

## Supplemental information

### **From Lead-Acid Batteries to Perovskite Solar Cells – Efficient Recycling of Pb-Containing Materials**

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## Materials

Sodium sulfite ( $\text{Na}_2\text{SO}_3$ , ACS reagent, 98%, Sigma-Aldrich), deionized water (Sigma-Aldrich), ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3$ , ACS reagent,  $\geq 30.0\%$   $\text{NH}_3$  basis, 98%, Sigma-Aldrich), nitric acid ( $\text{HNO}_3$ , ACS reagent, 70%, Sigma-Aldrich), potassium iodide (KI, ACS reagent,  $>99\%$ , Sigma-Aldrich), Chlorobenzene (anhydrous, 99.8%, Sigma-Aldrich),  $\text{SnO}_2$  colloidal solution (15 w% in water, Alfa Aesar), lead iodide (99.99%, trace metals basis, TCI), Formamidine hydroiodide (FAI, 99.99%, Dyenamo AB), methylammonium chloride (MACl, 99.99%, Dyenamo AB), dimethylformamide (DMF, anhydrous,  $>99\%$ , Acros), dimethyl sulfoxide (DMSO, anhydrous,  $>99\%$ , Acros), *n*-hexyl trimethylammonium bromide (HTMABr,  $>99\%$ , TCI), diethyl ether (anhydrous,  $>99\%$ , Sigma-Aldrich), P3HT (Ossila), carbon paste (Dyenamo AB).

## Lead recycling process

Lead chemicals were separately collected from the negative and positive plates from the lead acid battery. Both mixtures were then ground into powder using mortars for subsequent reactions and characterization.

Firstly, lead compounds ( $\text{PbSO}_4/\text{Pb}$ , 25 g) from negative plate and lead compounds ( $\text{PbSO}_4/\text{PbO}_2$ , 25 g) from positive plate were added into dilute  $\text{H}_2\text{SO}_4$  solution (10 %v/v in deionized water, 100 mL),  $\text{Na}_2\text{SO}_3$  (15.12 g, 120 mmol) was added slowly into above solution. After stirring vigorously for 24 hours, the remained solid from the reaction was collected by filtration and washed with deionized water (20 mL  $\times$  3). The solid was then dried at  $100^\circ\text{C}$  for 2 hours, yielding 55.4 g of powder. The filtered solution was recycled to repeat the reaction.

Secondly, above powder (30 g) and  $(\text{NH}_4)_2\text{CO}_3$  (14.4 g, 150 mmol) were added into deionized water (50 mL) and the mixed solution was stirred vigorously for 24 hours. The solid from the reaction was collected by filtration and washed with deionized water (10 mL  $\times$  3). The solid was then dried at  $100^\circ\text{C}$  for 2 hours, yielding 26.6 g of powder. The filtered solution was recycled to repeat the reaction. The recycling yield of second step is 100%.

Lastly, above lead compounds (20 g) was added into dilute nitric acid (2 M in deionized water, 100 mL). After stirring for 30 min, KI (33.2 g, 200 mmol) was added into the reaction. The yellow precipitate was collected by filtration and dried at  $60^\circ\text{C}$  for 24 hours. To further improve the purity of  $\text{PbI}_2$ , the yellow product was dissolved in DMF (50 mL) and the transparent solution was filtered by syringe filter (0.45  $\mu\text{m}$  pore size). Chlorobenzene (30 mL) was added slowly into the transparent solution. The yellow precipitate was collected by filtration and washed by anhydrous chlorobenzene (10 mL  $\times$  3). After being dried in vacuum overnight, the final product ( $\text{PbI}_2$ , 34.2 g) was obtained. The recycling yield of third step is 99.3%.

## Device fabrication process

Fluorine doped tin oxide (FTO) substrates (NSG-10) were chemically etched by zinc powder and 4 M HCl solution and sonicated in 2% Hellmanex water solution for 30 min, acetone for 15 min and ethanol for 15 min, respectively. Then, all substrates were further cleaned by UV-Ozone for 15 min.  $\text{SnO}_2$  colloidal solution (15 w% in water) was diluted with deionized water with 1:4 volume ratio. For the  $\text{SnO}_2$  layer, 150  $\mu\text{L}$  of above solution was deposited by spin-coating at 5000 rpm for 30 s. After the spin-coating, the substrates were dried at  $150^\circ\text{C}$  for 30 min in ambient air. The perovskite precursor solution was prepared by dissolving recycled or commercialized  $\text{PbI}_2$  (1.8 M), FAI (1.8 M) and MACl (0.63 M) into mixed solvent of DMF and DMSO (the volume ratio of DMF and DMSO is 4:1). 50  $\mu\text{L}$  of the above perovskite solution was spin-coated at 6000 rpm for 50 s, with diethyl ether (1 mL) poured as an anti-solvent at 15s into the spin-coat process. Then the substrates were annealed at  $150^\circ\text{C}$  for 10 min in ambient air

