



(51) International Patent Classification:

C30B 29/12 (2006.01) H01L 51/00 (2006.01)

(21) International Application Number:

PCT/CN2016/091992

(22) International Filing Date:

28 July 2016 (28.07.2016)

(25) Filing Language:

English

(26) Publication Language:

English

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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, 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))

(54) Title: FABRICATION OF PEROVSKITE PERIODIC ARRAYS FOR OPTOELECTRONIC APPLICATIONS

(57) Abstract: A solid-liquid-solid phase transformation (SLSPT) approach is used for fabrication of perovskite periodic nanostructures. The pattern on a mold is replicated by perovskite through phase change of perovskite from initially solid state, then to liquid state, and finally to solid state. The LED comprising perovskite periodic nanostructure shows better performance than that with flat perovskite. Further, the perovskite periodic nanostructure from SLSPT can be applied in many optoelectronic devices, such as solar cells, light emitting diodes (LED), laser diodes, transistors, and photodetectors.



FABRICATION OF PEROVSKITE PERIODIC ARRAYS FOR OPTOELECTRONIC APPLICATIONS

FIELD OF THE INVENTION

[0001] This invention relates to fabrication of perovskite periodic nanostructures and its application in optoelectronic devices.

BACKGROUND OF THE INVENTION

[0002] Organic-inorganic hybrid perovskite has attracted global attention in recent years for its extensive applications in optoelectronic devices. The demonstrated applications of three-dimensional organometallic halide perovskite thin film include solar cells, light emitting diodes (LEDs), lasers, transistors, and photodetectors. Such wide application of perovskite is intimately related to its unique chemical structure. The general formula of three-dimensional perovskite is ABX_3 ($A = CH_3NH_3$, $HC(NH_2)_2$, or Cs , $B = Pb$ or Sn , $X = Cl$, Br , or I). The band gap (E_g) of perovskite can be easily tuned from 1.17 eV to 3.0 eV by simply varying the constituent of A , B , and X .

[0003] Most of the uses of perovskite are based on the flat thin film of perovskite, which can be formed through a variety of methods, such as spin coating, thermal evaporation, and doctor blading. On the other hand, compared with flat thin film, the periodic nanostructure of semiconductors has incomparable optical properties. In the photovoltaic area, semiconductor periodic nanostructure associated with metal electrodes has been utilized to stimulate Surface Plasmon and also to increase the light path length within semiconductors in order to improve the power conversion efficiency (PCE) of corresponding solar cells. In addition, periodic nanostructure has been applied in LEDs to increase light extraction. Furthermore, distributed feedback (DFB) lasers and photonic crystal lasers can be realized after precisely designing semiconductor periodic nanostructure.

[0004] However, the challenge for directly patterning perovskite lies in its chemical instability. It is reported that perovskite will decompose after exposure to polar solvents, such as

water, methanol, and acetone. The photolithography usually used for nanofabrication can damage perovskite since the developer of the photoresist used in that process is normally dissolved in water. On the other hand, the high-power ions from a focused-ion beam used in photolithography will not only remove the perovskite that is unwanted but it will also decompose the nearby perovskite. In that case, the perovskite pattern obtained with photolithography may be quite different from the intended design. Besides, the crystal quality of perovskite can be damaged. It has been reported that the process of though gas-assisted focused-ion beam etching relieves the damage of perovskite during fabrication. However, the reduced photoluminescence (PL) of patterned perovskite compared with pristine flat perovskite indicates that the film quality of patterned perovskite is still worsened.

SUMMARY OF THE INVENTION

[0005] The present invention is directed to a novel solid-liquid-solid phase transformation (SLSPT) approach for the fabrication of perovskite periodic nanostructure with high crystal quality. In an exemplary embodiment, the approach includes forming flat perovskite thin film on a substrate, covering the perovskite thin film with a periodic mold, then converting the solid perovskite thin film into a liquid intermediate by reacting it with a chemical, subsequently recovering liquid intermediates into solid perovskite by removing the introduced chemical, and lifting up the mold. The result is the fabrication of a perovskite periodic nanostructure.

[0006] The high-quality perovskite periodic nanostructures are prepared through the phase transformation in which perovskite grows by itself into the periodic nanostructure. The approach used with the present invention does not need traditional and costly lithography nanofabrication technique which directly patterns the semiconductor and then etching it away. The latter heavily relies on skills, expensive equipment and uses a lot of chemicals in patterning.

[0007] The initial flat MAPbI_3 thin film can be prepared on a PEDOT:PSS/ITO substrate according to the solvent engineering approach.

