(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 August 2016 (11.08.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/126211 A1

(51) International Patent Classification:
H01G 9/20 (2006.01) *C01G 15/00* (2006.01)
H01L 51/42 (2006.01) *C01G 17/04* (2006.01)
C01G 21/16 (2006.01) *C01G 19/04* (2006.01)
C01B 33/40 (2006.01) *C01G 51/08* (2006.01)
C01G 9/04 (2006.01) *C01G 53/08* (2006.01)

(21) International Application Number:
PCT/SG2016/050060

(22) International Filing Date:
4 February 2016 (04.02.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10201500940Q 6 February 2015 (06.02.2015) SG

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,

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(54) Title: GEL, METHOD OF FORMING THE SAME, PHOTOVOLTAIC DEVICE AND METHOD OF FORMING THE SAME

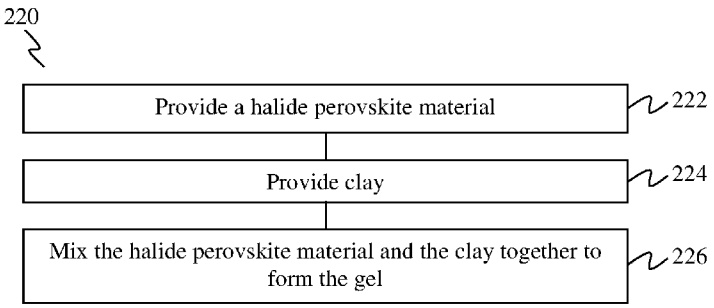


FIG. 2B

(57) Abstract: According to the embodiments of the present invention, a gel is provided. The gel has a composition including clay nanoparticles and a halide perovskite material of the general formula AMX_3, where A may be an organic or inorganic ion, M may be a metal cation or element, and X may be a halogen anion or element, such as methylammonium lead iodide ($CH_3NH_3PbI_2$). According to further embodiments of the present invention, a method of forming a gel, a photovoltaic device and a method of forming a photovoltaic device are also provided.

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LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

GEL, METHOD OF FORMING THE SAME, PHOTOVOLTAIC DEVICE AND METHOD OF FORMING THE SAME

Cross-Reference To Related Application

[0001] This application claims the benefit of priority of Singapore patent application No. 10201500940Q, filed 6 February 2015, the content of it being hereby incorporated by reference in its entirety for all purposes.

Technical Field

[0002] Various embodiments relate to a gel, a method of forming a gel, a photovoltaic device and a method of forming a photovoltaic device.

Background

[0003] Inorganic-organic lead halide perovskites have attracted enormous attention as a photovoltaic material due to their good electrical and optical properties as well as their solution processability. High power conversion efficiency (η) over 17% has been reported, which is comparable to that of commercialized solar cells made from silicon, copper indium gallium selenide (CIGS) or cadmium telluride (CdTe.).

[0004] Typically, the perovskite structure consists of a three-dimensional network of corner-corner connected MX_6 octahedra, where M (metal) cation is located at the centre of the octahedra and the X (Cl, Br, I) lies in the corners around M. The general formula for the inorganic-organic hybrid perovskite is AMX_3, where A may be an organic or inorganic ion, M may be a metal cation or element, and X may be a halogen anion or element. The perovskite acts as a sensitizer in perovskite based solar cell devices.

[0005] In general, an inorganic-organic heterojunction mesoscopic solar device is usually composed of a compact metal oxide layer as a hole blocking layer (bl.) (e.g., titanium dioxide, TiO_2), nanocrystalline metal dioxide as the photoanode (e.g., mesoporous TiO_2), an organometal halide perovskite as the light absorber (e.g., $CH_3NH_3PbI_2$), a p-type

material as hole transport material (HTM) (e.g., Spiro) and a noble metal film as the counter electrode(CE) (e.g., Au). An example of a perovskite sensitizer based solar cell device 180 is shown in FIG. 1. The solar cell device 180 includes a stack structure of a substrate (e.g., glass) 181, a layer of fluorine doped tin oxide (FTO) 182, a layer of titanium dioxide (TiO_2) 184 (e.g., as a hole blocking layer (bl)), a layer 186 of perovskite (e.g., $CH_3NH_3PbI_3$ or $CH_3NH_3PbI_{3-x}Cl_x$), a hole transport material (HTM) (not shown) and a noble metal film (e.g., Au) 188 as a counter electrode (CE). The device structure is FTO/bl/metal oxide layer/perovskite/HTM/ noble metal film.

[0006] As the fabrication technique, the perovskite layer is deposited either using a single-step or a two step deposition method. The single step deposition method involves direct spin coating of the perovskite sensitizer on the mesoporous metal oxide layer (e.g., TiO_2). The two-step process involves spin coating of the metal halide layer (e.g., lead(II) iodide, PbI_2), the infiltration of the TiO_2 mesoporous layer with PbI_2, and subsequent dipping into CH_3NH_3I (methylammonium iodide), which leads to the in-situ conversion to $CH_3NH_3PbI_3$ (methylammonium lead iodide).

[0007] However, there are main obstacles for large area production. Thus far, the demonstrated high efficiency perovskite solar cells have been fabricated on a smaller scale (up to 0.2 cm^2), employing the above mentioned processes. The spin coating process is a very popular technique deployed in research and development (R&D). However, the spin coating process reaches its limits when material usage and coating of large areas are taken into consideration.The rapid progress in the area has resulted in it being the most efficient solution processed solar cells to date. In order to scale up the perovskite based solar cell technology, large scale manufacturing processes such as printing need to be developed and employed.

Summary

[0008] According to an embodiment, a gel is provided. The gel may have a composition including a halide perovskite material and clay.

[0009] According to an embodiment, a method of forming a gel is provided. The method may include providing a halide perovskite material, providing clay, and mixing the halide perovskite material and the clay together to form the gel.

[0010] According to an embodiment, a photovoltaic device is provided. The photovoltaic device may include a substrate, and a perovskite layer on the substrate, wherein the perovskite layer is made of the gel as described herein, the gel having been heat treated to form the perovskite layer.

[0011] According to an embodiment, a method of forming a photovoltaic device is provided. The method may include applying a gel as described herein on a substrate, and performing a heat treatment on the gel to form a perovskite layer on the substrate.

Brief Description of the Drawings

[0012] In the drawings, like reference characters generally refer to like parts throughout the different views. The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the following description, various embodiments of the invention are described with reference to the following drawings, in which:

[0013] FIG. 1 shows the structure of a perovskite sensitizer based solar cell device.

[0014] FIG. 2A shows a schematic top view of a gel, according to various embodiments.

[0015] FIG. 2B shows a flow chart illustrating a method of forming a gel, according to various embodiments.

[0016] FIG. 2C shows a schematic cross sectional view of a photovoltaic device, according to various embodiments.

[0017] FIG. 2D shows a flow chart illustrating a method of forming a photovoltaic device, according to various embodiments.

[0018] FIG. 3A shows a method of forming a perovskite precursor solution, according to various embodiments.

[0019] FIG. 3B shows a method of forming a perovskite gel, according to various embodiments.

[0020] FIGS. 4A and 4B illustrate structures of cationic and anionic clays respectively.

[0021] FIG. 5A shows a photograph of an inverted sample bottle containing a perovskite gel of various embodiments.

[0022] FIGS. 5B and 5C show images of a perovskite film coated on a glass substrate using the perovskite gel precursor of various embodiments before and after sintering respectively.

[0023] FIGS. 6A and 6B show respective plots of representative current density-voltage (J-V) and incident photon to current conversion (IPCE) characteristic curves of the solar cell device of various embodiments.

[0024] FIG. 7 shows a cross sectional field emission scanning electron microscope (FESEM) image of a perovskite device fabricated using the perovskite gel of various embodiments.