(R. H. < 30%). After cooled to room temperature, 50  $\mu\text{L}$  of *n*-hexyl trimethylammonium bromide solution (0.1 mg/mL in chloroform) was deposited on the top of perovskite layer by spin-coating at 5000 rpm for 30 s. The substrate was followed by annealed at 150  $^{\circ}\text{C}$  for 1 min. After the substrate was cooled to room temperature, P3HT (10 mg/mL in chlorobenzene) was deposited on the top of substrate by spin-coating at 4000 rpm for 20 s. The carbon paste ( $\sim 40 \mu\text{m}$ ) was deposited on the perovskite film by doctor-blading and dried at 100  $^{\circ}\text{C}$  for 15 min.

#### **Other measurement**

The solar cell devices were measured under an irradiation intensity of 100 mW  $\text{cm}^2$  by Wave Labs SINUS-70 solar simulator with UV and IR range extenders. XPS measurements were carried out on a physical electronics quanter II scanning XPS microprobe. Scanning electron microscopy was performed on a Zeiss LEO 1550 with Oxford AZtec EDS.

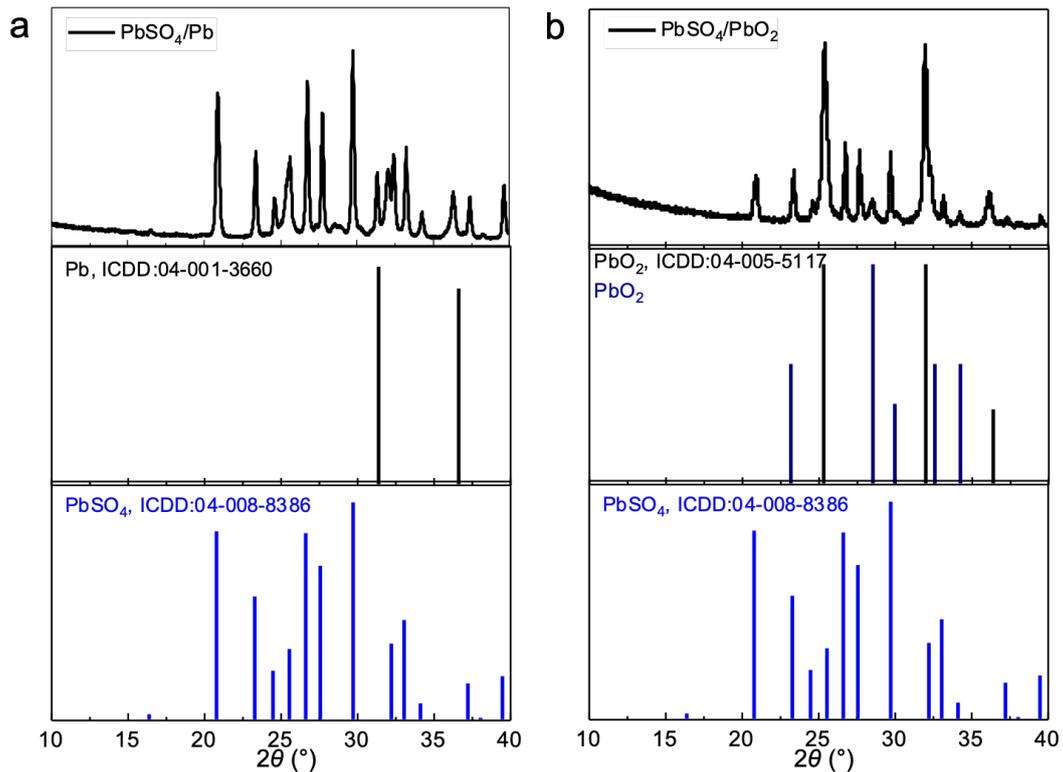
**a**



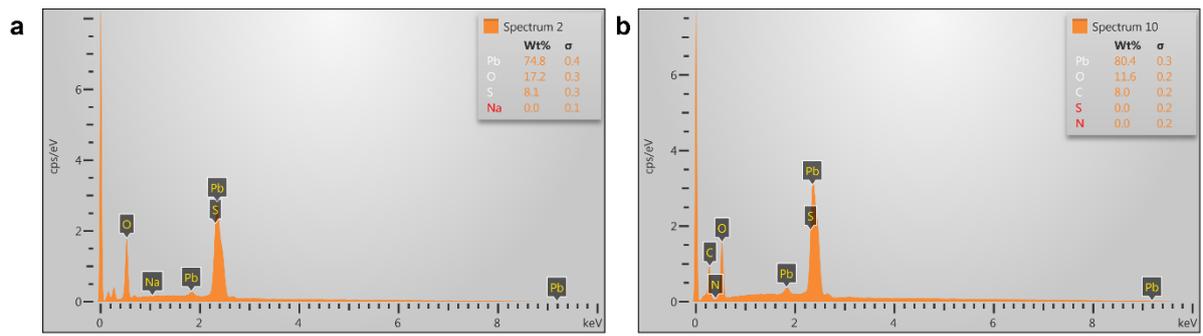
**b**



**Figure S1.** The voltage of the lead-acid battery **a)** before and **b)** after discharging process.



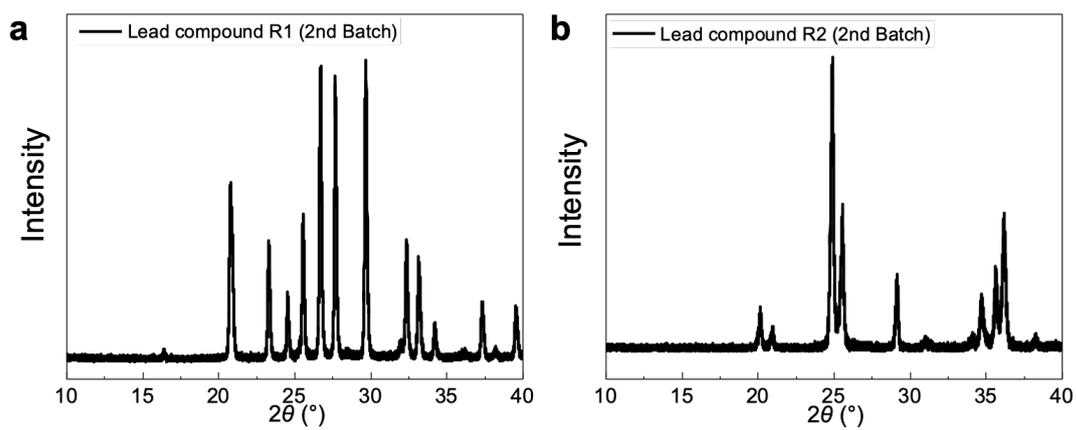
**Figure S2. a.** XRD patterns of lead-containing compounds from negative electrode and the reference XRD patterns of Pb and  $\text{PbSO}_4$ . **b.** XRD patterns of lead-containing compounds from positive electrode and the reference XRD patterns of  $\text{PbO}_2$  and  $\text{PbSO}_4$ .



**Figure S3.** EDS spectrum of lead-containing compounds after **a)** first step and **b)** second step of the recycling process.

**Table S1.** The solubility of lead compounds in aqueous solution at room temperature.

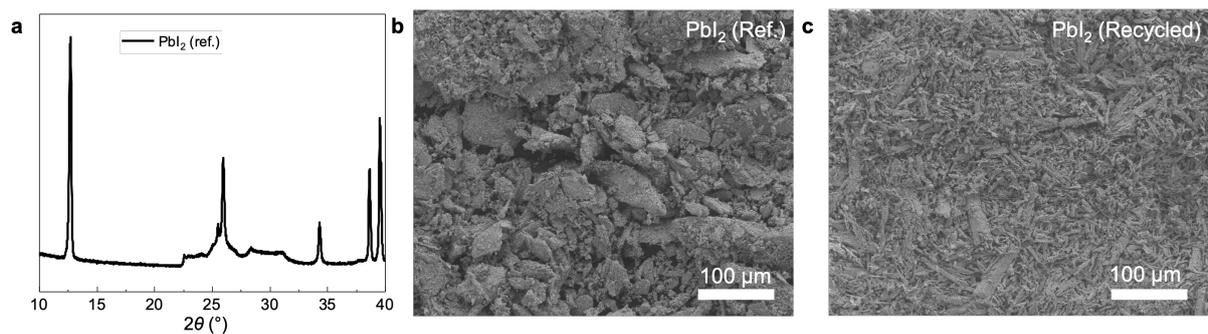
Lead compound	PbSO <sub>4</sub>	PbO <sub>2</sub>	Pb	PbCO <sub>3</sub>	PbI <sub>2</sub>
Solubility in water (g/100mL)	0.0404	<0.001	<0.001	0.00011	0.076