[0008] The present approach can provide several advantages. According to one aspect of the invention, the whole process avoids polar solvents (such as water), or high temperatures (>

150 °C), or high-power particles hitting and damaging the perovskite. According to another aspect of the invention, the initial flat perovskite thin film can be prepared by different approaches. It is not limited to a single certain approach. According to yet another aspect of the invention, the liquid intermediate forms a close contact with the periodic mold and thus contributes to accurate replication of the pattern from the mold. According to a further aspect of the invention, the visible grain boundary in pristine thin film disappears after forming the periodic nanostructure, which indicates the perovskite periodic nanostructure may have the property of a single crystal. Further benefits include, but are not limited to the crystal quality of the perovskite periodic nanostructure being improved in contrast with its flat thin film version. More importantly, a LED made with a perovskite periodic nanostructure is superior to that with a flat perovskite thin film. Last but not least, the perovskite periodic nanostructure created using the SLSPT approach is suitable for different optoelectronic devices, such as solar cells, LEDs, laser diodes, photodetectors, and transistors. More benefits will be understood and appreciated from embodiments as detailed below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The foregoing and other objects and advantages of the present invention will become more apparent when considered in connection with the following detailed description and appended drawings in which like designations denote like elements in the various views, and wherein:

[0010] FIG 1A is a cross-sectional Scanning Electron Microscope (SEM) image of flat methylammonium lead triiodide (MAPbI_3) thin film;

[0011] FIG 1B is a cross-sectional SEM image of MAPbI_3 periodic nanostructure with a period of 735 nm;

[0012] FIG 1C is a top-view SEM image of flat MAPbI_3 thin film;

[0013] FIG 1D is a top-view SEM image of MAPbI_3 periodic nanostructure with a period of 735 nm;

[0014] FIG 1E is an Atomic Force Microscopy (AFM) image of flat MAPbI_3 thin film;

[0015] FIG 1F is an AFM image of MAPbI_3 periodic nanostructure with a period of 735 nm;

- [0016] FIG 1G is an AFM height profile of flat MAPbI₃ thin film;
- [0017] FIG 1H is an AFM height profile of MAPbI₃ periodic nanostructure with a period of 735 nm;
- [0018] FIG 2 is an X-ray Diffraction (XRD) spectrum of flat MAPbI₃ thin film and MAPbI₃ periodic nanostructure with a period of 735 nm;
- [0019] FIG 3 is a photoluminescence (PL) spectra of flat MAPbI₃ thin film and MAPbI₃ periodic nanostructure with a period of 735 nm;
- [0020] FIG 4A is a top-view SEM image of flat MAPbI₃ thin film;
- [0021] FIG 4B is a top-view SEM image of MAPbI₃ periodic nanostructure with a period of 735 nm;
- [0022] FIG 5A is a cross-sectional SEM image of formamidinium lead triiodide (FAPbI₃) periodic nanostructure with 735 nm;
- [0023] FIG 5B is absorbance spectrum of MAPbI₃ periodic nanostructure with a period of 735 nm and FAPbI₃ periodic nanostructure with a period of 735 nm;
- [0024] FIG 6A is a graph of voltage-current density characteristics of a flat MAPbI₃ light emitting diode (LED) with different spin coating rates for phenyl-C61-butyric acid methyl ester (PC₆₁BM);
- [0025] FIG 6B is a graph of voltage-radiance characteristics of flat MAPbI₃ LED with different spin coating rates for PC₆₁BM.
- [0026] FIG 6C is a graph of voltage-current density characteristics of flat MAPbI₃ LED and a 735 nm-period MAPbI₃ LED; and
- [0027] FIG 6D is a graph of voltage-radiance characteristics of flat MAPbI₃ LED and a 735 nm-period MAPbI₃ LED.

DETAILED DESCRIPTION OF THE INVENTION

[0028] The invention provides a new solid-liquid-solid phase transformation (“SLSPT”) approach to fabricate perovskite periodic nanostructures with high crystal quality. In an illustrative embodiment, a method of forming perovskite periodic nanostructure starts with preparing flat perovskite thin film on a substrate. The top surface of the perovskite thin film is covered with a periodic mold. Rather than press the mold into the flat thin film, a chemical is

introduced to react with the solid perovskite in order to form a liquid intermediate. This liquid takes up the shape of the mold without pressing. After complete conversion into the liquid intermediate, the chemical is removed in order to convert the intermediate back into a solid perovskite. The solid will have the shape of the mold so that lifting up the mold reveals a perovskite periodic nanostructure. Before describing of the approach in detail, some specific terms need to be explained.

[0029] The term “SLSPT”, as used herein, refers to solid-liquid-solid phase transformation, which indicates the phase change of perovskite during the fabrication. The flat perovskite thin film is in solid state at the beginning and then becomes a liquid intermediate after reacting with an introduced chemical. Subsequently, the liquid intermediate returns back to a solid state after removal of the introduced chemical.

[0030] The term “perovskite”, as used herein, refers to a semiconductor material with the general chemical formula of ABX_3 ;

where A is an organic cation of the formula $(R_1R_2R_3R_4Na)^+$;

where R_1 is hydrogen, unsubstituted or substituted C_1 - C_{10} alkyl;

where R_2 is hydrogen, unsubstituted or substituted C_1 - C_{10} alkyl;

where R_3 is hydrogen, unsubstituted or substituted C_1 - C_{10} alkyl;

where R_4 is hydrogen, unsubstituted or substituted C_1 - C_{10} alkyl;

where a can be any value between 1 and 10(including 1 and 10).

B is at least one divalent metal cation; and

X is at least one halide anion.

