

Interface Materials For Perovskites

Technical Field

This invention relates to a device comprising a perovskite compound layer and a capping material layer. The invention also relates to a method preparing the device and the use for the device.

5 Background Art

The certified power conversion efficiency (PCE) of perovskite solar cells (PSCs) have exceeded 25%, which is comparable with commercialized silicon solar cells. However, the operational stability of PSCs still lags behind traditional silicon solar cells, which severely constrains their commercialization potential.

- 10 Bi-layered three-dimensional (3D)/low-dimensional (LD) perovskite solar cell (PSC) architecture recently emerged as an extremely promising approach to resolve the compromise between photovoltaic performance and operational stability.

The superincumbent LD capping layer plays a crucial role in not only surface passivation, but also heterojunction construction and environmental stress resistance. The most common LD capping materials are a type of halogenometallates, such as the popular two-dimensional (2D) Ruddlesden-Popper (RP) perovskites with the general formula of A_2MX_4 , where A is a bulky ammonium cation, M is a metal cation, and X is a halide anion. The LD material is capped on top of a 3D perovskite layer to not only passivate the 3D perovskite defects, but also to protect the 3D perovskite from environmental stressors such as moisture, oxygen, light and heat.

- 20 The widely adopted manufacturing process for the LD capping layer is to deposit a bulky ammonium halide such as phenethylammonium iodide (PEAI) on top of a 3D perovskite followed by a cation exchange reaction, which is known as the half precursor (HP) methodology. The metal cation of the LD capping materials is restricted to Pb^{2+}/Sn^{2+} and is almost irreplaceable with the current methodology since they are derived from the underlying 3D perovskite. Hence, the most popular strategy in new LD capping materials design is to engineer bulky molecular cations at the A site. Although an interesting solid-state in-plane growth method was recently demonstrated to have good controllability specifically for 2D BA_2PbI_4 (BA = butylammonium) on top of 3D perovskites, the intrinsically weak solid-state interaction/reaction and high pressure (60 MPa) requirements may limit its applicability to LD materials with metal cations distinct from the underlying 3D perovskite layer. To date, tailoring the metal cation of LD capping materials remains an open question and the restriction to Pb^{2+}/Sn^{2+} continues to pose environmental concerns.

Accordingly, there is a need to provide a device that overcomes, or at least ameliorates, one or more of the disadvantages described above.

Summary

In an aspect, there is provided a device comprising:

- a) a three-dimensional perovskite compound layer, comprising a three-dimensional perovskite compound having a formula $(A^1)B(X^1)_3$, wherein:

5 A^1 is selected from the group consisting of at least one ion of one or more group 1 elements of the Periodic Table of Elements, an organic cation having a structure of $R^1-(NH_x)_y^+$ wherein R^1 is CH or alkyl, x is 2 or 3 and y is 1 or 2, as valency allows, and any mixture thereof;

10 B is at least one ion of one or more group 14 elements of the Periodic Table of Elements or any mixture thereof; and

X^1 is a halide ion or any mixture thereof;

- b) a capping material layer comprising a capping material, provided on the three-dimensional perovskite compound layer, wherein the capping material is selected from a compound having a general formula $(A^2)_2M(X^2)_4$, $(A^2)_2(A^1)M_2(X^2)_7$, $(A^2)_mM_n(X^2)_{3n+m}$ or any mixture thereof, wherein:

A^2 is an ammonium cation having a structure of $R^2-NH_4^+$, wherein R^2 is an optionally substituted C_4 to C_{12} alkyl, an optionally substituted C_3 to C_{12} cycloalkyl, an optionally substituted arylalkyl, or any mixture thereof;

20 M is at least one ion of one or more group 2, group 3, group 7, group 8, group 9, group 10, group 11, group 12, group 13 or group 15 elements of the Periodic Table of Elements, or any mixture thereof;

X^2 is a halide ion or any mixture thereof;

m is an integer of 1, 2, 3, 4 or 5;

n is an integer of 1 or 2; and

25 a is 0 or an integer of 1, 2 or 3.

Advantageously, in the device as defined above, the metal present in the capping material may be the same or different from the metal present in the three-dimensional perovskite compound.

30 Advantageously, the device may comprise a capping material which may not only passivate defects in the three-dimensional perovskite compound, but also to protect the three-dimensional perovskite compound from environmental stressors such as moisture, oxygen, light and heat. More advantageously, the capping material layer of the device as defined above may induce more robust surface passivation for the three-dimensional perovskite compound and may form a stronger 3D/LD n-N isotype

heterojunction, which in turn may result in more significant suppression of charge recombination and enhancement of built-in potential.

The device as defined above may have an inverted structure (or a p-i-n type architecture) and may have a power conversion efficiency (PCE) of up to 24.1%, with a corresponding certified PCE of up to 23.25%. The device may advantageously also have an enhanced stability with 94.5% of the initial PCE retained after more than 1000 hours of operation at maximum power point (MPP) under and equivalent effective irradiance of 1 sun.

In another aspect, there is provided a method of preparing the device as defined above, comprising the steps of:

- 10 i) providing a three-dimensional perovskite compound layer, comprising a three-dimensional perovskite compound having a formula $(A^1)B(X^1)_3$ wherein:

A^1 is selected from the group consisting of at least one ion of one or more group 1 elements of the Periodic Table of Elements, an organic cation having a structure of $R^1-(NH_x)_y^+$ wherein R^1 is CH or alkyl, x is 2 or 3 and y is 1 or 2, as valency allows, and any mixture thereof;

B is at least one ion of one or more group 14 elements of the Periodic Table of Elements or any mixture thereof; and

X^1 is a halide ion or any mixture thereof;
- 20 ii) mixing a metal halide having a formula $M(X^2)_z$ with an ammonium halide having a formula $(A^2)(X^2)$ in a solvent to form a capping material solution, wherein

A^2 is an ammonium cation having a structure of $R^2-NH_a^+$, wherein R^2 is an optionally substituted C_4 to C_{12} alkyl, an optionally substituted C_3 to C_{12} cycloalkyl, an optionally substituted arylalkyl, or any mixture thereof;

M is at least one ion of one or more group 2, group 3, group 7, group 8, group 9, group 10, group 11, group 12, group 13 or group 15 elements of the Periodic Table of Elements, or any mixture thereof;

X^2 is a halide ion or any mixture thereof;

a is 0 or an integer of 1, 2 or 3; and

z is 2 or 3; and
- 30 iii) applying the capping material solution onto the three-dimensional perovskite compound layer to form a capping material layer comprising a capping material selected from a compound having a general formula $(A^2)_2M(X^2)_4$, $(A^2)_2(A^1)M_2(X^2)_7$, $(A^2)_mM_n(X^2)_{3n+m}$ or any mixture thereof;

wherein m is an integer of 1, 2, 3, 4 or 5; and

n is an integer of 1 or 2.

Advantageously, the method as defined herein requires the capping material solution comprising both a metal halide and an ammonium halide to be applied onto the three-dimensional perovskite compound.

- 5 Advantageously, this enables easier synthetic control of the capping material layer compared to the conventional half precursor (HP) methodology of preparing the device, whereby only the ammonium halide is applied onto the three-dimensional perovskite compound. By having the metal halide present in the capping material solution, the formation of the capping material does not rely on the upward diffusion of the metal from the underlying three-dimensional perovskite layer. Accordingly, the method
10 as defined herein allows unprecedented access to a vast variety of capping materials to be prepared on the three-dimensional perovskite compound, including capping materials that may be Pb-free.

Advantageously, since the method may allow the use of a variety of metals in the capping material, and may even be Pb-free, the method may allow fabrication of an enhanced range of efficient and stable 3D/LD PSCs that were previously not possible by the conventional HP method.

- 15 In another aspect, there is provide the use of the device as defined above in an optoelectronic device, photovoltaic cell, solar cell, light-emitting diode (LED), laser or photodetector, radiation detector, memristor, spintronic device, phototransistor, transistor, light emitting transistor (LET) or field-effect transistor (FET).

Definitions

- 20 The following words and terms used herein shall have the meaning indicated:

"Alkyl" as a group or part of a group refers to a straight or branched aliphatic hydrocarbon group, preferably a C₁-C₁₂ alkyl, more preferably a C₁-C₁₀ alkyl, most preferably C₁-C₆ unless otherwise noted. Examples of suitable straight and branched C₁-C₆ alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, t-butyl, hexyl, and the like. The group may be a terminal group or a bridging
25 group.

- "Cycloalkyl" refers to a saturated monocyclic or fused or spiro polycyclic, carbocycle preferably containing from 3 to 12 carbons per ring, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and the like, unless otherwise specified. It includes monocyclic systems such as cyclopropyl and cyclohexyl, bicyclic systems such as decalin, and polycyclic systems such as adamantane. A cycloalkyl group
30 typically is a C₃-C₁₂ alkyl group. The group may be a terminal group or a bridging group.

- "Arylalkyl" means an aryl-alkyl- group in which the aryl and alkyl moieties are as defined herein. Preferred arylalkyl groups contain a C₁₋₁₂ alkyl moiety. Exemplary arylalkyl groups include benzyl, phenethyl, 1-naphthalenemethyl and 2-naphthalenemethyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through
35 the alkyl group.

The term "optionally substituted" as used herein means the group to which this term refers may be unsubstituted, or may be substituted with one or more groups independently selected from acyl, alkyl, alkenyl, alkynyl, thiol, thioalkyl, cycloalkyl, cycloalkylalkyl, cycloalkenyl, cycloalkylalkenyl, heterocycloalkyl, cycloalkylheteroalkyl, cycloalkyloxy, cycloalkenyloxy, cycloamino, halo, carboxyl, carboxylate, haloalkyl, haloalkynyl, alkynyloxy, heteroalkyl, heteroalkenyl, heteroalkynyl, heteroalkyloxy, hydroxyl, hydroxyalkyl, alkoxy, thioalkoxy, alkenyloxy, haloalkoxy, haloalkenyl, haloalkynyl, haloalkenyloxy, nitro, amino, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroheterocyclyl, alkylamino, dialkylamino, alkenylamine, aminoalkyl, alkynylamino, acyl, alkyloxy, alkyloxyalkyl, alkyloxyaryl, alkyloxycarbonyl, alkyloxyheteroaryl, alkyloxyheterocycloalkyl, alkenoyl, alkynoyl, acylamino, diacylamino, acyloxy, alkylsulfonyloxy, heterocyclic, heterocycloalkenyl, heterocycloalkyl, heterocycloalkylalkyl, heterocycloalkylalkenyl, heterocycloalkylalkenyl, heterocycloalkylheteroalkyl, heterocycloalkyloxy, heterocycloalkenyloxy, heterocycloxy, heterocycloamino, haloheterocycloalkyl, alkylsulfinyl, alkylsulfonyl, alkylsulfenyl, alkylcarbonyloxy, alkylthio, acylthio, aminosulfonyl, phosphorus-containing groups such as phosphono and phosphinyl, sulfinyl, sulfinylamino, sulfonyl, sulfonylamino, aryl, arylalkyl, arylalkyloxy, arylamino, Arylheteroalkyl, heteroaryl, heteroarylalkyl, heteroarylalkenyl, heteroarylalkynyl, heteroarylheteroalkyl, heteroarylamino, heteroaryloxy, arylalkenyl, arylalkyl, alkylaryl, alkylheteroaryl, aryloxy, arylsulfonyl, cyano, cyanate, isocyanate, -C(O)NH(alkyl), and -C(O)N(alkyl)₂.

A "bond" is a linkage between atoms in a compound or molecule. The bond may be a single bond, a double bond, or a triple bond.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Detailed Description of Optional Embodiments

There is provided a device comprising:

- a) a three-dimensional perovskite compound layer, comprising a three-dimensional perovskite compound having a formula $(A^1)B(X^1)_3$ wherein:
 - A^1 may be selected from the group consisting of at least one ion of one or more group 1 elements of the Periodic Table of Elements, an organic cation having a structure of $R^1-(NH_x)_y^+$ wherein R^1 may be CH or alkyl, x may be 2 or 3 and y may be 1 or 2, as valency allows, and any mixture thereof;
 - B may be at least one ion of one or more group 14 elements of the Periodic Table of Elements or any mixture thereof; and
 - X^1 may be a halide ion or any mixture thereof;
 - b) a capping material layer comprising a capping material, provided on the three-dimensional perovskite compound layer, wherein the capping material may be selected from a compound having a general formula $(A^2)_2M(X^2)_4$, $(A^2)_2(A^1)M_2(X^2)_7$, $(A^2)_mM_n(X^2)_{3n+m}$ or any mixture thereof, wherein:
 - A^2 may be an ammonium cation having a structure of $R^2-NH_a^+$, wherein R^2 may be an optionally substituted C_4 to C_{12} alkyl, an optionally substituted C_3 to C_{12} cycloalkyl, an optionally substituted arylalkyl, or any mixture thereof;
 - M may be at least one ion of one or more group 2, group 3, group 7, group 8, group 9, group 10, group 11, group 12, group 13 or group 15 elements of the Periodic Table of Elements, or any mixture thereof;
 - X^2 may be a halide ion or any mixture thereof;
 - m may be an integer of 1, 2, 3, 4 or 5;
 - n may be an integer of 1 or 2; and
 - a may be 0 or an integer of 1, 2 or 3.
- A^1 may be selected from the group consisting of $CH_3NH_3^+$, $CH(NH_2)_2^+$, Cs^+ , Rb^+ and any mixture thereof.
- B may be selected from the group consisting of Pb^{2+} , Sn^{2+} , Ge^{2+} and any mixture thereof.

X¹ may be selected from the group consisting of I⁻, Br⁻, Cl⁻, F⁻ and any mixture thereof.

The three-dimensional perovskite compound may have the structure Cs_{0.15}FA_{0.85}PbI_{2.8}Cl_{0.2}, Rb_{0.05}Cs_{0.10}FA_{0.85}PbI_{2.8}Cl_{0.2}, or Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})₃, wherein MA may be CH₃NH₃⁺ and FA may be CH(NH₂)₂⁺.

- 5 The optionally substituted C₄ to C₁₂ alkyl, the optionally substituted C₃ to C₁₂ cycloalkyl, or the optionally substituted arylalkyl, may each independently be substituted or unsubstituted.

If substituted, the C₄ to C₁₂ alkyl, C₃ to C₁₂ cycloalkyl, or the arylalkyl, may each independently be substituted with a substituent selected from the group consisting of -OH, -SH, -COOH and any mixture thereof.

- 10 A² may be selected from the group consisting of phenethylammonium (PEA) ion, n-butylammonium (BA) ion, iso-butylammonium ion, phenylmethylammonium (PMA) ion, 1-naphthylmethylammonium (NMA) ion, and any mixture thereof.

M may be selected from the group consisting of Zn²⁺, Pb²⁺, Co²⁺, Mn²⁺, Cu²⁺, Sb³⁺, Bi³⁺, Al³⁺ and any mixture thereof.

- 15 X² may be selected from the group consisting of Cl⁻, Br⁻, I⁻, F⁻ and any mixture thereof.

The capping material layer may have a β -K₂SO₄ type, β -K₂PO₃F type, cubic, orthorhombic or tetragonal single crystal structure.

- 20 The capping material layer may have a perovskite-type single crystal structure. The cubic structure may have a space group Pm3m, no. 221. The orthorhombic structure may have a space group Pnma, no. 62 or Amm2, no. 68. The tetragonal structure may have a space group I4/mcm, no. 140, or P4mm, no. 99).

The capping material layer may be substantially free of Pb²⁺ or Sn²⁺.

The capping material layer may be zero-dimensional, one-dimensional, two-dimensional or three-dimensional.

- 25 The three-dimensional perovskite compound layer and the capping material layer may be each independently annealed. Advantageously, annealing may improve the workability of the respective layers, by increasing crystallinity, toughness, and machinability.

