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Recycling Spent Lead-acid Battery into Lead Halide for Resource Purification and Multifunctional Perovskite Diode

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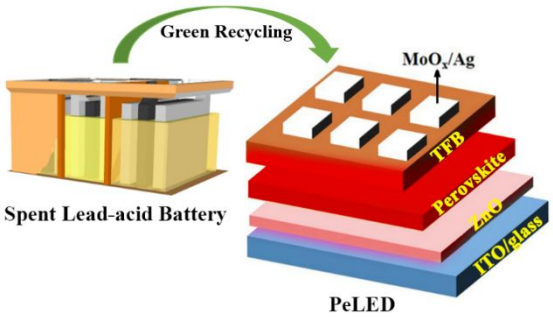
Green Recycling
MoO_x/Ag
TFB
Perovskite
ZnO
ITO/glass
Spent Lead-acid Battery
PeLED

Abstract Lead-acid battery is a reliable and cost-effective uninterrupted power supply (UPS) for cars, wheelchairs and et al. Recycling the discarded lead-acid batteries has increased the cost and could be a serious pollution issue after extensive use. It is important to exploit the new-generation application to reduce the cost and increase the value. In this article, we used a simple method to recycle spent lead-acid batteries for useful lead iodide resource with a high purity of over 99% and a recycling yield of 91.6% and then fabricated multifunctional $FAPbI_3$ perovskite diode using recycled lead iodide (PbI_2). The cost of recycled PbI_2 based on lab-grade chemicals is estimated to be only 17.4% that of lab-grade PbI_2, which undoubtedly greatly reduces the preparation cost of devices in the lab. The external quantum efficiencies (EQEs) of our perovskite diodes prepared with commercial and recycled PbI_2 are 19.0% and 18.7%, respectively, which shows that the performance of the device prepared from recycled PbI_2 is comparable to that of commercial lab-grade PbI_2. Based on the expense of industrial-grade chemicals, the cost of recycled PbI_2 is extrapolated to be 77.8% that of industrial-grade PbI_2. In addition, the dosage for thin film electronics is greatly diluted with respect to lead-acid batteries. Therefore, it can not only offer an approach to recycle hazardous solid waste, but also save the manufacturing cost of new-generation photoelectric devices, leading to earning additional value for lead waste.

Keywords: Spent lead-acid batteries; Recycling; Lead halide; Perovskite diode; Low cost.

INTRODUCTION

As a common energy storage device, lead-acid batteries are widely used in automobiles, aviation, and navigation due to high discharge rate, durable rechargeability, and low price[1, 2]. In the discharge state of a lead-acid battery, the main component of the positive electrode is lead dioxide and that of the negative electrode is lead. In the charged state, the main component of the positive electrode and the negative electrode is lead sulfate ($PbSO_4$). As more and more batteries die after extensive usage, a lot of solid-state lead-acid wastes are produced to occupy plenty of space. Particularly, the electrodes of lead-acid battery are mainly composed of Pb, $PbSO_4$ and its oxides, which are easy to produce lead pollution. Recycling the lead waster into battery will increase the additional cost. Aiming to start green development, governments are promoting to standardize the lead-acid battery industries and to recycle lead-acid batteries for advanced application[3, 4]. Therefore, how to recycle a large number of lead-acid batteries for utilization has become a new scientific and engineering problem. Most of industries resort it to pyrometallurgical process and wet chemistry for the recovery of the lead paste[5-7]. Because the pyrometallurgical process often requires carbonaceous reducing agents, and produces exhaust gases such as sulfur dioxide and carbon dioxide, which are seriously harmful to the environment and the human health[8, 9]. With the increasing requirements for environmental protection, the hydrometallurgical recycling of spent lead-acid batteries has displayed obvious advantages in this regard, but the existing hydrometallurgical recycling process needs large waste water treatment capacity, high energy consumption and complex production systems[10, 11]. Therefore, there is an urgent need for an economical and environmentally friendly way of recycling spent lead-acid batteries to mitigate the pollution and earn additional value.

The traditional recycling process for lead-acid battery is well established for reuse and the final lead product recovered is crude lead. The process is not so cost-efficient that its own economic value is not very high[12, 13]. Meanwhile, the industrially recovered crude lead contains more impurities, which needs to be further purified for advanced utilization. Halide lead perovskite materials have been widely used in the

research of solar cells and light-emitting diodes due to their abundant raw materials, low cost, superior photoelectric properties, higher color purity, solution processing, and low-temperature fabrication (<150 ^{o}C) [14-18]. Just in ten years, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has increased from the initial 3.8% to the most recent 25.5%, and the electroluminescent external quantum efficiencies (EQEs) of red and green light of perovskite light-emitting diodes (PeLEDs) have also exceeded 20%, which receive worldwide research interest[17, 19-23]. At present, the lead element occupies a pivotal position in the most efficient PSCs and PeLEDs, and thus the commercial lead source for lab use becomes more and more expensive, which could also restrict the commercialization in the future. Therefore, using lead resources from lead-acid batteries to fabricate the devices has two advantages: (1) reasonably and properly mitigate the environmental problems caused by spent lead-acid batteries, and realize the recycling of lead resources for advanced application; (2) increase the additional value of the lead resource and reduce manufacturing costs for advanced optoelectronic device. For example, PSC has demonstrated to be highly stable in outer space application and thus could be widely developed in low cost[24-26]. Therefore, it is feasible to recycle the lead source from spent lead-acid batteries for perovskite materials and devices[27-33].