[0031] As used herein, an alkyl group can be a substituted or unsubstituted, linear or branched chain saturated radical, it is often a substituted or an unsubstituted linear chain saturated radical, more often an unsubstituted linear chain saturated radical. A C_1 - C_{10} alkyl group is an unsubstituted or substituted, straight or branched chain saturated hydrocarbon radical having from 1 to 10 carbon atoms. Typically it is C_1 - C_{10} alkyl, for example methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl, or C_1 - C_6 alkyl, for example methyl, ethyl, propyl, butyl, pentyl or hexyl, or C_1 - C_4 alkyl, for example methyl, ethyl, i-propyl, n-propyl, t-butyl, s-butyl or n-butyl.

[0032] When an alkyl group is substituted it typically bears one or more substituents selected from substituted or unsubstituted C1-C10 alkyl, substituted or unsubstituted aryl, cyano, amino, C1-C10 alkylamino, di(C1-C10)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acylamido, hydroxy, oxo, halo, carboxy, ester, acyl, acyloxy, C1-C20 alkoxy, aryloxy, haloalkyl, sulfonic acid, sulfhydryl (i.e. thiol, -SH), C1-C10 alkylthio, arylthio, sulfonyl, phosphoric acid, phosphate ester, phosphonic acid and phosphonate ester. Examples of substituted alkyl groups include haloalkyl, hydroxyalkyl, aminoalkyl, alkoxyalkyl and alkaryl groups. The term alkaryl, as used herein, pertains to a C1-C20 alkyl group in which at least one hydrogen atom has been replaced with an aryl group. Examples of such groups include, but are not limited to, benzyl (phenylmethyl, PhCH_2 -), benzhydryl (Ph_2CH -), trityl (triphenylmethyl, Ph_3C -), phenethyl (phenylethyl, $\text{Ph-CH}_2\text{CH}_2$ -), styryl (Ph-CH=CH -), cinnamyl (Ph-CH=CH-CH_2 -).

[0033] Typically a substituted alkyl group carries 1, 2 or 3 substituents, for instance 1 or 2.

[0034] An aryl group is a substituted or unsubstituted, monocyclic or bicyclic aromatic group which typically contains from 6 to 14 carbon atoms, preferably from 6 to 10 carbon atoms in the ring portion. Examples include phenyl, naphthyl, indenyl and indanyl groups. An aryl group is unsubstituted or substituted. When an aryl group as defined above is substituted it typically bears one or more substituents selected from C1-C6 alkyl which is unsubstituted (to form an aralkyl group), aryl which is unsubstituted, cyano, amino, C1-C10 alkylamino, di(C1-C10)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acylamido, hydroxy, halo, carboxy, ester, acyl, acyloxy, C1-C20 alkoxy, aryloxy, haloalkyl, sulfhydryl (i.e. thiol, -SH), C1-10 alkylthio, arylthio, sulfonic acid, phosphoric acid, phosphate ester, phosphonic acid and phosphonate ester and sulfonyl. Typically it carries 0, 1, 2 or 3 substituents. A substituted aryl group may be substituted in two positions with a single C1-C6 alkylene group, or with a bidentate group represented by the formula $-\text{X}-(\text{C1-C6})\text{alkylene}$, or $-\text{X}-(\text{C1-C6})\text{alkylene-X}$, wherein X is selected from O, S and NR, and wherein R is H, aryl or C1-C6 alkyl. Thus a substituted aryl group may be an aryl group fused with a cycloalkyl group or with a heterocyclcyl group. The ring atoms of an aryl group may include one or more heteroatoms (as in a heteroaryl group). Such an aryl group (a heteroaryl group) is a substituted or unsubstituted mono- or

bicyclic heteroaromatic group which typically contains from 6 to 10 atoms in the ring portion including one or more heteroatoms. It is generally a 5- or 6-membered ring, containing at least one heteroatom selected from O, S, N, P, Se and Si. It may contain, for example, 1, 2 or 3 heteroatoms. Examples of heteroaryl groups include pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, furanyl, thienyl, pyrazolidinyl, pyrrolyl, oxazolyl, oxadiazolyl, isoxazolyl, thiadiazolyl, thiazolyl, isothiazolyl, imidazolyl, pyrazolyl, quinolyl and isoquinolyl. A heteroaryl group may be unsubstituted or substituted, for instance, as specified above for aryl. Typically it carries 0, 1, 2 or 3 substituents.

[0035] Typically the divalent metal cation may be selected from Ca^{2+} , Sr^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Pd^{2+} , Ge^{2+} , Sn^{2+} , Pb^{2+} , Yb^{2+} and Eu^{2+} . Usually, the divalent metal cation is selected from Sn^{2+} and Pb^{2+} .

