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Cyclic Utilization of Lead in Carbon-Based Perovskite Solar Cells

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KEYWORDS: Lead, NH$_3$·H$_2$O, Cyclic utilization, Carbon-based, Perovskite solar cells

ABSTRACT: An environmentally friendly dissolving-precipitating method is developed to recycle lead from carbon-based perovskite solar cells (PSCs). N, N-Dimethylformamide (DMF) was used to dissolve PSCs and to obtain lead containing lixivium. NH$_3$·H$_2$O was used as a precipitator to extract lead ions from the lixivium. The result analyzed by inductively coupled plasma optical emission (ICP-OES) shows that 99.9 % of lead can be extracted by NH$_3$·H$_2$O. Then, HI was used to generate PbI$_2$. ICP-OES analysis and thermodynamic calculation are used to analyze the lead content. The results show that few PbI$_2$ transforms into [PbI$_4$]$^{2-}$ due to the low concentration of hydroiodic acid (HI). The calculated lead recovery rate is 95.7 %. The recycled PbI$_2$ was used to fabricate carbon-based PSCs achieving an efficiency of 11.36 %, which is comparable to that (12.17 %) of carbon-based PSCs fabricated with commercial PbI$_2$. The developed process provides a new approach for the cyclic utilization of lead in carbon-based PSCs to avoid lead pollution.
INTRODUCTION

Perovskite solar cells (PSCs) have attracted considerable attention in recent years\textsuperscript{1-5}. The perovskite materials (ABX$_3$, A= Cs, CH$_3$NH$_3$, NH=CHNH$_3$, B = Pb, Sn; X = Cl, Br and I) have superior properties and have been applied to solar cells, light-emitting diode (LED), photodetectors, lasers, water-splitting and other electronic applications\textsuperscript{6}. Nowadays, with the improvement of the stability, PSCs would probably become the next-generation cheaper new energy. The efficiency plays an important role in reducing the cost and the stability is the key to the commercialization of PSCs\textsuperscript{7,8}. The silicon-perovskite tandem solar cells have an ultrahigh efficiency, which might be the direction of future new energy\textsuperscript{9-11}. And the theoretical efficiency of such structured solar cells can reach 35 %\textsuperscript{12,13}. However, the instability of perovskite materials can be a crucial factor hindering the commercialization of PSCs. Researchers are dedicated to studying two-dimensional (2D), all inorganic PSCs, all inorganic charge contacts as well as discrete iron(III) oxide nanoislands for PSCs, which improved the stability of PSCs\textsuperscript{14-18}. The 2D/3D carbon-based PSCs can even achieve one-year life\textsuperscript{19}. These technologies contribute to the commercialization of PSCs greatly, but the toxic property of PSCs still brings some environmental concern. Some efforts such as replacing lead with non-toxic element that has been put into the research of these problems\textsuperscript{20,21}. However, it seems that the toxic problem has not been addressed substantially. Replacing lead with non-toxic elements completely, such as Ge and Sn does not seem to be a good choice. And the PSCs fabricated with CH$_3$NH$_3$SnI$_3$ or NH=CHNH$_3$SnI$_3$ show poor performance with low efficiency and poor stability\textsuperscript{22}. Lead element is still indispensable element for perovskite
material of high performance PSCs, because the ionic size of lead ions is more suitable to sustain ABX$_3$ structure with a Goldschmidt tolerance factor$^{23}$. 

As we know, unfortunately, lead is unnecessary element to human body. The blood lead concentration is inversely and significantly associated with intelligence quotient (IQ)$^{24}$. Lead can destroy protein and has negative influence on children’ intelligence$^{25}$. In fact, if human are exposed to an environment containing high-concentration lead, their nerve immune, renal and cardiovascular systems would be affected negatively$^{26}$. Waste electrical and electronic equipment (WEEE) has updated its directive in August, 2012, ruling that waste photovoltaic modules should be recycled at their end of life$^{27}$. 

PbI$_2$ is an essential material to fabricate PSCs$^{28}$, which helps to fabricate high performance of PSCs$^{29}$. Carbon-based PSCs are most promising candidate to achieve commercialization, because the stability of carbon-based PSC shows superior stability compared with metal-based PSCs$^{19,30}$. The carbon-based PSCs with a structure of fluorine-doped tin oxide (FTO)/compact TiO$_2$ (c-TiO$_2$)/mesoporous TiO$_2$ (m-TiO$_2$)/CH$_3$NH$_3$PbI$_3$ film/carbon electrode can achieve the efficiency of over 14 % according to previous reports$^{31,32}$. Thus, it is necessary to develop a new method to recycle carbon-based PSCs firstly. It is reported that organic-inorganic perovskite material is easily dissolved in polarity solvent, especially in N, N-Dimethylformamide (DMF)$^{21}$. By this way, lead ions can be lixiviated from degraded carbon-based PSCs by immersing the cells into DMF. 

