

METHOD FOR RECYCLING, MANUFACTURING, AND REPAIRING
PEROVSKITE LIGHT-ELECTRIC CONVERSION MODULE

Technical field

The present description relates to a method for recycling,
5 manufacturing, and repairing perovskite light-electric conversion module. To
be specific, the present description relates to a method for recycling,
manufacturing, and repairing a perovskite layer of a perovskite photovoltaic
solar cell.

10 Background

Photovoltaics (PV) is a rapidly growing market to offer pollution-free
and low-cost electricity.^{1,2} Nevertheless, the surging growth of PV technology
raises a corresponding challenge: the mounting accumulation of end-of-life
PV modules, since the first massively installed silicon panels around year
15 2000, poses a growing concern for effective waste management.^{3,4} The
cumulative mass of end-of-life PV waste is projected to be about 80 million
tons by year 2050, constituting over 10% of global annual electronic waste.^{5,6}
To counteract this burgeoning issue, recycling these modules to recover
valuable raw materials and facilitate the creation of new modules emerges as
20 an economically viable and ecologically sound solution.^{7,8} Therefore, nations
worldwide are instituting recycling and waste regulations for PVs^{9,10}, such as
the EU's mandatory PV recycling regulation.¹¹

Metal halide perovskite (MHP) photovoltaic is an emerging technology
with advances in high power conversion efficiency (PCE), low-cost materials,
25 and solution processability.¹²⁻¹⁴ These advancements have spurred the
commercialization endeavours of several global entities.¹⁵ Drawing insights
from the evolution of silicon PV, the implementation of recycling technologies
for a circular photovoltaic system becomes a prerequisite prior to the
widespread utility-scale commercial adoption of a PV technology.¹⁶ For
30 perovskite PV, it can additionally help mitigate lead consumption and
effectively manage the toxic lead-containing waste associated with perovskite
devices.^{17,18}

Lead recycling has recently been raised for perovskite modules,
triggered by the concern of toxicity, to extract lead ions from the end-of-life
35 modules through lead absorbents and subsequently recovering to lead iodide

by introducing iodine.¹⁸⁻²² The lead recycling efficacy is optimized high, yet the atomic recycling efficacy is low. For example, the iodine elements, accounting for about 60 wt% of perovskite, are designed to be discarded.¹⁹ Note that, reserved iodine on the upper earth crust is even less abundant than the rare earths.²³ The low atomic efficacy not only compromises economic gains but also leaves residual waste unresolved.²⁴ More importantly, the reliance on hazardous solvents like dimethylformamide (DMF) and methylamine makes these recycling processes, aiming to protect the environment, themselves an environmental concern.²⁵ It also brings compatibility issues with industrial processes²⁶, given that DMF exposure in workplaces must be limited to 10 parts per million and methylamine can be flammable.^{27,28} Therefore, developing eco-friendly recycling strategies with high efficiency for perovskite PV remains challenging.

Hence, there is a need to provide an improved recycling method having not only a high recycling efficiency, but also less harmful to the environment.

Summary

An objective of the present description is to provide a method for recycling a perovskite light-electric conversion module with a high recycling efficiency, which is also less harmful to the environment.

The present description describes an all-green solvent-based holistic recycling strategy for establishing a circular perovskite photovoltaic system. With the strategy, all essential functional materials may be restored, including hole/electron transporting layers (HTL/ETL), the perovskite layer, ITO substrates, cover glasses, etc., with exceptional efficiency and purity.

Specifically, with a water-based recycling solution, an impressive 99.0 ± 0.4 wt% recycling efficiency for the perovskite layer has been achieved. Further, the same recycling solution can repair degraded perovskites affected by cation/halide deficiencies or I₂ formation.

The used recycling solution can still be reusable for recycling perovskite layers, as even when subjected to a rigorous 95 °C thermal stress test for over 3000 hours, it remains stable. This is advantageous in terms of both economy and environment.

Furthermore, a method for effectively recycling Spiro-OMeTAD (2,2',7,7'-Tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene) by

using ethyl acetate (EA) and ethanol (EtOH), yielding an outstanding purity of 99.82% and efficiency of 97.8 ± 0.3 wt% can be achieved.

The present description also extends to recycling SnO₂-coated ITO substrates and electrodes to demonstrate a comprehensive viability for

5 perovskite PV.

The perovskite light-electric conversion module manufactured with the recycled material exhibit comparable efficiency and stability to those manufactured with new raw materials.

According to a first aspect, there is provided a method for recycling a
10 perovskite layer of a perovskite light-electric conversion module. The method comprises:

(a) preparing a recycling solution by:

providing a polar solvent,

dissolving a first salt comprising lead-coordinative anions in the polar
15 solvent for dissolving lead-halide from perovskite of the perovskite layer,

dissolving a halogen element or a second salt comprising halide ions,

and

adding a reducing stabilizer for reducing a concentration of oxidized components of the recycling solution;

20 (b) immersing the module in the recycling solution for dissolving the perovskite from the perovskite layer; and

(c) precipitating perovskite crystals or growing a perovskite single crystal.

A perovskite light-electric conversion module may refer to a module comprising perovskite being able to convert light energy to electric energy.

25 The perovskite light-electric conversion module may be at least a part of a perovskite opto-electronic device, such as a perovskite photovoltaic solar cell.

The perovskite light-electric conversion module may be a waste module, such as a broken module.

The first salt may be an additive which can improve perovskite solubility of
30 the recycling solution.

The second salt may be an additive which can improve phase purity of the recycling solution.

The perovskite of the perovskite layer may be recycled in the form as perovskite crystals, or as a perovskite single crystal of high quality.

35 Step (b) may comprise:

heating the recycling solution and immersing the module in the heated recycling solution, or

immersing the module in the recycling solution and heating the recycling solution.

Step (b) may comprise heating the recycling solution to a temperature within a range from about 25 °C to about 100 °C, more preferably from about 5 45 °C to about 90 °C, most preferably from about 65 °C to about 80 °C.

Step (b) may comprise immersing the module for a period of at least about 5 minutes, more preferably of at least about 20 minutes, most preferably of at least about 60 minutes.