[0036] In general, the perovskites are selected from $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbBr}_3$, $\text{CH}_3\text{NH}_3\text{PbCl}_3$, $\text{CH}_3\text{NH}_3\text{PbF}_3$, $\text{CH}_3\text{NH}_3\text{PbBrI}_2$, $\text{CH}_3\text{NH}_3\text{PbBrCl}_2$, $\text{CH}_3\text{NH}_3\text{PbIBr}_2$, $\text{CH}_3\text{NH}_3\text{PbICl}_2$, $\text{CH}_3\text{NH}_3\text{PbClBr}_2$, $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$, $\text{CH}_3\text{NH}_3\text{SnBrI}_2$, $\text{CH}_3\text{NH}_3\text{SnBrCl}_2$, $\text{CH}_3\text{NH}_3\text{SnF}_2\text{Br}$, $\text{CH}_3\text{NH}_3\text{SnIBr}_2$, $\text{CH}_3\text{NH}_3\text{SnICl}_2$, $\text{CH}_3\text{NH}_3\text{SnF}_2\text{I}$, $\text{CH}_3\text{NH}_3\text{SnClBr}_2$, $\text{CH}_3\text{NH}_3\text{SnI}_2\text{Cl}$, $\text{CH}_3\text{NH}_3\text{SnF}_2\text{Cl}$, $\text{HC}(\text{NH}_2)_2\text{PbI}_3$, $\text{HC}(\text{NH}_2)_2\text{PbBr}_3$, $\text{HC}(\text{NH}_2)_2\text{PbCl}_3$, $\text{HC}(\text{NH}_2)_2\text{PbF}_3$, $\text{HC}(\text{NH}_2)_2\text{PbBrI}_2$, $\text{HC}(\text{NH}_2)_2\text{PbBrCl}_2$, $\text{HC}(\text{NH}_2)_2\text{PbIBr}_2$, $\text{HC}(\text{NH}_2)_2\text{PbClBr}_2$, $\text{HC}(\text{NH}_2)_2\text{PbI}_2\text{Cl}$, $\text{HC}(\text{NH}_2)_2\text{PbICl}_2$, $\text{HC}(\text{NH}_2)_2\text{SnI}_3$, $\text{HC}(\text{NH}_2)_2\text{SnBr}_3$, $\text{HC}(\text{NH}_2)_2\text{SnCl}_3$, $\text{HC}(\text{NH}_2)_2\text{SnF}_3$, $\text{HC}(\text{NH}_2)_2\text{SnBrI}_2$, $\text{HC}(\text{NH}_2)_2\text{SnBrCl}_2$, $\text{HC}(\text{NH}_2)_2\text{SnIBr}_2$, $\text{HC}(\text{NH}_2)_2\text{SnClBr}_2$, $\text{HC}(\text{NH}_2)_2\text{SnI}_2\text{Cl}$, and $\text{HC}(\text{NH}_2)_2\text{SnICl}_2$. For instance, in the optoelectronic device of the invention, the perovskites may be selected from $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbBr}_3$, $\text{CH}_3\text{NH}_3\text{PbCl}_3$, $\text{CH}_3\text{NH}_3\text{PbF}_3$, $\text{CH}_3\text{NH}_3\text{PbBrI}_2$, $\text{CH}_3\text{NH}_3\text{PbBrCl}_2$, $\text{CH}_3\text{NH}_3\text{PbIBr}_2$, $\text{CH}_3\text{NH}_3\text{PbICl}_2$, $\text{CH}_3\text{NH}_3\text{PbClBr}_2$, $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$, $\text{CH}_3\text{NH}_3\text{SnBrI}_2$, $\text{CH}_3\text{NH}_3\text{SnBrCl}_2$, $\text{CH}_3\text{NH}_3\text{SnF}_2\text{Br}$, $\text{CH}_3\text{NH}_3\text{SnIBr}_2$, $\text{CH}_3\text{NH}_3\text{SnICl}_2$, $\text{CH}_3\text{NH}_3\text{SnF}_2\text{I}$, $\text{CH}_3\text{NH}_3\text{SnClBr}_2$, $\text{CH}_3\text{NH}_3\text{SnI}_2\text{Cl}$, $\text{CH}_3\text{NH}_3\text{SnF}_2\text{Cl}$, $\text{HC}(\text{NH}_2)_2\text{PbI}_3$, $\text{HC}(\text{NH}_2)_2\text{PbBr}_3$, $\text{HC}(\text{NH}_2)_2\text{PbCl}_3$, $\text{HC}(\text{NH}_2)_2\text{PbF}_3$, $\text{HC}(\text{NH}_2)_2\text{PbBrI}_2$, $\text{HC}(\text{NH}_2)_2\text{PbBrCl}_2$, $\text{HC}(\text{NH}_2)_2\text{PbIBr}_2$, $\text{HC}(\text{NH}_2)_2\text{PbClBr}_2$, $\text{HC}(\text{NH}_2)_2\text{PbI}_2\text{Cl}$, $\text{HC}(\text{NH}_2)_2\text{PbICl}_2$, $\text{HC}(\text{NH}_2)_2\text{SnI}_3$, $\text{HC}(\text{NH}_2)_2\text{SnBr}_3$, $\text{HC}(\text{NH}_2)_2\text{SnCl}_3$, $\text{HC}(\text{NH}_2)_2\text{SnF}_3$, $\text{HC}(\text{NH}_2)_2\text{SnBrI}_2$, $\text{HC}(\text{NH}_2)_2\text{SnBrCl}_2$, $\text{HC}(\text{NH}_2)_2\text{SnIBr}_2$, $\text{HC}(\text{NH}_2)_2\text{SnClBr}_2$, $\text{HC}(\text{NH}_2)_2\text{SnI}_2\text{Cl}$, and $\text{HC}(\text{NH}_2)_2\text{SnICl}_2$. Typically, the perovskite is selected from $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbBr}_3$, $\text{CH}_3\text{NH}_3\text{PbCl}_3$, $\text{CH}_3\text{NH}_3\text{PbF}_3$, $\text{CH}_3\text{NH}_3\text{PbBrI}_2$, $\text{CH}_3\text{NH}_3\text{PbBrCl}_2$, $\text{CH}_3\text{NH}_3\text{PbIBr}_2$,