[0025] FIG. 8 shows a method for perovskite gel formation using various metal oxide nanoparticles.

Detailed Description

[0026] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0027] Embodiments described in the context of one of the methods or devices are analogously valid for the other methods or devices. Similarly, embodiments described in the context of a method are analogously valid for a device, and vice versa.

[0028] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments.

Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0029] In the context of various embodiments, the articles "a", "an" and "the" as used with regard to a feature or element include a reference to one or more of the features or elements.

[0030] In the context of various embodiments, the phrase "at least substantially" may include "exactly" and a reasonable variance.

[0031] In the context of various embodiments, the term "about" or "approximately" as applied to a numeric value encompasses the exact value and a reasonable variance.

[0032] As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

[0033] Various embodiments may relate to processable perovskite gel formulation for large area processes (e.g., screen printing/coating) in photovoltaic devices, for example, various embodiments may provide a processable perovskite gel formulation for large area printable photovoltaics.

[0034] Various embodiments may provide one or more of the following: (i) a composite perovskite gel as a material for printable perovskite photovoltaic devices; (ii) perovskite gel formation with nanoclay particles (particle size <50nm) precursors; (iii) a low temperature perovskite gel formation method; (iv) screen printable/coatable perovskite formulation using nanoclays; or (v) application of nanoclay based perovskite gels in photovoltaic.

[0035] FIG. 2A shows a schematic top view of a gel 200, according to various embodiments. The gel 200 has a composition including a halide perovskite material 202 and clay 204.

[0036] In other words, a gel 200 may be provided. The gel 200 may be made of a halide perovskite material 202 and clay 204, for example, the gel 200 may include a mixture of the halide perovskite material 202 and clay 204. This may mean that the gel 200 may be a perovskite gel or a composite perovskite gel.

[0037] The clay 204 may include clay nanoparticles 204a having a size (e.g., diameter)of less than 50nm (i.e., < 50 nm), for example, < 40 nm, < 30 nm, < 20 nm, < 10 nm, e.g., a

size that is more than 1 nm and less than 50 nm, e.g., between about 1 nm and about 45 nm, between about 1 nm and about 30 nm, between about 1 nm and about 20 nm, between about 1 nm and about 10 nm, between about 1 nm and about 5 nm, between about 10 nm and about 45 nm, or between about 20 nm and about 45 nm. This may mean that each clay nanoparticle 204a may have a size (e.g., diameter) of less than 50 nm. Therefore, the gel 200 may be a nanoclay based perovskite gel.

[0038] In various embodiments, a weight of the clay 204 may be between about 1% and about 3% of a weight of the halide perovskite material 202, for example, between about 1% and about 2%, or between about 2% and about 3%. This may mean that the weight ratio of the halide perovskite material 202 to the clay 204 may be between about 100:1 and about 100:3.

[0039] In various embodiments, the halide perovskite material 202 may be in the form of a halide perovskite precursor solution, with the clay 204 added into the halide perovskite precursor solution.

[0040] In various embodiments, the gel 200 may include a solvent. The solvent may include but not limited to dimethylformamide (DMF), dimethyl sulfoxide (DMSO), γ-Bulyrolacton (GBL), acetonitrile, etc., or a mixture of solvents in various volume (ml) proportions, e.g., DMF:DMSO : 0.9:0.1, 0.8:0.2, 0.7:0.3, 0.6:0.4, 0.5:0.5 and vice versa.

[0041] In various embodiments, the clay 204 may include or may be cationic clay or anionic clay. The cationic clay may include smectite (montmorillonite), vermiculite, illite, kaolinite, etc. The hydrotalcite-based anionic clay may include anions such asNO_3^-, Cl^-, Br^-, I^-, SO_4^{2-}, CO_3^{2-}, etc.

[0042] In various embodiments, the halide perovskite material 202 may include an organic cation. The organic cation may include an organic ammonium cation. As non-limiting examples, the organic cation may include $CH_3NH_3^+$, $C_2H_5NH^{3+}$, $CH(NH_2)_3$, $C(NH_3)_3$, Cs, RNH_3, where R= $(CH_3(CH_2)n)$, where n= 1, 2, 3, 4, etc., or mixed cations in different stoichiometric ratios. However, it should be appreciated that other organic cations may also be employed.

[0043] In various embodiments, the halide perovskite material 202 may include a metal cation. The metal cation may correspond to a metal selected from the group consisting of

lead (Pb), tin (Sn), cobalt (Co), nickel (Ni), zinc (Zn), gallium (Ga), and germanium (Ge). However, it should be appreciated that other metal cations may also be employed.

[0044] In various embodiments, thehalide perovskite material 202 may include one or more halide anions selected from the group consisting of F^- (fluoride), I^- (iodide), Cl^- (chloride) and Br^-(bromide). This may mean that the halide perovskite material 202 may include one or more halogen elements selected from the group consisting of F, I, Cl and Br.

[0045] In various embodiments, the halide perovskite material 202 may be represented by the general formula AMX_3, where "A" represents an organic cation, "M" represents a metal and "X" represents a halide or halide mixture.

[0046] In the context of various embodiments, the gel 200 may provide a precursor (perovskite) material or composition for manufacturing, for example, a photovoltaic device.

[0047] In the context of various embodiments, the gel 200 may be employed for large area printable photovoltaic devices, for example, the gel 200 may be a processable perovskite gel formulation for large area processes (e.g., screen printing/coating) for photovoltaic devices.

[0048] FIG. 2B shows a flow chart 220 illustrating a method of forming a gel (e.g., 200, FIG. 2A), according to various embodiments.

[0049] At 222, a halide perovskite material is provided.

[0050] At 224, clay is provided. For example, the clay provided may be in the form of clay powder.

[0051] At 226, the halide perovskite material and the clay are mixed together to form the gel.

[0052] In various embodiments, at 224, clay including clay nanoparticles having a size of less than 50 nm (i.e., < 50 nm) may be provided. For example, the clay provided may be in the form of a clay nanoparticle powder (or nanoclay powder).

[0053] In various embodiments, the halide perovskite material and the clay may be provided such that a weight of the clay may be between about 1% and about 3% of a weight of the halide perovskite material.

[0054] In various embodiments, at 222, one or more precursor materials of the halide perovskite material may be mixed in a solvent to form the halide perovskite material. In this way, the halide perovskite material may be a halide perovskite (precursor) solution. Subsequently, at 226, clay may be added into the halide perovskite solution for mixing with the halide perovskite material to form the gel.

[0055] The one or more precursor materials may include a metal halide, e.g., lead iodide (PbI_2), lead bromide ($PbBr_2$), lead chloride ($PbCl_2$), one or more tin halides (e.g., SnI_2, $SnBr_2$, $SnCl_2$), one or more germanium halides (e.g., GeI_2, $GeBr_2$, $GeCl_2$) etc., and an organic or inorganic halide, e.g., methyl ammonium iodide/bromide/chloride (CH_3NH_3I, CH_3NH_3Br, CH_3NH_3Cl), formamidinium iodide/bromide/chloride ($CH(NH_2)_2I$, $CH(NH_2)_2Br$, $CH(NH_2)_2Cl$), cesium iodide/bromide/chloride (CsI, CsBr, CsCl), guanidinium iodide/bromide/chloride ($C(NH_2)_3I$, $C(NH_2)_3Br$, $C(NH_2)_3Cl$), etc. The one or more precursor materials may be provided in the form of powder.

[0056] The solvent may include but not limited to dimethylformamide (DMF), dimethyl sulfoxide (DMSO), γ-Bulyrolacton (GBL), acetonitrile, etc., or a mixture of solvents in various volume (ml) proportion, e.g., DMF:DMSO : 0.9:0.1, 0.8:0.2, 0.7:0.3, 0.6:0.4 0.5:0.5 and vice versa.