In this work, we adopt the "wet-fire-wet" recycle process combining pyrometallurgical and hydrometallurgical methods to recycle the spent lead-acid batteries, which neither produces a mass of sulfur dioxide fumes that is harmful to the environment like the pyrometallurgical method, nor does it produce a large amount of waste water like the hydrometallurgical method. Firstly, we demonstrated the preparation of lead iodide (PbI_2) powder from the lead source of lead-acid battery through "wet-fire-wet" recycle process and the recycling yield is as high as 91.6%. The extracted PbI_2 product is highly soluble in polar aprotic solvent but undissolved in water and thus is facile for device utilization and environmental disposal. Then, the as-prepared PbI_2 powder was used as the precursor solution to fabricate high-brightness PeLEDs. The result shows that PbI_2 extracted by recycling lead in spent lead-acid batteries has the same material characteristics as commercial PbI_2, but

its cost is only 17.4% that of commercial lab-grade PbI_2. By industrial scale-up, this is extrapolated to be 77.8% that of industrial-grade PbI_2. Therefore, we can develop appropriate methods to recycle the waste lead sources for the fabrication of PeLEDs, which not only saves the cost of device fabrication and earn additional value, but also achieves the purpose of waste utilization and reduces environmental pollution.

EXPERIMENTAL

Materials and Chemicals. Ammonium carbonate ($(NH_4)_2CO_3$) (Cas no. 506-87-6, purity: ＞99%), Hydrobromic acid (Cas no. 10035-10-6, ACS: 48%), Zn $(Ac)_2{\cdot}2H_2O$ (Cas no. 557-34-6, purity: ＞98%), KOH (Cas no. 1310-58-3, purity: 99.99%) and Hydroiodic acid (Cas no. 10034-85-2, ACS: 55-58%) were purchased from Sigma-Aldrich. Nitric acid (Cas no. 7697-37-2, AR: 65-68%), Methanol (Cas no. 67-56-1, AR: 99.5%) and N, N-dimethylformamide (DMF) (Cas no. 68-12-2, purity: ＞99%) were purchased from Aldrich. PbI_2 (Cas no. 10101-63-0, purity: 99.99%) and Lead bromide ($PbBr_2$) (Cas no. 10031-22-8, purity: 99.99%) were purchased from Xi'an Polymer Light Technology Corp.

Extracting the lead resource for PbI_2. The spent lead-acid battery was obtained from an abandoned electric bicycle. After removing the battery top cover, the battery is mechanically disassembled. The acidic electrolyte was carefully poured out and collected, and the inner wall of the battery and the electrode plate were repeatedly washed with deionized water and dried. Scraped lead and its compounds from the electrode plate were grinded into powder. The collected 21.6098 g powder scraped from the electrode plate was firstly reacted with the slightly excessive ammonium carbonate solution to desulfurize and placed overnight. After removing the supernatant, the precipitate was collected. The precipitate obtained was dried in an oven at 60 ^{o}C, and its main components are lead metal, lead dioxide, and lead carbonate. The 19.04 g precipitate was calcinated in a tube furnace at 600 ^{o}C for 5 hours to obtain 15.4817 g yellow powder. The calcinated yellow powder (the main component is PbO) was reacted with 2 mol/L dilute nitric acid diluted by 40 mL thick nitric acid, stood for 2 hours, removed a small amount of impurity from the bottom.

The supernatant was reacted with 76 mL hydroiodic acid to obtain yellow PbI_2 crystal powder, which was washed three times with ethanol, then recrystallized with DMF, finally dried in a vacuum drying oven at 60 °C for 24 hours.

Synthesis of ZnO NPs. 2.95 g of Zn $(Ac)_2 \cdot 2H_2O$ was dissolved in 125 mL of methanol and 1.48 g of KOH was dissolved in 65 mL of methanol. Zn $(Ac)_2 \cdot 2H_2O$ solution was added into a 250 mL three-neck round bottom flask and kept it to 60 °C, and then KOH solution was poured to react for 2 hours. After keep overnight, the supernatant was removed to collect the precipitate. After washing and centrifuging for three times, it is finally dissolved in the mixed solution of methanol and chloroform for use.

Device fabrication. The patterned ITO glass was washed with cleaning agent, deionized water, acetone, isopropanol, absolute ethanol, and dried with nitrogen, and then the substrate was further cleaned with UV-Ozone. In a fumehood, 8 mg/mL ZnO as an electron transport material was spin-coated on the substrate at 4000 rpm for 60 s, and then annealed at 130 °C for 15 min. After cooling to room temperature, the substrate was transferred to a nitrogen glove box for further device fabrication. FAI, PbI_2 and 5AVA were dissolved in DMF at a molar ratio of 2: 1: 0.5 to prepare the precursor solution with a concentration of 0.5 M. 30 μL of the perovskite precursor solution was spin-coated on the substrate at 3000 rpm for 60 s, and TFB as the hole transport material was spin-coated on the perovskite substrate at 2000 rpm for 30 s. 8 nm MoO_x and 100 nm Ag were sequentially deposited by vacuum evaporation equipment (vacuum degree is 1.0×10^{-5} Pa), in which the effective area of the device (the overlapping area of ITO and Ag electrodes) is 8 mm^2.

Characterization. For PbO and PbI_2 powders, we use inductively coupled plasma optical emission spectrometer (ICP-OES) (Model: CAP 7000) and ion chromatograph (Model: ICS-1500) to conduct elemental composition analysis, and use X-ray polycrystalline powder diffractometer (XRD) (Model: Empyrean) to verify the material composition. For PbI_2 and precursor liquid films, we use XRD (Model: Empyrean) for crystallinity analysis, and use ultra-high resolution field emission

scanning electron microscope (SEM) (Model: Merlin) to characterize the surface morphology, using ultraviolet visible (UV) spectrophotometer (Model: UV-2600) measures its absorbance value. In addition, we used a 590 nm laser, an integrating sphere and a flame spectrometer to measure the photoluminescence quantum yield of the film.