CH₃NH₃PbICl₂, CH₃NH₃PbClBr₂, CH₃NH₃PbI₂Cl, CH₃NH₃SnF₂Br, CH₃NH₃SnICl₂, CH₃NH₃SnF₂I, CH₃NH₃SnI₂Cl, CH₃NH₃SnF₂Cl, HC(NH₂)₂PbI₃, HC(NH₂)₂PbBr₃, HC(NH₂)₂PbCl₃, HC(NH₂)₂PbF₃, HC(NH₂)₂PbBrI₂, HC(NH₂)₂PbBrCl₂, HC(NH₂)₂PbIBr₂, HC(NH₂)₂PbClBr₂, HC(NH₂)₂PbI₂Cl, HC(NH₂)₂PbICl₂, HC(NH₂)₂SnI₃, HC(NH₂)₂SnBr₃, HC(NH₂)₂SnCl₃, HC(NH₂)₂SnF₃, HC(NH₂)₂SnBrI₂, HC(NH₂)₂SnBrCl₂, HC(NH₂)₂SnIBr₂, HC(NH₂)₂SnClBr₂, HC(NH₂)₂SnI₂Cl, and HC(NH₂)₂SnICl₂. More typically, the perovskite is selected from CH₃NH₃PbI₃, CH₃NH₃PbBr₃, CH₃NH₃PbCl₃, CH₃NH₃PbF₃, CH₃NH₃PbBrI₂, CH₃NH₃PbBrCl₂, CH₃NH₃PbIBr₂, CH₃NH₃PbICl₂, CH₃NH₃PbClBr₂, CH₃NH₃PbI₂Cl, CH₃NH₃SnF₂Br, CH₃NH₃SnF₂I and CH₃NH₃SnF₂Cl. Usually, the perovskite is selected from CH₃NH₃PbBrI₂, CH₃NH₃PbBrCl₂, CH₃NH₃PbIBr₂, CH₃NH₃PbICl₂, CH₃NH₃SnF₂Br, CH₃NH₃SnF₂I, HC(NH₂)₂PbI₃, HC(NH₂)₂PbBr₃, HC(NH₂)₂PbCl₃, HC(NH₂)₂PbF₃, HC(NH₂)₂PbBrI₂, HC(NH₂)₂PbBrCl₂, HC(NH₂)₂PbIBr₂, HC(NH₂)₂PbClBr₂, HC(NH₂)₂PbI₂Cl, HC(NH₂)₂PbICl₂, HC(NH₂)₂SnI₃, HC(NH₂)₂SnBr₃, HC(NH₂)₂SnCl₃, HC(NH₂)₂SnF₃, HC(NH₂)₂SnBrI₂, HC(NH₂)₂SnBrCl₂, HC(NH₂)₂SnIBr₂, HC(NH₂)₂SnClBr₂, HC(NH₂)₂SnI₂Cl, and HC(NH₂)₂SnICl₂.

[0037] The term “periodic nanostructures”, or “periodic arrays”, as used herein, refers to repeated units in nanoscale with a certain period. It can be a one dimensional periodic nanostructure or a two dimensional pillar or hole.

[0038] The term “mold”, or “periodic mold”, as used herein is made from one of PDMS, PMMA, Silicon, Nickel, or Silicon dioxide. It can be one dimensional periodic nanostructure with any period or two dimensional hole or pillar structure with any configuration.

[0039] First, an exemplary method of forming a flat perovskite thin film utilizes a reported one-step solvent engineering approach. See, N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu and S. I. Seok, *Nat Mater*, 2014, 13, 897-903, which is incorporated herein by reference in its entirety. This approach is one of the most reported methods for fabricating smooth perovskite thin film with high-quality crystal. This approach starts with dissolving lead halide and organic halide simultaneously in a combinational solvent of dimethyl sulfoxide (DMSO) and gamma-butyrolactone (GBL). Subsequently this solution is spin coated on a substrate. During coating, a weak polar solvent (such as toluene, or chlorobenzene, or 1, 2-dichlorobenzene) is dripped on the substrate. The spin coated substrate is then annealed to form a

flat perovskite thin film. It should be noticed that, the method for fabrication of the flat perovskite thin film is not limited to the one-step solvent engineering approach. Other approaches, including but not limited to two-step sequential deposition, dual-source thermal evaporation, and doctor blading, can also be utilized to fabricate flat perovskite thin film. Any of these formed perovskite thin films is suitable for the SLSPT approach to fabrication of perovskite periodic nanostructure.