The metal present in the capping material (M) may be different from the metal present in the three-dimensional perovskite compound (B).

- 30 For the purposes of this disclosure, the three-dimensional perovskite compound layer may be referred to as the “three-dimensional layer” or the “3D layer” and the capping material layer may be referred to as the “low-dimensional layer” or the “LD layer”.

The device may further comprise a hole transport layer comprising a hole transport material, wherein the three-dimensional perovskite compound layer may be provided on the hole transport layer.

The hole transport material may be selected from the group consisting of poly(triarylamine) (PTAA), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), (2-(9H-carbazol-9-yl)ethyl)phosphonic acid (2PACZ), [2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACZ), [4-(3,6-dimethyl-9H-carbazol-9-yl)butyl]phosphonic acid (Me-4PACZ), (2-(3,6-dimethyl-9H-carbazol-9-yl)ethyl)phosphonic acid (Me-2PACZ), NiO, CuSCN, CuO and any mixture thereof.

The device may further comprise an electrode, wherein the hole transport layer may be provided on the electrode.

The electrode may be selected from the group consisting of indium tin oxide (ITO), fluorine-doped tin oxide (FTO) and any mixture thereof.

The device may further comprise an electron transport layer comprising an electron transport material, provided on the capping material layer.

The electron transport material may be selected from the group consisting of C₆₀/bathocuproine ([6,6]-phenyl-C61-butyric acid methyl ester, BCP), methyl 4-[3'-phenyl-3'H-cyclopropa[1,9](C₆₀-I_h)[5,6]fulleren-3'-yl]butanoate (PC61BM), (6,6)-phenyl C71 butyric acid methyl ester (PC71BM), 1',1'',4',4''-tetrahydro-di[1,4]methanonaphthaleno[5,6]fullerene-C60 (ICBA), tin(IV) oxide, zinc oxide, and any mixture thereof.

The device may further comprise a counter electrode, provided on the electron transport layer.

The counter electrode may comprise an element selected from the group consisting of gold, silver, platinum, aluminium, copper, carbon and any mixture thereof.

The electron transport layer, the capping material layer, the three-dimensional perovskite compound layer and the hole transport layer may be independently in a form of a film.

The device may comprise the respective layers as defined above, in the following order:

- 25 - counter electrode
- electron transport layer
- capping material layer
- three-dimensional perovskite layer
- hole transport layer
- 30 - electrode

The device may have an inverted structure or a p-i-n type architecture.

The counter electrode may have a thickness in the range of about 100 nm to about 200 nm, about 100 nm to about 120 nm, about 100 nm to about 140 nm, about 100 nm to about 160 nm, about 100 nm to about 180 nm, about 120 nm to about 140 nm, about 120 nm to about 160 nm, about 120 nm to about

180 nm, about 120 nm to about 200 nm, about 140 nm to about 160 nm, about 140 nm to about 180 nm, about 140 nm to about 200 nm, about 160 nm to about 180 nm, about 160 nm to about 200 nm, or about 180 nm to about 200 nm.

5 The electron transport layer may have a thickness in the range of about 45 nm to about 75 nm, about 45 nm to about 60 nm or about 60 nm, to about 75 nm.

The capping material layer may have a thickness in the range of about 15 nm to 25 nm, about 15 nm to about 20 nm or about 20 nm to about 25 nm.

10 The three-dimensional perovskite compound layer may have a thickness in the range of about 400 nm to about 700 nm, about 400 nm to about 500 nm, about 400 nm to about 600 nm, about 500 nm to about 600 nm, about 500 nm to about 700 nm, or about 600 nm to about 700 nm.

The hole transport layer may have a thickness in the range of about 20 nm to about 80 nm, about 20 nm to about 40 nm, about 20 nm to about 60 nm, about 40 nm to about 60 nm, about 40 nm to about 80 nm, or about 60 nm to about 80 nm.

15 The electrode may have a thickness in the range of about 150 nm to about 300 nm, about 150 nm to about 200 nm, about 150 nm to about 250 nm, about 200 nm to about 250 nm, about 250 nm to about 300 nm or about 250 nm to about 300 nm.

The device may be an optoelectronic device, photovoltaic cell, solar cell, light-emitting diode (LED), laser or photodetector, radiation detector, memristor, spintronic device, phototransistor, transistor, light emitting transistor (LET) or field-effect transistor (FET).

20 There is also provided a method of preparing the device as defined above, comprising the steps of:

- 25 i) providing a three-dimensional perovskite compound layer, comprising a three-dimensional perovskite compound having a formula $(A^1)B(X^1)_3$ wherein:
A¹ may be selected from the group consisting of at least one ion of one or more group 1 elements of the Periodic Table of Elements, an organic cation having a structure of R¹-(NH_x)_y⁺ wherein R¹ may be CH or alkyl, x may be 2 or 3 and y may be 1 or 2, as valency allows, and any mixture thereof;

B may be at least one ion of one or more group 14 elements of the Periodic Table of Elements or any mixture thereof; and

X¹ may be a halide ion or any mixture thereof;
- 30 ii) mixing a metal halide having a formula $M(X^2)_z$ with an ammonium halide having a formula $(A^2)(X^2)$ in a solvent to form a capping material solution, wherein
A² may be an ammonium cation having a structure of R²-NH_a⁺, wherein R² may be an optionally substituted C₄ to C₁₂ alkyl, an optionally substituted C₃ to C₁₂ cycloalkyl, an optionally substituted arylalkyl, or any mixture thereof;

M may be at least one ion of one or more group 2, group 3, group 7, group 8, group 9, group 10, group 11, group 12, group 13 or group 15 elements of the Periodic Table of Elements, or any mixture thereof;

X^2 may be a halide ion or any mixture thereof;

5 a may be 0 or an integer of 1, 2 or 3; and

z may be 2 or 3; and

10 iii) applying the capping material solution onto the three-dimensional perovskite compound layer to form a capping material layer comprising a capping material selected from a compound having a general formula $(A^2)_2M(X^2)_4$, $(A^2)_2(A^1)M_2(X^2)_7$, $(A^2)_mM_n(X^2)_{3n+m}$ or any mixture thereof;

wherein m may be an integer of 1, 2, 3, 4 or 5; and

n may an integer of 1 or 2.

The metal halide having the formula $M(X^2)_z$ may be selected from the group consisting of $Pb(X^2)_2$, $Zn(X^2)_2$, $Sn(X^2)_2$, $Co(X^2)_2$, $Mn(X^2)_2$, $Cu(X^2)_2$, $Sb(X^2)_3$, $Bi(X^2)_3$, $Al(X^2)_3$ and any mixture thereof.

15 The ammonium halide having the formula $(A^2)(X^2)$ may be selected from the group consisting of phenethylammonium halide ($PEA(X^2)$), n-butylammonium halide ($BA(X^2)$), iso-butylammonium halide, phenylmethyl ammonium halide ($PMA(X^2)$), 1-naphthylmethylammonium halide ($NMA(X^2)$) and any mixture thereof.

20 The solvent may be selected from the group consisting of acetonitrile (ACN), acetone, dimethylformamide (DMF), dimethylsulfoxide (DMSO), methanol, t-butyl alcohol, ethanol, isopropyl alcohol, tetrahydrofuran, methylamine and any mixture thereof.

The capping material solution, the metal halide having the formula $M(X^2)_z$ and ammonium halide having the formula $(A^2)(X^2)$ may be present at a molar ratio in the range of about 1:1 to about 1:3, about 1:1 to about 1:2, or about 1:2 to about 1:3.

25 In the capping material solution, the concentration of the metal halide having the formula $M(X^2)_z$ in the solvent may be in the range of about 5 mM to about 50 mM, about 5 mM to about 15 mM, about 5 mM to about 30 mM, about 15 mM to about 30 mM, about 15 mM to about 50 mM, or about 30 mM to about 50 mM.

30 The applying step may comprise applying the capping material solution directly onto the three-dimensional perovskite compound layer.

The applying step may comprise spin-coating, spray coating or slot-die coating the capping material solution onto the three-dimensional perovskite compound layer or dipping the three-dimensional perovskite compound layer in the capping material solution.

The method may further comprise the step of each independently annealing the capping material layer and the three-dimensional perovskite compound layer.

The method may further comprise the step of providing a hole transport layer comprising a hole transport material, wherein the three-dimensional perovskite compound layer may be provided on the hole transport layer.

The method may further comprise the step of providing an electrode, wherein the hole transport layer is provided on the electrode.

The method may further comprise the step of applying an electron transport layer comprising an electron transport material on the capping material layer.

The method may further comprise the step of applying a counter electrode on the electron transport layer.

There is also provided the use of the device as defined above in an optoelectronic device, photovoltaic cell, solar cell, light-emitting diode (LED), laser or photodetector, radiation detector, memristor, spintronic device, phototransistor, transistor, light emitting transistor (LET) or field-effect transistor (FET).

Brief Description of Figures

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the disclosure.

Fig. 1A

Fig. 1A is a schematic comparison of the FP process as disclosed herein and the conventional HP processes for preparing the 3D/LD stack films.

Fig. 1B

Fig. 1B shows the crystal structures of the 2D PEA_2PbI_4 and 0D PEA_2ZnX_4 ($\text{X} = \text{Cl/I}$).

Fig. 1C

Fig. 1C is a series of X-ray diffraction (XRD) patterns of pristine LD materials. The vertical grey shades with numbers mark the main peak positions of 0D PEA_2ZnX_4 . The symbols (asterisk, octothorp and plus) indicate the main peak positions of PEAI , 2D PEA_2PbI_4 , and quasi-2D $\text{PEA}_2\text{FAPb}_2\text{I}_7$, respectively.

Fig. 1D

Fig. 1D is a series of full-range XRD patterns of the pristine LD materials ($\text{PEA}_2\text{ZnCl}_4$, $\text{PEA}_2\text{ZnI}_2\text{Cl}_2$, PEA_2ZnI_4 , $\text{PEA}_2\text{FAPb}_2\text{I}_7$, PEA_2PbI_4 and PEAI).

Fig. 1E

Fig. 1E is a series of XRD patterns of control $\text{Rb}_5\text{Cs}_{10}$ and $\text{Rb}_5\text{Cs}_{10}/\text{LD}$ stack films. The vertical grey shades with numbers and vertical dotted lines mark the main peak positions of 0D PEA_2ZnX_4 and 3D perovskites, respectively. The symbols (asterisk, octothorp and plus) indicate the main peak positions of PEA₁, 2D PEA_2PbI_4 , and quasi-2D $\text{PEA}_2\text{FAPb}_2\text{I}_7$, respectively.

Fig. 1F

Fig. 1F is a series of full-range XRD patterns of the control $\text{Rb}_5\text{Cs}_{10}$ and $\text{Rb}_5\text{Cs}_{10}/\text{LD}$ stack films.

Fig. 1G

Fig. 1G is a series of XRD patterns of control Cs_{15} and Cs_{15}/LD stack films. The vertical grey shades with numbers and vertical dotted lines mark the main peak positions of 0D PEA_2ZnX_4 and 3D perovskites, respectively. The symbols (asterisk, octothorp and plus) indicate the main peak positions of PEA₁, 2D PEA_2PbI_4 , and quasi-2D $\text{PEA}_2\text{FAPb}_2\text{I}_7$, respectively.

Fig. 1H

Fig. 1H is a series of full-range XRD patterns of the control Cs_{15} and Cs_{15}/LD stack films.

Fig. 2

Fig. 2 is a series of XRD patterns of the pristine NMAI, $(\text{NMA})_2\text{PbI}_4$, $(\text{NMA})_2\text{FAPb}_2\text{I}_7$ films, and the 3D/NMAI and 3D/ $(\text{NMA})_2\text{PbI}_4$ stack films.

Fig. 3

Fig. 3 is a series of XRD patterns of the $\text{RbCl}/\text{PEA}_2\text{ZnI}_2\text{Cl}_2$ stack film and the pristine RbCl, PEA₁, and $\text{PEA}_2\text{ZnI}_2\text{Cl}_2$ films.

Fig. 4A

Fig. 4A is a fitting plot of low-angle XRD peaks of $\text{Rb}_5\text{Cs}_{10}/\text{PEA}_2\text{PbI}_4$ stack films. The fit is based on the Pearson VII function. The A value indicates the relative peak area. The relative intensity is raw and acquired under the same measurement conditions.

Fig. 4B

Fig. 4B is a fitting plot of low-angle XRD peaks of $\text{Cs}_{16}/\text{PEA}_2\text{ZnI}_4$ stack films. The fit is based on the Gaussian function. The A value indicates the relative peak area. The relative intensity is raw and acquired under the same measurement conditions.

Fig. 4C

Fig. 4C is a fitting plot of low-angle XRD peaks of $\text{Rb}_5\text{Cs}_{10}/\text{PEA}_2\text{ZnI}_4$ stack films. The fit is based on the Gaussian function. The A values indicate the relative peak area. The relative intensity is raw and acquired under the same measurement conditions.

5 **Fig. 5A**

Fig. 5A refers to UV-Vis spectra of PEA_2PbI_4 and $\text{PEA}_2\text{FAPb}_2\text{I}_7$. The films were prepared using the precursor solution of Example 1 with the same metal ion concentration of 17 mM.

Fig. 5B

10 Fig. 5B refers to UV-Vis spectra of PEA_2ZnI_4 and $\text{PEA}_2\text{ZnI}_2\text{Cl}_2$. The films were prepared using the precursor solution of Example 1 with the same metal ion concentration of 17 mM.

Fig. 5C

Fig. 5C refers to UV-Vis spectra of the control $\text{Rb}_5\text{Cs}_{10}$ and $\text{Rb}_5\text{Cs}_{10}/\text{LD}$ stack films based on a relatively thin $\text{Rb}_5\text{Cs}_{10}$ layer. The relatively thin $\text{Rb}_5\text{Cs}_{10}$ film was prepared using a precursor solution of Example 1 but with a metal ion concentration of 0.1 M.

15 **Fig. 6A**

Fig. 6A is a schematic diagram from the prior art of the geometry of grazing incidence wide/small angle X-ray scattering (GIWAXS/GISAXS).

Fig. 6B

20 Fig. 6B is a graphic representation from the prior art of the GIWAXS and GISAXS scattering pattern for an organic photovoltaic thin film sample.

Fig. 6C

Fig. 6C shows images indicating the GIWAXS patterns (at $\Psi = 0^\circ$, out of plane) of (a) control 3D and 3D/LD stack films (b) 3D/PEAI, (c) 3D/PEA₂PbI₃, (d) 3D/PEA₂ZnI₄ and (e) 3D/PEA₂ZnI₂Cl₂. Labels are Pb-LD: quasi-2D PEA₂FAPb₂I₇, Zn-LD: 0D PEA₂ZnX₄.

25 **Fig. 6D**

Fig. 6D is a series of images of the GIWAXS and GISAXS patterns at different Ψ angles of the control 3D (CsI_5) film. (a) is $\Psi = 0^\circ$ GIWAX, (b) is $\Psi = 90^\circ$ GIWAX in plane, (c) is 90° GISAXS in plane and out of plane; and (d) is 180° GISAXS out of plane.

Fig. 6E

Fig. 6E is an image of the GIWAXS and GISAXS patterns at different Ψ angles of the 3D/PEAI stack film. (a) is $\Psi = 0^\circ$ GIWAX, (b) is $\Psi = 90^\circ$ GIWAX in plane, (c) is 90° GISAXS in plane and out of plane; and (d) is 180° GISAXS out of plane.

5 Fig. 6F

Fig. 6F is an image of the GIWAXS and GISAXS patterns at different Ψ angles of the 3D/PEA₂PbI₄ stack film. (a) is $\Psi = 0^\circ$ GIWAX, (b) is $\Psi = 90^\circ$ GIWAX in plane, (c) is 90° GISAXS in plane and out of plane; and (d) is 180° GISAXS out of plane.