We set up self-made test fixtures to test the electroluminescence performance of devices in an integrating sphere. Using Keithley 2400 instrument, at a step voltage of 0.05 V, the *J-V* data from 0 V to 9 V is tested, and flame spectrometer (Ocean Optics) recorded electroluminescence characteristics.

Results and discussion

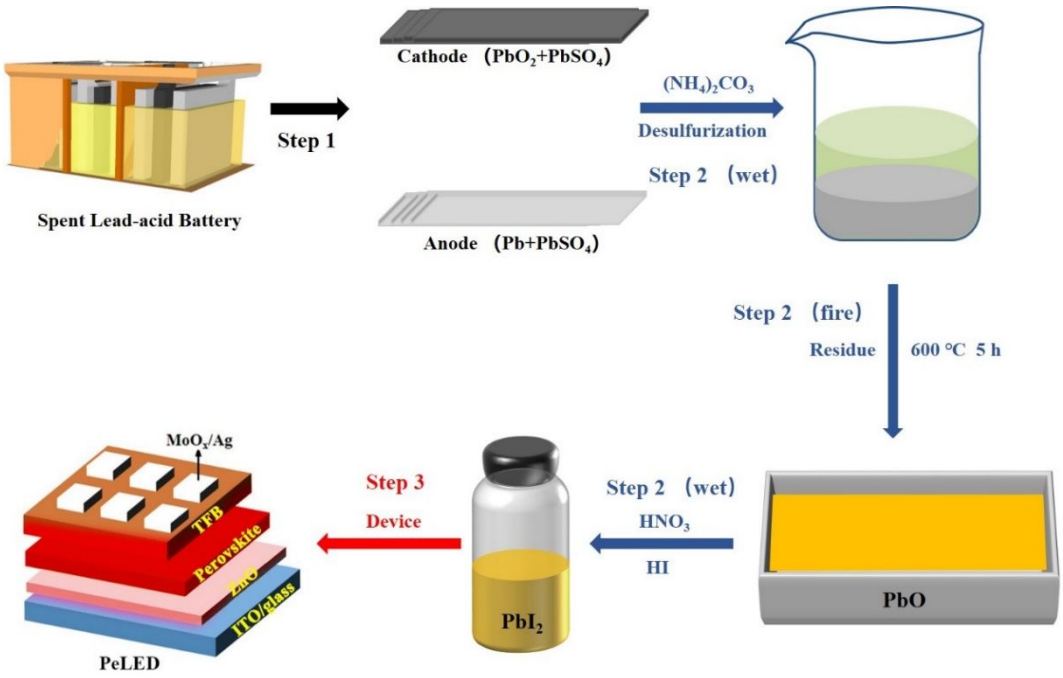

Figure 1. The recycling process of lead resource from spent lead-acid batteries for the fabrication of PeLED. Step 1: disassembly process; Step 2: "wet-fire-wet" recycling, including desulfurization, calcination and halide processes; Step 3: resource utilization for PeLED device.

Simple process, high yield and clean product are the grand goals for recycling the spent lead-acid battery. Figure 1 mainly shows the new recycling strategy for extracting high-purity PbI_2 powder by recycling spent lead-acid batteries and

fabricating high-brightness PeLEDs by using the recycled lead halide resource. Unlike traditional pyrometallurgical methods, this method not only contain no harmful flue gas (SO_x) and waste water, but also can extract high-purity lead halide powder with high productive yield due to the orthometric dissolution characteristic of lead halide (soluble in DMF but insoluble in water). This process is divided into three steps. Step 1 is the disassembly process, namely, removing the cathode and anode from the spent lead-acid battery. We took down the lead source electrode of the spent lead-acid battery and crushed it for standby. In Pb paste, it contains 50 wt% $PbSO_4$, 28 wt% PbO_2, 9 wt% PbO, 4 wt% Pb, and the total amount of Pb element is 70.76 wt%. Step 2 is the "wet-fire-wet" recycle process for the high-purity PbI_2, including wet-chemical desulphurization, fire calcination and wet-chemical halide through a series of chemical reactions. Step 3 is to utilize the extracted PbI_2 powder to prepare the perovskite precursor solution for fabricating PeLEDs.

In Step 2, the main chemical reactions are as follows:

$$PbSO_4 + (NH_4)_2CO_3 \rightarrow PbCO_3 + (NH_4)_2SO_4 \quad (1)$$

$$PbCO_3 \xrightarrow{600℃} PbO + CO_2 \quad (2)$$

$$PbO_2 \xrightarrow{600℃} PbO + {}^1/_2O_2 \quad (3)$$

$$Pb + {}^1/_2O_2 \xrightarrow{600℃} PbO \; ; \; Pb + PbO_2 \xrightarrow{600℃} PbO \quad (4)$$

$$PbO + 2HI \rightarrow PbI_2 + H_2O \quad (5)$$

Due to the continuous charge-discharge cycle of lead-acid batteries, a large amount of $PbSO_4$ will be produced in both the anode and cathode, so when we process the electrode plate, we must first consider removing the sulfur element for subsequent treatment. In reaction (1), we add ammonium carbonate solution to the lead paste to make lead ions and carbonate ions produce insoluble precipitates, and then take the precipitates for later use to achieve the purpose of removing sulfur. The ICP test results of the reaction products show that the surface of the products may also be coated with a small amount of carbonate and ammonium ions and a very small amount of iron and antimony impurities (Sb: 0.01%; Fe: 0.1%), which may be caused

by the residual of unreacted ammonium carbonate in the precipitation process (Figure S1). The ammonium sulfate produced is not only harmless to the environment, but also can be used as a fertilizer for plants.