[0040] The substrate on which the flat perovskite thin film is deposited can be rigid or flexible. The rigid substrate can be chosen from glass, silicon, ITO coated glass, fluorine-doped tin oxide (FTO) coated glass, and any thereof coated with semiconductor material. On the other hand, the flexible substrate can be ITO coated polyethylene terephthalate (PET), ITO coated polyethylene-naphthalate (PEN), ITO coated polyimide (PI), FTO coated PET, FTO coated PEN, and FTO coated PI, and any thereof coated with semiconductor material.

[0041] Second, the perovskite thin film is covered with a periodic mold. An exemplary embodiment of a mold is a one dimensional periodic nanostructure on polydimethylsiloxane (PDMS). For example, a PDMS periodic nanostructure with a period of 735 nm is used to fabricate a MAPbI_3 periodic nanostructure. However, other molds, including but not limited to quartz, silicon, silicon oxide, nickel, and poly(methyl methacrylate) (PMMA) can also be suitable for the SLSPT approach. It should be noted that, to form better contact between the perovskite thin film and the mold, the use of soft molds, such as PMMA and PDMS, is suggested.

Subsequently, to convert the solid perovskite thin film into a liquid state in order to replicate the pattern on the mold, a chemical is introduced. The introduced chemical reacts with perovskite and forms a liquid intermediate, accompanied with a color change of the perovskite. This is one of a crucial part of the SLSPT approach. The recipe for choosing a chemical should satisfy following requirements: First, the chemical must react with perovskite to form a liquid intermediate. Second, the intermediate must decompose into perovskite and other byproducts. In general, the chemical can be nitrogen-containing compound, such as amines. These amines include monoamines, diamines, triamines and polyamines. Specific examples of monoamines added include aliphatic monoamines such as methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, 2-ethylhexylamine, nonylamine, decylamine,

undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, octadecylamine, octadecyleneamine, eicosylamine or docosylamine, alicyclic monoamines such as cyclohexylamine or methylcyclohexylamine, aromatic monoamines such as benzylamino or β -phenylmethylamine, symmetrical secondary amines such as N,N-dimethylamine, N,N-diethylamine, N,N-dipropylamine, N,N-dibutylamine, N,N-diethylamine or N,N-dioctylamine, and mixed secondary amines such as N-methyl-N-ethylamine, N-methyl-N-butylamine, N-methyl-N-dodecylamine, N-methyl-N-octadecylamine, N-ethyl-N-hexadecylamine, N-ethyl-N-octadecylamine, N-propyl-N-hexadecylamine or N-propyl-N-benzylamine. The chemical can be any one selected from the group consisting of ammonia, methylamine, formamidine, ethylamine, n-butylamine, tert-butylamine, octylamine etc. An exemplary embodiment of a chosen chemical is methylamine (MA) gas. MA gas is produced by heating its solution in water and purifying the gas with a drier. The MA gas reacts with solid methylammonium lead triiodide (MAPbI_3) and forms the liquid intermediate of $\text{MAPbI}_3 \cdot \text{MA}$. Other than the change of state from solid to liquid, the color of perovskite changes from brown to transparent. This is the indication of the completion of the reaction. The time for complete conversion of perovskite into the intermediate depends on the heating temperature of MA and the number of perovskite thin film devices. In general, the higher the temperature and the fewer perovskite devices, reduces the time. Usually, the reaction time is within ten minutes.

[0042] As part of the SLSPT process, the chemical must be removed from the intermediate in order to convert the liquid intermediates into solid perovskite. The chemical can be removed by annealing or volatilization at room temperature. The heating temperature can be any value between 25 °C and 150 °C. The higher the temperature, the shorter the time required for complete conversion. Besides, a higher temperature results in better crystallization of perovskite. However, a temperature higher than 100 °C might decompose the perovskite. As a result, the preferred annealing temperature should be in the range of 80 °C to 100 °C. After complete conversion, the liquid intermediate turns back into solid perovskite, accompanied with the replication of the pattern from the mold.

[0043] Moreover, the prepared perovskite periodic nanostructure can be used in different optoelectronic devices, such as solar cells, LEDs, laser diodes, transistors, and photodetectors.

An exemplary embodiment of the application of a prepared perovskite periodic nanostructure is in a perovskite LED. In general, an LED device comprises a bottom electrode, a hole transporting layer, an emissive layer, an electron transporting layer, and a top electrode. For example, the bottom electrode can be ITO or FTO on a rigid or flexible substrate, and the top electrode can be aluminum (Al), silver (Ag), or gold (Au). The hole transporting layer can be chosen from PEDOT:PSS and NiO_x . The electron transporting layer can be phenyl-C61-butyric acid methyl ester (PC_{61}BM), C60, ZnO, and SnO_x . The PEDOT:PSS and PC_{61}BM thin film can be formed via spin coating and doctor blading. C60 thin film could also be deposited through spin coating and thermal evaporation. Besides, NiO_x , ZnO, and SnO_x thin films could be prepared via spin coating, doctor blading, and atomic layer deposition. Finally, the Al, Ag, or Au electrode could be deposited via thermal evaporation.