Fig. 6G

- 10 Fig. 6G is an image of the GIWAXS and GISAXS patterns at different Ψ angles of the 3D/PEA₂ZnI₄ stack film. (a) is $\Psi = 0^\circ$ GIWAX, (b) is $\Psi = 90^\circ$ GIWAX in plane, (c) is 90° GISAXS in plane and out of plane; and (d) is 180° GISAXS out of plane.

Fig. 6H

- 15 Fig. 6H is an image of the GIWAXS and GISAXS patterns at different Ψ angles of the 3D/PEA₂ZnI₂Cl₂ stack film. (a) is $\Psi = 0^\circ$ GIWAX, (b) is $\Psi = 90^\circ$ GIWAX in plane, (c) is 90° GISAXS in plane and out of plane; and (d) is 180° GISAXS out of plane.

Fig. 7A

Fig. 7A is a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of a cross-section of the FP-based 3D/PEA₂ZnX₄ PSC.

20 Fig. 7B

Fig. 7B is a Zn energy-dispersive X-ray spectroscopy (EDX) elemental map of a cross-section of the FP-based 3D/PEA₂ZnX₄ PSC.

Fig. 7C

- 25 Fig. 7C is an EDX spectrum from Region 1 as indicated on Fig. 7A. The characteristic Zn K α peak at 8.63 eV is visible in Region 1, indicating Region 1 is the location of the Zn-LD (PEA₂ZnX₄) capping layer. No lattice fringes were visible in the Zn-LD layer (Region 1), which is likely due to the relatively low crystallinity of the 0D PEA₂ZnX₄ and/or damage by the FIB during sample lamella preparation.

Fig. 7D

Fig. 7D is an EDX spectrum from Region 2 as indicated on Fig. 7A.

Fig. 8A

Fig. 8A is a graph showing the time-of-flight secondary-ion mass spectroscopy (ToF-SIMS) elemental depth profiles of the control 3D PSCs. The relative intensities of the Pb, In and Zn elements are scaled up or down proportionally for clarity, as indicated within the legend.

5 **Fig. 8B**

Fig. 8B is a graph showing a ToF-SIMS elemental depth profiles of the control 3D/PEA₂ZnX₄ PSCs. The relative intensities of the Pb, In and Zn elements are scaled up or down proportionally for clarity, as indicated within the legend.

Fig. 9A

- 10 Fig. 9A is a scanning electron microscope (SEM) image of the PEA₂ZnX₄ capping layer deposited on a bare ITO glass substrate. The representative PEA₂ZnX₄ sufficiently covered region and insufficiently covered region (bare ITO region) were indicated respectively. Scale bar represents 500 nm.

Fig. 9B

- 15 Fig. 9B is a C EDX elemental map of the PEA₂ZnX₄ capping layer deposited on a bare ITO glass substrate. Scale bar represents 500 nm.

Fig. 9C

Fig. 9C is a Zn EDX elemental map of the PEA₂ZnX₄ capping layer deposited on a bare ITO glass substrate. Scale bar represents 500 nm.

Fig. 10

- 20 Fig. 10 is a series of SEM images consisting of planar SEM images of (a) pristine 3D perovskite, (b) HP-based 3D/PEAI, (c) FP-based 3D/PEA₂PbI₄, (d) 3D/PEA₂ZnI₄, and (e) 3D/PEA₂ZnI₂Cl₂ films; and cross-sectional SEM images of (f) 3D/PEAI, (g) 3D/PEA₂PbI₄, (h) 3D/PEA₂ZnI₄, and (i) 3D/PEA₂ZnI₂Cl₂ films. The 3D perovskite is Rb₅Cs₁₀. Scale bar represents 500 nm.

Fig. 11A

- 25 Fig. 11A is an atomic force microscopy (AFM) image of the Rb₅Cs₁₀ film. RMS refers to surface root mean square roughness. Scale bar represents 2 μm.

Fig. 11B

Fig. 11B is an atomic force microscopy (AFM) image of the HP-based 3D/PEAI film. RMS refers to surface root mean square roughness. Scale bar represents 2 μm.

Fig. 11C

Fig. 11C is an atomic force microscopy (AFM) image of the FP-based 3D/PEA₂PbI₄ film. RMS refers to surface root mean square roughness. Scale bar represents 2 μm .

Fig. 11D

- 5 Fig. 11D is an atomic force microscopy (AFM) image of the 3D/PEA₂ZnI₄ film. RMS refers to surface root mean square roughness. Scale bar represents 2 μm .

Fig. 11E

Fig. 11E is an atomic force microscopy (AFM) image of the 3D/PEA₂ZnI₂Cl₂ film. RMS refers to surface root mean square roughness. Scale bar represents 2 μm .

10 **Fig. 12A**

Fig. 12A is a schematic illustration and cross-sectional SEM image of the disclosed 3D/LD PSC. The charge and terminal symbols indicate photoinduced electron/hole and device anode/cathode, respectively. The LD capping material in the cross-sectional SEM image is PEA₂ZnX₄. Scale bar represents 200 nm.

15 **Fig. 12B**

Fig. 12B is a box and whisker plot of the statistical distribution of open-circuit voltage (V_{OC}) for the PSCs without (control) or with the capping materials fabricated by HP or FP process (25 individual devices for each type were used in the statistics). The centre dotted line, box and whisker plots indicate the mean values, the 75th (top edge) and 25th (bottom edge) percentiles, and the outliers, respectively.

20 **Fig. 12C**

Fig. 12C is a box and whisker plot of the statistical distribution of short-circuit current density (J_{SC}) for the PSCs without (control) or with the capping materials fabricated by HP or FP process (25 individual devices for each type were used in the statistics). The centre dotted line, box and whisker plots indicate the mean values, the 75th (top edge) and 25th (bottom edge) percentiles, and the outliers, respectively.

25 **Fig. 12D**

Fig. 12D is a box and whisker plot of the statistical distribution of fill factor (FF) for the PSCs without (control) or with the capping materials fabricated by HP or FP process (25 individual devices for each type were used in the statistics). The centre dotted line, box and whisker plots indicate the mean values, the 75th (top edge) and 25th (bottom edge) percentiles, and the outliers, respectively.

Fig. 12E

Fig. 12E is a box and whisker plot of the statistical distribution of power-conversion efficiency (PCE) for the PSCs without (control) or with the capping materials fabricated by HP or FP process (25 individual devices for each type were used in the statistics). The centre dotted line, box and whisker plots indicate the mean values, the 75th (top edge) and 25th (bottom edge) percentiles, and the outliers, respectively.

Fig. 13A

Fig. 13A is a pseudo-colour time-resolved photoluminescence (TRPL) plots of the control 3D perovskite, 3D/PEAI and 3D/PEA₂ZnX₄ stack films deposited on glass substrates excited at 640 nm with a fluence of 0.177 $\mu\text{J cm}^{-2}$. The colour scale stands for normalized PL intensity ranging from 0 to unity. Both 3D/PEAI and 3D/PEA₂ZnX₄ stack films exhibit long tails (white regions) in their pseudo-colour TRPL plots relative to the control 3D film, indicating longer photoluminescence lifetimes.

Fig. 13B

Fig. 13B is a graph of normalized photoluminescence against decay time.

Fig. 14A

Fig. 14A is a series of images showing the fluence-dependent TRPL of control 3D perovskite film. (a) to (f) are pseudo-colour TRPL plots excited at 640 nm with various fluences, specifically (a) 0.071 μJcm^2 , (b) 0.177 μJcm^2 , (c) 0.354 μJcm^2 , (d) 0.707 μJcm^2 , (e) 1.415 μJcm^2 , and (f) 2.829 μJcm^2 . With an increase in the excited fluence, the tails (white regions) exhibit a noticeable reduction, indicating shorter photoluminescence lifetimes.

Fig. 14B

Fig. 14B is a TRPL decay kinetics graph of the square root of photoluminescence intensity against delay time with various excitation fluences and their global fits.

Fig. 15A

Fig. 15A is a series of images showing the fluence-dependent TRPL of 3D/PEAI stack film. (a) to (f) are pseudo-colour TRPL plots excited at 640 nm with various fluences, specifically (a) 0.071 μJcm^2 , (b) 0.177 μJcm^2 , (c) 0.354 μJcm^2 , (d) 0.707 μJcm^2 , (e) 1.415 μJcm^2 , and (f) 2.829 μJcm^2 . With an increase in the excited fluence, the tails (white regions) exhibit a noticeable reduction, indicating shorter photoluminescence lifetimes.

Fig. 15B

Fig. 15B is a TRPL decay kinetics graph of the square root of photoluminescence intensity against delay time with various excitation fluences and their global fits.

Fig. 16A

Fig. 16A is a series of images showing the fluence-dependent TRPL of 3D/PEA₂ZnX₄ stack film. (a) to (f) are pseudo-colour TRPL plots excited at 640 nm with various fluences, specifically (a) 0.071 μJcm^{-2} , (b) 0.177 μJcm^{-2} , (c) 0.354 μJcm^{-2} , (d) 0.707 μJcm^{-2} , (e) 1.415 μJcm^{-2} , and (f) 2.829 μJcm^{-2} . With an increase in the excited fluence, the tails (white regions) exhibit a noticeable reduction, indicating shorter photoluminescence lifetimes.

Fig. 16B

Fig. 16B is a TRPL decay kinetics graph of the square root of photoluminescence intensity against delay time with various excitation fluences and their global fits.

Fig. 17A

Fig. 17A is a schematic diagram showing the passivating interactions of $-\text{NH}_3^+$ groups in PEA₂FAPb₂I₇ passivators with the negatively charged A site cation vacancy (VA) defects. Only representative fragments of the PEA₂FAPb₂I₇ passivators taken from their single crystal structures are presented here for simplicity.

Fig. 17B

Fig. 17B is a schematic diagram showing passivating interactions of $-\text{NH}_3^+$ groups in PEA₂ZnX₄ passivators with the negatively charged A site cation vacancy (VA) defects. Only representative fragments of the PEA₂ZnX₄ passivators taken from their single crystal structures are presented here for simplicity.

Fig. 17C

Fig. 17C is a schematic diagram showing passivating interactions of halide anions in octahedral [PbI₆] of PEA₂FAPb₂I₇ with the positively charged halide vacancy (V_X) defects. Only representative fragments of the PEA₂FAPb₂I₇ passivators taken from their single crystal structures are presented here for simplicity.

Fig. 17D

Fig. 17D is a schematic diagram showing passivating interactions of halide anions in tetrahedral [ZnI₄] of PEA₂ZnX₄ with the positively charged halide vacancy (V_X) defects. Only representative fragments of the PEA₂ZnX₄ passivators taken from their single crystal structures are presented here for simplicity.

Fig. 18A

Fig. 18A is a 2D ESP map of the N atoms in $-\text{NH}_3^+$ passivating groups in PEA₂FAPb₂I₇. All the 2D planes are extracted according to the target atom coordinates, and only representative fragments of the PEA₂FAPb₂I₇ passivators taken from their single crystal structures are presented here for simplicity.

Fig. 18B

Fig. 18B is a 2D ESP map of the N atoms in -NH_3^+ passivating groups in PEA_2ZnX_4 . All the 2D planes are extracted according to the target atom coordinates, and only representative fragments of the PEA_2ZnX_4 passivators taken from their single crystal structures are presented here for simplicity.

5 **Fig. 18C**

Fig. 18C is a 2D ESP map of the I atoms in octahedral $[\text{PbI}_6]$ of $\text{PEA}_2\text{FAPb}_2\text{I}_7$.

Fig. 18D

Fig. 18D is a 2D ESP map of the I atoms in tetrahedral $[\text{ZnI}_4]$ of PEA_2ZnX_4 .

Fig. 19A

- 10 Fig. 19A is a schematic diagram of the quasi-2D $\text{PEA}_2\text{FAPb}_2\text{I}_7$ passivator from (i) the side view and (ii) the (001) plane.

Fig. 19B

Fig. 19B is a schematic diagram of the 0D PEA_2ZnX_4 passivator from (i) the side view and (ii) the (010) plane.

15 **Fig. 20A**

Fig. 20A is a series of Kelvin probe force microscopy (KPFM) images of the perovskite films deposited on ITO-coated glass substrates ((i) control, (ii) PEA₂I and (iii) PEA_2ZnX_4), where the colour scale stands for CPD intensity ranging from 1.0 V to 2.8 V.

Fig. 20B

- 20 Fig. 20B is a distribution plot of the CPD statistical distribution of the perovskite films deposited on ITO-coated glass substrates corresponding to Fig. 20A ((i) control, (ii) PEA₂I and (iii) PEA_2ZnX_4).

Fig. 20C

- 25 Fig. 20C is the UPS spectra of the perovskite films deposited on ITO-coated glass substrates corresponding to that shown in Fig. 20A ((i) control, (ii) PEA₂I and (iii) PEA_2ZnX_4). E_f represents Fermi level. The small vertical lines on left and right panels of the UPS spectra mark the secondary electron cutoff and valence band edge, respectively.

Fig. 21A

Fig. 21A is a UV-vis spectrum of $\text{Rb}_5\text{Cs}_{10}$ 3D perovskite film.

Fig. 21B

Fig. 21B is a UV-vis spectrum of $\text{PEA}_2\text{FAPb}_2\text{I}_7$ film.

Fig. 21C

Fig. 21C is a UV-vis spectrum of PEA_2ZnI_3 film.

5 **Fig. 22A**

Fig. 22A is a schematic diagram of charge transport across the n-N isotype heterojunction interface based on the intrinsic thermionic emission and quantum tunneling mechanisms.

Fig. 22B

10 Fig. 22B is a schematic diagram of LD capping layer distribution on 3D perovskite surface. There are both thin and thick regions of the LD capping layer, the former can be thin enough for charge transport by tunneling, and the charge carriers in the thick regions can also diffuse to adjacent thin regions for the transport.

Fig. 22C

15 Fig. 22C is a schematic illustration of the formation of the n-N isotype heterojunction. E_{vac} represents vacuum level and $E_{\text{built in}}$ represents built-in electric field at the junction, with units eV. The plus and minus signs indicate the positively and negatively charged regions at the junction, respectively, and the dashed arrows indicate direction of $E_{\text{built in}}$. The top arrows show the photoinduced electron transfer direction, and the bottom arrows with red cross signs indicate the photoinduced hole blocking direction. The delta sign indicates the Fermi level difference at the junction.

20 **Fig. 23**

Fig. 23 is a graph of null voltage as a function of irradiance for the control, 3D/PEAI, and 3D/ PEA_2ZnX_4 PSCs at room temperature. The horizontal lines indicate the saturated voltage levels. The V_{bi} estimated from the saturated null voltage are 1.13 V, 1.19 V, and 1.23 V, respectively.

Fig. 24

25 Fig. 24 is an energy-level diagram illustrating the possible field-effect passivation mechanism in the 3D perovskite surface, 3D/Pb-LD heterojunction and 3D/Zn-LD heterojunction.

Fig. 25

Fig. 25 is an energy-level diagram illustrating the perovskite/C60 interface recombination comparison between the 3D perovskite surface, 3D/Pb-LD structures and 3D/Zn-LD structures.

Fig. 26

Fig. 26A is a cross-sectional SEM image of the disclosed 3D/LD PSC, with a magnified image to indicate the LD layer thickness. The LD capping material is PEA_2ZnX_4 and the thickness of the LD capping layer is estimated to be approximately 20 nm. Scale bar represents 200 nm in the full image and 100 nm in expansion.

Fig. 27

Fig. 27 is a 3D AFM image of the control 3D perovskite film. Some of the valleys with depth exceeding the estimated capping layer thickness (approximately 20 nm) are indicated.

Fig. 28

Fig. 28 is a chemical structure of the TPPi molecule.