The period of time for immersing the module in the recycling solution may 10 be related to the temperature of the recycling solution. The lower the temperature of the recycling solution, the longer the time for immersing for dissolving the perovskite from the perovskite layer.

For example, when the temperature is about room temperature, e.g., 25 °C, the module may be immersed for about 60 minutes. When the 15 temperature is about 80 °C, the module may be immersed for about 20 minutes.

In one example, the temperature is about 80 °C for a period of at least about 20 minutes.

The term "about" when referring to a value or range in the present 20 application should be understood as a margin of differences above or below the specific value or range. For example, about 25 °C may be understood as 24 °C to 26 °C.

Step (c) may comprise cooling the recycling solution for precipitating perovskite crystals or growing the perovskite single crystal.

25 The method may further comprise (d) separating the perovskite crystals or the perovskite single crystal from the mixture of step (c).

The method may further comprise (e) washing the perovskite crystals or the perovskite single crystal, preferably with any of methanol, ethanol, isopropanol, chlorobenzene, toluene, dichlorobenzene, methyl acetate, ethyl 30 acetate, and combination thereof.

Washing may improve the purity of the perovskite crystals or the perovskite single crystal.

The method may further comprise (f) drying the perovskite crystals or the perovskite single crystal under vacuum or in an inert gas environment.

35 The drying may be preferably for a period of at least about 20 hours, more preferably of at least about 22 hours, most preferably of at least about 24 hours.

The drying may be preferably at a temperature within a range from about 40 °C to about 150 °C, more preferably from about 50 °C to about 90 °C, most preferably from about 55 °C to about 80 °C.

The condition for drying may be selected to improve the drying speed.

- 5 Both vacuum and the inert gas environment may increase the drying speed.

When the drying temperature is lower than 100 °C, preferably lower than 90 °C, it is easier to control the drying process.

In one example, the drying is performed at 60 °C, for about 24 hours, under vacuum, e.g., within a vacuum oven.

- 10 Step (d) may comprise centrifuging the mixture of step (c) to separate the perovskite crystals or the perovskite single crystal.

Step (d) may comprise filtering the mixture of step (c) with a filter to separate the perovskite crystals or the perovskite single crystal.

- 15 The mixture of step (c) may comprise the recycling solution, and the precipitated perovskite crystals or the grown perovskite single crystal. Thus, either centrifuging or filtrating can separate the perovskite crystals.

Prior to centrifuging the mixture of step (c), the method may comprise removing the module from the recycling solution.

- 20 In one example, the centrifuging is performed at a speed of about 1000 rpm (rotations per minute) to about 5000 rpm for about 3 minutes.

The perovskite light-electric conversion module may be at least a part of a perovskite opto-electronic device, such as a perovskite photovoltaic solar cell.

- 25 The polar solvent may be any of water, methanol, ethanol, isopropanol, acetonitrile, acetone, N,N-Dimethylacetamide, formic acid, acetic acid, nitromethane, sulfoane, glycerol, and combination thereof.

- 30 The first salt may comprise any anions of acetate, nitride, chloride, iodide, bromide, carbonate, and cations of sodium, lithium, potassium, calcium, barium, copper, iron, aluminium, magnesium, strontium, zinc, manganese, ammonium, methylammonium, ethylammonium, quaternary ammonium, tetramethylammonium, dimethylammonium, trimethylammonium, and combination thereof.

A concentration of the first salt comprising anions of acetate may be within a range of about 0.1 mmol/L to about 15 mol/L.

- 35 A concentration of the first salt comprising anions of nitride may be within a range of about 0.1 mmol/L to about 10 mol/L.

A concentration of the first salt comprising anions of chloride may be within a range of about 0.1 mmol/L to about 6 mol/L.

A concentration of the first salt comprising anions of iodide may be within a range of about 0.1 mmol/L to about 11 mol/L.

A concentration of the first salt comprising anions of bromide may be within a range of about 0.1 mmol/L to about 9 mol/L.

- 5 A concentration of the first salt comprising anions of carbonate may be within a range of about 0.1 mmol/L to about 1 mol/L.

The halogen element may be any of iodine, bromine, chlorine, and combination thereof.

- 10 The second salt may comprise any anions of iodide, triiodide, bromide, tribromide, chloride, trichloride, and cations of sodium, lithium, potassium, calcium, barium, copper, iron, aluminium, magnesium, strontium, zinc, manganese, ammonium, methylammonium, ethylammonium, quaternary ammonium, tetramethylammonium dimethylammonium, trimethylammonium, and combination thereof.

- 15 A concentration of the second salt comprising anions of iodide or triiodide may be within a range of about 0.1 mmol/L to about 11 mol/L.

A concentration of the second salt comprising anions of bromide or tribromide may be within a range of about 0.1 mmol/L to about 9 mol/L.

- 20 A concentration of the second salt comprising anions of chloride or trichloride may be within a range of about 0.1 mmol/L to about 6 mol/L.

The reducing stabilizer may be any of hypophosphorous acid (H_3PO_2), hydroxylamine, hydrazine, ascorbic acid (vitamin C), sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), sodium bisulfite (NaHSO_3), and combination thereof.

- 25 The reducing stabilizer can improve the stability of the recycling solution in a long term and under a high temperature. The recycling solution can be reused due to its exceptional stability. This is advantageous as the recycling solution is costly to recycle.

- 30 For example, even when subjected to a rigorous 95 °C thermal stress test for over 3000 hours, the recycling solution can remain stable and reusable.

A volume concentration of the hypophosphorous acid (H_3PO_2) may be about 0.1 % v/v to about 30 % v/v.

A concentration of the hydroxylamine may be about 0.1 to about 100 mg/mL.

- 35 A volume concentration of the hydrazine may be about 0.1% v/v to 20 % v/v.

A concentration of the ascorbic acid (vitamin C) may be about 0.1 to about 200 mg/mL.

A concentration of the sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) may be about 0.1 to about 300 mg/mL.

- 5 A concentration of the sodium bisulfite (NaHSO_3) may be about 0.1 to about 300 mg/mL.