As shown in reaction (2-4), the lead carbonate, lead, and lead dioxide obtained by the desulfurization reaction were calcinated in a tube furnace at 600 ^{o}C for 5 hours to obtain yellow PbO powder without releasing harmful gas[34]. In view of the new pollution caused by the lead vapor generated by the oxidation of lead powder at 600 ^{o}C, the tail gas of lead powder was treated by using hydrogen iodic acid. On the one hand, it can eliminate the environmental pollution caused by lead vapor. On the other hand, the product of tail gas treatment and excess hydrogen iodic acid can be reused to prepare PbI_2 without introducing impurities. Figure S2 shows the image of PbO powder obtained by calcination. We further used various methods to characterize the purity of PbO obtained by calcination. First, we used Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) to initially characterize the purity of PbO. Through SEM, it can be seen that the PbO powder appears as large and uniform crystals (Figure S3). As shown in Figure S4, the proportion of elements in the PbO powder is analyzed by EDS. The proportion of lead element is 92.78%, the proportion of oxygen element is 7.22%, and the atomic percentages of the two are 49.80% and 50.20%, which are close to 1: 1. It is preliminarily proved that the yellow powder after calcination is PbO with a purity of about 100%. In addition, in order to better verify the purity of PbO, the as-prepared PbO powder passed the ICP test (Figure S5). The test results showed that the Pb content in the PbO powder reached 92.37%, and the purity exceeded 99.5%, reaching the purity of commercial PbO, laying a good foundation for the next step to prepare high-purity lead halide.

Normally, we directly put the PbO powder beaker to react with hydroiodic acid according to the stoichiometric ratio (reaction (5)). After a period of time, there is no obvious change in the PbO powder. We speculate that PbI_2 is formed on the surface of the PbO powder, which hinders the normal progress of the reaction.

$$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O \quad (6)$$

$$Pb(NO_3)_2 + 2HI \rightarrow PbI_2 + 2HNO_3 \quad (7)$$

Therefore, we modified the process. The as-prepared PbO powder was first reacted with 2 mol/L of dilute nitric acid according to the stoichiometric ratio to obtain a clear solution, and there is no residue at the bottom of the beaker. 55-58 wt% HI was then added dropwise to the clear solution until yellow PbI_2 crystals no longer formed (reaction (6-7)). The HNO_3 generated by equation (7) can be reused to react with PbO.

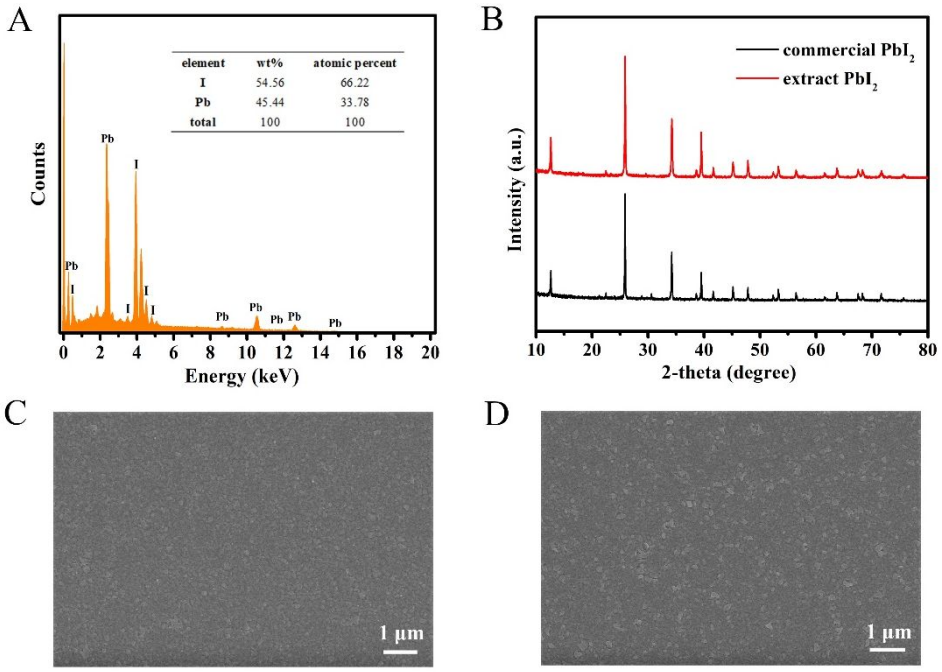

Figure 2. Material characterization for PbI_2 extracted from lead-acid batteries. (A) EDS analysis of PbI_2 powder. (B) XRD spectrum analysis of commercial and extracted PbI_2 powder. (C) SEM of the commercial PbI_2 film. (D) SEM of the extracted PbI_2 film.

The high purity of lead halide is the prerequisite for the preparation of performance PeLEDs. Further, since both antimony triiodide and ferrous iodide are soluble in ethanol and lead iodide is insoluble in ethanol, we washed PbI_2 powder with anhydrous ethanol for three times, and then recrystallized and purified with DMF to remove a small amount of iron and antimony impurities that may still exist. Finally, we dried in a vacuum oven at 60 ^oC for 24 hours to obtain pure yellow PbI_2 crystal powder (Figure S6). We performed the purity characterization of the extracted yellow PbI_2 crystal powder. We first performed EDS characterization of the extracted PbI_2