Fig. 29A

Fig. 29A is a series of images showing the fluence-dependent TRPL of 3D perovskite film with TPPi passivation. (a) to (f) are pseudo-colour TRPL plots excited at 640 nm with various fluences, specifically (a) $0.071 \mu\text{Jcm}^2$, (b) $0.177 \mu\text{Jcm}^2$, (c) $0.354 \mu\text{Jcm}^2$, (d) $0.707 \mu\text{Jcm}^2$, (e) $1.415 \mu\text{Jcm}^2$, and (f) $2.829 \mu\text{Jcm}^2$.

Fig. 29B

Fig. 29B is a TRPL decay kinetics graph of the square root of photoluminescence intensity against delay time with various excitation fluences and their global fits.

Fig. 30A

Fig. 30A is a graph of current density against voltage (J - V curves) of the champion 3D/ PEA_2ZnX_4 PSC with additional TPPi passivation. FS represents forward scan while RS represents reverse scan.

Fig. 30B

Fig. 30B is a graph of stable power output (SPO) of the target 3D/ PEA_2ZnX_4 PSC with additional TPPi passivation against time, measured at a bias of 1.02 V.

Fig. 30C

Fig. 30C is a PCE distribution histogram of 103 individual target PSCs, where the curve indicates the probability density function of normal distribution.

Fig. 30D

Fig. 30D is the external quantum efficiency (EQE) spectrum of the target PSC.

Fig. 31A

Fig. 31A is a graph of normalized PCE over time, which represents the operational stability of the control and target PSCs at MPP in N₂ under a white light-emitting diode (LED) illumination with an equivalent effective irradiance of one sun. The initial PCEs for the control and target PSCs were (18.6 ± 0.1)% and (21.7 ± 0.1)%, respectively. The device temperature was around 40 °C during test. The error bars denote standard deviations for 3 different measurements, and the centre for the error bars indicates the mean values.

Fig. 31B

Fig. 31B is a graph of current density against voltage (*J-V* curves) of the target PSC before and after MPP tracking for 1009 hours.

Fig. 32A

Fig. 32A is (i) an AFM image and (ii) graph showing the morphology of the control 3D perovskite film before aging under one sun illumination for 13 hours in air (relative humidity approximately 64%) without encapsulation. Scale bar represents 20 μm.

Fig. 32B

Fig. 32B is (i) an AFM image and (ii) graph showing the morphology of the control 3D perovskite film after aging under one sun illumination for 13 hours in air (relative humidity approximately 64%) without encapsulation, showing the change in morphology. Scale bar represents 20 μm.

Fig. 33A

Fig. 33A is (i) an AFM image and (ii) graph showing the morphology of the target 3D/LD stack film before aging under one sun illumination for 13 hours in air (relative humidity approximately 64%) without encapsulation. Scale bar represents 20 μm.

Fig. 33B

Fig. 33B is (i) an AFM image and (ii) graph showing the morphology of the target 3D/LD stack film after aging under one sun illumination for 13 hours in air (relative humidity approximately 64%) without encapsulation, showing the change in morphology. Scale bar represents 20 μm.

Fig. 34

Fig. 34 is a schematic illustration demonstrating the stability improvement of the 3D/LD structure.

Fig. 35A

Fig. 35A is an image of the steady-state contact angle of deionized water on top of a Glass/PEA₂ZnI₄ film.

Fig. 35B

Fig. 35B is an image of the steady-state contact angle of deionized water on top of a Glass/PEAI film.

Fig. 35C

Fig. 35C is an image of the steady-state contact angle of deionized water on top of a Glass/ZnI₂ film.

5 **Fig. 36**

Fig. 36 is a series of photoluminescence (PL) images consisting of PL images of the control 3D perovskite film (a) before and (b) after aging under one sun illumination for 13 hours in air (relative humidity approximately 64%) without encapsulation; PL images of the target 3D/LD stack film (c) before and (d) after aging under the same conditions; enlarged PL images of (e) region indicated in (c) and (f) region indicated in (d). The samples were excited by a 473 nm continuous wave laser. Scale bar represents 100 μm.

Fig. 37

Fig. 37 is a graph of normalized PCE against time, which tests the heat stability of the control 3D and the target 3D/LD PSCs under 85 °C, with relative humidity approximately 50%. The error bars denote standard deviations for 3 individual devices, and the centre for the error bars indicate the mean values.

Fig. 38

Fig. 38 is a series of XRD patterns of pristine BA₂ZnI₂Cl₂ and Cs₁₅/BA₂ZnI₂Cl₂ stack films.

Fig. 39

Fig. 39 is a series of XRD patterns of pristine PEA₂CoI₂Cl₂ and Cs₁₅/PEA₂CoI₂Cl₂ stack films. The slight shift of the low-angle characteristic XRD peak position of PEA₂CoI₂Cl₂ was due to the halogen exchange between I- in PEA₂CoI₂Cl₂ and Cl- in the Cs₁₅ perovskite, which was similar to the PEA₂ZnX₄.

Examples

Non-limiting examples of the disclosure will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the disclosure.

25 **Example 1: Half precursor (HP) and full precursor (FP) capping solution preparation**

The conventional HP capping solution was prepared by dissolving PEAI (purchased from Greatcell Energy Ltd, Australia) in isopropanol (IPA) (purchased from Sigma-Aldrich, St. Louis, Missouri, United States of America).

The FP capping solution of the present disclosure was prepared as follows:

- The PEA_2PbI_4 FP capping solution was prepared by dissolving 31.3 mg PbI_2 (purchased from TCI, Chuo-ku, Tokyo, Japan) and 33.9 mg phenethylammonium iodide (PEAI) (purchased from Greatcell Energy Ltd, Australia) in 4 mL acetonitrile (ACN) (17 mM) (purchased from Sigma-Aldrich, St. Louis, Missouri, United States of America). The other FP capping solutions including BA_2PbI_4 , PMA_2PbI_4 , $(\text{NMA})_2\text{PbI}_4$, BA_2ZnX_4 ($\text{X} = \text{Cl/I}$), PEA_2ZnX_4 ($\text{X} = \text{Cl/I}$) and PEA_2CoX_4 ($\text{X} = \text{Cl/I}$) ($\text{BA} = n$ -butylammonium; $\text{PMA} = \text{phenylmethylammonium}$; $\text{NMA} = 1$ -naphthylmethylammonium), and were prepared in the same way with an identical concentration of 17 mM as the PEA_2PbI_4 FP capping solution. A mixed solvent containing 50 μL methylamine (purchased from Sigma-Aldrich, St. Louis, Missouri, United States of America) in 1 mL ACN was specially used to dissolve the $(\text{NMA})_2\text{PbI}_4$ precursors.
- The PEA_2PbI_4 - PEA_2ZnX_4 hybrid FP capping solution was prepared by dissolving 62.7 mg PbI_2 , 18.5 mg ZnCl_2 (purchased from Sigma-Aldrich, St. Louis, Missouri, United States of America), and 135.5 mg PEA in 8 mL ACN.

Example 2: Device fabrication and characterization

Device fabrication

- The patterned ITO-coated glass substrates (purchased from Shenzhen Huayu Union Technology Co., Ltd, China) were ultrasonically cleaned with an aqueous detergent (Alconox[®] detergent, purchased from Sigma-Aldrich, St. Louis, Missouri, United States of America), deionized water, acetone, and ethyl alcohol for about 20 minutes in sequence, followed by ultraviolet ozone treatment for 15 minutes before next use. All the spin-coating processes were conducted in a N_2 -filled glovebox ($\text{O}_2 < 10$ ppm, $\text{H}_2\text{O} < 1.0$ ppm).

The hole transporting poly(triarylamine) (PTAA) layer was deposited by spin-coating the PTAA (purchased from Xi'an Polymer Light Technology Corp, Xi'an, Shaanxi, China) solution (2 mg mL^{-1} in toluene) on cleaned ITO substrates at a speed of 2000 rpm for 60 seconds, and then annealed at 100 °C for 10 min.

- The $\text{Rb}_{0.05}\text{Cs}_{0.10}\text{FA}_{0.85}\text{PbI}_{2.8}\text{Cl}_{0.2}$ ($\text{Rb}_5\text{Cs}_{10}$) perovskite precursor contained 414.9 mg PbI_2 , 27.8 mg PbCl_2 (purchased from Sigma-Aldrich, St. Louis, Missouri, United States of America), 146.2 mg formamidinium iodide (FAI) (purchased from Greatcell Energy Ltd, Australia), 26.0 mg CsI (purchased from Sigma-Aldrich, St. Louis, Missouri, United States of America), and 10.6 mg RbI (purchased from Sigma-Aldrich, St. Louis, Missouri, United States of America) in 1 mL anhydrous DMF : DMSO (4 : 1, v/v) (both solvents purchased from Sigma-Aldrich, St. Louis, Missouri, United States of America).
- The $\text{Cs}_{0.15}\text{FA}_{0.85}\text{PbI}_{2.8}\text{Cl}_{0.2}$ (Cs_{15}) perovskite precursor contained 414.9 mg PbI_2 , 27.8 mg PbCl_2 , 146.2 mg FAI, 39.0 mg CsI in 1 mL anhydrous DMF : DMSO (4 : 1, v/v). The $\text{Cs}_{0.05}(\text{MA}_{0.15}\text{FA}_{0.85})_{0.95}\text{PbI}_{2.55}\text{Br}_{0.45}$ (CsMAFA) perovskite precursor contained 780.3 mg PbI_2 , 112.9 mg PbBr_2 , 277.8 mg FAI, 26.0 mg CsI, and 31.9 mg MABr (purchased from Greatcell Energy Ltd, Australia) in 2 mL anhydrous DMF: DMSO (4 : 1, v/v). The $\text{Rb}_5\text{Cs}_{10}$, Cs_{15} and CsMAFA perovskite films were deposited by spin-coating the corresponding precursor solution on the ITO/PTAA substrates at 1000 rpm for 10 seconds (5 second ramp) and 4000 rpm for 45 seconds (1 second ramp), and 150 μL of 1,2-dichlorobenzene (DCB) (purchased from Sigma-Aldrich, St. Louis, Missouri, United States of America) was rapidly dropped on the substrates at 10 seconds before the end of the program to induce fast

crystallization of perovskites. The as-prepared perovskite films were then annealed at 110 °C for 10 min.

Next, the HP or FP capping solution was spin-coated on top of the perovskite films at a speed of 5000 rpm (1500 rpm was used for XRD and GIWAXS/GISAXS samples for better signals) for 30 seconds.

- 5 The FP capping solution was rapidly injected on the 3D perovskite surface after the substrate started spinning to minimize the possible erosion to the underlying 3D perovskite. The films were then annealed at 100 °C for 10 minutes.

- 10 The additional tris(2,4-di-tert-butylphenyl) phosphite (TPPi) passivation layer was prepared by spin-coating the TPPi toluene solution (6 mg mL⁻¹) (both TPPi and toluene purchased from Sigma-Aldrich, St. Louis, Missouri, United States of America) at a speed of 5000 rpm for 30 seconds as required. Finally, 50 nm C₆₀ (purchased from Puyang Yongxin Fullerene Technology Co., Ltd, Puyang, China), 6 nm bathocuproine (BCP) (purchased from Xi'an Polymer Light Technology Corp, Xi'an, Shaanxi, China), and 100 nm Ag were thermally evaporated (under a vacuum < 5.0 × 10⁻⁴ Pa) in sequence on the films through a metal shadow mask with an active area of 6.0 mm² for small-area devices or 1.218 cm² for large-area devices. To minimize the unaccounted reflecting and possible edge effect, a 100 nm LiF (purchased from Sigma-Aldrich, St. Louis, Missouri, United States of America) layer was evaporated onto the glass side of ITO substrates as an anti-reflection layer, and a non-reflective black metal aperture mask with an aperture area around 4.0 mm² for small-area devices or 0.973 cm² for large-area devices was also affixed on the glass side of ITO substrates as required. The Ag electrode was replaced with the Cr (5 nm)/Au (100 nm) electrode in the PSCs for the stability tests.
- 20

Device characterization

- 25 The current density–voltage (*J*–*V*) curves of the PSCs were recorded with a Keithley 2400 source meter (Keithley Instruments, Cleveland, Ohio, United States of America) under simulated AM 1.5 G solar illumination from a ScienceTech UHE-NSC AAA solar simulator (Sciencetech, Ontario, Canada). The effective irradiance of the solar simulator for the disclosed PSCs was adjusted to one sun (100 mW cm⁻²) by using an Oriel PV Reference Cell System (91150V) (Newport, Irvine, California, United States of America) with calibration of possible spectral mismatch. The *J*–*V* curves were measured in either forward or reverse scan direction from –0.2 V to 1.25 V/1.20 V or 1.25 V/1.20 V to –0.2 V at a scan rate of approximately 0.5 V s⁻¹. The presented *J*–*V* curves were obtained in reverse scan direction at room temperature in a N₂-filled glovebox (O₂ < 10 ppm, H₂O < 1.0 ppm) unless specified otherwise. The *J*–*V* curves were initially measured without an aperture mask. The measured *J*_{SC} was then calibrated against the value obtained with aperture mask by subtracting the obtained *J*_{SC} difference between the measurements without and with aperture mask in the specific photovoltaic system, although the *J*_{SC} difference was as small as 0.37 mA cm⁻² caused by the unaccounted reflecting and possible edge effect
- 30 Table 1. The final presented *J*–*V* curves were obtained from the measurement with an aperture mask or based on the calibrated *J*_{SC} accordingly. The spectral response and external quantum efficiency analysis was performed on a Zolix Solar Cell Scan100 measurement system (Zolix Instruments Co., Ltd., Beijing, China) and QEPVSI-b set-up (Newport, Irvine, California, United States of America).
- 35

Table 1. Comparison of photovoltaic parameters for the target 3D/PEA₂ZnX₄PSC with additional TPPI passivation measured without and with aperture mask.^a The 3D perovskite and PEA₂ZnX₄ here are Rb₅CS₁₀ and PEAZnI₂Cl₂, respectively.

Aperture mask	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)	ΔJ _{SC} (mA cm ⁻²) ^b
With	1.174 ± 0.010 ^a	23.98 ± 0.24	82.6 ± 0.8	23.3 ± 0.3	0.37
Without	1.181 ± 0.010	24.35 ± 0.19	81.2 ± 0.7	23.4 ± 0.3	

^aThe data include average values and standard deviations calculated from 22 individual devices. ^bThe ΔJ_{SC} is the J_{SC} difference between the measurements without and with aperture mask.

Example 3: Stability tests

Operational Stability test

The operational stability test for the disclosed PSCs was conducted in a N₂-filled glovebox (O₂ < 10 ppm, H₂O < 1.0 ppm) at maximum power point (MPP) under illumination of a white LED lamp with an equivalent effective irradiance of one sun. An example of the detailed tracking process is as follows and the involved data are shown in Table 2: (1) The initial PCE of the PSC was measured under the simulated AM 1.5 G AAA solar simulator with an effective irradiance of one sun as described above. The obtained initial PCE and J_{SC} were labelled as PCE_(0h,SS) and J_{SC(0h,SS)} (SS denotes solar simulator). (2) The PSC was then subjected to the operational test under the white LED lamp irradiation. The effective irradiance of the white LED lamp for the specific PSC was identified as one sun when the measured J_{SC} (labelled as J_{SC(0h,LED)}) was adjusted to approximate the J_{SC(0h,SS)} in step (1). A certain voltage bias was then selected and applied to the PSC to generate MPP output by a Keithley 2602B source meter (Keithley Instruments, Cleveland, Ohio, United States of America). The PSC was left to continuously operate under this MPP for around 22 hours. (3) After the first 22 hours of MPP operation, the J_{SC} was measured again under the white LED lamp and labelled as J_{SC(22h,LED)}. The J_{SC} was also measured for the same device under solar simulator irradiation and labelled as J_{SC(22h,SS)}. The possible difference between J_{SC(22h,LED)} and J_{SC(22h,SS)} may be caused by the irradiance change of the white LED lamp after 22 hours of operation but not due to the device performance change between the two measurements, because both J_{SC(22h,LED)} and J_{SC(22h,SS)} were measured at the same time. The negligible difference between J_{SC(22h,LED)} and J_{SC(22h,SS)} indicated the relatively stable irradiance of the white LED lamp. (4) The longer operational tests were similarly conducted by repeating steps (2) and (3). The presented operational stability results were based on the PCE data measured under the solar simulator irradiation.