Lead can also be sequestrated by resin or by removing DMF under vacuum in order to obtain PbI$_2$ in lead leaching solvent$^{33,34}$ However, on the one hand, solvent extraction requires heating and vacuum, which may have potential harm to workers and pollute the environment. On
the other hand, the structure of carbon-based PSCs is different from that of metal-based PSCs in which the former has no hole conductor layer. Thus, it is not necessary to use toxic chlorobenzene to remove the hole conductor layer. The carbon electrode is directly contacted with the perovskite film. It will not be peeled off until the perovskite film dissolving in DMF, which is different from the method of recycling metal-based PSCs with two-step process\textsuperscript{20,24}.

Here, we developed an environmentally friendly method to cyclically utilize lead ions from carbon-based PSCs for the first time. NH\textsubscript{3}·H\textsubscript{2}O was used as a precipitator to precipitate lead ions and HI was used to react with Pb(OH)\textsubscript{2} to obtain PbI\textsubscript{2} which can be re-used as raw materials for fabricating PSCs.

EXPERIMENTAL SECTION

**Materials.** DMF (Sinopharm Chemical Reagent Co. Ltd, 99.5 %), Commercial PbI\textsubscript{2} (Borun New Material Technology Co. Ltd, 99.9985 %), CH\textsubscript{3}NH\textsubscript{3}I (Tokyo Chemical Industry, 98 %), discarded aged carbon-based perovskite solar cells (home-made), NH\textsubscript{3}·H\textsubscript{2}O (Sinopharm Chemical Reagent Co. Ltd, 25 ~ 28 wt%), Dimethyl sulfoxide (DMSO) (Sigma Aldrich, 99.9 %), Carbon paste (home-made), HI (Aladdin 57 wt% in water).

**Lead recycling process.** 120 pieces of aged carbon-based PSCs were washed for three times by using 50.0, 30.0 and 20.0 mL of DMF, each for 5 min, respectively. After that, the mixture solution was centrifuged at 9800 rpm for 20 min in order to get a lixivium containing lead ions and remove carbon electrode at the same time. The carbon electrode needs to be washed for three times with 10.0 mL of DMF and centrifuged for three times and the supernatant needs to be collected as well. Then, the collected supernatant was filtered through a
polytetrafluoroethylene (PTFE) filter (0.22 µm). Finally, 130.0 mL of lixivium containing lead ions was collected.

20.0 mL of the obtained lead lixivium mentioned above was treated with the following method: 2.0 mL of NH₃·H₂O solution was dropped into 20.0 mL of the obtained lixivium and stirred vigorously for 25 min. The lixivium became turbid immediately and white precipitation was formed. Then, the precipitate was separated by centrifugation. 22.0 mL of supernatant (Supernatant I, was obtained by centrifuging the solution that was obtained by dropping 2.0 mL of NH₃·H₂O into 20.0 mL of lead lixivium) was collected for ICP-OES analysis. The white precipitate was washed for four times by using deionized water. Then 20.1 mL of 0.038 M of HI solution was dropped into the obtained white precipitate. Yellow precipitate was formed. After that, the mixture solution was centrifuged at 9800 rpm for 20 min in order to get a supernatant (Supernatant II, was obtained by centrifuging the solution that was obtained by dropping 20.1 mL of HI solution into the white precipitate). And then the yellow precipitate was centrifuged and washed with deionized water. Finally, yellow powder was obtained after drying at 80 °C overnight.