[0057] In various embodiments, at 226, the one or more precursor materials may be stirred in the solvent to mix the one or more precursor materials in the solvent.

[0058] In various embodiments, the mixture of the one or more precursor materials and the solvent may be subjected to a heating process.

[0059] The heating process may be carried out at a predetermined temperature between about 40°C and about 120°C, for example, between about 40°C and about 100°C, between about 40°C and about 70°C, between about 70°C and about 120°C, or between about 60°C and about 100°C. As a non-limiting example, the heating process may be carried out at about 70°C - 100 °C.

[0060] The heating process may be carried out for a predetermined duration between about 0.5 hr and about 24hrs, for example, between about 0.5 hour and about 18hours, between about 0.5 hour and about 12 hours, between about 0.5 hour and about 2 hours, between about 2 hours and about 24 hours, between about 12 hours and about 24 hours,

or between about 2 hours and about 12 hours. As a non-limiting example, the heating process may be carried out for about 12 hours.

[0061] In various embodiments, at 226, the halide perovskite material and the clay may be subjected to a sonication process to mix the halide perovskite material and the clay. The sonication process may be carried out for a predetermined duration between about 0.5 hr and about 12 hrs, for example, between about 0.5 hour and about 8 hours, between about 0.5 hour and about 4 hours, between about 0.5 hour and about 1 hour, between about 1 hour and about 4 hours, or between about 1 hour and about 2 hours. As a non-limiting example, the sonication process may be carried out for about 1 hour. The sonication process may be carried out at room temperature.

[0062] In various embodiments, at 226, the halide perovskite material and the clay may be stirred prior to the sonication process. The stirring process may be carried out for a predetermined duration between about 0.5 hr and about 24 hrs, for example, between about 0.5 hour and about 18 hours, between about 0.5 hour and about 12 hours, between about 0.5 hour and about 2 hours, between about 2 hours and about 24 hours, between about 12 hours and about 24 hours, or between about 2 hours and about 12 hours. As a non-limiting example, the stirring process may be carried out for about 1 hour. The stirring process may be carried out at room temperature.

[0063] In various embodiments, at 224, a cationic clay or anionic clay may be provided.

[0064] In various embodiments, the halide perovskite material may include an organic cation. The organic cation may include an organic ammonium cation. As non-limiting examples, the organic cation may include $CH_3NH_3^+$, $C_2H_5NH^{3+}$. $CH(NH_2)_3$, $C(NH_3)_3$, Cs, RNH_3, where R= $(CH_3(CH_2)n)$, where n= 1, 2, 3, 4, etc., or mixed cations in different stoichiometric ratios. However, it should be appreciated that other organic cations may also be employed.

[0065] In various embodiments, the halide perovskite material may include a metal cation. The metal cation may correspond to a metal selected from the group consisting of lead (Pb), tin (Sn), cobalt (Co), nickel (Ni), zinc (Zn), gallium (Ga), and germanium (Ge). However, it should be appreciated that other metal cations may also be employed.

[0066] In various embodiments, thehalide perovskite material may include one or more halide anions selected from the group consisting of F^- (fluoride), I^- (iodide), Cl^-(chloride) and Br^-(bromide).

[0067] In various embodiments, the halide perovskite material may represented by the general formula AMX_3, where "A" represents an organic cation, "M" represents a metal and "X" represents a halide or halide mixture.

[0068] FIG. 2C shows a schematic cross sectional view of a photovoltaic device 230, according to various embodiments. The photovoltaic device 230 includes a substrate 232, and a perovskite layer 234 on the substrate 232, wherein the perovskite layer 234 is made of the gel as described herein (e.g., 200, FIG. 2A), the gel having been heat treated to form the perovskite layer 234.

[0069] In other words, a photovoltaic device (e.g., a solar cell) 230 may be provided. The photovoltaic device 230 may include a substrate (or carrier) 230 and a gel (e.g., 200, FIG. 2A) that may be applied on the substrate 232 and which has undergone a heat treatment to form the perovskite layer 234 on the substrate 232. In this way, the perovskite layer 234 may have a composition at least substantially similar to that of the gel. The gel may be applied on the substrate 232 by printing or coating.

[0070] In various embodiments, the perovskite layer 234 may act as a light absorber.

[0071] In various embodiments, the heat treatment may be carried out at a predetermined temperature between about 40°C and about 120°C, for example, between about 40°C and about 100°C, between about 40°C and about 70°C, between about 70°C and about 120°C, or between about 60°C and about 100°C. As a non-limiting example, the heat treatment may be carried out at about 70°C.

[0072] In various embodiments, the heat treatment may be carried out for a predetermined duration between about 0.1hr and about 24hrs,between about 0.1hour and about 10 hours, between about 0.1 hour and about 5 hours, between about 0.1 hour and about 1 hour, between about 0.1 hour and about 0.5 hour, between about 0.5hour and about 10 hours, between about 0.5 hour and about 1 hour, or between about 10 hours and about 24 hours. As a non-limiting example, the heat treatment may be carried out for about 30 minutes (0.5 hour).

[0073] In various embodiments, the heat treatment may include a sintering process.

[0074] In the context of various embodiments, the substrate 232 may include a glass substrate.

[0075] In various embodiments, a thickness of the perovskite layer 234 may be between about 100 nm and about 2 μm (2000 nm), for example, between about 100 nm and about 1000 nm, between about 100 nm and about 500 nm, between about 100 nm and about 200 nm, between about 500 nm and about 2000 nm, between about 1000 nm and about 2000 nm, or between about 500 nm and about 1000 nm.

[0076] The photovoltaic device 230 may include a pair of electrodes, where the perovskite layer 234 may be sandwiched between the pair of electrodes.

[0077] The photovoltaic device 230 may include one or more other layers, for example, a metal oxide layer as a hole blocking layer, a hole transport material, etc. The one or more other layers may be sandwiched between the pair of electrodes.

[0078] In various embodiments, the perovskite layer 234 may include mesoporous titanium oxide (TiO_2). As a non-limiting example, mesoporous TiO_2 may be infiltrated or penetrated with the gel, and then heat treated to form the perovskite layer 234 with the mesoporous TiO_2.

[0079] In the context of various embodiments, the photovoltaic device 230 may be a perovskite photovoltaic device or a perovskite solar module.

[0080] FIG. 2D shows a flow chart 240 illustrating a method of forming a photovoltaic device, according to various embodiments.

[0081] At 242, a gel as described herein is applied on a substrate. The substrate may be, for example, a glass substrate.

[0082] At 244, a heat treatment is performed on the gel to form a perovskite layer on the substrate. In this way, the perovskite layer may be made of the gel, and may have a composition at least substantially similar to that of the gel.

[0083] In various embodiments, at 242, the gel may be applied on a substrate by printing (e.g., screen printing) the gel on the substrate. However, it should be appreciated that other processes may also be used to apply the gel to the substrate, for example, by coating.

[0084] In various embodiments, the heat treatment may be carried out at a predetermined temperature between about 40°C and about 120°C, for example, between about 40°C and

about 100°C, between about 40°C and about 70°C, between about 70°C and about 120°C, or between about 60°C and about 100°C. As a non-limiting example, the heat treatment may be carried out at about 70°C.

[0085] In various embodiments, the heat treatment may be carried out for a predetermined duration between about 0.1hr and about 24 hrs, between about 0.1 hour and about 10 hours, between about 0.1 hour and about 5 hours, between about 0.1 hour and about 1 hour, between about 0.1 hour and about 0.5 hour, between about 0.5hour and about 10 hours, between about 0.5 hour and about 1 hour, or between about 10 hours and about 24 hours. As a non-limiting example, the heat treatment may be carried out for about 30 minutes (0.5 hour).