Table 2. Comparison of the representative photovoltaic parameters for the target PSC before and after the first 22 hours of MPP operation.

Operational time (hour)	J _{SC(SS)} (mA cm ⁻²) ^a	J _{SC(LED)} (mA cm ⁻²) ^b	PCE _(SS) (%) ^c	ΔJ _{SC} (mA cm ⁻²) ^d
0	22.51 ± 0.16 ^e	22.64 ± 0.00	21.7 ± 0.1	0.13
22	22.35 ± 0.11	22.36 ± 0.02	21.4 ± 0.1	0.01

^a J_{SC(SS)} denotes the measured J_{SC} under the solar stimulator. ^b J_{SC(LED)} denotes the measured J_{SC} under the white LED. ^c PCE_(SS) denotes the measured PCE under the solar stimulator. ^d ΔJ_{SC} denotes the difference between J_{SC(LED)} and J_{SC(SS)}.

^eThe data include average values and standard deviations calculated from 3 measurements.

Heat stability test

The 85 °C heat stability test was conducted under ambient conditions (relative humidity approximately 50%) or in a N₂-filled glovebox (O₂ < 10 ppm, H₂O < 1.0 ppm). A simple base encapsulation was made for the device before start of the test in air, and there was no encapsulation for the device tested in N₂.

- 5 The simple base encapsulation was done by direct storing the original device in a small commercial air-tight box, which was then put into an 85 °C oven for the test. It should be noted that the simple base encapsulation was unable to strictly insulate the air. The widely used triple-cation CsMAFA 3D perovskite was used in the relevant device for the test.

Example 4: Fabrication and characterization of 3D/LD stack films

- 10 A comparison between the proposed FP and traditional HP processes is shown in Fig 1A. The solvent of the HP solution was generally prepared using an antisolvent, such as IPA, whereas a slightly more polar solvent acetonitrile (ACN) was used to dissolve the FP components, especially the metal halide, as mentioned in Example 1. For simplicity, PEA₂PbI₄ and PEA₂ZnX₄ (X = Cl/I) with structures given in Fig. 1B were chosen as representatives of the FP-based LD capping materials for further discussion.
- 15 On the other hand, the ubiquitous PEAI was chosen as a representative for the HP capping method. Notably, the distinguishable characteristic low-angle XRD peaks (Fig. 1C and Fig. 1D) provided strong and direct evidence to verify the presence of corresponding LD materials in the 3D/LD films. As a result, the deposited PEA₂PbI₄ was fully converted into the quasi-2D PEA₂FAPb₂I₇ through a reaction with the bottom 3D perovskite of either Rb_{0.05}Cs_{0.10}FA_{0.85}PbI_{2.8}Cl_{0.2} (abbreviated as Rb₅Cs₁₀) (Fig. 1E and Fig. 1F) or Cs_{0.15}FA_{0.85}PbI_{2.8}Cl_{0.2} (abbreviated as Cs₁₅) (Fig. 1G and Fig. 1H). However, for the conventional capping method, PEAI salt still partially remained on both 3D perovskites under the same post-treatment although most were transformed into PEA₂FAPb₂I₇ (Fig. 1E and Fig. 1G). The superior controllability of the FP technique for growth of the LD overlayer in this disclosure was further confirmed by the successful realization of a 2D (NMA)₂PbI₄ capping layer with superior intrinsic stability on a 3D perovskite (Fig. 2), which was inaccessible with the traditional HP process due to the difficult reaction between the NMAI salt and the 3D perovskite. Interestingly, it was found that both PEA₂ZnX₄ and PEA₂FAPb₂I₇ phases were detected in the Rb₅Cs₁₀/PEA₂ZnX₄ film (Fig. 1E), but only PEA₂ZnX₄ was present in the Cs₁₅/PEA₂ZnX₄ film (Fig. 1G). It was also noted that a halogen exchange between I⁻ in PEA₂ZnX₄ and Cl⁻ in either Rb₅Cs₁₀ or Cs₁₅ perovskite always occurred, ultimately leading to a Cl-rich composition of PEA₂ZnI_{4-x}Cl_x (x ≥ 2) (Fig. 1E and Fig. 1G), where the estimated x values are presented in Table 3. Henceforth, the Zn-based capping component is represented by the simplified formula of PEA₂ZnX₄ unless specified otherwise, where X is Cl⁻, I⁻, or their mixture.
- 25
- 30

Table 3. The estimated x values in the capping product of $\text{PEA}_2\text{ZnI}_{4-x}\text{Cl}_x$ in the 3D/ PEA_2ZnX_4 (X = Cl/I) stack films according to the characteristic XRD peak position of PEA_2ZnX_4 (see Fig. 1C, 1E and 1G).

Film	Characteristic XRD peak position 2θ ($^\circ$)	Product	x value
PEA_2ZnI_4	6.6		0
$\text{PEA}_2\text{ZnI}_2\text{Cl}_2$	6.9		2
$\text{PEA}_2\text{ZnCl}_4$	7.2		4
$\text{Rb}_5\text{Cs}_{10}/\text{PEA}_2\text{ZnI}_4$	6.9	$\text{PEA}_2\text{ZnI}_{4-x}\text{Cl}_x$	2
$\text{Rb}_5\text{Cs}_{10}/\text{PEA}_2\text{ZnI}_2\text{Cl}_2$	7.1		approximately 3 ^a
$\text{Cs}_{15}/\text{PEA}_2\text{ZnI}_4$	7.0		approximately 3
$\text{Cs}_{15}/\text{PEA}_2\text{ZnI}_2\text{Cl}_2$	7.1		approximately 3

^aThe x value here is estimated to be around 3 as the characteristic XRD peak position is between those of $\text{PEA}_2\text{ZnI}_2\text{Cl}_2$ and $\text{PEA}_2\text{ZnCl}_4$.

5 To reveal the possible reaction pathways between PEA_2ZnX_4 and $\text{Rb}_5\text{Cs}_{10}$ perovskite, the $\text{RbCl}/\text{PEA}_2\text{ZnX}_4$ stack film was investigated under similar conditions and it was discovered that Rb^+ partially exchanged with PEA^+ to generate PEAX salt (Fig. 3). The exchanged Rb^+ was likely incorporated into the PEA_2ZnX_4 structure to form $(\text{PEA}_{1-3}\text{Rb}_3)_2\text{ZnX}_4$, which was a reasonable deduction as the full-width at half-maximum (FWHM) value for the characteristic diffraction peak of PEA_2ZnX_4 was almost doubled (Fig. 3) and considering Rb_2ZnX_4 had the same $\beta\text{-K}_2\text{SO}_4$ type crystal structure to PEA_2ZnX_4 . Hence, it was concluded that the capped PEA_2ZnX_4 partially reacted with the $\text{Rb}_5\text{Cs}_{10}$ perovskite to generate $(\text{PEA}_{1-3}\text{Rb}_3)_2\text{ZnX}_4$ and $\text{PEA}_2\text{FAPb}_2\text{I}_7$ via the cation exchange between Rb^+ and PEA^+ . The possible reactions between the disclosed LD capping materials and the 3D perovskites are summarized in Table 4.

10

15

Table 4. Comparison of the possible reactions between the capping materials and the 3D perovskites, and the corresponding products/residues.

Capping Material	3D perovskite	Possible reaction	Possible product/residue
PEAX	APbX ₃ ^a	$2\text{PEAX} + \text{APbX}_3 \rightarrow \text{PEA}_2\text{PbX}_4 + \text{AX}$	PEA ₂ APb ₂ X ₇ ,
		$\text{PEA}_2\text{PbX}_4 + \text{APbX}_3 \rightarrow \text{PEA}_2\text{APb}_2\text{X}_7$	PEA ₂ PbX ₄ , AX, PEAX
PEA ₂ PbX ₄	APbX ₃	$\text{PEA}_2\text{PbX}_4 + \text{APbX}_3 \rightarrow \text{PEA}_2\text{APb}_2\text{X}_7$	PEA ₂ APb ₂ X ₇
PEA ₂ ZnX ₄	(Cs _x FA _{1-x})PbX ₃	—	PEA ₂ ZnX ₄
	(Rb _{2y} Cs _x FA _{1-x-2y})PbX ₃	$\text{PEA}_2\text{ZnX}_4 + (\text{Rb}_{2y}\text{Cs}_x\text{FA}_{1-x-2y})\text{PbX}_3 \rightarrow$ $(\text{PEA}_{1-y}\text{Rb}_y)_2\text{ZnX}_4 + 2y\text{PEAX} +$ $(\text{Cs}_x\text{FA}_{1-x-2y})\text{Pb}_{1-2y}\text{X}_{3(1-2y)} + 2y\text{PbX}_2$	PEA ₂ ZnX ₄ , (PEA _{1-y} Rb _y) ₂ ZnX ₄ ,
		$2\text{PEAX} + \text{PbX}_2 \rightarrow \text{PEA}_2\text{PbX}_4$	PEA ₂ APb ₂ X ₇ ,
		$\text{PEA}_2\text{PbX}_4 + \text{APbX}_3 \rightarrow \text{PEA}_2\text{APb}_2\text{X}_7$	PEA ₂ PbX ₄ , PbX ₂

^aA = Rb, Cs, FA; X = Cl/I.

- 5 The possible conversion ratio of PEA₂ZnX₄ in the Rb₅Cs₁₀/PEA₂ZnX₄ stack film was further determined by means of a rough quantitative XRD analysis (Fig. 4A – 4C and Table 5), in which the relative amount of the phases present was estimated by using the integral intensity of the corresponding characteristic diffraction peak. Considering the identical preparation and measurement conditions, and similar chemical environments for both Rb₅Cs₁₀/PEA₂ZnX₄ and Rb₅Cs₁₀/PEA₂PbI₄ stack films, it was plausible to assume that the crystallinity and texture of PEA₂FAPb₂I₇ in both stack films were roughly consistent,
- 10 suggesting that the ratio of PEA₂FAPb₂I₇ in Rb₅Cs₁₀/PEA₂ZnX₄ to that in Rb₅Cs₁₀/PEA₂PbI₄ could be estimated by directly comparing the corresponding integral intensities of the PEA₂FAPb₂I₇ diffraction peak. It was also inferred that the PEA₂FAPb₂I₇ diffraction peak intensity of Rb₅Cs₁₀/PEA₂ZnX₄ should approach that of Rb₅Cs₁₀/PEA₂PbI₄ if the PEA₂ZnX₄ was fully converted into PEA₂FAPb₂I₇. This was because PEA₂PbI₄ showed a complete transformation into PEA₂FAPb₂I₇ in Rb₅Cs₁₀/PEA₂PbI₄, and the
- 15 contents of PEA⁺ in both stack films were probably equivalent due to the same fabrication conditions. Accordingly, a conversion ratio of approximately 10% of PEA₂ZnX₄ in Rb₅Cs₁₀/PEA₂ZnX₄ was obtained by simply comparing the PEA₂FAPb₂I₇ diffraction peak intensity of Rb₅Cs₁₀/PEA₂ZnX₄ to that of Rb₅Cs₁₀/PEA₂PbI₄ (Table 5), indicating that approximately 90% of PEA₂ZnX₄ in Rb₅Cs₁₀/PEA₂ZnX₄ was retained.
- 20 To examine the reliability of the results, a similar analysis was performed to directly calculate the retention ratio of PEA₂ZnX₄ in Rb₅Cs₁₀/PEA₂ZnX₄ by comparing the PEA₂ZnX₄ diffraction peak intensity of Rb₅Cs₁₀/PEA₂ZnX₄ to that of Cs₁₅/PEA₂ZnX₄, which led to a similar retention ratio of approximately 90% (Table 5). Meanwhile, ultraviolet-visible (UV-Vis) absorption spectra of both Rb₅Cs₁₀/PEAI and Rb₅Cs₁₀/PEA₂PbI₄ films based on a relatively thin Rb₅Cs₁₀ layer exhibited a clear
- 25 and strong excitonic absorption peak at approximately 570 nm corresponding to PEA₂FAPb₂I₇, which was barely observed for the Rb₅Cs₁₀/PEA₂ZnX₄ film (Fig. 5A – 5C). Therefore, it could be deduced

that the $\text{PEA}_2\text{FAPb}_2\text{I}_7$ was a minor capping by-product in the $\text{Rb}_5\text{Cs}_{10}/\text{PEA}_2\text{ZnX}_4$ film, though it was difficult to directly identify PEA_2ZnX_4 in the UV-Vis spectrum of the $\text{Rb}_5\text{Cs}_{10}/\text{PEA}_2\text{ZnX}_4$ film due to the intrinsic weak absorption of PEA_2ZnX_4 (Fig. 5C). This was in accordance with the above quantitative XRD analysis results. In summary, the capped PEA_2ZnX_4 primarily remained on the $\text{Rb}_5\text{Cs}_{10}$ perovskite, and there was only a slight reaction with $\text{Rb}_5\text{Cs}_{10}$ perovskite to produce a small amount of $\text{PEA}_2\text{FAPb}_2\text{I}_7$ by-product.

Table 5. The estimated proportion of each component in the capping products according to quantitative XRD analysis (see Fig. 4).

3D/LD stack	Capping product	XRD peak area	Capping product proportion
$\text{Rb}_5\text{Cs}_{10}/\text{PEA}_2\text{PbI}_4$	$\text{PEA}_2\text{FAPb}_2\text{I}_7$	3553	100%
$\text{Cs}_{15}/\text{PEA}_2\text{ZnI}_4$	PEA_2ZnX_4	83.7	100%
$\text{Rb}_5\text{Cs}_{10}/\text{PEA}_2\text{ZnI}_4$	$\text{PEA}_2\text{FAPb}_2\text{I}_7$	391	$\sim 10\%^a$
	PEA_2ZnX_4	76.5	approximately 90% ^b

^aThe proportion is estimated by comparing the $\text{PEA}_2\text{FAPb}_2\text{I}_7$ peak area in the $\text{Rb}_5\text{Cs}_{10}/\text{PEA}_2\text{ZnI}_4$ to that in $\text{Rb}_5\text{Cs}_{10}/\text{PEA}_2\text{PbI}_4$.

^bThe proportion is estimated by comparing the PEA_2ZnX_4 peak area in $\text{Rb}_5\text{Cs}_{10}/\text{PEA}_2\text{ZnI}_4$ to that in $\text{Cs}_{15}/\text{PEA}_2\text{ZnI}_4$.

The orientation of the LD capping material was further assessed with respect to the substrate using grazing incidence wide/small angle X-ray scattering (GIWAXS/GISAXS) (Fig. 6A – 6H). Grazing incidence X-ray scattering (GIXS) techniques are widely used to analyze the crystal orientation/crystalline lattice spacing/crystalline correlation length, domain size/domain shape, and phase separation/phase purity of functional materials in photovoltaic devices. Fig. 6A shows the reflection geometry of GIXS. The X-ray beam impinged onto the sample surface under a very shallow incident angle α_i (typically $\alpha_i < 1^\circ$) and scattered under an existing angle α_f and out of plane angles Ψ . Typically, the x-axis would be along the X-ray beam direction, the y-axis would be parallel to the sample surface, the z-axis would be along with the surface normal, and the scattering plane is the (x,z)-plane. Scattering signal coming from sample was then recorded on 2D X-ray detector. The GIWAXS/GISAXS signals could be obtained by changing the sample-detector distance.