powder to determine its element content. As shown in the Figure 2A, the EDS spectrum of extracted PbI_2 powder contains no other elements except Pb and I. The mass fraction of I and Pb are 54.56% and 45.44%, respectively, so the purity of extracted powder is close to 100%. The atomic percentages of I and Pb are 66.22% and 33.78% by calculating, respectively, which are close to 2: 1. It is further confirms that the molecular formula of the extracted white powder is PbI_2. Figure 2B is the XRD pattern of extracted PbI_2 from the spent lead-acid battery[35]. It can be seen from the XRD pattern that the extracted PbI_2 has the same crystal structure as the commercial PbI_2 without redundant peaks and the intensity of the peaks varies slightly, which indicates that the extracted PbI_2 with high purity will lay a foundation for us to further prepare high-performance PeLED devices. The SEM images of PbI_2 powder shows that PbI_2 has a good cubic crystal structure, with a crystal size of about 500 nm (Figure S7). In order to verify the film-forming state of PbI_2 powder, we used DMF as a solvent to prepare a 0.5 M PbI_2 solution and spin-coated it on a transparent glass substrate. From Figure 2C, it can be seen that the SEM image of commercial PbI_2 film exhibits good coverage without pinholes. Comparing the SEM images, we can observe that the quality of extracted PbI_2 film is similar to that of commercial PbI_2 film (Figure 2D). It is further verified that the extracted PbI_2 has good film-forming ability, which is conducive to obtain high-quality perovskite films. We also used an ultraviolet spectrophotometer to test the absorption spectra of the PbI_2 films, and the results showed that the commercial and extracted PbI_2 films have the similar absorption spectrum (Figure S8).

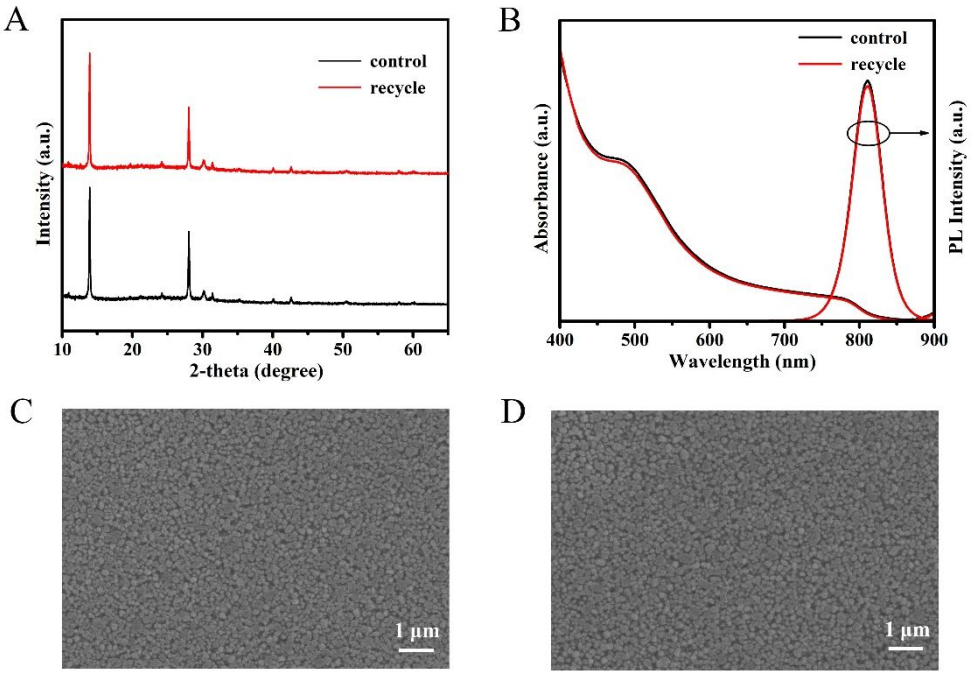

Figure 3. Film characterization of perovskite precursors. (A) XRD spectrum analysis of perovskite precursor. (B) The absorption peak and PL intensity of thin film of perovskite precursor. (C) SEM image of control perovskite precursor. (D) SEM image of recycle perovskite precursor.

We then used commercial and recycled PbI_2 as raw materials to prepare the $FAPbI_3$ perovskite films. Through XRD analysis of the perovskite films prepared by commercial and extracted PbI_2, we can see that two perovskite samples have good crystallinity and the same crystal structure (Figure 3A) [36-38]. It is well known that the optical properties of perovskite thin films affect the luminescence properties of PeLEDs. Therefore, it is necessary to study the absorption and fluorescence spectra of different $FAPbI_3$ perovskite films by UV-vis spectroscopy and photoluminescence (PL). Figure 3B shows the absorption spectra and PL spectra of the different perovskite films. It can be seen that two samples have a narrow PL peak at 809 nm and the absorption edge is also at 810 nm. We also studied the surface morphology of $FAPbI_3$ films prepared from different PbI_2 materials by SEM as shown in Figure 3C and D. Through SEM images, we can see that the perovskite film prepared from the extracted PbI_2 formed a uniform and dense thin film on the ZnO substrate, with a grain size of about 100 nm. The compact perovskite film with small size perovskite crystal is beneficial to increase the charge injection and reduce the non-radiative

recombination, so as to improve the electroluminescence performance of the device. Compared with the commercialized PbI_2, the two samples have similar film states, which indicates that the PbI_2 extracted from the spent lead-acid battery will not affect the final efficiency of the device because of the quality of the light-emitting layer film, and can meet the preparation of perovskite film requirements.