**Fabrication of carbon-based perovskite solar cells.** The perovskite (CH₃NH₃PbI₃) precursor was prepared with the proportion of 0.006 mol of PbI₂ and 0.006 mol of CH₃NH₃I powder dissolving in 0.425 mL of DMSO and 3.890 mL of DMF. Fluorine-doped tin oxide (FTO, 7Ω/□) glasses were purchased from Pilkington company and were cleaned by deionized water, acetone and ethyl alcohol respectively in an ultrasonic bath for 30 min and were treated in ultraviolet ozone system (UV-O₃) for 15 min to remove the organic residues subsequently. About 40 nm-thick c-TiO₂ was
prepared by spin-coating with home-made TiO$_2$ sol. Then the film was annealed at 510 °C for 30 min. After that, the substrates were dipped in 40 mM TiCl$_4$ solution at 70 °C for 30 min. After cooling, the substrates were washed with deionized water and ethanol, and then the substrates were dried and sintered again at 510 °C for 30 min. Then the m-TiO$_2$ was spin-coated on the c-TiO$_2$ layer and annealed at 510 °C for 30 min. CH$_3$NH$_3$PbI$_3$ solution was then spin-coated on the m-TiO$_2$ layer with a speed of 4000 rpm for 30 s and the substrate was annealed at 100 °C for 10 min. After that, about 24 µm-thick of carbon electrode was screen-printed on the perovskite film.

**CHARACTERIZATIONS**

Scanning electron microscopy (SEM) images of the perovskite films were obtained using field emission scanning electron microscope (FEI Magellan 400). X-ray diffraction (XRD) measurements were performed with a Bruker, D8-Advance X-ray diffractometer using Cu Kα radiation under the operation conditions of 40 kV and 40 mA from 10° to 80°, with a scanning speed of 5°/min. UV-vis spectra were recorded on a Shimadzu UV-2550PC spectrometer. The current density-voltage (I-V) curves were measured under AM 1.5G illumination of 100 mW/cm$^2$ with a Yokogawa-7563 source meter in combination with a solar simulator (YSS-150A, Yamashita Denso Corporation, Japan) equipped with a 1000 W xenon lamp. The exact light intensities of the measurements were calibrated with a silicon photo-detector (BS-520). The I-V curves were obtained by applying an external voltage bias with a scan rate of 40 mV/s. Incident photon-to-current conversion efficiency (IPCE) curves were measured with CEP1500 from 300-900 nm using a Xe source (BSO-X300LC). And the signal was recorded as a function of the wavelength using a SM-250 system (Bunkoh-keiki, Japan) and calibrated using a standard Si photodiode (S13370-
1010BQ). Steady photoluminescence (PL) spectroscopy was recorded on a Horiba Jobinyvon (Horiba-Ltd) Nanolog device with an excitation wavelength of 466 nm. The purity of recycled PbI$_2$ and the lead content in lixivium and supernatant were measured by ICP-OES (Agilent Technologies 5100).

RESULTS AND DISCUSSION

The dissolution-precipitation method for cyclic utilization of lead from aged carbon-based PSCs is illustrated in Figure 1. DMF was used to dissolve the perovskite material in aged carbon-based PSCs (CH$_3$NH$_3$PbI$_3$). The structure of the carbon-based PSCs that we recycled is FTO/c-TiO$_2$/m-TiO$_2$/CH$_3$NH$_3$PbI$_3$ film/carbon electrode. As far as the structure is concerned, the independent degraded perovskite (CH$_3$NH$_3$PbI$_3$) film can separate carbon electrode and substrate of FTO/c-TiO$_2$/m-TiO$_2$. Organic-inorganic perovskite can be easily dissolved in polar solvent, especially in DMF$^7$. According to the experimental section, the perovskite films degraded partly or entirely are easily dissolved in DMF. When the aged carbon-based PSCs were immersed into DMF, the degraded perovskite film was dissolved into DMF immediately and the carbon electrode peeled off from the substrate simultaneously. After centrifugation, insoluble material such as carbon electrode was removed. And the insoluble material was washed by DMF subsequently and centrifuged for three times in order to make sure that the perovskite material was dissolved into DMF thoroughly. PTFE filter (0.22 µm) was used to filter supernatant solution to obtain clean lixivium containing lead ions. After filtration, the liquid supernatant containing lead ions was collected.
XRD was used to characterize the discarded cells washed by DMF and substrate with fresh m-TiO$_2$ (Figure 2a). It is obvious to find that the diffraction peaks of TiO$_2$ substrate washed by DMF are in good agreement with the fresh one, which means the majority of perovskite material can be washed by DMF thoroughly. We also characterized the transmittance of the substrates. The transmittance of aged carbon-based PSCs washed by DMF is quite the same as that of the fresh one (FTO/c-TiO$_2$/m-TiO$_2$), which means that little undissolved residual material exists in the m-TiO$_2$ electrode (Figure 2b). The substrate with m-TiO$_2$ can be recycled for fabricating new carbon-based PSCs. When the device gets degraded, it can be washed with DMF in order to remove the degradable part. Then the fresh perovskite film can be prepared on the m-TiO$_2$. The I-V curves of original device, degraded one, and device fabricated with the old substrate are shown in Figure 3, respectively. The corresponding parameters are listed in Table 1. The efficiency of carbon-based PSC only decreases by 1.5 %, which means that the old substrates can function well.