Based on the Nano-inXider of Xenocs system, Ψ rotation enabled the sample to rotate around the beam and achieved different configurations (GIWAXS/GISAXS in plane/out of plane) (see Fig. 6B). For $\Psi = 90^\circ$, the pattern recorded corresponded to GIWAXS and GISAXS in-plane with an overlap in the q scattering vector. For $\Psi = 0^\circ$, GIWAXS out-of-plane is achievable. For $\Psi = 180^\circ$, GIWAXS out-of-plane is measured.

The incident monochromatic X-ray beam with a wave vector $\mathbf{k}_i$ and a wave number $k_0 = 2\pi/\lambda$ (λ is the wavelength of the X-rays, and its value is intrinsic to the metal anode) was scattered along $\mathbf{k}_f$ direction. The scattering wave vector $\mathbf{q}$ and the related three components (q_x , q_y and q_z) are defined by the following equations:

$$\mathbf{q} = (q_x, q_y, q_z) = \mathbf{k}_f - \mathbf{k}_i \quad (\text{E1})$$

$$q_x = \frac{2\pi}{\lambda} (\cos \Psi \cos \alpha_f - \cos \alpha_i) \quad (\text{E2})$$

$$q_y = \frac{2\pi}{\lambda} (\sin \Psi \cos \alpha_f) \quad (\text{E3})$$

$$q_z = \frac{2\pi}{\lambda} (\sin \alpha_f + \sin \alpha_i) \quad (\text{E4})$$

- 5 When the lateral structures were absent, it met $\alpha_i = \alpha_f$ due to the pure specular scattering. The diffuse scattering results from the lateral deviation of the refractive index, which leads to $\alpha_i \neq \alpha_f$.

The control 3D film exhibited Debye-Scherrer-like rings, and the 3D/LD stack films showed additional Bragg spots whose positions corresponded to those of the relevant peaks in their XRD patterns. Interestingly, all the Bragg spots shown in the disclosed 3D/LD stack films were located along the Q_z direction, indicating that the LD capping materials were oriented preferentially with the (0k0) planes parallel to the substrate, i.e., the b-axis was oriented perpendicular to the substrate. This was consistent with the orientation of most reported LD capping materials prepared by the conventional HP methodology.

15 The presence and distribution of the Zn-based capping layer on 3D perovskite surface was further identified using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDX) (Fig. 7A – 7D), as well as time-of-flight secondary-ion mass spectroscopy (ToF-SIMS) (Fig. 8A and 8B). In Fig. 7C, it was observed that no lattice fringes were visible in the Zn-LD layer, which was probably due to the relatively low crystallinity of the 0D PEA_2ZnX_4 and/or damage by the FIB during sample lamella preparation. In Fig. 8B, the Zn signal was only observed in between the C and Pb signals in the 3D/ PEA_2ZnX_4 device, which was absent in the control device, indicating that the PEA_2ZnX_4 capping material was mainly distributed at the interface between C_{60} and the 3D perovskite. It should be noted that the onset of both the Zn and Pb signals was almost simultaneous at the point of sputtering. This was because the PEA_2ZnX_4 capping layer with a small optimum thickness on top of the relatively rough 3D perovskite surface was probably discontinuous rather than conformal, thus it cannot sufficiently cover the 3D perovskite surface.

In addition, the Zn-based capping material probably formed a film on the 3D perovskite surface, inferred from its distribution form on the ITO substrate (Fig. 9A – 9C). From Fig. 9A – 9C, it was noted that direct identification of the PEA_2ZnX_4 capping layer on 3D perovskite surface via possible different morphologies between them was quite difficult as the PEA_2ZnX_4 capping layer was relatively thin and the 3D perovskite surface was relatively rough, which resulted in the PEA_2ZnX_4 capping layer appearing almost “invisible” under SEM, and thus the 3D perovskite morphology was observed everywhere.

35 The ITO/ PEA_2ZnX_4 film was also investigated to estimate the possible coverage of PEA_2ZnX_4 in the 3D/ PEA_2ZnX_4 film and it was noted that most areas of the 3D perovskite surface were probably sufficiently covered by the PEA_2ZnX_4 capping layer, but there was also a small amount of imperfectly covered areas. Lattice micro strain analysis (Table 6) suggested that the Zn-based capping layer hardly

induced any additional lattice strain for the bottom 3D perovskite although their crystal structures were different. It was also noted that the FP-based capping solution hardly changed the cross-sectional morphology of the underlying 3D perovskite (Fig. 10), which indicated negligible damage to the underlying 3D perovskite. Additionally, all the capping layers were found to effectively reduce the roughness of the 3D perovskite film (Fig. 11A – 11E), which was probably attributed to the filling of 3D perovskite surface valley regions by the capping materials.

Table 6. Lattice micro strain analysis for the control 3D and 3D/PEA₂ZnI₄ stack films. The 3D perovskite here is CsI₅.

3D perovskite lattice plane	Peak position (2θ) (°)		β _{hkl} (°) ^a		Micro strain (%) ^b	
	3D	3D/PEA ₂ ZnI ₄	3D	3D/PEA ₂ ZnI ₄	3D	3D/PEA ₂ ZnI ₄
001	13.996	13.400	0.121	0.123	0.43	0.44
110	19.858	19.865	0.093	0.095	0.253	0.24
002	28.211	28.212	0.127	0.120	0.22	0.21
012	31.636	31.637	0.133	0.125	0.20	0.19
220	40.332	40.340	0.136	0.113	0.16	0.13

^a β_{hkl} is the full width at half maximum of the peak, which is related to the lattice micro strain, crystalline domain size and instrumental contribution. Considering the same instrument being used and similar crystalline domain size for the control 3D and 3D/PEA₂ZnI₄ samples, it is reasonable that any difference in β_{hkl} between the two samples is mainly attributed to the different lattice micro strain. ^bThe lattice micro strain can be estimated using β_{hkl}/4tanθ based on the Debye-Scherrer method.

Example 5: Photovoltaic performance comparison of 3D/LD PSCs

The p–i–n structured 3D/LD PSCs were then investigated with a general configuration of ITO/PTAA/3D/LD/C₆₀/BCP/Ag (Fig. 12A), and the 3D perovskite was Rb₅Cs₁₀ unless specified otherwise. The values of the open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF) and power-conversion efficiency (PCE) for the control and target PSCs with the various capping materials fabricated by traditional HP or the FP process of this disclosure were compared in Fig. 12B – 12E and Table 7. The capping layers were prepared using their respective optimum conditions for a fair comparison (Table 8). Compared to the control device with an average PCE of 19.3 ± 0.3%, both the traditional HP-based 3D/PEAI device and the FP-based 3D/PEA₂PbI₄ device showed improved performance of 20.5 ± 0.8% and 20.8 ± 0.5%, respectively, while the 3D/PEA₂ZnX₄ device showed even greater improvement with a remarkable PCE of 22.2 ± 0.3%. These improvements were mainly ascribed to the enhanced V_{OC}. The comparable performance between the FP-based 3D/PEA₂PbI₄ and HP-based 3D/PEAI devices was attributed to the similar ultimate capping component (PEA₂FAPb₂I₇). The better reproducibility (narrower PCE distribution) of the FP-based 3D/PEA₂PbI₄ device was likely due to the superior synthetic control of the LD capping layer by the FP technique. These results validated the feasibility and superiority of our FP technique for efficient 3D/LD PSCs. The outstanding

performance of the 3D/PEA₂ZnX₄ device advocated potential advantages of PEA₂ZnX₄ in serving as the LD capping material in 3D/LD PSCs, which was also applicable in relatively large-area (approximately 1 cm²) devices (Table 9). It was noted that the key capping component for the high-performance 3D/PEA₂ZnX₄ device should be the intrinsic PEA₂ZnX₄ and not the PEA₂FAPb₂I₇ by-product since the PEA₂ZnX₄ residual was the main capping component (accounting for approximately 90%) in the 3D/PEA₂ZnX₄ stack film, as demonstrated above. To eliminate the interference from the small amount of PEA₂FAPb₂I₇ by-product, similar PSCs based on the Cs₁₅ perovskite were also investigated, considering that PEA₂ZnX₄ could fully remain on the Cs₁₅ perovskite, as demonstrated above. Consequently, similar performance improvement was demonstrated (Table 10), further confirming the intrinsic superiority of PEA₂ZnX₄ as the LD capping material in 3D/LD PSCs.

Table 7. Statistics of photovoltaic parameters for PSCs without or with different capping materials. The 3D perovskite and PEA₂ZnX₄ here are Rb₅Cs₁₀ and PEAZnI₂Cl₂, respectively.

Capping material	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
Control	1.037 ± 0.018 ^a	23.8 ± 0.3	78.2 ± 1.1	19.3 ± 0.3
PEAI	1.112 ± 0.024	23.4 ± 0.4	78.7 ± 1.2	20.5 ± 0.8
PEA ₂ PbI ₄	1.134 ± 0.006	23.3 ± 0.2	78.6 ± 1.5	20.85 ± 0.5
PEA ₂ ZnI ₄	1.159 ± 0.007	23.9 ± 0.2	80.4 ± 0.6	22.2 ± 0.3

^aThe data include average values and standard deviations calculated from 25 individual devices.

Table 8. Statistics of photovoltaic parameters for PSCs based on the capping materials with various concentrations. The 3D perovskite and PEA₂ZnX₄ here are Rb₅Cs₁₀ and PEAZnI₂Cl₂, respectively.

Capping material	Concentration (mM)	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
PEAI	10	1.072 ± 0.023 ^a	23.5 ± 0.1	79.7 ± 0.8	20.1 ± 0.4
	20	1.119 ± 0.017	23.4 ± 0.4	78.4 ± 0.5	20.6 ± 0.6
	30	1.126 ± 0.017	22.5 ± 0.8	75.3 ± 4.0	19.1 ± 1.8
PEA ₂ PbI ₄	12	1.107 ± 0.006	23.4 ± 0.2	79.6 ± 0.7	20.6 ± 0.4
	17	1.135 ± 0.008	23.4 ± 0.3	78.4 ± 1.4	20.8 ± 0.5
	23	1.142 ± 0.013	21.4 ± 0.3	79.0 ± 1.5	19.3 ± 0.5
PEA ₂ ZnX ₄	17	1.158 ± 0.006	23.8 ± 0.2	80.6 ± 0.5	22.2 ± 0.2

26	1.169 ± 0.005	22.9 ± 0.3	79.3 ± 1.8	21.2 ± 0.8
----	-------------------	----------------	----------------	----------------

^aThe data include average values and standard deviations calculated from 8 individual devices.

Table 9. Statistics of photovoltaic parameters for the 3D/PEAI and 3D/PEA₂ZnX₄ PSCs with a relatively large aperture area of 0.973 cm².

Device structure	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
3D/PEAI	1.104 ± 0.008^a	23.2 ± 0.3	74.4 ± 2.85	19.0 ± 0.8
3D/PEA ₂ ZnX ₄	1.134 ± 0.010	23.3 ± 0.3	78.4 ± 1.2	20.8 ± 0.4

5 ^aThe data include average values and standard deviations calculated from 10 individual devices.

Table 10. Statistics of photovoltaic parameters for PSCs without or with different capping materials. The 3D perovskite and PEA₂ZnX₄ here are Rb₅CS₁₀ and PEAZnI₂Cl₂, respectively.

Capping material	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
Control	1.048 ± 0.005^a	22.4 ± 0.2	77.41 ± 1.2	18.2 ± 0.3
PEAI	1.132 ± 0.009	22.0 ± 0.5	78.7 ± 1.1	19.6 ± 0.6
PEA ₂ PbI ₄	1.135 ± 0.006	22.7 ± 0.4	79.2 ± 1.0	20.4 ± 0.4
PEA ₂ ZnX ₄	1.150 ± 0.005	22.7 ± 0.4	81.0 ± 1.3	21.2 ± 0.4

^aThe data include average values and standard deviations calculated from 13 individual devices.

10 **Example 6: Optoelectronic properties evolution in 3D/LD PSCs**

To explicate the underlying reasons for the extraordinary enhancement of device performance by the PEA₂ZnX₄ capping material, time-resolved photoluminescence (TRPL) analysis was conducted to characterize the nonradiative recombination losses of charge carriers in the perovskite films.

15 In view of similar ultimate capping component and comparable performance for both HP-based 3D/PEAI and FP-based 3D/PEA₂PbI₄ devices, the 3D/PEAI stack film was taken as the representative of the Pb-based counterpart for comparison. As shown in Fig. 13A, both 3D/PEAI and 3D/PEA₂ZnX₄ stack films exhibited ‘long tails’ in their pseudo-colour TRPL plots relative to the control film under the same excitation fluence of 0.177 μJ cm⁻² at 640 nm, indicating longer PL lifetimes. A more distinct comparison of TRPL decay kinetics was illustrated in Fig. 13B. To extract the specific rate constant (*k*₁) and lifetime (*τ*) for trap-mediated nonradiative recombination, i.e., Shockley–Read–Hall (SRH)
20 recombination, fluence-dependent TRPL analysis and corresponding global fits were also carried out

(Fig. 14 – 16). The TRPL delay kinetics correlate to charge carrier recombination channels, which are dependent on excitation pulse fluences (initial charge carrier densities). At very low excitation fluences, trap-mediated nonradiative monomolecular recombination (first-order) channel is dominated, leading to a mono-exponential relationship of TRPL decay kinetics. As excitation fluence increases, higher-order recombination channels such as bimolecular electron-hole radiative recombination (second-order) and trimolecular Auger recombination (third-order) start to contribute, resulting in accelerated TRPL decay kinetics, which can be generally governed by the following rate equation:

$$\frac{dN}{dt} = -k_1N - k_2N^2 - k_3N^3 \quad (E5)$$

where N is photoexcited charge carrier density, k_1 , k_2 and k_3 are rate constants for the first-order, second-order, and third-order recombination, respectively.

To extract specific recombination rate constants, fluence-dependent TRPL analysis under excitation of 640nm femtosecond laser pulses with various fluences (0.071, 0.177, 0.354, 0.707, 1.415 and 2.829 $\mu\text{J cm}^{-2}$) were carried out for the disclosed perovskite films. The excitation fluences used were relatively low, under which the third-order Auger recombination was negligible. So, the k_1 and k_2 values could be extracted by globally fitting the TRPL delay kinetics with various excitation fluences by using the simplified rate equation (E6):

$$\frac{dN}{dt} = -k_1N - k_2N^2 \quad (E6)$$

The lifetime ($\tau = 1/k_1$) of the first-order trap-mediate recombination can then be calculated.

In comparison with the control 3D perovskite, more significant decrease of k_1 and increase of τ for 3D/PEA₂ZnX₄ than conventional 3D/PEAI were observed (Table 11), implying the superiority of PEA₂ZnX₄ over traditional Pb-based counterpart for surface passivation to suppress charge recombination. The chemical passivation effect of the halogenometallate family of capping materials had been known to be mainly rooted in their interactions with the A site cation vacancy (V_A) and halide vacancy (V_X) defects, which were regarded as the dominant types of defects on 3D perovskite surface. Similarly, in this disclosure, both the main surface capping component PEA₂FAPb₂I₇ in the conventional 3D/PEAI film and PEA₂ZnX₄ in the 3D/PEA₂ZnX₄ film enabled the interactions with the V_A and V_X defects depending on the cationic ammonium group (i.e., $-\text{NH}_3^+$) and halide anion in their structures (Fig. 17A – 17D). Although both the PEA₂FAPb₂I₇ and PEA₂ZnX₄ passivators possessed the same passivating groups, their interactions with defects may vary due to different chemical environments and structures, leading to discrepant passivation effects.

Table 11. The extracted constants from global fits for the fluence-dependent TRPL decay kinetics of the 3D perovskite films without or with different capping materials (see Fig. 14 – 16).