The perovskite may be any of formamminium lead iodide, formamminium lead bromide, formamminium lead chloride, methylammonium lead iodide, methylammonium lead bromide, methylammonium lead chloride, cesium lead
10 iodide, cesium lead bromide, cesium lead chloride, and combination thereof.

The perovskite light-electric conversion module may comprise a hole transporting layer comprising spiro-OMeTAD (2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene). The method may comprise recycling the spiro-OMeTAD, comprising:

- 15 (1) immersing the module in a spiro-OMeTAD recycling solution comprising a solvent selectively dissolving the spiro-OMeTAD from the hole transporting layer, the solvent having a polarity lower than a polarity of acetonitrile;
(2) adding a reducing agent in the spiro-OMeTAD recycling solution to
20 reduce oxidized spiro-OMeTAD of the spiro-OMeTAD recycling solution; and
(3) precipitating the spiro-OMeTAD by adding an anti-solvent in the spiro-OMeTAD recycling solution.

According to second aspect, there is provided a method for manufacturing a perovskite light-electric conversion module using the
25 perovskite crystals precipitated according to the first aspect, or the perovskite single crystal grown according to the first aspect.

According to third aspect, there is provided a method for repairing a perovskite layer of a perovskite light-electric conversion module. The method comprises:

- 30 - preparing a recycling solution by:
 providing a polar solvent,
 dissolving a first salt comprising lead-coordinative anions in the polar solvent for dissolving lead-halide from perovskite of the perovskite layer,
35 dissolving a halogen element or a second salt comprising halide ions, and

adding a reducing stabilizer for reducing a concentration of oxidized components of the recycling solution;

- immersing the module in the recycling solution for repairing the perovskite layer.

5 The perovskites of the perovskite layer may be affected by cation/halide deficiencies or I₂ formation. By immersing the module in the recycling solution, the damaged perovskite layer may be repaired.

The second and third aspects may generally present the same or corresponding advantages as the first aspect.

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Brief description of the drawings

The above, as well as additional objects, features, and advantages of the present description, will be better understood through the following illustrative and non-limiting detailed description, with reference to the appended drawings. In the drawings like reference numerals will be used for like elements unless stated otherwise.

15

Fig. 1 is an example perovskite PV-based circular power system.

Fig. 2A illustrate an example recycling solution.

Fig. 2B is a diagram of ¹H-NMR spectrum of sodium acetate (NaOAc) with and without PbI₂.

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Fig. 2C is a diagram of absorption curves of an example recycling solution with various NaI concentrations.

Fig. 3A is a diagram of XRD pattern of FAPbI₃ films manufactured with new and recycled FAPbI₃ perovskite.

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Fig. 3B is a diagram of PL spectra of FAPbI₃ films manufactured with new and recycled FAPbI₃ perovskite.

Fig. 3C is a diagram of J-V curves of perovskite opto-electronic devices manufactured with new and recycled FAPbI₃ perovskite.

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Fig. 3D is a diagram of statistic efficiency chart of perovskite opto-electronic devices manufactured with new and recycled FAPbI₃ perovskite.

Fig. 4A is an example spiro-OMeTAD recycling process.

Fig. 4B is a diagram of ¹H-NMR spectrum of new and recycled spiro-OMeTAD.

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Fig. 4C is a diagram of conductivity of new and recycled spiro-OMeTAD doped with same ionic-modulated doping method.

Fig. 4D is a diagram of J-V curves of perovskite opto-electronic devices manufactured with new and recycled spiro-OMeTAD.

Fig. 5 is a diagram of J-V curves of perovskite opto-electronic devices manufactured with new and recycled gold electrode.

Fig. 6A is a diagram of transmission characteristics of perovskite opto-electronic devices manufactured with new and recycled SnO₂-coated ITO glasses.

Fig. 6B is a diagram of XRD pattern of perovskite opto-electronic devices manufactured with new, recycled SnO₂-coated ITO glasses, and bare ITO.

Fig. 6C is a diagram of J-V curves of perovskite opto-electronic devices manufactured with new and recycled SnO₂-coated ITO glasses.

Fig. 7A is a diagram of J-V curves of perovskite opto-electronic devices manufactured with new and 5th recycled materials.

Fig. 7B is a diagram of statistic efficiency chart of perovskite opto-electronic devices manufactured with new and 5th recycled materials.

Detailed description

Fig. 1 illustrates a perovskite PV-based circular power system. A solar farm may produce and supply clean energy to support society operations.

Once a perovskite light-electric conversion module is broken or reaches the end of its lifespan, it may be repaired or recycled, e.g., layer by layer as shown in Fig. 1. The multiple layers may include: a hole/electron transporting layers (HTL/ETL), a perovskite layer, an ITO substrate, a cover glass layer, etc. The recycled materials may be used to manufacture new modules for building new solar farms.

The module may be subject to a 150°C heat treatment for 3 minutes for facilitating delamination of the multiple layers of the module, e.g., by softening the ethylene vinyl acetate (EVA) encapsulant.

The EVA encapsulant is used as an example because it is a widely commercialized product in silicon photovoltaics and its potential compatibility with perovskite light-electric conversion module, such as PV solar cells.

The delaminated modules may be layer-by-layer recycled to recycle different materials, such as glass, spiro-OMeTAD, perovskite crystal powders, and SnO₂-coated ITO substrates, etc.

These recycled materials may be subsequently used for manufacturing new modules, thereby completing a full circular loop for the modules.

In connection with Figs 2A- 2C, the method for recycling a perovskite layer of a perovskite light-electric conversion module will be discussed in detail.

The example recycling solution of fig. 2A is a water-based solution.

5 The recycling of the lead-containing perovskite layer constitutes a critical aspect of the circular perovskite PV process. In contrast to using hazardous organic solvents, the recycling solution of the present description is an eco-friendly solution based on water.

The method comprises preparing a recycling solution by:

10 providing a polar solvent,
dissolving a first salt comprising lead-coordinative anions in the polar solvent for dissolving lead-halide from perovskite of the perovskite layer,
dissolving a second salt comprising halide ions, and
adding a reducing stabilizer for reducing a concentration of oxidized
15 components of the recycling solution.