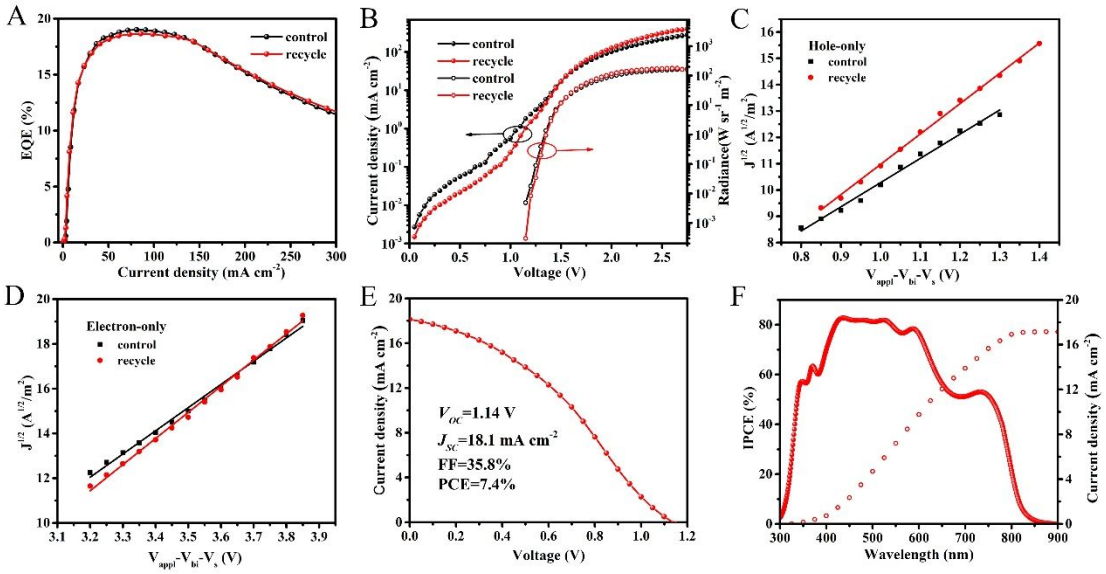

Figure 4. Device characterization of PeLEDs. (A) EQE diagrams of devices. (B) Current Density-Voltage-Radiance curves of devices. (C) $J^{1/2}$-V_{appl}-V_{bi}-V_s curves of hole-only devices. (D) $J^{1/2}$–V_{appl}-V_{bi}-V_s curves of electron-only devices. (E) J-V characteristic curves of corresponding device. (F) incident photon-to-electron conversion efficiency (IPCE) spectra of corresponding device.

In order to further evaluate the performance of the PeLEDs based on different sources of PbI_2, we have fabricated the structure of PeLEDs with Glass/ITO/ZnO/$FAPbI_3$/TFB/MoO_x/Ag. As shown in Figure 4A, the commercial and extracted PbI_2 perovskite devices reached 19.0% and 18.7% peak EQE at a current density of 75 mA cm^{-2}, respectively, which further shows that the efficiency of the devices prepared by the recycled PbI_2 and commercial PbI_2 is almost the same. Figure 4B shows the Current Density-Voltage-Radiance curves of the two devices from commercial and extracted PbI_2. Due to the better carrier mobility of the device, when the bias voltage is applied to 1.2 V, the current density and radiance of the device prepared by the commercial PbI_2 increase rapidly, and the high brightness of 178 W

343 sr^{-1} m^{-2} is reached at 2.6 V. Through comparison, it can be found that the maximum
344 brightness of the device prepared by the recycled PbI_2 is 173 W sr^{-1} m^{-2} and the
345 brightness at the maximum EQE is 78 W sr^{-1} m^{-2}. In order to understand the
346 characteristics of PeLEDs based on different PbI_2 as raw materials, the hole and
347 electron mobilities of $FAPbI_3$ film (Figure 4C and D) were measured through the
348 space charge-limited current (SC-LC) model with a hole-only device of ITO/PEDOT:
349 PSS/$FAPbI_3$ (250 nm)/TFB/Ag structure and an electron-only device of
350 ITO/ZnO//$FAPbI_3$ (250 nm)/$PC_{61}BM$/Ag structure. Here the SC-LC is calculated by
351 the equation[39]:

352 $$J = \frac{9}{8}\varepsilon_r\varepsilon_o\mu_e\frac{V^2}{d^3} \quad (8)$$

353 The results show that the hole mobility of $FAPbI_3$ films based on commercial and
354 extracted PbI_2 are 4.24×10^{-4} and 6.91×10^{-4} cm^2 V^{-1} s^{-1}, and the electron mobilities of
355 them are 5.60×10^{-4} and 7.11×10^{-4} cm^2 V^{-1} s^{-1}, respectively, which are of the same
356 order of magnitude and both have higher hole/electron mobility. A more matched
357 hole/electron mobility can improve the charge transport characteristics of the device,
358 thereby reducing nonradiative recombination and enhancing the performance of the
359 device. We also investigated the PV performance of PeLED. Figure 4E shows the *J-V*
360 curve of the corresponding LED device. We can observe that the device has a power
361 conversion efficiency (PCE) of 7.4% with a fill factor of 35.8%, an open circuit
362 voltage of 1.14 V, a short circuit current of 18.1 mA cm^{-2}. Figure 4F shows the IPCE
363 of the corresponding device, whose integral current is 17.2 mA cm^{-2}, which is
364 consistent with the current in the previous *J-V* curve.

365 In addition, we also use calcinated PbO to react with dilute nitric acid and
366 hydrobromic acid to prepare high-purity $PbBr_2$ (Figure S9). In order to verify the
367 purity of $PbBr_2$, we performed EDS characterization on the $PbBr_2$ powder (Table S1).
368 The results showed that the white powder only contains Pb and Br, and the atomic
369 percentages of the two are 34.71% and 65.29%, respectively. The element ratio is
370 close to 2: 1. Further, we also compare the extracted $PbBr_2$ with commercial $PbBr_2$,
371 the XRD analysis showed that the two have the same crystal structure, and the

absorption spectrum further verified that the purity of the $PbBr_2$ we extracted is comparable to that of commercial $PbBr_2$ (Figure S10 and S11). In order to verify the optical properties of $PbBr_2$, we used the extracted and commercial $PbBr_2$ to prepare $CsPbBr_3$ precursor to prepare PeLED of structure Glass/ITO/PEDOT: PSS/ $CsPbBr_3$/B3PyMPM/LiF/Al, in which the concentration of the active layer is 0.5 M. We also tested the electrical performance of the prepared devices, and the brightness of the commercial and extracted devices were 2288 and 2174 cd m^{-2}, respectively, indicating that the extracted $PbBr_2$ could achieve the photoelectric performance similar to that of the commercial $PbBr_2$ (Figure S12 and Video S1). We recovered lead from spent lead-acid batteries and extracted yellow PbI_2 and white $PbBr_2$ powders to prepare high-performance PeLEDs. Through comparison, it is found that the PeLEDs prepared from the extracted perovskite raw materials and commercial raw materials have the same photoelectric properties, which provides a new idea for the recycling of used lead-acid batteries in the future.