Capping material	First-order		Second-order
	$k_1 (10^8 \text{ s}^{-1})$	$\tau \text{ (ns)}$	$k_2 (10^{-11} \text{ cm}^3 \text{ s}^{-1})$
Control	19.7 ± 0.1	506 ± 2	3.14 ± 0.03
PEAI	5.1 ± 0.1	1950 ± 50	3.69 ± 0.03
PEA ₂ ZnX ₄	3.8 ± 0.1	2600 ± 100	3.06 ± 0.03

Density-functional theory (DFT) calculation was also conducted to assess the electronic structure of PEA₂FAPb₂I₇ and PEA₂ZnI₄. The electrostatic potential (ESP) maps of PEA₂FAPb₂I₇ and PEA₂ZnI₄ based on their single crystal structures were calculated using Vienna Ab initio Simulation Package (VASP). All-electron-like projector augmented wave (PAW) method was used and the PW86R exchange and PBE correlation potential was implemented in the VASP code. The semicore of Pb atoms (5d-orbital) was treated as valence electrons, i.e., 14 valence electrons for Pb (5d¹⁰6s²6p²) atom. The cut-off energy for the plane wave expansion of the wave functions was 500 eV. The lattice constants of PEA₂FAPb₂I₇ and PEA₂ZnI₄ were listed in Table 12. All atoms in the unit cell were fully optimized. The Hellman-Feynman forces were less than 1 meV Å⁻¹. The 4×4×1 and 4×1×3 Monkhorst-Pack grid of k-points for Brillouin zone integration of PEA₂FAPb₂I₇ and PEA₂ZnI₄ were employed in the DFT calculations, respectively. The method of vdW-DF2 was used to calculate the van der Waals (VDW) interaction. The related ESP maps were generated using the Visualization for Electronic and STructural Analysis (VESTA) software.

On one hand, the calculated ESP maps of PEA₂FAPb₂I₇ and PEA₂ZnX₄ showed almost identical ESP for the -NH₃⁺ groups in both passivators (Fig. 18A and 18B), indicating that the passivation effects induced by the -NH₃⁺ groups were probably similar for both passivators. A slightly more negative ESP for the halide anion in the tetrahedral [ZnI₄] than in the octahedral [PbI₆] was also observed (Fig. 18C and 18D), which was in accordance with the smaller electronegativity of Zn relative to Pb. This was conducive to inducing relatively stronger interaction between the halide anion in PEA₂ZnX₄ and the positively charged V_X defect, and thus contributing to the superior passivation effect. On the other hand, the isolated tetrahedral [ZnI₄] structure in the 0D PEA₂ZnX₄ was relatively relaxed compared to the strained connected octahedral [PbI₆] structure in the quasi-2D PEA₂FAPb₂I₇ (Fig. 19A and 19B), which was easier to form effective interactions between passivating groups and the defects. Another possible reason for the superiority of PEA₂ZnX₄ may be related to modification of interface energy level alignment, which is discussed below.

Table 12. The lattice constants of $\text{PEA}_2\text{FAPb}_2\text{I}_7$ and PEA_2ZnI_4 .

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
$\text{PEA}_2\text{FAPb}_2\text{I}_7$	8.722	8.726	22.533	97.6	93.5	90.4
PEA_2ZnI_4	8.205	26.832	10.988	90.0	90.2	90.0

Kelvin probe force microscopy (KPFM) analysis was performed to explore surface potential evolution of the perovskite films with different capping materials. Fig. 20A presented the KPFM images of control 3D, 3D/PEAI and 3D/ PEA_2ZnX_4 stack films with the same colour scale standing for contact potential difference (CPD) between tip and sample surface. The highest average CPD value of 3D/ PEA_2ZnX_4 (Fig. 20B) implied a more significant decrease in surface work function induced by PEA_2ZnX_4 than the traditional Pb-based counterpart. In addition, ultraviolet photoelectron spectroscopy (UPS) analysis was carried out to determine the Fermi levels and valence band maximum (VBM) of the surfaces of pristine 3D, 3D/PEAI and 3D/ PEA_2ZnX_4 stack films (Fig. 20C). It should be noted that the mentioned Fermi levels here are actually quasi-Fermi levels. The conduction band minimum (CBM) was then extrapolated in relation to the optical bandgaps, which were estimated from UV-Vis spectra of the pristine 3D perovskite, $\text{PEA}_2\text{FAPb}_2\text{I}_7$ and PEA_2ZnI_4 (Fig. 21A – 21C). It should be noted that in this case, the bandgaps of the surface capping components in 3D/PEAI and 3D/ PEA_2ZnX_4 stack films were approximated from those of the pristine $\text{PEA}_2\text{FAPb}_2\text{I}_7$ and PEA_2ZnI_4 films. This was because the initially capped PEAI and PEA_2ZnX_4 would mostly convert into $\text{PEA}_2\text{FAPb}_2\text{I}_7$ and PEA_2ZnI_4 (Table 3) after post-treatment respectively, as shown above.

The charge transport across the n-n isotype heterojunction interface was illustrated in Fig. 22A and Fig. 22B. Based on Anderson's model, the heterojunctions between two contacting semiconductors can be classified as isotype and anisotype according to the type of conductivity present on either side of the junction. The former involves two semiconductors with similar types of conductivity, which includes n-n and p-p types. In the specific n-n isotype heterojunction, there are four cases of energy band profiles depending on the relation between electron affinities (χ), work functions (ϕ) and band gaps (E_g) of the two contacting semiconductors, as shown below.

Case I:

$$\chi_1 > \chi_2, \phi_1 > \phi_2, \chi_1 + E_{g1} < \chi_2 + E_{g2}$$

Case II:

$$\chi_1 > \chi_2, \phi_1 < \phi_2, \chi_1 + E_{g1} < \chi_2 + E_{g2}$$

Case III:

$$\chi_1 < \chi_2, \phi_1 < \phi_2, \chi_1 + E_{g1} > \chi_2 + E_{g2}$$

Case IV:

$$\chi_1 > \chi_2, \phi_1 > \phi_2, \chi_1 + E_{g1} > \chi_2 + E_{g2}$$

The disclosed 3D/LD structures conformed to the Case I energy band profile of n-n isotype heterojunction (Fig. 22C). In this situation, an accumulation layer was formed on the 3D side of the interface and a depletion layer on the LD side of the interface, accompanied with a self-consistent quantum well at the interface (Fig. 22A). According to various models proposed by Anderson and other researchers, thermionic emission and quantum tunnelling over the heterojunction barrier are two probable intrinsic mechanisms for the charge transport across the heterojunction interface.

As presented in the resulting energy level diagram (Fig. 22C), all Fermi levels of the 3D perovskite and surface capping components are much closer to their CBM, revealing n-type properties. Furthermore, the Fermi level of the surface capping component in 3D/PEA₂ZnX₄ (−3.98 eV) was relatively higher than that in 3D/PEAI (−4.15 eV), and both are effectively enhanced relative to the control 3D perovskite (−4.42 eV), which agreed with the KPFM results.

Importantly, the specific energy level alignment in either 3D/PEAI or 3D/PEA₂ZnX₄ conduced to construct an n-N isotype heterojunction with an additional built-in electric field pointing from the surface to the bulk (Fig. 22C), which was responsible for enhancement of V_{bi} and thus V_{OC} . As the additional V_{bi} was dominated by the Fermi level difference at the junction, 3D/PEA₂ZnX₄ could theoretically induce a stronger n-N isotype heterojunction and produce a higher additional V_{bi} by virtue of a larger Fermi level difference relative to the conventional 3D/PEAI. The possible V_{bi} variation was further investigated by the photosaturation method for the control, 3D/PEAI and 3D/PEA₂ZnX₄ PSCs. The photosaturation method was a non-destructive and non-invasive technique for measuring the V_{bi} of photovoltaic devices. Generally, for an ideal classical p-n junction, the V_{OC} can be calculated by:

$$V_{OC} = \frac{kT}{q} \ln \left(\frac{J_{ph}}{J_{th}} + 1 \right) \quad (E7)$$

Where k , T , q , J_{ph} and J_{th} are Boltzmann constant, absolute temperature, elementary charge, photocurrent density, and thermally generated current density (or dark current density), respectively. In fact, the V_{OC} does not indefinitely increase with the enhancement of J_{th} according to the E7 relation, especially under relatively high irradiance, because the V_{OC} is also limited by:

$$V_{OC} = \frac{kT}{q} \ln \left[\frac{L_p + L_n + W}{(L_p/\tau_p)p_n + (L_n/\tau_n)n_p} g_{ph} + 1 \right] \quad (E8)$$

where L_p , L_n , W , p_n and n_p are hole diffusion length, electron diffusion length, depletion width, hole concentration on the n side of the junction, electron concentration on the p side of the junction, respectively. The τ_p and τ_n are the corresponding hole and electron lifetimes, respectively. The g_{ph} is the photo generation rate. As the τ_p and τ_n get shorter significantly under illumination with relatively high intensities, the V_{OC} cannot increase indefinitely with increased photo generation rate and is expected to saturate close to the V_{bi} of the junction. Therefore the V_{bi} can be estimated from the photosaturated V_{OC} . The V_{OC} here was identified by measuring the null voltage where the output current of the device is zero.

As predicted, the 3D/PEA₂ZnX₄ led to a larger increase of V_{bi} compared to the traditional 3D/PEAI (Fig. 23), which was consistent with the V_{OC} evolution. On the other hand, the specific built-in electric field at the n-N isotype heterojunction likely induced departure of holes at the 3D perovskite surface, resulting in decreased hole concentration, which was advantageous for reducing the SRH recombination at the surface (Fig. 24), as the SRH recombination rate was strongly dependent on the surface concentration of the minority carrier. This effect is commonly known in silicon solar cells as field-effect passivation. Accordingly, there was likely stronger field-effect passivation in 3D/PEA₂ZnX₄ on account of a relatively larger built-in electric field at the corresponding n-N isotype heterojunction, which was also responsible for the superior passivation effect of PEA₂ZnX₄. Furthermore, the relatively deeper VBM of the surface capping component could also induce a barrier for holes between the 3D perovskite layer and the C₆₀ electron transporting layer, which effectively restrained undesired recombination at the perovskite/C₆₀ interface caused by the adverse band tail states of C₆₀ (Fig. 25). The slightly higher hole barrier in 3D/PEA₂ZnX₄ (0.42eV as compared to 0.35eV in 3D/Pb-LD) also contributed to greater suppression of charge recombination, thus improving the device performance.

Example 7: Device performance and stability of 3D/LD PSCs

The LD capping layer of this disclosure, with a small optimum thickness (approximately 20 nm, estimated from Fig. 26) was deposited on a relatively rough 3D perovskite surface (Fig. 11 and 37) via the solution process, which made the LD capping layer likely discontinuous rather than conformal. As illustrated in Fig. 22B, both thin and thick regions of the LD capping layer likely coexisted. The thin capping region was advantageous for charge transport by tunnelling. For the thick capping region, the charge carriers can also diffuse to adjacent thin capping regions to transfer across the interface.

To further improve device performance, TPPI, a traditional surface passivation molecule, was introduced to the best-performing 3D/PEA₂ZnX₄ PSCs, considering that the relatively rough 3D perovskite surface likely cannot be sufficiently covered by the PEA₂ZnX₄ capping layer with a small optimum thickness (approximately 20 nm) (Fig. 9, 11, 26 and 27). The chemical structure of the TPPI molecule is presented in Fig. 28, and its passivation efficacy was confirmed by the reduced k_1 and increased τ of the 3D/TPPI film compared to the pristine 3D perovskite film (Fig. 14 and 29, and Table 13), as well as a slight increase in PCE of the 3D/TPPI PSCs (Table 14), which had also been demonstrated by other similar molecules. As a result, a maximum PCE of 24.1% was obtained with a V_{OC} of 1.198 V, a J_{SC} of 24.0 mA cm⁻², an FF of 83.9%, and negligible hysteresis (Fig. 30A). The device also exhibited an average stable power output (SPO) of 23.5% at the maximum power point (MPP) (Fig. 30B) and good reproducibility with an average PCE of 22.9% over 103 individual cells (Fig. 30C and Table 15). The measured J_{SC} was validated by the integrated J_{SC} from the external quantum efficiency (EQE) spectrum (Fig. 30D), with a reasonable relative discrepancy less than 2%. In addition, the PSCs of this disclosure were evaluated by an independent national institute, Solar Energy Research Institute of Singapore (SERIS), which offers a high-precision solar simulator with an almost ideal spectral mismatch factor of 1.01 for the PSCs of this disclosure (complying with IEC 60904-9). A certified PCE of 23.25% was obtained when measured in reverse scan direction, and 22.81% was obtained when measured in forward scan direction based on a non-reflective black aperture with a certified area of 4.03 mm² (the device active area is 6.0 mm²).

Table 13. The extracted constants from global fits for the fluence-dependent TRPL decay kinetics of the 3D perovskite films without or with TPPi passivation (see Fig. 13 and 28).

Passivation condition	First-order		Second-order
	k_1 (10^8 s ⁻¹)	τ (ns)	k_2 (10^{-11} cm ³ s ⁻¹)
Control	19.7 ± 0.1	506 ± 2	3.14 ± 0.03
TPPi passivation	18.5 ± 0.1	541 ± 2	3.00 ± 0.02

5 Table 14. Statistics of photovoltaic parameters for the control 3D PSCs without or with TPPi. The 3D perovskite is Cs₁₅.

Device structure	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
3D	1.048 ± 0.005 ^a	22.4 ± 0.2	77.4 ± 1.2	18.2 ± 0.3
3D/TPPi	1.064 ± 0.004	22.7 ± 0.2	80.1 ± 0.9	19.4 ± 0.1

^aThe data include average values and standard deviations calculated from 13 individual devices

Table 15. Statistics of photovoltaic parameters for the target 3D/PEA₂ZnX₄ PSC with additional TPPi passivation. The 3D perovskite and PEA₂ZnX₄ here are Rb₅Cs₁₀ and PEA₂ZnI₂Cl₂.

V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
1.184 ± 0.010 ^a	23.9 ± 0.3	81.0 ± 0.9	22.9 ± 0.3

10 ^aThe data include average values and standard deviations calculated from 103 individual devices

15 Lastly, the operational stability of the 3D/LD PSCs was examined based on the FP technology. The operational stability tests were carried out at MPP in a N₂-filled glovebox (O₂ < 10 ppm, H₂O < 1.0 ppm) under illumination of a white light-emitting diode (LED) lamp with an equivalent effective irradiance of one sun. It was noted that the Cs₁₅ 3D perovskite and the hybrid LD capping layer of PEA₂PbI₄–PEA₂ZnX₄ were included in the PSCs for the stability tests, considering that a comparable device performance was achieved for the 3D/PEA₂PbI₄–PEA₂ZnX₄ PSC relative to the 3D/PEA₂ZnX₄ PSC (Table 16), which was due to the intrinsic superiority of PEA₂ZnX₄, as demonstrated above. Similar tests were also conducted for BA₂PbI₄, PMA₂PbI₄, PEA₂CoX₄ and BA₂ZnX₄, which also highlighted the intrinsic superiority of PEA₂ZnX₄ (Tables 17 and 18). Consequently, 94.5% of the initial PCE was maintained after 1009 hours of MPP operation for the target PSC, which was remarkably enhanced compared to the control PSC (Fig. 31A and 31B). To reveal the possible reasons for the stability improvement induced by the LD capping layer, the surface morphology and defects evolution

20

of the relevant perovskite films were investigated after aging them under one sun illumination in air without encapsulation. As illustrated in Fig. 32A, 32B, 33A and 33B, the LD capping layer effectively inhibited the generation of surface pinholes on the 3D perovskite film, which likely resulted from the blocking of H₂O/O₂ penetration/erosion by the hydrophobic organic bulky cations within the structure of the LD capping layer (Fig. 34). To this end, Fig. 35A-35C show the steady state contact angles of deionized water on top of glass/PEA₂ZnI₄, glass/PEAI and glass/ZnI₂ films. The contact angles of the glass/ PEA₂ZnI₄ and glass/PEAI films remained almost unchanged after one hour of measurement, suggesting relatively good water resistance properties. Additionally, the steady-state water contact angle of the glass/ PEA₂ZnI₄ film was found to be much larger than that of the glass/ZnI₂ film but slightly smaller than that of the glass/PEAI film, which suggested that the water resistance property of PEA₂ZnI₄, likely results from the hydrophobic organic bulky cation (PEA⁺).