The polar solvent may be any of water, methanol, ethanol, isopropanol, acetonitrile, acetone, N,N-Dimethylacetamide, formic acid, acetic acid, nitromethane, sulfoane, glycerol, and combination thereof.

20 Three main additives, the first salt sodium acetate (NaOAc), the second salt sodium iodide (NaI), the reducing stabilizer hypophosphorous acid (H₃PO₂) are added to address perovskite solubility, phase purity and solution stability problems of the recycling solution.

It is known that water exhibits a limited solubility towards lead iodide (about 0.044 g per 100 mL at 20 °C)²⁹, despite its ability to dissolve organic
25 iodide salts like methylammonium iodide and formamidinium iodide. To enhance lead iodide dissolution, we introduced acetate ions (the first salt) which readily complex with lead ions, forming highly soluble lead acetate (about 44.31 g per 100 mL at 20 °C)³⁰.

Fig. 2B is a diagram of ¹H-NMR spectrum of sodium acetate (NaOAc)
30 with and without PbI₂. The chelating effect is evident in Fig. 2B.

A distinct chemical shift in the acetate group indicates a strong interaction with lead ions. To visually demonstrate the efficacy of acetate ions in enhancing dissolution, 100 mg of methylammonium lead iodide (MAPbI₃) was initially added to 4 mL of pure water. After 10 minutes, undissolved yellow
35 powder remained, highlighting the limited solubility of lead iodide in water. Subsequently, with the introduction of a 500 mg/mL sodium acetate into solution, the lead iodide powder readily dissolved within about 10 seconds of

shaking. Thus, it conclusively establishes that acetate ions facilitate lead iodide dissolution in water through effective chelation.

Therefore, the first salt can improve perovskite solubility in the recycling solution.

5 The first salt may comprise any anions of acetate, nitride, chloride, iodide, bromide, carbonate, and cations of sodium, lithium, potassium, calcium, barium, copper, iron, aluminium, magnesium, strontium, zinc, manganese, ammonium, methylammonium, ethylammonium, quaternary ammonium, tetramethylammonium, dimethylammonium, trimethylammonium, and combination thereof.

10 A concentration of the first salt comprising anions of acetate may be within a range of about 0.1 mmol/L to about 15 mol/L.

 A concentration of the first salt comprising anions of nitride may be within a range of about 0.1 mmol/L to about 10 mol/L.

15 A concentration of the first salt comprising anions of chloride may be within a range of about 0.1 mmol/L to about 6 mol/L.

 A concentration of the first salt comprising anions of iodide may be within a range of about 0.1 mmol/L to about 11 mol/L.

20 A concentration of the first salt comprising anions of bromide may be within a range of about 0.1 mmol/L to about 9 mol/L.

 A concentration of the first salt comprising anions of carbonate may be within a range of about 0.1 mmol/L to about 1 mol/L.

 Apart from addressing solubility challenges, the iodine ions (second salt) are added to the recycling solution to regulate lead coordination for facilitating the extraction of phase-pure perovskite from the solution. By gradually substituting solvent and acetate coordinators with iodine ions, the phase of lead species in the solution was systematically tuned. This transitioned from $[PbI]^+$ to $[PbI_2]^0$ and eventually to $[PbI_3]^-$ is for forming the perovskite framework.³¹ While acetate ions partially retained their coordination to enhance solubility, the addition of iodine ions played a central role in phase control.

35 Fig. 2C is a diagram of absorption curves of an example recycling solution with various NaI concentrations. 1 μ mol of formamidinium lead iodide (FAPbI₃) was dissolved in a 500 mg/mL NaOAc aqueous solution, and progressively introduced NaI for iodine ions.

 The enlarged portion of Fig. 2C is solution with 35 mg/mL NaI fitted with $[PbI_2]^0$ and $[PbI_3]^-$ peaks.

The $[\text{PbI}]^+$ peak located at about 290 nm is beyond the measurable range of the instrument used. The transition from $[\text{PbI}_2]^0$ (absorption peak at about 320 nm) to dominant $[\text{PbI}_3]^-$ peak at about 360 nm was observed by increasing the iodine concentration.³¹ A similar phase transition was observed
5 with MAPbI_3 under different NaI concentrations.

For a visual demonstration of lead coordination changes and the resulting precipitates, an excessive amount (400 mg/mL) of MAPbI_3 was introduced into the NaOAc aqueous solution. The yellow powder of PbI_2 could be transformed into the black perovskite phase of MAPbI_3 upon the addition
10 of NaI . These outcomes highlight the precise control of phase purity in precipitates from the recycling solution by adjusting the iodine concentration.

Thus, the second salt can improve the phase purity of the recycling solution.

The halogen element may be any of iodine, bromine, chlorine, and
15 combination thereof.

The second salt may comprise any anions of iodide, triiodide, bromide, tribromide, chloride, trichloride, and cations of sodium, lithium, potassium, calcium, barium, copper, iron, aluminium, magnesium, strontium, zinc, manganese, ammonium, methylammonium, ethylammonium, quaternary
20 ammonium, tetramethylammonium dimethylammonium, trimethylammonium, and combination thereof.

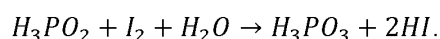
A concentration of the second salt comprising anions of iodide or triiodide may be within a range of about 0.1 mmol/L to about 11 mol/L.

A concentration of the second salt comprising anions of bromide or
25 tribromide may be within a range of about 0.1 mmol/L to about 9 mol/L.

A concentration of the second salt comprising anions of chloride or trichloride may be within a range of about 0.1 mmol/L to about 6 mol/L.

The reducing stabilizer, e.g., H_3PO_2 was introduced as a stabilizer to ensure a long-term and high-temperature stability of the recycling solution.³²
30 In aqueous solutions with high iodide ion concentrations, iodide ions can be rapidly oxidized to iodine (I_2), particularly under elevated temperatures. This oxidation can significantly reduce the iodide concentration, thereby destroy the recycling solution.