[0086] In various embodiments, at 244, the heat treatment may include a sintering process.

[0087] While the methods described above are illustrated and described as a series of steps or events, it will be appreciated that any ordering of such steps or events are not to be interpreted in a limiting sense. For example, some steps may occur in different orders and/or concurrently with other steps or events apart from those illustrated and/or described herein. In addition, not all illustrated steps may be required to implement one or more aspects or embodiments described herein. Also, one or more of the steps depicted herein may be carried out in one or more separate acts and/or phases.

[0088] It should be appreciated that descriptions in the context of the gel 200and the photovoltaic device 230 may be correspondingly applicable to each other, and may also be correspondingly applicable in relation to the method of forming a gel and the method of forming a photovoltaic device, and vice versa.

[0089] Various embodiments may employ clay nanoparticles powder with a suitable size, e.g., less than 50nm (< 50 nm) to form perovskite gels.

[0090] In general, in various embodiments, gel formation may be carried out by mixing clay powder with a halide perovskite precursor (solution) in dimethylformamide (DMF). The clay to perovskite ratio may be fixed to about 1 - 3 % (e.g., weight%, or weight ratio), for example, about 10-30 mg of clay per ml (~1 g) of perosvkite (precursor) solution. The mixture of clay and perovskite may be stirred for approximately 1 hour, followed by sonication for approximately 1 hour to form the desired perovskite gel with

controlled viscosity. The specific double layer structure of the clay along with the appropriate size (e.g., less than about 50 nm) may favour the gel formation.

[0091] As non-limiting examples of gel formation, FIG. 3A shows a method 350a of forming a (halide) perovskite precursor solution and FIG. 3B shows a method 350b of forming a (halide) perovskite gel, illustrating perovskite + clay nanoparticles gel formation.

[0092] Referring to FIG. 3A, in order to form a perovskite precursor solution ($MAPbX_3$), perovskite precursor powder, for example, lead iodide, PBI_2 352 (weight about 461mg) and methyl ammonium iodide, CH_3NH_3I354 (weight about 158mg) may be mixed together in approximately 1 ml dimethylformaide (DMF) solvent 356, for example in a bottle 359. The solution or mixture of PBI_2 352, CH_3NH_3I354 and DMF 356 may be stirred at about 70°C for about 12 hours. As a result, a perovskite precursor solution 358 may be obtained.

[0093] Referring to FIG. 3B, using the prepared perovskite precursor solution 358, approximately 1 ml of perovskite precursor solution 358b in DMF may be prepared in a sample bottle 359b. About 3 wt% (e.g. 30 mg) of clay powder 360 (particle size < 50 nm) may be added into the perovskite precursor solution 358b. Subsequently, the solution or mixture of perovskite precursor solution 358b and clay powder 360 may be stirred for about 1 hour at room temperature, followed by sonication for about 1 hour at room temperature to form a homogenous halide perovskite gel 362a in the sample bottle 359b, as shown in the image 364a. The perovskite gel formation may be tested by inverting the sample bottle 359, and testing whether the gel 362a stays atop, as may be observed in the image 364b.

[0094] As described above, the gel 362a composition may include about 1ml perovskite solution (~42 %) in DMF + 3% (e.g., 30 mg) of clay nanoparticle powder (particle size < 50nm).

[0095] In various embodiments, gel formation is plausible using the clay nanoparticles and halide based perovskite precursors, as decribed herein. In general perovskite formula of $MAPbX_3$, MA = an organic cation such as $CH_3NH_3^+$, $C_2H_5NH^{3+}$, etc, and X = halide or halide mixture. In various embodiments, Pb (lead) may be replaced by a metal such as tin (Sn), cobalt (Co), nickel (Ni), zinc (Zn), gallium (Ga), etc.

[0096] Clay is a natural material with a layered structure, which is mainly composed of layered silicates. For example, clay may include tetrahedrally and octahedrally organised layered structures.

[0097] Referring to FIG. 4A showing the structure of a cationic clay, cations that may be entrapped between clay layers, such as Li^+(lithium ion), Na^+ (sodium ion), Ca^+ (calcium ion), Mg^+ (magnesium ion), Ba^+ (barium ion), La^+(lanthanum ion), Ce^+(cerium ion),Ru^+ (rubidium ion),etc., may be easily replaced with other cations.These other cations that may replace the entrapped cations may depend on the charge, size and affinity of the entrapped cations.

[0098] Similarly, referring to FIG. 4B showing the structure of an anionicclay, in anion exchangeable clay (e.g., hydrotalcite), anions may be entrapped between clay layers, such as CO_3^{2-} (carbonateion), NO_3^{2-} (trioxidonitrate(.2-)), I_3^- (triiodide ion), etc, where these charge-balancing anions may be easily exchanged with various anions (see FIG. 4B). The replacement of existing anionsin the anionic clay may be possible based on the charge, size and affinity of the entrapped anions.

[0099] These two types of clay (i.e., cationic and anionic clays) may be employed as a gel forming agent with the perovskite precursor. Clay with specific sizes, e.g., less than 50 nm is suitable for gel formation.

[0100] FIG. 5A shows a photograph of an inverted sample bottle 559 containing a perovskite gel 562. As may be observed, the perovskite (precursor) gel 562 staying or remaining at the top of the inverted sample bottle 559 confirms gel formation.

[0101] FIGS. 5B and 5C show images of a perovskite film 566a, 566b coated on a glass substrate using the perovskite gel precursor (e.g., 362a, FIG. 3B; 562, FIG. 5A) of various embodiments before and after sintering at about 70°C for approximately 30 minutes respectively.

[0102] In various embodiments, after forming the gel, the gel may be applied, for example, onto a substrate for making a device. After being applied, the gel may be sintered at about 70°C for about 30 minutes in order to make or obtain a crystalline film from the gel. The time and temperature for the sintering process may be varied, for example, between about 10 minutes and about 2 hours and between about 40°C and about 120°C.

[0103] Solar cell devices (or photovoltaic devices) may be fabricated using the perovskite gel coated films, where after being applied onto the devices, the films may be subsequently sintered at about70°C for about 30 minutes. The time and temperature for the sintering process may be varied, for example, 10 minutes - 2 hours and 40°C - 120°C. FIGS. 6A and 6B show respective plots 670, 678 of representative current density-voltage (J-V) and incident photon to current conversion (IPCE) characteristic curves of the solar cell device of various embodiments, illustrating the characteristic J-V curves (plot 670) of the perovskite devices fabricated using the perovskite gel of various embodiments and the corresponding IPCE (plot 678) under 1 sun illumination. The J-V curves in plot 670 were obtained under standard solar full sun test conditions (e.g., 1000 W/m^2, AM 1.5) (curve 672) and dark conditions (curve 674).

[0104] The obtained J-V performance parameters are shown in Table 1. As may be seen, the photovoltaic device based on the gel coated films of various embodiments may achieve conversion efficiencies up to approximately 9%.

Table 1:J-V characteristic parameters of the photovoltaic devices fabricated using the perovskite gel

Sr. No.	Jsc (mA/cm^2)	Voc (mV)	FF (%)	Efficiency (%)
1	15.8	890	66.2	9.09
2	16.6	867	58.1	8.34
3	15.7	912	64.4	8.96

where Jsc refers to the short-circuit current density, Voc refers to the open-circuit voltage and FF refers to fill factor.

