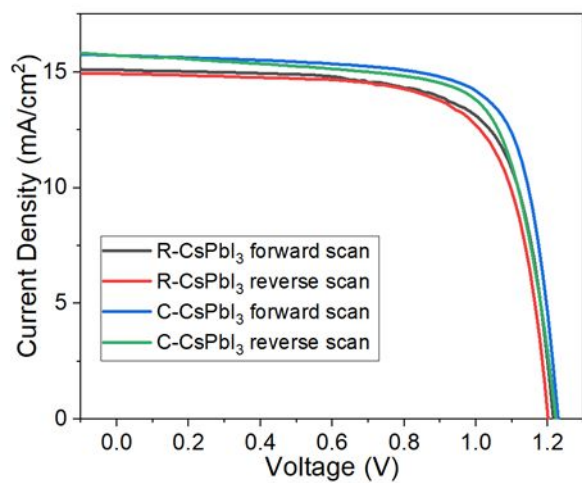


Figure S3. J-V curves of the C-CsPbI₃ and R-CsPbI₃ QD solar cells under forward and reverse direction scans.

Table S1. The reported state of the art efficiencies and device structures of CsPbI₃ QD solar cells.

Device Structure	Voc (V)	Jsc (mA/cm ²)	FF	PCE (%)	Ref
FTO/c-TiO ₂ /CsPbI ₃ /PTAA/MoOx/Ag	1.25	15.85	0.77	15.21	⁵
FTO/c-TiO ₂ /Zn:CsPbI ₃ /Spiro/MoO ₃ /Ag	1.23	17.58	0.74	16.07	⁶
FTO/c-TiO ₂ /M-TiO ₂ /CsPbI ₃ /Spiro/Au	1.06	17.77	0.75	14.32	⁷
ITO/SnO ₂ /PCBM/PCBM:CsPbI ₃ hybrid/PTB7/MoOx/Ag	1.26	15.6	0.78	15.1	⁸
ITO/SnO ₂ /CsPbI ₃ /Spiro/Ag	1.27	17.71	0.72	16.21	⁹
FTO/c-TiO ₂ /CsPbI ₃ /PTAA/MoO ₃ /Ag	1.24	16.0	0.74	14.7	This work

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