According to our experiment, the carbon-based PSCs degraded following with the efficiency of the cell dropping by a half of its original efficiency. And the perovskite films degraded seriously. We define them as aged carbon-based solar cells. The color of perovskite films would change from dark to yellow, which means that CH$_3$NH$_3$PbI$_3$ would gradually collapse and transfer into PbI$_2$ under the condition of moisture, high temperature or light$^{35,36}$.

Actually, the degradation degree of carbon-based PSCs has no influence on lead recycling. Because both of CH$_3$NH$_3$PbI$_3$ and PbI$_2$ can be dissolved in DMF and precipitated by NH$_3$·H$_2$O. The reported recycling method can be applied to carbon-based
PSCs degradation entirely and cells degrade partly in which CH$_3$NH$_3$PbI$_3$ partly transformed into the PbI$_2$ entirely and partly.

2.0 mL of NH$_3$·H$_2$O (25~28 wt%) was used as the reactant to precipitate lead ions to form Pb(OH)$_2$ precipitate. When NH$_3$·H$_2$O was dropped into 20.0 mL of lixivium containing lead ions and stirred, the lixivium became turbid and white precipitate was formed (Equation 1). Here, an excessive amount of NH$_3$·H$_2$O need to be dipped in the lixivium to make sure a complete reaction. The lead content in the lixivium is 220.0 µg/g according to ICP-OES analysis. By comparison, the lead content in 22.0 mL of supernatant □ is 0.2 µg/g, which means that 99.9 % of lead ions were precipitated by dropping NH$_3$·H$_2$O into the lixivium (Table 2).

The white precipitate needs to be washed with deionized water for three times to remove soluble ions. NaOH and H$_2$S are also considered as precipitators to react with Pb$^{2+}$ ions from the lixivium containing lead. However, Pb(OH)$_2$ can be dissolved in strong base to form [Pb(OH)$_4$]$^{2-}$ ions. They will be dissolved into water and form clean solution when the precipitate was washed with deionized water. Thus, we think that NH$_3$·H$_2$O is better than NaOH for precipitating lead ions. H$_2$S may also be another choice for the quite low $K_{sp}$ of PbS$^{37}$. Considering the toxicity of H$_2$S, it is also not suitable for the precipitation process. In addition, the precipitate of PbS is too stable to form PbI$_2$ by reacting with HI.

In order to form PbI$_2$, appropriate concentration (0.038M) of HI solution was used to react with the white precipitate to form PbI$_2$ (Equation 2). The main reactions are listed as following:

\[
Pb^{2+} + 2 \text{NH}_3\cdot\text{H}_2\text{O} \rightleftharpoons \text{Pb(OH)}_2\downarrow + 2 \text{NH}_4^+ \quad (1)
\]
\[
\text{Pb(OH)}_2 + 2 \text{HI} \rightleftharpoons \text{PbI}_2 + 2 \text{H}_2\text{O} \quad (2)
\]

The colors of reactants change from white to yellow, which implies that Equation 2 would happen. To give a theoretical explanation, the Gibbs free energy of the reaction \((\Delta_r G_m^\theta)\) is calculated with Equation 3. The standard Gibbs free energy of the formation values of chemicals in Equation 2 are listed in Table 3\textsuperscript{37}.

\[
\Delta_r G_m^\theta = [\Delta_f G_m^\theta (\text{PbI}_2) + 2\Delta_f G_m^\theta (\text{H}_2\text{O})] - [\Delta_f G_m^\theta (\text{Pb(OH)}_2) + 2\Delta_f G_m^\theta (\text{HI})] \quad (3)
\]

The calculated \(\Delta_r G_m^\theta = -436.58 \text{ kJ/mol} < 0\), which means that Equation 2 would move in the forward direction.