[0105] FIG. 7 shows a cross sectional field emission scanning electron microscope (FESEM) image of a (gel) perovskite device fabricated using the perovskite gel of various embodiments. The perovskite device includes a structure having a layer 780 of perovskite gel and TiO_2 (e.g., mesoporous TiO_2) (the gel having been sintered at about 70°C for about 30 minutes) sandwiched between a layer 782 of spiro and a layer 784 of fluorine doped tin oxide (FTO). The perovskite gel layer thickness may vary depending on the amount of the gel precursor used in the fabrication step. The device performance

may depend on the thickness of the perovskite gel layer, where a thinner film thickness offers a better performance.

[0106] Various metal oxide nanoparticle powders such as aluminium oxide (Al_2O_3), titanium oxide (TiO_2), and tin oxide (SnO_2), etc. were employed in a method to form aperovskite gel. FIG. 8 shows a method 890 for perovskite gel formation using various metal oxide nanoparticles (e.g., Al_2O_3, TiO_2, SnO_2). For example, metal oxide nanoparticle powder 894 may be mixed with a perovskite precursor (e.g., $MAPbX_3$, X= Cl, Br and I) in DMF (solution 892, for example prepared according to FIG. 3A) in different weight amounts (or weight ratios) (e.g., 10mg of metal oxide powder 894 /1g of perovskite precursor solution 892 (equivalent to 1% weight ratio), 20mg/1g (2% weight ratio), 30mg/1g (2% weight ratio), etc), followed by sonication for about 1 hr to form gel. However, it was found that metal oxide nanoparticle powders were not well mixed with the perovskite precursors. As may be observed in FIG. 8, the separation of the perovskite precursor (top layer 896 in the bottle 893) and the metal oxide nanoparticle powder (bottom layer 897) may be clearly seen. Therefore, metal oxide nanoparticles are not a suitable candidate to form a gel with the perovskite precursor.

[0107] Various embodiments may provide an immense advantage in commercialization of perovskite solar modules. Various embodiments may ease the large scale manufacturing process for deposition of perovskite layer, which is a critical fabrication step in this type of solar cells.

[0108] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A gel having a composition comprising a halide perovskite material and clay.

2. The gel as claimed in claim 1, wherein the clay comprises clay nanoparticles having a size of less than 50 nm.

3. The gel as claimed in claim 1, wherein a weight of the clay is between about 1% and about 3% of a weight of the halide perovskite material.

4. The gel as claimed in claim 1, wherein the gel comprises a solvent.

5. The gel as claimed in claim 1, wherein the clay comprises cationic clay or anionic clay.

6. The gel as claimed in claim 1, wherein the halide perovskite material comprises an organic cation.

7. The gel as claimed in claim 1, wherein the halide perovskite material comprises one or more halide anions selected from the group consisting of F^-, I^-, Cl^- and Br^-.

8. A method of forming a gel comprising:
providing a halide perovskite material;
providing clay; and
mixing the halide perovskite material and the clay together to form the gel.

9. The method as claimed in claim 8, wherein providing clay comprises providing clay including clay nanoparticles having a size of less than 50 nm.

10. The method as claimed in claim 8, wherein a weight of the clay is between about 1% and about 3% of a weight of the halide perovskite material.

11. The method as claimed in claim 8, wherein providing a halide perovskite material comprises mixing one or more precursor materials of the halide perovskite material in a solvent to form the halide perovskite material.

12. The method as claimed in claim 11, further comprising subjecting the mixture of the one or more precursor materials and the solvent to a heating process.

13. The method as claimed in claim 8, wherein mixing the halide perovskite material and the clay comprises subjecting the halide perovskite material and the clay to a sonication process.

14. The method as claimed in claim 13, wherein mixing the halide perovskite material and the clay further comprises stirring the halide perovskite material and the clay prior to the sonication process.

15. The method as claimed in claim 8, wherein providing clay comprises providing a cationic clay or an anionic clay.

16. The method as claimed in claim 8, wherein the halide perovskite material comprises an organic cation.

17. The method as claimed in claim 8, wherein the halide perovskite material comprises one or more halide anions selected from the group consisting of F^-, I^-, Cl^- and Br^-.

18. A photovoltaic device comprising:

a substrate; and

a perovskite layer on the substrate, wherein the perovskite layer is made of the gel as claimed in claim 1, the gel having been heat treated to form the perovskite layer.

19. A method of forming a photovoltaic device, the method comprising:
applying a gel as claimed in claim 1 on a substrate; and
performing a heat treatment on the gel to form a perovskite layer on the substrate.

20. The method as claimed in claim 19, wherein applying a gel comprises printing the gel on the substrate.

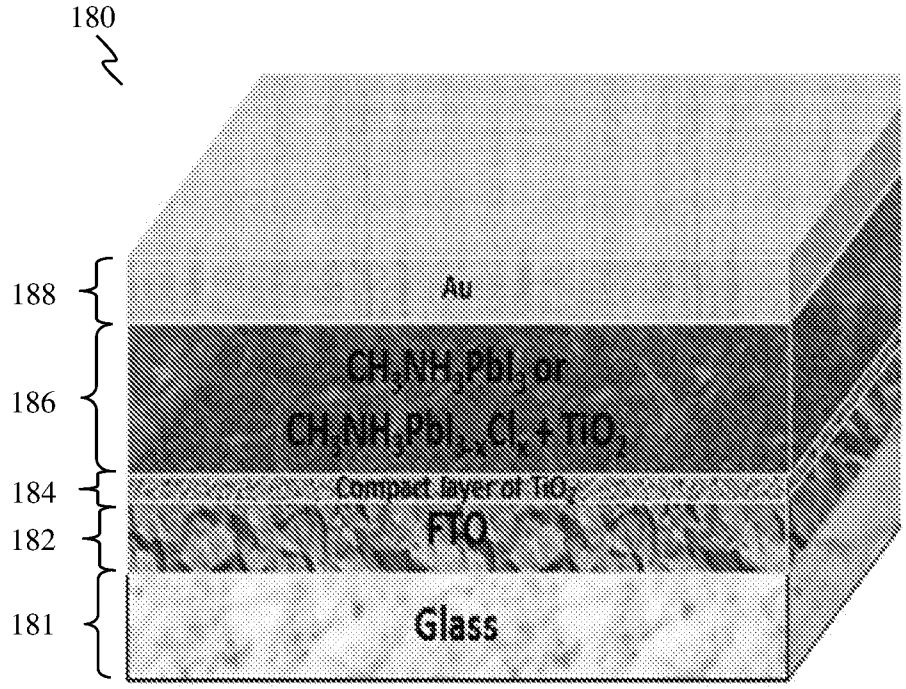

180
188
186
184
182
181
Au
$CH_3NH_3PbI_3$ or
$CH_3NH_3PbI_{3-x}Cl_x + TiO_2$
Compact layer of TiO_2
FTO
Glass