Thus, the reducing stabilizer, e.g., H_3PO_2 , is added to the recycling
35 solution to reduce iodine back to iodide ions through the reaction of:



This process effectively enhanced the stability of the recycling solution.

The reducing stabilizer may be any of hypophosphorous acid (H_3PO_2), hydroxylamine, hydrazine, ascorbic acid (vitamin C), sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), sodium bisulfite (NaHSO_3), and combination thereof.

A volume concentration of the hypophosphorous acid (H_3PO_2) may be
5 about 0.1 % v/v to about 30 % v/v. A concentration of the hydroxylamine may be about 0.1 to about 100 mg/mL. A volume concentration of the hydrazine may be about 0.1% v/v to 20 % v/v. A concentration of the ascorbic acid (vitamin C) may be about 0.1 to about 200 mg/mL. A concentration of the sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) may be about 0.1 to about 300 mg/mL. A
10 concentration of the sodium bisulfite (NaHSO_3) may be about 0.1 to about 300 mg/mL.

The recycling solution was separated into a first and a second bottle, H_3PO_2 was added to the first bottle. The recycling solution of both bottles underwent a thermal stress test at 95 °C. It was evident that the recycling of
15 the first bottle displayed no colour change even after enduring over 3000 hours of thermal stress. In contrast, the recycling of the second bottle without H_3PO_2 exhibited a shift to brown color within the first 72 hours, progressing to a dark red hue with extended treatment time, indicating rapid iodine formation.

20 The results validate the substantial improvement in solution stability achieved through the use of the H_3PO_2 additive. This exceptional stability also endows the recycling solution reusability. Importantly, the recycling of perovskite with the same composition in this work was accomplished using the same recycled solution.

25 Hence, by adding these three types of additives, the recycling solution can be improved to feature enhanced perovskite solubility, the capability for tuning phase-pure perovskite, and excellent thermal stability.

The method comprises immersing the module in the recycling solution for dissolving the perovskite from the perovskite layer. The module may be
30 immersed into the heated recycling solution (about 80 °C). The heating can be performed prior to or after the module being immersed to the heated solution. The heating may facilitate the dissolution of perovskites.

The recycling solution may be heat to a temperature within a range from about 25 °C to about 100 °C, more preferably from about 45 °C to about
35 90 °C, most preferably from about 65 °C to about 80 °C.

The module may be immersed for a period of at least about 5 minutes, more preferably of at least about 20 minutes, most preferably of at least about 60 minutes.

The recycling solution may be cooled to precipitate high-purity
5 perovskite crystals, or a perovskite single crystal, for recycling.

The method may comprise separating the perovskite crystals or the perovskite single crystal, e.g., by centrifuging or by filtering with a filter to separate the perovskite crystals or the perovskite single crystal.

The method may comprise washing the perovskite crystals or the
10 perovskite single crystal, preferably with ethanol and/or ethyl acetate.

The method may comprise drying the perovskite crystals or the perovskite single crystal under vacuum or in an inert gas environment.

The drying may be performed preferably for a period of at least about 20 hours, more preferably of at least about 22 hours, most preferably of at
15 least about 24 hours.

The drying may be performed preferably at a temperature within a range from about 40 °C to about 150 °C, more preferably from about 50 °C to about 90 °C, most preferably from about 55 °C to about 80 °C.

The devices based on MAPbI₃ was recycled, following by X-ray
20 diffraction (XRD) analysis of the recycled powder, which revealed peaks corresponding to phase-pure perovskite. The XRD pattern of the films produced with recycled perovskite crystals powders closely matched that of new MAPbI₃.

Perovskite recycling efficiency was assessed over three independent
25 recycling iterations, yielding a remarkable recycling efficiency of 99.0 ± 0.4 wt%. This high efficiency can be attributed to the solution reliable stability.

FAPbI₃ perovskite, which is renowned for its record-high efficiency³³, was recycled according to the method.

Figs 3A- 3B are respectively a diagram of XRD pattern, and of PL
30 (photoluminescence) spectra of FAPbI₃ films made of new and recycled FAPbI₃ perovskite.

As can be seen in Figs 3A- 3B, the FAPbI₃ film manufactured using recycled FAPbI₃ perovskite exhibited almost identical XRD patterns, PL spectra, and morphology as new FAPbI₃ perovskite.

35 Figs 3C- 3D are respectively a diagram of J-V curves and statistic efficiency chart, of perovskite opto-electronic devices manufactured with new and recycled FAPbI₃ perovskite.

It can be seen that the perovskite opto-electronic devices manufactured with recycled FAPbI₃ perovskite achieved an average power conversion efficiency of $21.9 \pm 1.1\%$, with a top value of 23.4%. These results equate to a recovery of over 99% of the efficiency obtained using new perovskite materials ($22.1 \pm 0.9\%$).

The low efficiency loss may be benefit from the high-quality crystal growth during recycling and the defect tolerance nature of perovskite materials.

Additionally, the recycling of the mixed-cation perovskite, FA_{0.5}MA_{0.5}PbI₃ according to the method was also verified.

There was negligible difference in the XRD patterns of perovskite films manufactured with new and recycled perovskite. Thus, the method for recycling a perovskite layer of a perovskite light-electric conversion module using the recycling solution has a wide application for various perovskite compositions.

The method can also be used to repair a perovskite layer of a perovskite light-electric conversion module. The perovskite light-electric conversion module may be a degraded module of two degraded states: FAI deficiency and excess of I₂.

In one example, FAPbI₃ raw materials with a simulated 10% FAI deficiency or an additional 10 wt% I₂ was used for replicating the conditions found in degraded perovskites. The recycled perovskite crystal powders were used to manufacture thin films for testing. In these films, high crystalline peaks similar to those observed in films manufactured by new perovskites can be identified.

Thus, the results suggest that the I₂ can be effectively reduced/repared to I⁻ for crystal growth with the aid of H₃PO₂, while the recycling solution can provide the small amount of FAI needed to address any deficiency.