In order to calculate the lost lead in the process of dropping HI solution into Pb(OH)_2 to form PbI_2, ICP-OES was also used to analyze the collected supernatant. The measured lead content in 20.1 mL of supernatant \(\square\) is 8.9 \(\mu\)g/g. Considering the transformation of PbI_2 to [PbI_4]^{2-} ions due to an excess HI solution used to form PbI_2 precipitate, the calculated concentration of [PbI_4]^{2-} ions is \(1.35 \times 10^{-7}\) M. And considering the lead loss after dropping NH_3·H_2O to form Pb(OH)_2, the calculated lead recovery rate is 95.7 %. The adsorption methods with poly (acrylic acid) organo-montmorillonite nanocomposites, magnetic nanocarbon adsorbents as well as nanocarbon adsorbents, graphene had been used to reduce heavy metal such as lead and hexavalent chromium in waste water\textsuperscript{26,38,39}. Some reports have discussed the methods of recycling aged metal-based PSCs, ion exchange with hydroxyapatite effectively reduced the lead content in residual-lead-containing solution\textsuperscript{20,40}. The methods mentioned above can also be applied to recycle lead in supernatant \(\square\).

The yellow precipitate was characterized by XRD. The result shows that the yellow precipitate is PbI_2 (Figure 4). The recycled PbI_2 and the commercial PbI_2 were both dissolved in DMF to form solutions with the same concentration of 1.25 M. And the
prepared solutions were spin-coated on FTO glasses and then the substrate was heated at 80 °C for 30 min to form PbI₂ film. The XRD peaks of recycled PbI₂ film are in good agreement with those of the commercial one. The intensities of their peaks are quite different, which should be attributed to their different crystallinity. The results confirm that the yellow precipitate is PbI₂. The purity of PbI₂ was analyzed by ICP-OES. According to the calculation, its purity is 99.9 % (Table 4) which is quite lower than that of the commercial PbI₂ (Experiment section).

To avoid environmental pollution and achieve a cyclic utilization of lead, the recycled PbI₂ was used to fabricate a carbon-based PSC. For comparison, commercial PbI₂ was also used to prepare a carbon-based PSC. Figure 5 shows the SEM images of the surfaces of perovskite films on m-TiO₂. Both of the two films show rough and porous surfaces, and no obvious difference can be observed. The UV-vis spectra of two perovskite films deposited on m-TiO₂ is shown in Figure 6a. It can be seen that the absorptance of the perovskite film fabricated with recycled PbI₂ is only slightly lower than that of the perovskite film fabricated with commercial PbI₂. The PL spectrum of the porous perovskite films are shown in Figure 6b. The emission peak can be observed at 760 nm under the condition of excitation wavelength of 466 nm. The quenching intensity of perovskite film fabricated with commercial PbI₂ is stronger, which means that more efficient charge transfer is achieved in this film⁴¹. This result can help to achieve a better performance of carbon-based PSCs. The I-V curves of two carbon-based perovskite solar cells fabricated with recycled PbI₂ and with commercial one is shown in Figure 7a. And the corresponding parameters of the two carbon-based PSCs are listed in Table 5. The device fabricated by recycled PbI₂ shows an open-circuit voltage (V_{oc}) of 0.87 V, a short-
circuit current ($J_{sc}$) of 20.54 mA/cm$^2$, a fill factor (FF) of 63.61 % and a power conversion efficiency (PCE) of 11.36 %. Compared with the parameters ($V_{oc} = 0.92$ V, $J_{sc} = 20.89$ mA/cm$^2$, FF = 63.64 % and PCE = 12.17 %) of the device fabricated by commercial PbI$_2$, the device fabricated by recycled PbI$_2$ shows comparable properties. The corresponding IPCE action curves of the two devices are shown in Figure 7b. The IPCE of the device fabricated with the recycled PbI$_2$ is lower than that of the device fabricated with the commercial one, which results in a lower integrated current (19.36 mA/cm$^2$) of the device fabricated with the recycled PbI$_2$. However, this value achieves to 93.71 % of that (20.66 mA/cm$^2$) of the device fabricated with the commercial PbI$_2$, showing an effective cyclic utilization of lead in carbon-based PSCs.

CONCLUSIONS

In conclusion, we developed a dissolution-precipitation method for the cyclic utilization of lead from carbon-based PSCs. The result shows that 99.9 % of lead ion can be extracted by NH$_3$·H$_2$O solution. The PbI$_2$ was obtained by using an appropriate concentration of HI. The calculated lead recovery rate is 95.7 %. The recycled PbI$_2$ was used to fabricate a carbon-based PSC with an efficiency of 11.36 %, which is comparable to that (12.17 %) of carbon-based PSC fabricated with commercial PbI$_2$. The developed process provides a new approach to the cyclic utilization of lead in carbon-based PSCs to avoid lead pollution in soil and water.