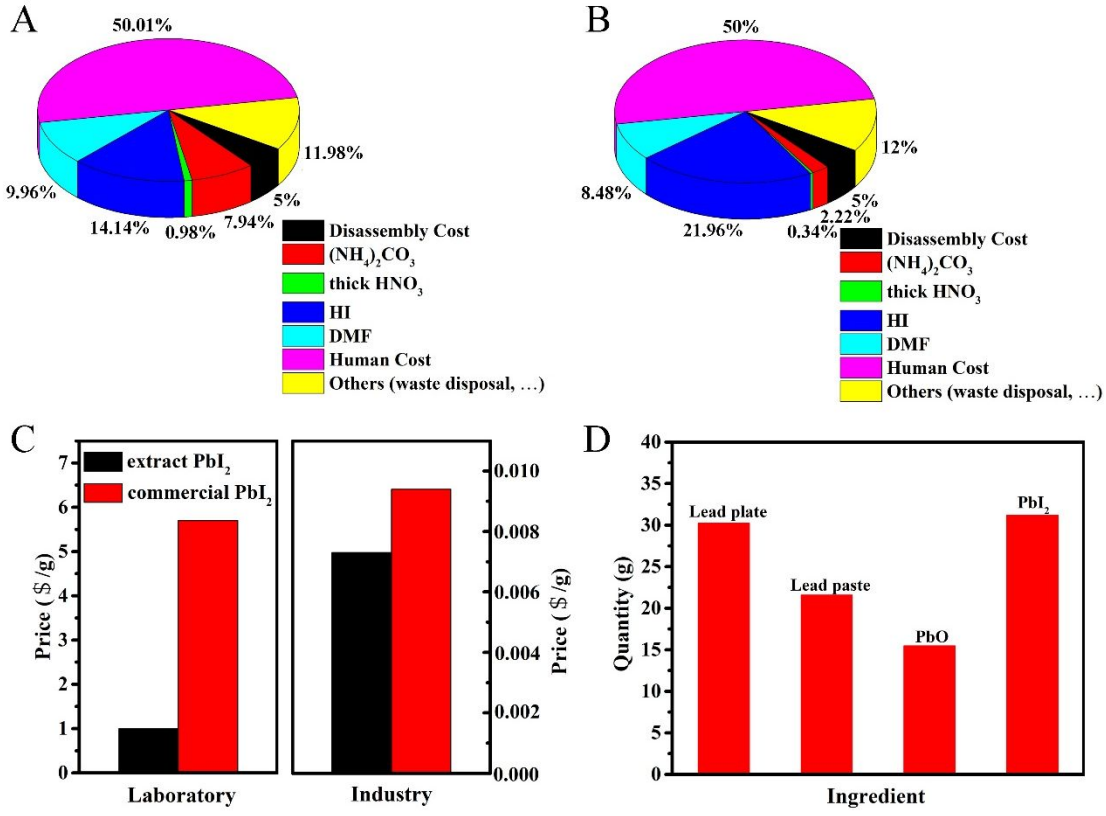

Figure 5. Analysis on the benefits of lead recycling from spent lead-acid batteries. (A) Various costs associated with the laboratory recycling process. (B) Various costs in the industrial recycling

process. (C) Comparison of recycling and commercial price of PbI_2. (D) Yield analysis during recycling.

In the manufacturing process of PeLEDs components, the main expense is the cost of raw materials and human cost[40-42]. By extracting PbI_2 from spent lead-acid batteries, we not only save the manufacturing cost and increase the value, but also make an important contribution to resource recovery and environmental pollution reduction. We calculated the material consumption during the recycling process on the basis of 100 g lead paste (Table 1). In the first disassembly process, the cost is set to be 5% of the total budget. In the second step, the amount of ammonium carbonate, thick nitric acid and hydroiodic acid are 0.033 kg, 0.04 L and 0.076 L, and the costs are \$11.4, \$1.4 and \$20.3, respectively. DMF, used to purify PbI_2 multiple times, costs about \$14.3, and other costs like waste disposal, pure water and lab equipment costs are about \$17.2. It is worth noting that the human cost of extracting PbI_2 is set to 50% of the total cost, which is based on the budgeting of normal research project. Finally, we calculated that the total cost of 100 g of paste for laboratory and industrial recycling were \$143.6 and \$1.0555, respectively. As shown in Figure 5A and B, we separately calculated the cost of each material in the whole battery in the laboratory and the industrial recycling process. Compared with the laboratory recycling process, the cost of $(NH_4)_2CO_3$ in the industrial recycling process is significantly reduced, while the cost of HI is slightly increased. Meanwhile, DMF and nitric acid can be reused in the extraction process of PbI_2, so the actual recycling cost is even lower. Further comparisons are made between the cost of recycled PbI_2 and the commercial price of PbI_2 (Figure 5C). The price of known chemical reagent company's PbI_2 is 5.7 \$/g, while the laboratory recycling cost of our PbI_2 is 0.99 \$/g, which is only 17.4% of the commercial cost. Even more surprising is that if we use industrial-grade raw materials, the cost of extracting PbI_2 is only 77.8% that of industrial-grade PbI_2, which greatly saves the preparation cost of PeLEDs.