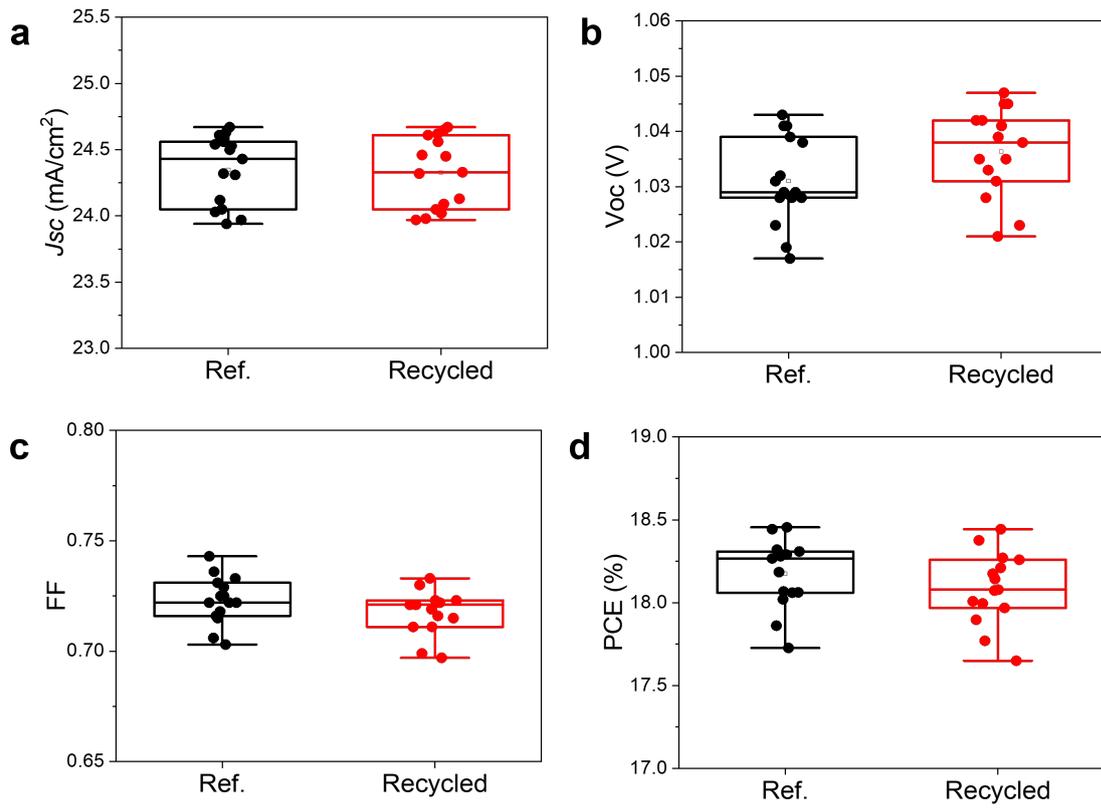
**Figure S4.** XRD patterns of lead-containing compounds after a) first step and b) second step react with recycled solutions.

**Table S2.** Material quantities and costs relevant to the lead recycling process

Chemical	Weight of reagent (g/g PbI <sub>2</sub> )	Volume of solvent (mL/g PbI <sub>2</sub> )	Price of chemical (USD/kg or USD/L)	Material cost (USD/g PbI <sub>2</sub> )
H <sub>2</sub> SO <sub>4</sub>		0.8	100.3	0.080
Na <sub>2</sub> SO <sub>3</sub>	0.18		73.6	0.013
deionized H <sub>2</sub> O		6.5	15.3	0.099
(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	0.32		311.8	0.099
HNO <sub>3</sub>		0.37	55.6	0.021
KI	0.97		416.4	0.423
DMF		1.47	170	0.249
Chlorobenzene		1.75	164.8	0.288
Recycled PbI <sub>2</sub>				1.272



**Figure S5.** a. XRD patterns of commercially obtainable  $\text{PbI}_2$  powder. SEM images of b) commercially available and c) recycled  $\text{PbI}_2$  powder.



**Figure S6.** The photovoltaic parameters of a)  $J_{sc}$ , b)  $V_{oc}$ , c) FF, and d) PCE of the C-PSCs fabricated from the commercially available and recycled  $PbI_2$ , 15 devices in each condition.