AUTHOR INFORMATION

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NOTES

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

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Tables

Table 1. The I-V parameter of carbon-based PSCs (original one), its degraded one and the carbon-based PSCs fabricated with the substrate of degraded one.

<table>
<thead>
<tr>
<th>Carbon-based PSCs</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
<th>FF (%)</th>
<th>Max. Eff (%)</th>
</tr>
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<tbody>
<tr>
<td>Original one</td>
<td>0.934</td>
<td>20.04</td>
<td>65.25</td>
<td>12.21</td>
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<tr>
<td>Degraded one</td>
<td>0.709</td>
<td>18.17</td>
<td>51.26</td>
<td>6.61</td>
</tr>
<tr>
<td>Old substrate</td>
<td>0.912</td>
<td>20.88</td>
<td>63.19</td>
<td>12.03</td>
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Table 2. The lead contents in lixivium and supernatant analyzed by ICP-OES.

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<tr>
<th>Component</th>
<th>Lead content (µg/g)</th>
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<tr>
<td>Lead contained lixivium</td>
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<tr>
<td>Supernatant I (collected after reaction with NH$_3$·H$_2$O)</td>
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<tr>
<td>Supernatant II (collected after reaction with HI)</td>
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Table 3 The Gibbs free energy of formation values of chemicals in Equation 2.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Pb(OH)$_2$</th>
<th>HI</th>
<th>PbI$_2$</th>
<th>H$_2$O</th>
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<tbody>
<tr>
<td>$\Delta G_m^\theta$ (kJ/mol)</td>
<td>-108.1</td>
<td>-51.59</td>
<td>-173.58</td>
<td>-237.14</td>
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Table 4. The impurity contents of PbI₂ analyzed by ICP-OES.

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<thead>
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<th>Component</th>
<th>Content (µg/g)</th>
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<td>B</td>
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<tr>
<td>Ca</td>
<td>&lt; 40.0</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt; 10.0</td>
</tr>
<tr>
<td>Mg</td>
<td>1.8</td>
</tr>
<tr>
<td>P</td>
<td>&lt; 20.0</td>
</tr>
<tr>
<td>S</td>
<td>840</td>
</tr>
<tr>
<td>Ti</td>
<td>6.8</td>
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Table 5. I-V parameters of carbon-based PSCs fabricated with commercial PbI$_2$ and recycled PbI$_2$.

<table>
<thead>
<tr>
<th>Carbon-based PSCs</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA·cm$^{-2}$)</th>
<th>FF (%)</th>
<th>Max. Eff (%)</th>
<th>Ave±std. Eff (%)</th>
</tr>
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<tbody>
<tr>
<td>Commercial PbI$_2$</td>
<td>0.92</td>
<td>20.89</td>
<td>63.64</td>
<td>12.17</td>
<td>12.02±0.12</td>
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<td>Recycled PbI$_2$</td>
<td>0.87</td>
<td>20.54</td>
<td>63.61</td>
<td>11.36</td>
<td>10.48±1.28</td>
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Figure captions

Figure 1. Illustrated cyclic utilization process of lead from carbon-based PSCs.

Figure 2. (a) XRD patterns of fresh m-TiO$_2$ substrate and degraded carbon-based PSCs washed by DMF, (b) transmittance spectra of FTO glass; FTO/c-TiO$_2$/m-TiO$_2$ substrate and degraded carbon-based PSCs washed by DMF.

Figure 3. I-V curves of original carbon-based PSC, degraded one and the carbon-based PSC fabricated with the substrate of degraded one.

Figure 4. XRD patterns of the recycled PbI$_2$ film and commercial PbI$_2$ film.

Figure 5. SEM images of CH$_3$NH$_3$PbI$_3$ films fabricated with (a) commercial PbI$_2$ and (b) recycled PbI$_2$.

Figure 6. (a) UV-Vis spectra and (b) PL spectra of CH$_3$NH$_3$PbI$_3$ films fabricated with commercial PbI$_2$ and recycled PbI$_2$.

Figure 7. (a) I-V curves of carbon-based PSCs fabricated with recycled PbI$_2$ and commercial PbI$_2$, (b) corresponding IPCE curves and integrated current of carbon-based PSCs.
Figures

Figure 1
Figure 2
Figure 4
Figure 5
Figure 6
Figure 7
Cyclic utilization of lead from carbon-based perovskite solar cells with dissolving-precipitating method achieves environmental protection and resource utilization.