Table 1 The material consumption of 100 g lead paste.

Materials	Price		Dosage	Cost ($)	
	Laboratory	Industry		Laboratory	Industry
$(NH_4)_2CO_3$	230 $/kg	0.71 $/kg	0.033 kg	11.4	0.0234
HNO_3 (thick)	36 $/L	0.09 $/L	0.04 L	1.4	0.0036
HI	267 $/L	3.05 $/L	0.076 L	20.3	0.2318
DMSO	286 $/L	1.79 $/L	0.05 L	14.3	0.0895
Disassembly Cost				7.2	0.0528
Human Cost				71.8	0.5277
Others (Waste disposal …)				17.2	0.1267
Total				143.6	1.0555

In the recycling process, the final recycling rate is an important indicator for our evaluation of the recycling of used lead-acid batteries. For this, we calculated the recycling rate by weighing the recycling amount at each step (Figure 5D). The lead paste of the spent lead battery is mainly the paste-like substance formed by the active material on the two poles after repeated charging and discharging. Its main components are $PbSO_4$, PbO_2, Pb, and the mass fraction of $PbSO_4$ exceeds 50%. We first take the active material off the electrode plate and obtain 21.6098 g powder. In step 2, we transfer the powder through desulfurization reaction and calcination reaction successively to obtain 15.4817 g of yellow PbO powder with a yield of about 94%. The PbO powder is further reacted with dilute nitric acid and hydroiodic acid, and finally washing and vacuum drying, 31.1930 g of PbI_2 yellow crystal powder was obtained with a yield of about 97.5%. After calculation, the final yield was about 91.6%.

Table 2 Lead consumption of lead-acid battery and perovskite device.

		Dosage (million unit)	Lead (each) (kg)	Lead (total) (thousand tons)
lead-acid battery	electric moped	400	1	400
	car	1000	2	2000
perovskite device	display screen	5000	4.5×10^{-4}	2.25

Reusing the lead source of spent lead-acid batteries for PeLEDs or perovskite display technology can not only reduce the economic cost of perovskite devices, but

also greatly reduce the environmental hazards because of the diluted concentration. A preliminary evaluation of lead-acid batteries and perovskite display applications can be made in terms of lead consumption and service life. From the perspective of dosage, the application of lead-acid battery in the field of transportation is mainly to provide power for electric moped and car. As shown in Table 2, there are about 400 million electric mopeds driven by lead-acid battery in the world, among which the lead content of each lead-acid battery is calculated by 1 kg, which consumes a total of 400,000 tons of lead. What is even more surprising is that about 1 billion cars in the world use lead-acid batteries as their uninterrupted power supply systems, and the lead content of each uninterrupted power supply system is as high as 2 kg. So, just for daily transportation, the amount of lead used is staggering 2.4 million tons. On the other hand, the perovskite display screens mainly used for computer display in the future, the size of each display screen is about 40 cm×50 cm, the thickness of the perovskite active layer is 500 nm, and the concentration of lead in the perovskite film is 4.5 g/cm^3. If the number of laptops and PCs are 5 billion, the amount of lead used is only 2,250 tons, which is only 0.1% of the amount of lead used in lead-acid batteries. Therefore, if the lead source used in lead-acid batteries is recycled or directly used in display technology, the amount of lead used will be greatly reduced, thereby reducing the environmental problems caused by lead leakage. In terms of service life, the longest service life of lead-acid batteries is 5 years, while the average life of display screens is 8-10 years. Therefore, using recycled lead in perovskite display technology is also a more low-carbon and environmentally friendly energy recycling method.

With the development of the economy, vehicles such as electric mopeds and cars have gradually become the main means of transportation for people to travel. However, lead-acid batteries, the scrap products of these vehicles, have become a problem of environmental pollution to be solved. Therefore, recycling the lead in spent lead-acid batteries has become an important research topic. The utilization of lead resource for advanced devices may offer more opportunity to enhance the additional value for hazardous wastes.

We use a combination of pyrometallurgical and hydrometallurgical methods to

466 recycle spent lead-acid batteries. Firstly, yellow PbO powder with purity more than
467 99.5% was obtained by treating spent lead-acid battery and calcinating at high
468 temperature. Then, the PbO powder was sequentially reacted with dilute nitric acid
469 and hydroiodic acid to obtain yellow PbI_2 crystals, washed with absolute ethanol for
470 multiple times, and recrystallized with DMF to obtain high-purity PbI_2 crystals with a
471 purity of more than 99% and a yield of 91.6%. This method of combining wet and fire
472 metallurgy methods to extract lead from spent lead-acid batteries can not only extract
473 high-purity perovskite raw materials, but also save energy consumption. Further, we
474 used extracted PbI_2 as raw materials to prepare the PeLEDs. Through the analysis of
475 the thin film and optical properties of the device, we found that the extracted PbI_2 has
476 the same physical and chemical properties as the commercial PbI_2, and the EQEs of
477 the devices prepared with extracted and commercial PbI_2 are 19.0% and 18.7%,
478 respectively, which shows that we can completely use the extraction of lead source
479 from the spent lead acid battery as the raw material for perovskite research. It not only
480 saves the cost problem, but also effectively reduces the environmental pollution
481 caused by the spent lead-acid batteries, leading to the lead source recycling and
482 utilization.
483

484 **ASSOCIATED CONTENT**

485 **Supporting Information**

486 Supporting Information is available free of charge on the ACS Publications website or
487 from the author.
488

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494 **Notes**

Any additional relevant notes should be placed here.

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