[0044] Following are examples of the present invention to illustrate the SLSPT approach for fabrication of perovskite periodic nanostructures.

EXAMPLE 1

Perovskite periodic nanostructure fabrication and characterization

[0045] MAPbI_3 periodic nanostructure with a period of 735 nm was prepared using the SLSPT approach. At the beginning, a flat thin film was prepared using the one-step solvent engineering approach. More specifically, 0.5 mol/l precursor of PbI_2/MAI (molar ratio = 1:1) in a combinational solvent of DMSO/GBL ($v/v = 3:7$) was heated at 80 °C for 1 hour and then spin coated on a PEDOT:PSS/ITO substrate at a speed of 1000 rpm for a first duration of 10 seconds and then 5000 rpm for a second duration of 40 s. Toluene was dripped on to the spin coating substrate at 17 s of the second duration (also at 27 s of the whole coating time). After coating, the substrate was baked at 100 °C for 10 min, which led to the formation of flat MAPbI_3 thin film. The above process was completed in a laboratory glove box.

[0046] The mold with a period of 735 nm was prepared by transfer from a periodic nanostructure by photolithography and placed on the prepared flat MAPbI_3 thin film. The MAPbI_3 thin film with the PDMS mold atop was transferred, perhaps in a plastic bag, into a chamber where dry gaseous MA was prepared through heating its aqueous solution at 60 °C. The

MA gas was dried with calcium oxide (CaO) powder and then introduced to the perovskite thin film. After less than 10 min of MA gas treatment, brown MAPbI₃ became transparent, indicating formation of a liquid intermediate of MAPbI₃.MA. Subsequently, the device was brought back to the glove box, followed by annealing at 100 °C for 5 min. The color of the device gradually changed from transparent to brown during annealing, indicating the conversion of MAPbI₃.MA to MAPbI₃. When the PDMS mold was lifted off, the MAPbI₃ periodic nanostructure was revealed.

[0047] As can be seen from FIG 1A, 1C, and 1E, the flat MAPbI₃ thin film from the one-step solvent engineering approach was quite smooth with root mean square (RMS) roughness of 6.28 nm. After being patterned, the flat MAPbI₃ thin film formed a satisfactory periodic nanostructure with a period of 735 nm, as shown in FIG 1B, 1D, 1F. Besides, the grain boundary which was obvious in the flat thin film (FIG 1C) was invisible in the patterned device (FIG 1D), which indicated that the patterned MAPbI₃ might have single crystal properties. What's more, an interesting phenomenon was that the depth of MAPbI₃ changed from 60-80 nm in the flat thin film to 100-120 nm after forming periodic nanostructure. This could be understood as the MAPbI₃ previously located at the space region being pushed to the line region by the PDMS mold, resulting in an increased thickness of line region. The crystal quality of MAPbI₃ before and after being patterned was investigated by XRD technique. See FIG 2 which shows that the characteristic peaks of reported MAPbI₃ were observed in the flat MAPbI₃ device at 13.95°, 28.38°, and 31.74°, which corresponded to (110), (220), and (310) lattice phase. After being patterned, the MAPbI₃ exhibited a higher intensity in the XRD spectrum at lattice phase of (110) and (220) compared with the flat one, indicating better crystal quality for the MAPbI₃ periodic nanostructure. The increased crystal quality can be explained by the reported defect healing of MA to MAPbI₃. In addition, as shown in FIG 3, the improved photoluminescence (PL) of the 735 nm-period MAPbI₃ device in comparison to the flat one could be attributed to the improved crystal quality of the MAPbI₃ periodic nanostructure and the light out coupling of the periodic nanostructure.

[0048] FAPbI₃ periodic nanostructure can be fabricated by cation exchange of the MAPbI₃ periodic nanostructure by dipping MAPbI₃ in a FAI solution as described in the article,

G. E. Eperon, C. E. Beck and H.J. Snaith, *Mater Horiz*, 2016, 3, 63-71, which is incorporated herein by reference in its entirety. After 5 min cation exchange, the sharp edge in the MAPbI₃ periodic nanostructure becomes much smoother, as shown in FIG. 5A. However, the line depth and width are almost the same for MAPbI₃ and the FAPbI₃ periodic nanostructure, which demonstrates the feasibility of fabricating a FAPbI₃ periodic nanostructure from a MAPbI₃ periodic nanostructure. Besides, the absorbance onset is red shifted from 780 nm in MAPbI₃ periodic nanostructure to 810 nm in FAPbI₃ periodic nanostructure, as shown in FIG. 5B. The red-shifted absorption onset originated from lower band gap of FAPbI₃ ($E_g = 1.45$ eV), in comparison to that of MAPbI₃ with E_g of 1.5 eV.