The ion species and concentration of the recycling solution can be readily monitored and restored during high-volume production in the fabrication process. The crystal growth process during recycling also serves to automatically rectify deficiencies and defects formation.

In connection with Figs 4A- 4D, the method for recycling a hole transporting layer of a perovskite light-electric conversion module will be discussed in detail.

As shown in Fig. 1, the hole transporting layer of the module comprising spiro-OMeTAD (2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene) may also be recycled to recover spiro-OMeTAD of a high purity, which is an efficient hole transporting material.

5 Fig. 4A is an example recycling process of spiro-OMeTAD, where in a reducing agent is iodide salt, a dissolving solvent is ethyl acetate, and an anti-solvent is ethanol.

By immersing the module in a spiro-OMeTAD recycling solution comprising a solvent selectively dissolving the spiro-OMeTAD from the hole
10 transporting layer, the spiro-OMeTAD may be dissolved from the hole transporting layer.

The solvent may have a polarity lower than a polarity of acetonitrile. The solvent may be any of ethyl acetate, methyl acetate, toluene, chlorobenzene, dichlorobenzene, dichloromethane, chloroform, anisole,
15 tetrahydrofuran, 2-methyltetrahydrofuran, and combination thereof.

A reducing agent may be added in the spiro-OMeTAD recycling solution to reduce oxidized spiro-OMeTAD of the spiro-OMeTAD recycling solution. The reducing agent may be any of iodide salts, borane, diborane, Lithium N,N-(dimethylamino)borohydride, Catecholborane, hydrazine, and
20 combination thereof.

By adding an anti-solvent, e.g., ethanol (EtOH), crystallization may be induced such that the spiro-OMeTAD may be precipitated. The anti-solvent may be any of ethanol, methanol, propanol, isopropanol, butanol, and combination thereof.

25 Given the importance of efficient doping of spiro-OMeTAD during use, impurities within the EA solution may include the spiro-OMeTAD radical-cation and salt-based dopant additives. To address this, a reduction process using reductants, such as iodine salts, can convert it to a neutral state.

Iodine salts may be used as reducing agents due to their by-products,
30 which can be readily eliminated through subsequent purification steps. Moreover, NMR signals suggesting the presence of EVA encapsulant in the recycled spiro-OMeTAD were observed, possibly indicating slight EVA dissolution in EA.

Optionally, the spiro-OMeTAD recycling solution may be filtrated with
35 an adsorbent, e.g., silica gel, for eliminating the EVA impurity from the solution. The adsorbent material may be any of any of silica gel, celite,

aluminum oxide, polyamide, magnesium silicate, talc, calcium oxide, activated carbon, and combination thereof.

Optionally, the spiro-OMeTAD recycling solution may be concentrated, by e.g., evaporating the spiro-OMeTAD recycling solution. The evaporating
5 may be performed in an environment having a pressure lower than one standard atmosphere (1 atm).

The method may comprise cooling the spiro-OMeTAD recycling solution for precipitating the spiro-OMeTAD. The cooling may be preferably to a temperature within a range from about 2 °C to about 20 °C, more preferably
10 from about 3 °C to about 15 °C, most preferably from about 4 °C to about 10 °C. The cooling may be last preferably for a period of at least about 10 minutes, more preferably of at least about 15 minutes, most preferably of at least about 20 minutes.

Further purification and drying processes may be applied to achieve
15 high-purity neutral state spiro-OMeTAD.

The method may comprise separating the spiro-OMeTAD after the spiro-OMeTAD has been precipitating, e.g., by centrifuging or filtering a filter to separate the spiro-OMeTAD.

The method may comprise washing the spiro-OMeTAD, preferably with
20 the anti-solvent.

The method may comprise drying the spiro-OMeTAD under vacuum or in an inert gas environment. The drying may be performed preferably for a period of at least about 1 hour, more preferably of at least about 1.5 hours, most preferably of at least about 2 hours. The drying may be performed
25 preferably at a temperature within a range from about 25 °C to about 100 °C, more preferably from about 35 °C to about 80 °C, most preferably from about 45 °C to about 60 °C.

The method may comprise sonicating the spiro-OMeTAD recycling solution for accelerating the reducing action.

30 The sonicating may be performed preferably for a period of at least about 1 minutes, more preferably of at least about 3 minutes, most preferably of at least about 5 minutes.

The sonicating may be performed preferably at a temperature within a range from about 25 °C to about 60 °C, more preferably from about 35 °C to
35 about 55 °C, most preferably from about 45 °C to about 50 °C.

From Fig. 4B, it can be seen that the ^1H -NMR spectrum of new and recycled spiro-OMeTAD show almost identical purity. No significant impurity peaks can be found for recycled spiro-OMeTAD.

The purity of recycled spiro-OMeTAD was measured with High-
5 performance liquid chromatography (HPLC) to be 99.82%, very close to the new spiro-OMeTAD (99.84%).

The radical-cation, i.e. TFSI $^+$, was confirmed to be removed in recycled spiro-OMeTAD with ^{19}F -NMR spectra.

As can be seen in Figs 4C and 4D, the recycled spiro-OMeTAD
10 exhibited nearly identical conductivity after doping and device efficiency compared to new spiro-OMeTAD.

In addition, the method may comprise recycling gold electrode by centrifuging the spiro-OMeTAD recycling solution (EA) after spiro-OMeTAD recycling to collect the solid electrode.

15 The perovskite opto-electronic devices manufactured with new and recycled gold electrode showed negligible differences in Fig. 5. An image of the recycled gold electrode is also shown in Fig. 5.

It should be noted that the primary loss of the electrode likely results from thermal evaporation process. More effective electrode deposition
20 techniques, such as inkjet-printing, can significantly reduce this loss.

In addition, the method may comprise recycling SnO_2 -coated ITO glasses by cleaning and UV-Ozone treatment to remove degraded species after perovskite recycling.

The recycled SnO_2 -coated ITO glasses exhibit similar optical and
25 crystalline properties compared to new ones, as well as similar device performance, as shown in Figs 6A- 6C.

In connection with Figs 7A- 7B, multiple rounds of recycling of a perovskite light-electric conversion module will be discussed in detail.