FIG. 1

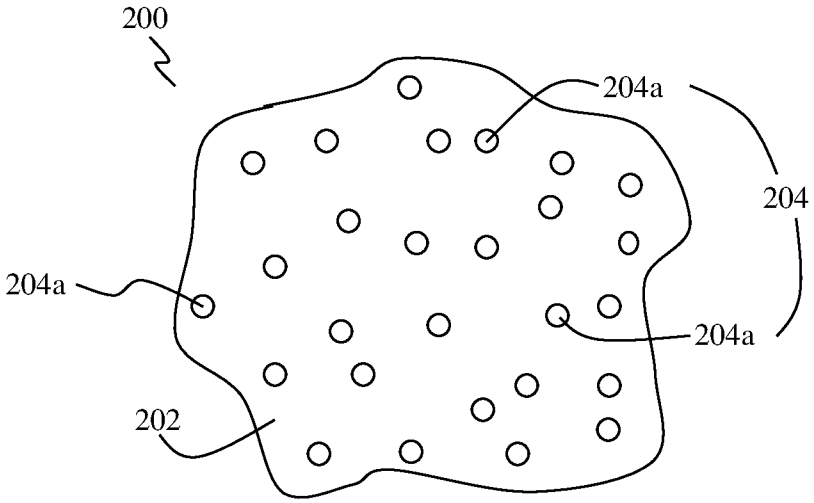

200
204a
204
204a
204a
202

FIG. 2A

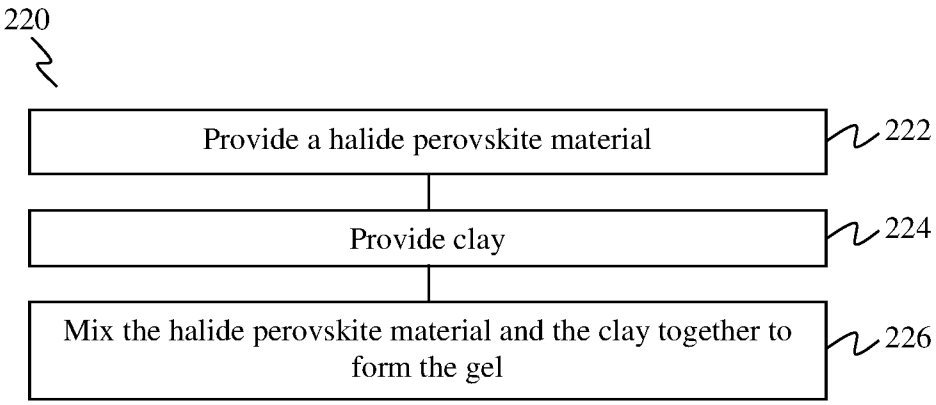

220
Provide a halide perovskite material
222
Provide clay
224
Mix the halide perovskite material and the clay together to form the gel
226

FIG. 2B

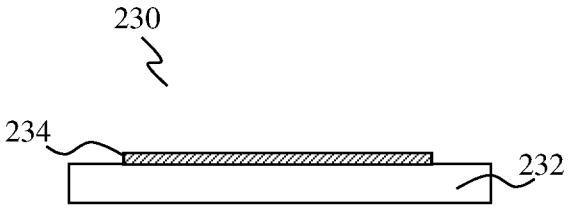

230
234
232

FIG. 2C

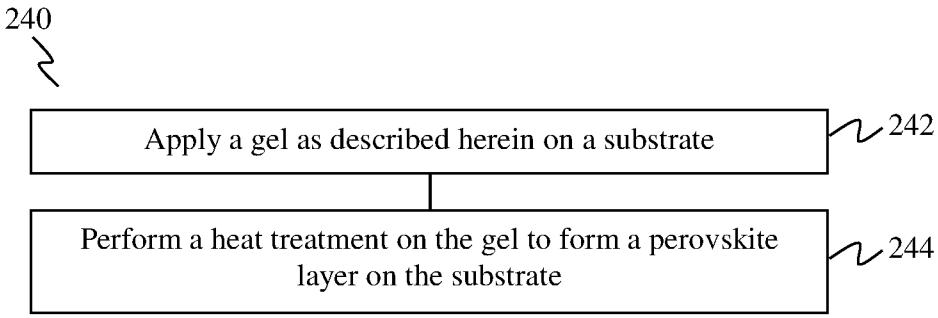

240
Apply a gel as described herein on a substrate
242
Perform a heat treatment on the gel to form a perovskite layer on the substrate
244

FIG. 2D

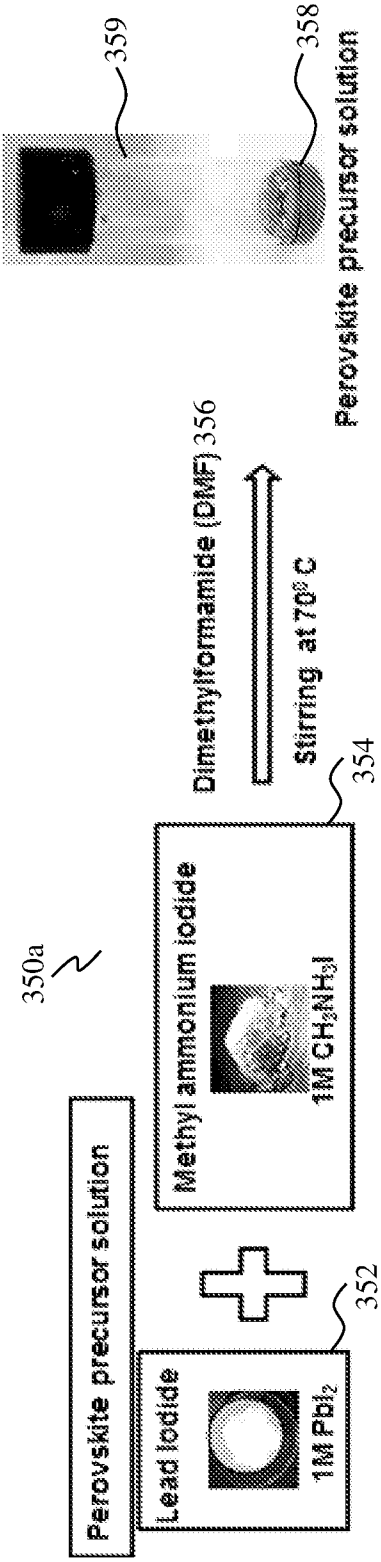

350a
Perovskite precursor solution
Lead Iodide
1M PbI_2
352
Methyl ammonium iodide
1M CH_3NH_3I
354
Dimethylformamide (DMF) 356
Stirring at 70° C
Perovskite precursor solution
358
359

FIG. 3A

350b
Perovskite gel formulation using clay nanoparticles
359b
358b
Perovskite precursor solution
1 ml
Nanoclay powder
3% (30mg)
360
Stirring and sonication
for 1hr
Room temperature
364a
359b
362a
Gel formation
364b
362a
359b