Moreover, a relatively larger decrease in surface PL intensity for the control 3D perovskite film was also observed (Fig. 36), indicating that the LD capping layer was probably favourable for suppressing light-induced production of surface defects due to the robust interaction between the LD capping material and the 3D perovskite surface (Fig. 34).

It should be noted that some local degradation spots were still observed in the target 3D/LD stack film (indicated by the circles in Fig. 36f), which was likely due to the imperfect coverage of the LD layer for the 3D perovskite surface. To further verify the role of the LD capping layer in device stability improvement, the 85 °C heat stability tests were also performed for the disclosed PSCs under ambient conditions or in N₂ (refer to Example 3). The relatively quick drop of PCE for the target device when tested in air, relative to that in N₂, was probably due to the poor encapsulation. The initial average PCE for the control 3D device is (18.5 ± 0.1)%. The initial average PCEs for the target 3D/LD devices tested under ambient condition or in N₂ are (20.1 ± 0.1)% and (20.9 ± 0.2)%, respectively. As predicted, the target 3D/LD device also showed enhanced heat stability, compared to the control 3D device (Fig. 37).

Table 16. Statistics of photovoltaic parameters for the target 3D/PEA₂ZnX₄ and 3D/PEA₂PbI₄-PEA₂ZnX₄ PSCs. The 3D perovskite and PEA₂ZnX₄ here are CsI₃ and PEA₂ZnI₂Cl₂, respectively.

Capping material	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
PEA ₂ ZnX ₄	1.150 ± 0.005 ^a	22.7 ± 0.4	81.0 ± 1.3	21.2 ± 0.4
PEA ₂ PbI ₄ -PEA ₂ ZnX ₄	1.156 ± 0.005	23.0 ± 0.5	80.8 ± 1.2	21.5 ± 0.5

^aThe data include average values and standard deviations calculated from 13 individual devices

Table 17. Statistics of photovoltaic parameters for the 3D/BA₂PbI₄ and 3D/PMA₂PbI₄ and 3D/PEA₂CoX₄ PSCs based on the FP technology of this disclosure. The 3D perovskite here is Rb₅Cs₁₀.

Capping material	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
BA ₂ PbI ₄	1.103 ± 0.006 ^a	22.6 ± 0.4	81.0 ± 1.7	20.2 ± 0.4
PMA ₂ PbI ₄	1.093 ± 0.005	23.3 ± 0.1	79.3 ± 0.7	20.2 ± 0.2
PEA ₂ CoX ₄	1.142 ± 0.007	23.3 ± 0.2	75.7 ± 1.1	20.1 ± 0.5

^aThe data include average values and standard deviations calculated from 8 individual devices

5 Table 18. Statistics of photovoltaic parameters for PSCs without or with different capping materials. The 3D perovskite, BA₂ZnX₄ and PEA₂ZnX₄ here are Cs₁₅, BA₂ZnI₂Cl₂ and PEA₂ZnI₂Cl₂, respectively.

Capping material	V _{OC} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)
Control	1.048 ± 0.005 ^a	22.4 ± 0.2	77.4 ± 1.2	18.2 ± 0.3
BA ₂ ZnX ₄	1.125 ± 0.008	22.9 ± 0.3	80.3 ± 1.0	20.7 ± 0.3
PEA ₂ ZnX ₄	1.150 ± 0.005	22.7 ± 0.4	81.0 ± 1.3	21.2 ± 0.4

^aThe data include average values and standard deviations calculated from 13 individual devices

10 Although only the representative PEA₂PbI₄ and PEA₂ZnX₄ were presented here in detail, the FP technology of this disclosure also demonstrated broad applicability for other commonly used LD capping materials such as BA₂PbI₄ and PMA₂PbI₄ (Table 17), as well as BA₂ZnX₄ (Fig. 38 and Table 18). Apart from the Zn²⁺ cation, the FP technology of this disclosure could potentially unlock access to many other divalent metal cations such as Co²⁺ (PEA₂CoX₄) (Fig. 39 and Table 17), Mn²⁺, Cu²⁺, etc. as well as trivalent cations such as Sb³⁺, Bi³⁺, and Al³⁺ for use in the LD layer, which are promising for tuning energy level alignments at 3D/LD interfaces and/or enhancing the interface stability more

15 effectively.

Industrial Applicability

The device as defined above may be useful in perovskite optoelectronics such as LEDs, lasers, photodetectors, radiation detectors, memristors, spintronic devices, phototransistors, transistors, LETs or FETs.

- 5 The methods as defined above may also be useful for developing superior LD capping materials from the vast family of halogenometallates, including the Pb-free capping materials, for more efficient and stable PSCs.

- 10 It will be apparent that various other modifications and adaptations of the disclosure will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the disclosure and it is intended that all such modifications and adaptations come within the scope of the appended claims.

CLAIMS

1. A device comprising:
 - a) a three-dimensional perovskite compound layer, comprising a three-dimensional perovskite compound having a formula $(A^1)B(X^1)_3$, wherein:

5 A^1 is selected from the group consisting of at least one ion of one or more group 1 elements of the Periodic Table of Elements, an organic cation having a structure of $R^1-(NH_x)_y^+$ wherein R^1 is CH or alkyl, x is 2 or 3 and y is 1 or 2, as valency allows, and any mixture thereof;

10 B is at least one ion of one or more group 14 elements of the Periodic Table of Elements or any mixture thereof; and

X^1 is a halide ion or any mixture thereof;
 - b) a capping material layer comprising a capping material, provided on the three-dimensional perovskite compound layer, wherein the capping material is selected from a compound having a general formula $(A^2)_2M(X^2)_4$, $(A^2)_2(A^1)M_2(X^2)_7$, $(A^2)_mM_n(X^2)_{3n+m}$ or any mixture thereof, wherein:

15 A^2 is an ammonium cation having a structure of $R^2-NH_a^+$, wherein R^2 is an optionally substituted C_4 to C_{12} alkyl, an optionally substituted C_3 to C_{12} cycloalkyl, an optionally substituted arylalkyl, or any mixture thereof;

20 M is at least one ion of one or more group 2, group 3, group 7, group 8, group 9, group 10, group 11, group 12, group 13 or group 15 elements of the Periodic Table of Elements, or any mixture thereof;

X^2 is a halide ion or any mixture thereof;

m is an integer of 1, 2, 3, 4 or 5;

n is an integer of 1 or 2; and

25 a is 0 or an integer of 1, 2 or 3.
2. The device according to claim 1, wherein A^1 is selected from the group consisting of $CH_3NH_3^+$, $CH(NH_2)_2^+$, Cs^+ , Rb^+ and any mixture thereof, B is selected from the group consisting of Pb^{2+} , Sn^{2+} , Ge^{2+} and any mixture thereof, and X^1 is selected from the group consisting of I, Br, Cl, F and any mixture thereof.
- 30 3. The device according to claim 1 or 2, wherein the three-dimensional perovskite compound has the structure $Cs_{0.15}FA_{0.85}PbI_{2.8}Cl_{0.2}$, $Rb_{0.05}Cs_{0.10}FA_{0.85}PbI_{2.8}Cl_{0.2}$, or $Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$, wherein MA is $CH_3NH_3^+$ and FA is $CH(NH_2)_2^+$.

4. The device according to any one of the preceding claims, wherein:

A^2 is selected from the group consisting of phenethylammonium (PEA) ion, n-butylammonium (BA) ion, iso-butylammonium ion, phenylmethylammonium (PMA) ion, 1-naphthylmethylammonium (NMA) ion, and any mixture thereof;
5. M is selected from the group consisting of Zn^{2+} , Pb^{2+} , Co^{2+} , Mn^{2+} , Cu^{2+} , Sb^{3+} , Bi^{3+} , Al^{3+} and any mixture thereof; or

X^2 is selected from the group consisting of Cl^- , Br^- , I^- , F^- and any mixture thereof.
5. The device according to any one of the preceding claims, wherein the capping material layer has a β - K_2SO_4 type, β - K_2PO_3F type, cubic, orthorhombic or tetragonal single crystal structure.
10. 6. The device according to any one of the preceding claims, wherein the capping material layer is substantially free of Pb^{2+} or Sn^{2+} .
7. The device according to any one of the preceding claims, wherein the three-dimensional perovskite compound layer and the capping material layer are each independently annealed.
15. 8. The device according to any one of the preceding claims, further comprising a hole transport layer comprising a hole transport material, wherein the three-dimensional perovskite compound layer is provided on the hole transport layer.
9. The device according to claim 8, wherein the hole transport material is selected from the group consisting of poly(triarylamine) (PTAA), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), (2-(9H-carbazol-9-yl)ethyl)phosphonic acid (2PACZ), [2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACZ), [4-(3,6-dimethyl-9H-carbazol-9-yl)butyl]phosphonic acid (Me-4PACz), (2-(3,6-dimethyl-9H-carbazol-9-yl)ethyl)phosphonic acid (Me-2PACz), NiO, CuSCN, CuO and any mixture thereof.
20. 10. The device according to claim 8 or 9, further comprising an electrode, wherein the hole transport layer is provided on the electrode.
25. 11. The device according to claim 10, wherein the electrode is selected from the group consisting of indium tin oxide (ITO), fluorine-doped tin oxide (FTO) and any mixture thereof.
12. The device according to any one of the preceding claims, further comprising an electron transport layer comprising an electron transport material, provided on the capping material layer.
30. 13. The device according to claim 12, wherein the electron transport material is selected from the group consisting of C_{60} /bathocuproine ([6,6]-phenyl-C61-butyric acid methyl ester, BCP), methyl 4-[3'-phenyl-3'H-cyclopropa[1,9](C_{60} - I_h)[5,6]fulleren-3'-yl]butanoate (PC61BM), (6,6)-phenyl C71 butyric acid methyl ester (PC71BM), 1',1'',4',4''-tetrahydro-

di[1,4]methanonaphthaieno[5,6]fullerene-C60 (ICBA), tin(IV) oxide, zinc oxide, and any mixture thereof.

14. The device according to claim 12 or 13, further comprising a counter electrode, provided on the electron transport layer.
- 5 15. The device according to claim 14, wherein the counter electrode comprises an element selected from the group consisting of gold, silver, platinum, aluminium, copper, carbon and any mixture thereof.
16. The device according to any one of claims 8 to 15, wherein the electron transport layer, the capping material layer, the three-dimensional perovskite compound layer and the hole transport layer are independently in a form of a film.
- 10 17. The device according to any one of claims 8 to 16, wherein the counter electrode has a thickness in the range of about 100 nm to about 200 nm, the electron transport layer has a thickness in the range of about 45 nm to about 75 nm, the capping material layer has a thickness in the range of about 15 nm to 25 nm, the three-dimensional perovskite compound layer has a thickness in the range of about 400 nm to about 700 nm, the hole transport layer has a thickness in the range of about 20 nm to about 80 nm, or the electrode has a thickness in the range of about 150 nm to about 300 nm.
- 15 18. The device according to any one of the preceding claims, wherein the device is an optoelectronic device, photovoltaic cell, solar cell, light-emitting diode (LED), laser or photodetector, radiation detector, memristor, spintronic device, phototransistor, transistor, light emitting transistor (LET) or field-effect transistor (FET).
- 20 19. A method of preparing the device of any one of the preceding claims, comprising the steps of:
 - i) providing a three-dimensional perovskite compound layer, comprising a three-dimensional perovskite compound having a formula $(A^1)B(X^1)_3$ wherein:
 - 25 A^1 is selected from the group consisting of at least one ion of one or more group 1 elements of the Periodic Table of Elements, an organic cation having a structure of $R^1-(NH_x)_y^+$ wherein R^1 is CH or alkyl, x is 2 or 3 and y is 1 or 2, as valency allows, and any mixture thereof;
 - B is at least one ion of one or more group 14 elements of the Periodic Table of Elements or any mixture thereof; and
 - 30 X^1 is a halide ion or any mixture thereof;
 - ii) mixing a metal halide having a formula $M(X^2)_z$ with an ammonium halide having a formula $(A^2)(X^2)$ in a solvent to form a capping material solution, wherein

A^2 is an ammonium cation having a structure of $R^2-NH_a^+$, wherein R^2 is an optionally substituted C_4 to C_{12} alkyl, an optionally substituted C_3 to C_{12} cycloalkyl, an optionally substituted arylalkyl, or any mixture thereof;

5 M is at least one ion of one or more group 2, group 3, group 7, group 8, group 9, group 10, group 11, group 12, group 13 or group 15 elements of the Periodic Table of Elements, or any mixture thereof;

X^2 is a halide ion or any mixture thereof;

a is 0 or an integer of 1, 2 or 3; and

z is 2 or 3; and

10 iii) applying the capping material solution onto the three-dimensional perovskite compound layer to form a capping material layer comprising a capping material selected from a compound having a general formula $(A^2)_2M(X^2)_4$, $(A^2)_2(A^1)M_2(X^2)_7$, $(A^2)_mM_n(X^2)_{3n+m}$ or any mixture thereof;

wherein m is an integer of 1, 2, 3, 4 or 5; and

15 n is an integer of 1 or 2.

20. The method according to claim 19, wherein:

the metal halide having the formula $M(X^2)_z$ is selected from the group consisting of $Pb(X^2)_2$, $Zn(X^2)_2$, $Sn(X^2)_2$, $Co(X^2)_2$, $Mn(X^2)_2$, $Cu(X^2)_2$, $Sb(X^2)_3$, $Bi(X^2)_3$, $Al(X^2)_3$ and any mixture thereof;

20 the ammonium halide having the formula $(A^2)(X^2)$ is selected from the group consisting of phenethylammonium halide (PEA(X^2)), n-butylammonium halide (BA(X^2)), isobutylammonium halide, phenylmethyl ammonium halide (PMA(X^2)), 1-naphthylmethylammonium halide (NMA(X^2)) and any mixture thereof; or

25 the solvent is selected from the group consisting of acetonitrile (ACN), acetone, dimethylformamide (DMF), dimethylsulfoxide (DMSO), methanol, t-butyl alcohol, ethanol, isopropyl alcohol, tetrahydrofuran, methylamine and any mixture thereof.

21. The method according to claim 19 or 20, wherein in the capping material solution, the metal halide having the formula $M(X^2)_z$ and ammonium halide having the formula $(A^2)(X^2)$ are present at a molar ratio in the range of about 1:1 to about 1:3.

30 22. The method according to any one of claims 19 to 21, wherein in the capping material solution, the concentration of the metal halide having the formula $M(X^2)_z$ in the solvent is in the range of about 5 mM to about 50 mM.

23. The method according to any one of claims 19 to 22, wherein the applying step comprises spin-coating, spray coating or slot-die coating the capping material solution onto the three-dimensional perovskite compound layer or dipping the three-dimensional perovskite compound layer in the capping material solution.
- 5 24. The method according to any one of claims 19 to 23, comprising the step of annealing the capping material layer onto the three-dimensional perovskite compound layer.
- 10 25. Use of the device according to any one of claims 1 to 17 in an optoelectronic device, photovoltaic cell, solar cell, light-emitting diode (LED), laser, photodetector, radiation detector, memristor, spintronic devices, phototransistor, transistor, light emitting transistor (LET) or field-effect transistor (FET).