The degraded perovskite light-electric conversion modules were
30 subjected 5 rounds of recycling processes, the recycled materials (5th recycled materials) were subsequently used for manufacturing new perovskite light-electric conversion modules.

As can be seen in Figs 7A- 7B, the manufactured perovskite light-electric conversion modules made of the 5th recycled materials achieved an
35 average power conversion efficiency (PCE) of $21.8 \pm 0.8\%$, with a top efficiency of 23.5%.

The performance of these modules was proved comparable to that of devices fabricated with new materials, affirming the high reproducibility and stability of the recycling method of the present description.

In this example, the recycling solution for perovskite has been reused
5 more than 30 times, consistently producing high-quality perovskites for multi-round recycling. This multi-round recycling capability significantly reduces the average cost of recycling and the total consumption of lead-containing materials in perovskite photovoltaics.

10 **One example of the method will be discussed below in detail.**

1. Materials:

The materials used were as follows: lead iodide (PbI_2) (>98%, TCI materials), Methylammonium iodide (MAI) (greatcell solar), Formamidinium iodide (FAI) (greatcell solar), sodium acetate (NaOAc) (Sigma-Aldrich),
15 sodium iodide (NaI) (Sigma-Aldrich), Hypophosphorous acid (H_3PO_2) (Sigma-Aldrich), Ethyl acetate (EA) (Sigma-Aldrich), Ethanol (EtOH) (96%, Solveco), Spiro-OMeTAD (99.5%, Xi'an P-oled).

2. Preparation for perovskite recycling:

Three additives (NaOAc, NaI, H_3PO_2) were dissolved/added in DI
20 water. The optimized concentrations are 100-700 mg/mL, 300-900 mg/mL, and 1-10 v/v% for NaOAc, NaI, and H_3PO_2 respectively.

3. Recycling of perovskite:

Each waste perovskite module was soaked in the 20 mL prepared solution at 80 °C for 20 mins. Then, the module after the perovskite layer
25 dissolved was rinsed and removed from the solution with bare SnO_2 on the ITO substrate. The solution was gradually cool down at a rate of about 10 °C per hour to room temperature to grow the perovskite crystals. The solid crystal and liquid solution were then separated by centrifuging at 5000 rpm for 3 minutes. The obtained crystals were then washed with ethanol and ethyl
30 acetate for several times, and dried in a vacuum oven at 60 °C for 24 hours.

4. Recycling of spiro-OMeTAD:

The de-encapsulated 20 modules were individually immersed in 10 mL of ethyl acetate, allowing them to soak for 3 minutes. Afterward, each module was rinsed with 5 mL of ethyl acetate. The resulting brown solutions, totalling
35 110 mL in volume, were combined, and 8 mg of tetrabutylammonium iodide was introduced into the solution. The solution was sonicated at 50 °C for 5 minutes, during which time it gradually transitioned from brown to light yellow.

Following sonication, the solution was passed through a 0.5 cm thick silica gel pad for filtration. Subsequently, the filtrate rotary evaporated under reduced pressure until it reached a final volume of 1 mL. To this concentrated solution, 10 mL of 95% ethanol was added, resulting in a significant amount of white solid precipitating from the solution. This suspension was stored in a refrigerator at 4 °C for 20 minutes, then centrifuged at 4000 rpm for 3 minutes. The supernatant was carefully decanted, and the white solid at the bottom was washed once with ethanol. Next, the white solid was dried in a vacuum oven set to 50 °C for 2 hours.

10 In summary, a recycling method for recycling a perovskite light-electric conversion module utilising environmentally friendly solvents to restore and recover almost all valuable components from waste modules. The recycling efficiencies reach 99.0 ± 0.4 wt% for perovskite, and 97.8 ± 0.3 wt% for spiro-OMeTAD. Notably, the recycling solution demonstrates stability and reusability even after enduring thermal stress at 95 °C for 3000 hours. Modules manufactured with recycled materials/components successfully recover more than 99% of their initial efficiency compared to those manufactured with new materials. Furthermore, the multi-round recycling process enables these modules to achieve efficiencies similar to those manufactured with new materials.

20 In the above the inventive concept has mainly been described with reference to a limited number of examples. However, as is readily appreciated by a person skilled in the art, other examples than the ones disclosed above are equally possible within the scope of the inventive concept, as defined by the appended claims.

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CLAIMS

1. A method for recycling a perovskite layer of a perovskite light-electric conversion module, the method comprising:
 - (a) preparing a recycling solution by:
 - 5 providing a polar solvent,
dissolving a first salt comprising lead-coordinative anions in the polar solvent for dissolving lead-halide from perovskite of the perovskite layer,
dissolving a halogen element or a second salt comprising halide ions,
and
 - 10 adding a reducing stabilizer for reducing a concentration of oxidized components of the recycling solution;
 - (b) immersing the module in the recycling solution for dissolving the perovskite from the perovskite layer; and
 - (c) precipitating perovskite crystals or growing a perovskite single crystal.
- 15 2. The method according to claim 1, wherein step (b) comprises:
 - heating the recycling solution and immersing the module in the heated recycling solution, or
 - immersing the module in the recycling solution and heating the
 - 20 recycling solution.
3. The method according to claim 2, wherein step (b) comprises:
 - heating the recycling solution to a temperature within a range from about 25 °C to about 100 °C, more preferably from about 45 °C to about 90
 - 25 °C, most preferably from about 65 °C to about 80 °C; and/or
 - immersing the module for a period of at least about 5 minutes, more preferably of at least about 20 minutes, most preferably of at least about 60 minutes.
- 30 4. The method according to any of claims 1- 3, wherein step (c) comprises:
 - cooling the recycling solution for precipitating perovskite crystals or growing the perovskite single crystal.
- 35 5. The method according to any of claims 1- 4, wherein the method further comprises:

(d) separating the perovskite crystals or the perovskite single crystal from the mixture of step (c);

(e) washing the perovskite crystals or the perovskite single crystal, preferably with any of methanol, ethanol, isopropanol, chlorobenzene, toluene,

5 dichlorobenzene, methyl acetate, ethyl acetate, and combination thereof; and

(f) drying the perovskite crystals or the perovskite single crystal under vacuum or in an inert gas environment,

preferably for a period of at least about 20 hours, more preferably of at least about 22 hours, most preferably of at least about 24 hours, and/or

10 preferably at a temperature within a range from about 40 °C to about 150 °C, more preferably from about 50 °C to about 90 °C, most preferably from about 55 °C to about 80 °C.