FIG. 3B

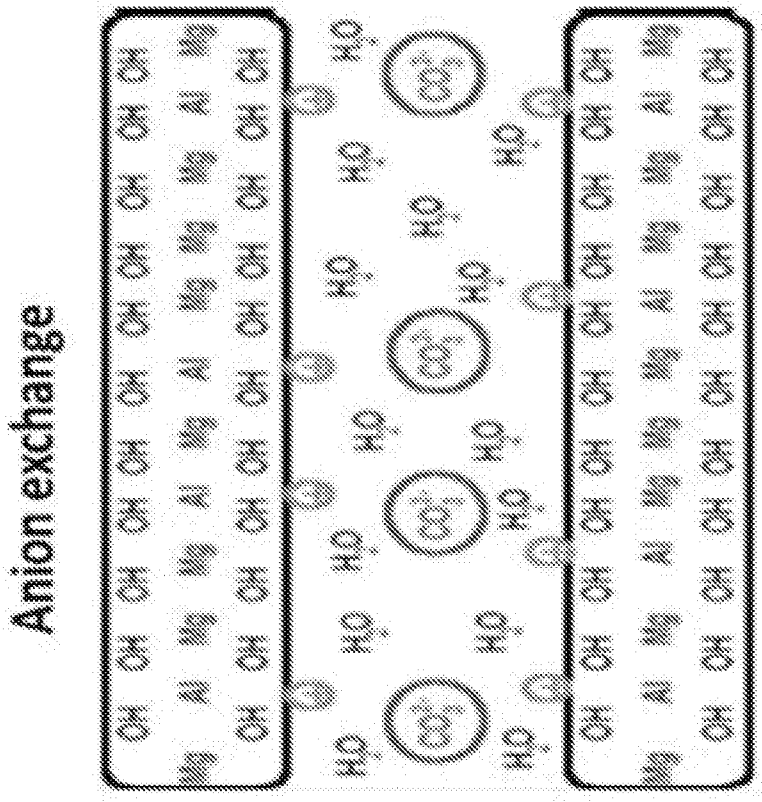

Anion exchange

FIG. 4B

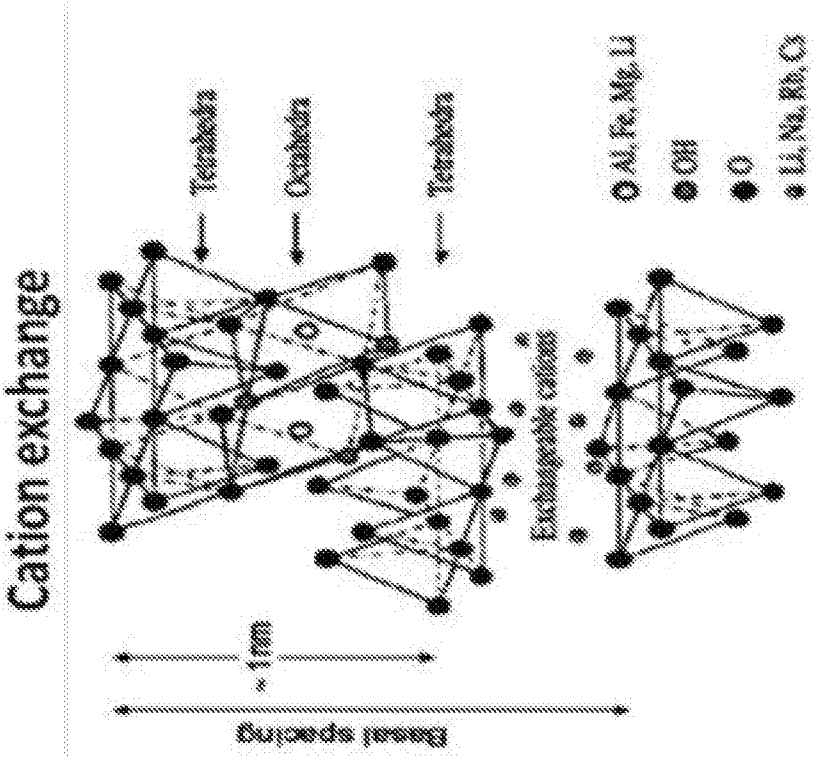

Cation exchange
Tetrahedra
Octahedra
Tetrahedra
Exchangeable cations
Basal spacing
~1nm
Al, Fe, Mg, Li
OH
O
Li, Na, Rb, Cs

FIG. 4A

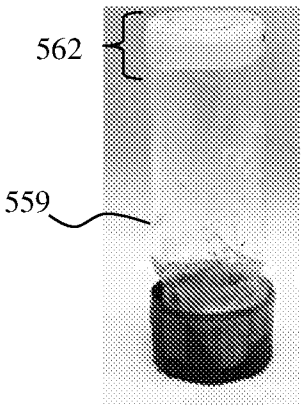


FIG. 5A

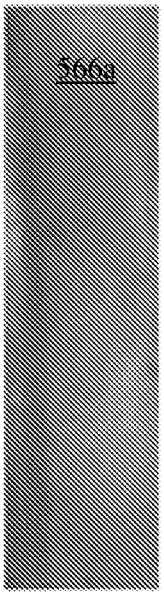


FIG. 5B

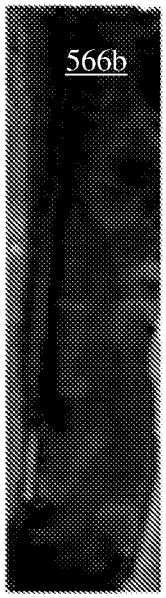


FIG. 5C

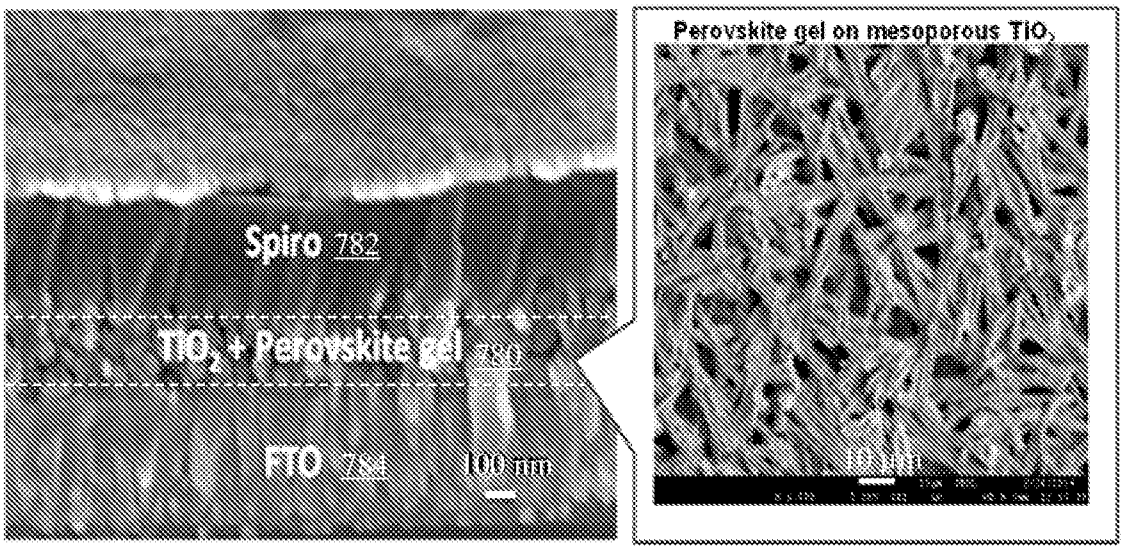


FIG. 7

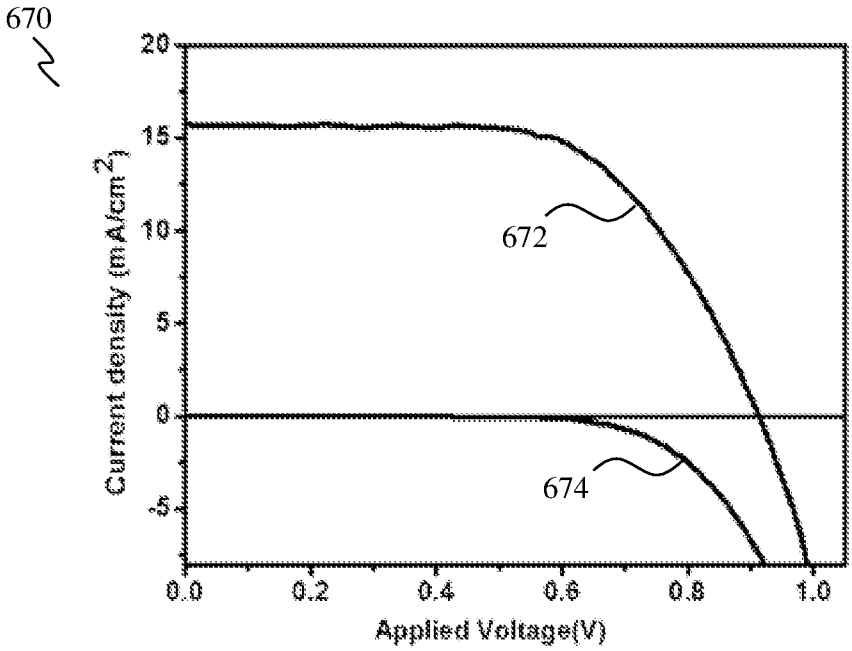

670
20
15
10
5
0
-5
Current density (mA/cm^2)
672
674
0.0
0.2
0.4
0.6
0.8
1.0
Applied Voltage(V)

FIG. 6A

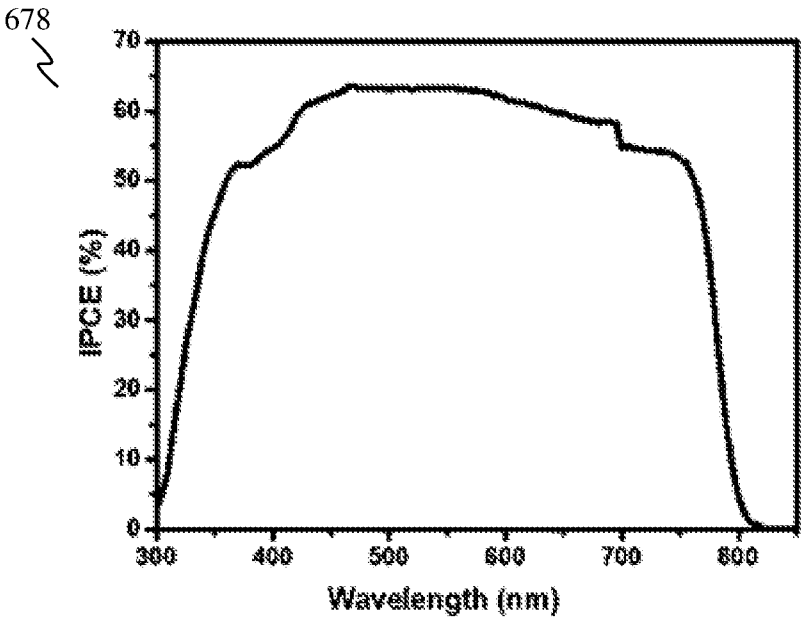

678
70
60
50
40
30
20
10
0
IPCE (%)
300
400
500
600
700
800
Wavelength (nm)

FIG. 6B

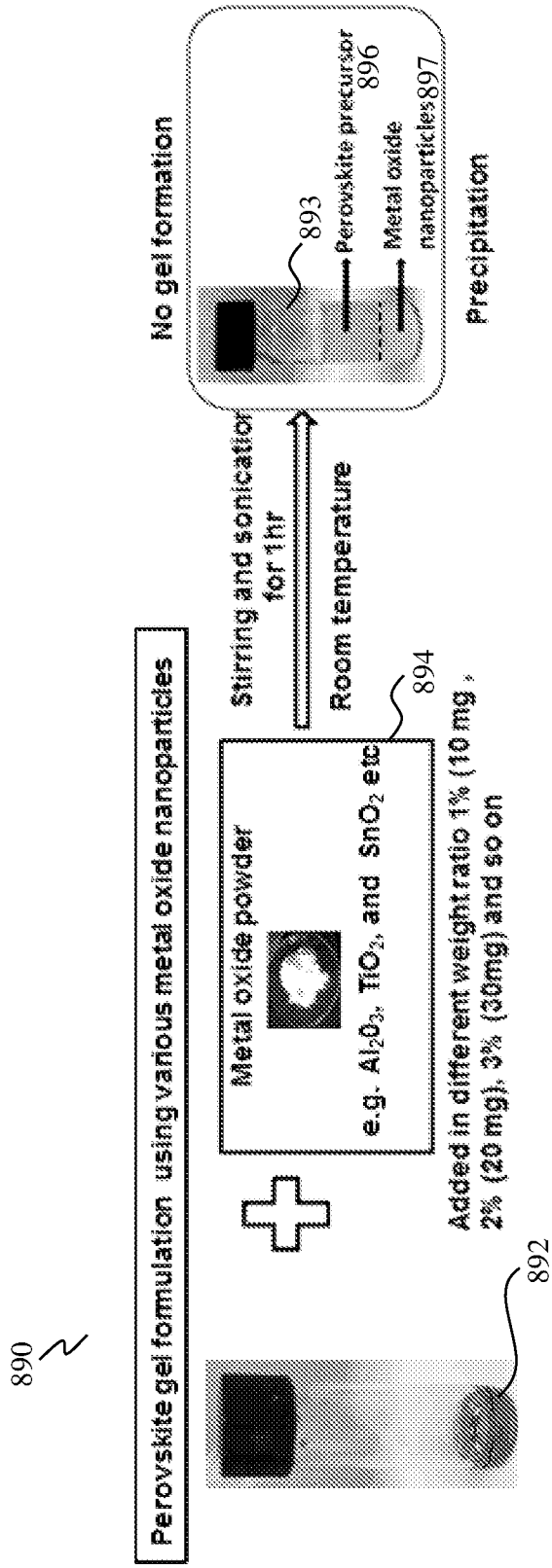

890
Perovskite gel formulation using various metal oxide nanoparticles
892
Perovskite precursor solution
1 ml
Metal oxide powder
e.g. Al_2O_3, TiO_2, and SnO_2 etc
894
Added in different weight ratio 1% (10 mg),
2% (20 mg), 3% (30mg) and so on
Stirring and sonication
for 1hr
Room temperature
No gel formation
893
Perovskite precursor
896
Metal oxide
nanoparticles 897
Precipitation

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2016/050060

A. CLASSIFICATION OF SUBJECT MATTER

See Supplemental Box

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC/WPI/CAPLUS: perovskite, halide, iodide, solar, photovoltaic, clay, gel and like terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SUM, T. C. ET AL., Advancements in Perovskite Solar Cells: Photophysics Behind the Photovoltaics. *Energy & Environmental Science*, 2 May 2014, Vol. 7, No. 8, pages 2518-2534 [Retrieved on 2016-03-03] (DOI: 10.1039/C4EE00673A) See entire document.	1-20
A	BOIX, P. P. ET AL., Current Progress and Future Perspectives for Organic/Inorganic Perovskite Solar Cells. *Materials Today*, 11 February 2014, Vol. 17, No. 1, pages 16-23 [Retrieved on 2016-03-03] (DOI: 10.1016/J.MATTOD.2013.12.002) See entire document.	
A	GREEN, M. A. ET AL., The Emergence of Perovskite Solar Cells. *Nature Photonics*, 27 June 2014, Vol. 8, No. 7, pages 506-514 [Retrieved on 2016-03-03] (DOI: 10.1038/NPHOTON.2014.134) See abstract.	

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04/03/2016 *(day/month/year)*	16/03/2016 *(day/month/year)*

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2016/050060

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GRÄTZEL, M., The Light and Shade of Perovskite Solar Cells. *Nature Materials*, 21 August 2014, Vol. 13, No. 9, pages 838-842 [Retrieved on 2016-03-03] (DOI: 10.1038/NMAT4065) See abstract.	
A	WANG, X. ET AL., Nanoclay Gelation Approach Toward Improved Dye-Sensitized Solar Cell Efficiencies: An Investigation of Charge Transport and Shift in the TiO_2 Conduction Band. *Applied Materials & Interfaces*, 19 December 2012, Vol. 5, No. 2, pages 444-450 [Retrieved on 2016-03-03] (DOI: 10.1021/AM3025454) See abstract.	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2016/050060

Supplemental Box
(Classification of Subject Matter)

Int. Cl.
H01G 9/20 (2006.01)
H01L 51/42 (2006.01)
C01G 21/16 (2006.01)
C01B 33/40 (2006.01)
C01G 9/04 (2006.01)
C01G 15/00 (2006.01)
C01G 17/04 (2006.01)
C01G 19/04 (2006.01)
C01G 51/08 (2006.01)
C01G 53/08 (2006.01)