6. The method according to claim 5, wherein step (d) comprises:

15 centrifuging the mixture of step (c) to separate the perovskite crystals or the perovskite single crystal; or

filtering the mixture of step (c) with a filter to separate the perovskite crystals or the perovskite single crystal.

20 7. The method according to any of claims 1- 6, wherein the perovskite light-electric conversion module is at least a part of a perovskite opto-electronic device, such as a perovskite photovoltaic solar cell.

8. The method according to any of claims 1- 7, wherein the polar solvent
25 is any of water, methanol, ethanol, isopropanol, acetonitrile, acetone, N,N-Dimethylacetamide, formic acid, acetic acid, nitromethane, sulfoane, glycerol, and combination thereof.

9. The method according to any of claims 1- 8, wherein the first salt
30 comprises any anions of acetate, nitride, chloride, iodide, bromide, carbonate, and cations of sodium, lithium, potassium, calcium, barium, copper, iron, aluminium, magnesium, strontium, zinc, manganese, ammonium, methylammonium, ethylammonium, quaternary ammonium, tetramethylammonium, dimethylammonium, trimethylammonium, and
35 combination thereof.

10. The method according to claim 9,

wherein a concentration of the first salt comprising anions of acetate is within a range of about 0.1 mmol/L to about 15 mol/L;

wherein a concentration of the first salt comprising anions of nitride is within a range of about 0.1 mmol/L to about 10 mol/L;

5 wherein a concentration of the first salt comprising anions of chloride is within a range of about 0.1 mmol/L to about 6 mol/L;

wherein a concentration of the first salt comprising anions of iodide is within a range of about 0.1 mmol/L to about 11 mol/L;

10 wherein a concentration of the first salt comprising anions of bromide is within a range of about 0.1 mmol/L to about 9 mol/L;

wherein a concentration of the first salt comprising anions of carbonate is within a range of about 0.1 mmol/L to about 1 mol/L.

11. The method according to any of claims 1- 10, wherein the halogen
15 element is any of iodine, bromine, chlorine, and combination thereof.

12. The method according to any of claims 1- 11, wherein the second salt comprises any anions of iodide, triiodide, bromide, tribromide, chloride, trichloride, and cations of sodium, lithium, potassium, calcium, barium,
20 copper, iron, aluminium, magnesium, strontium, zinc, manganese, ammonium, methylammonium, ethylammonium, quaternary ammonium, tetramethylammonium dimethylammonium, trimethylammonium, and combination thereof.

25 13. The method according to claim 12,
wherein a concentration of the second salt comprising anions of iodide or triiodide is within a range of about 0.1 mmol/L to about 11 mol/L;
wherein a concentration of the second salt comprising anions of bromide or tribromide is within a range of about 0.1 mmol/L to about 9 mol/L;
30 wherein a concentration of the second salt comprising anions of chloride or trichloride is within a range of about 0.1 mmol/L to about 6 mol/L.

14. The method according to any of claims 1- 13, wherein the reducing stabilizer is any of hypophosphorous acid (H_3PO_2), hydroxylamine, hydrazine,
35 ascorbic acid (vitamin C), sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), sodium bisulfite (NaHSO_3), and combination thereof.

15. The method according to claim 14,
wherein a volume concentration of the hypophosphorous acid (H_3PO_2) is about 0.1 % v/v to about 30 % v/v;
wherein a concentration of the hydroxylamine is about 0.1 to about 100
5 mg/mL;
wherein a volume concentration of the hydrazine is about 0.1% v/v to 20 % v/v;
wherein a concentration of the ascorbic acid (vitamin C) is about 0.1 to about 200 mg/mL;
10 wherein a concentration of the sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) is about 0.1 to about 300 mg/mL;
wherein a concentration of the sodium bisulfite (NaHSO_3) is about 0.1 to about 300 mg/mL.
- 15 16. The method according to any of claims 1- 14, wherein the perovskite is any of formamdinium lead iodide, formamdinium lead bromide, formamdinium lead chloride, methylammonium lead iodide, methylammonium lead bromide, methylammonium lead chloride, cesium lead iodide, cesium lead bromide, cesium lead chloride, and combination thereof.
- 20 17. The method according to any of claims 1- 16, wherein the perovskite light-electric conversion module comprises a hole transporting layer comprising spiro-OMeTAD (2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene);
25 wherein the method comprises recycling the spiro-OMeTAD, comprising:
(1) immersing the module in a spiro-OMeTAD recycling solution comprising a solvent selectively dissolving the spiro-OMeTAD from the hole transporting layer, the solvent having a polarity lower than a polarity of
30 acetonitrile;
(2) adding a reducing agent in the spiro-OMeTAD recycling solution to reduce oxidized spiro-OMeTAD of the spiro-OMeTAD recycling solution; and
(3) precipitating the spiro-OMeTAD by adding an anti-solvent in the spiro-OMeTAD recycling solution.
- 35 18. A method for manufacturing a perovskite light-electric conversion module using the perovskite crystals precipitated according to any of the

claims 1- 17 or the perovskite single crystal grown according to any of the claims 1- 17.

19. A method for repairing a perovskite layer of a perovskite light-electric
5 conversion module, the method comprising:
- preparing a recycling solution by:
 - providing a polar solvent,
 - dissolving a first salt comprising lead-coordinative anions in the
polar solvent for dissolving lead-halide from perovskite of the
10 perovskite layer,
 - dissolving a halogen element or a second salt comprising halide
ions, and
 - adding a reducing stabilizer for reducing a concentration of
oxidized components of the recycling solution;
 - 15 - immersing the module in the recycling solution for repairing the
perovskite layer.