MAPbI₃ periodic nanostructure LED fabrication and characterization

[0049] The MAPbI₃ periodic nanostructure was manufactured into an LED and compared with flat MAPbI₃ LED. The structure of the MAPbI₃ LED is ITO/PEDOT:PSS/MAPbI₃/PC₆₁BM/Ag. First, ITO coated glass was successively cleaned with detergent, water, acetone, and ethanol. After treatment with ultraviolet-ozone (UVO) for 15 min, the ITO glass was spin coated with PEDOT:PSS at rate of 3000 rpm and annealed at 130 °C for 10 min. The MAPbI₃ periodic nanostructure with a period of 735 nm was fabricated on PEDOT:PSS via above SLSPT approach. The device with the flat MAPbI₃ thin film was used as reference. PC₆₁BM in 1, 2-Dichlorobenzene (DCB) was spin coated on the MAPbI₃ periodic nanostructure and thin film, followed by thermal evaporation of 100 nm Ag. For the flat MAPbI₃ device, PC₆₁BM was dissolved in DCB with a concentration of 20 mg/ml. The spin coating rate of PC₆₁BM was investigated to obtain optimized electroluminescence. FIG. 6A and 6B show the voltage-current density characteristic and voltage-radiance of flat MAPbI₃ LED under different spin coating rates for the PC₆₁BM. The optimal spin coating rate of 1000 rpm for PC₆₁BM resulted in a radiance of 0.27 W/(m²sr) for the flat MAPbI₃ LED. As for the device with MAPbI₃ periodic nanostructure, PC₆₁BM was dissolved in DCB with a concentration of 30 mg/ml and its spin coating rate was as low as 500 rpm in order to fully cover the perovskite. The radiance of the LED with the 735 nm-period MAPbI₃ reached 0.52 W/(m²sr), which was approximate two times that of the flat MAPbI₃ LED, as shown in FIG. 6D. This increased electroluminescence in the MAPbI₃ LED with the periodic nanostructure matched well with the improved PL in the MAPbI₃ periodic

nanostructure. The improvement can be attributed to the improved crystal quality of perovskite after being patterned and the light out coupling of the periodic nanostructure.

EXAMPLE 2

[0050] Another method for fabrication of flat MAPbI₃ thin film was investigated and utilized to fabricate a MAPbI₃ periodic nanostructure. More specifically, 0.15 mol/l precursor of PbI₂/MAI (molar ratio = 1:1) was dissolved in dimethylformamide (DMF). After complete dissolution, the precursor was spin coated on a PEDOT:PSS/ITO substrate with a speed of 5000 rpm for 50 seconds. After coating, the substrate was annealed at 100 °C for 10 min. A PDMS mold with a period of 735 nm was placed on prepared flat MAPbI₃ thin film. The MAPbI₃ thin film with PDMS mold atop was transferred into a chamber where dry gaseous MA was prepared through heating its aqueous solution at 60 °C. The MA gas was dried with CaO powder and then introduced to the perovskite thin film. After less than 10 min of MA gas treatment, brown MAPbI₃ became transparent. Subsequently, the device was brought back to the glove box, followed by annealing at 100 °C for 5 min. After removal of the PDMS mold, the MAPbI₃ periodic nanostructure was revealed. FIG 4A and 4B show the MAPbI₃ thin film from this method and its corresponding MAPbI₃ periodic nanostructure with a period of 735 nm. It also should be noticed that the small crystals in the thin film disappeared after forming the MAPbI₃ periodic nanostructure.

[0051] The present invention has been described herein using molds having period of 735 nm. However, the present inventors have also demonstrated successful operation using molds with periods of 1500 nm.

[0052] While the present invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A method of fabricating perovskite periodic nanostructures, the method comprising steps of:

forming a flat perovskite thin film on a substrate;
covering the perovskite thin film with a periodic mold having a nanostructure pattern;
converting the perovskite into a liquid intermediate by reacting it with a chemical
recovering the liquid intermediate into solid perovskite by removing the introduced chemical; and
removing the mold.

2. The method according to claim 1, wherein the perovskite has a general formula of ABX_3 ,

where A is an organic cation;

where B is at least one divalent metal cation, preferably selected from Ca^{2+} , Sr^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Pd^{2+} , Ge^{2+} , Sn^{2+} , Pb^{2+} , Yb^{2+} and Eu^{2+} ; and

where X is at least one halide anion, and preferably the perovskite is selected from $CH_3NH_3PbI_3$, $CH_3NH_3PbBr_3$, $CH_3NH_3PbCl_3$, $CH_3NH_3PbF_3$, $CH_3NH_3PbBrI_2$, $CH_3NH_3PbBrCl_2$, $CH_3NH_3PbIBr_2$, $CH_3NH_3PbICl_2$, $CH_3NH_3PbClBr_2$, $CH_3NH_3PbI_2Cl$, $CH_3NH_3SnBrI_2$, $CH_3NH_3SnBrCl_2$, $CH_3NH_3SnF_2Br$, $CH_3NH_3SnIBr_2$, $CH_3NH_3SnICl_2$, $CH_3NH_3SnF_2I$, $CH_3NH_3SnClBr_2$, $CH_3NH_3SnI_2Cl$, $CH_3NH_3SnF_2Cl$, $HC(NH_2)_2PbI_3$, $HC(NH_2)_2PbBr_3$, $HC(NH_2)_2PbCl_3$, $HC(NH_2)_2PbF_3$, $HC(NH_2)_2PbBrI_2$, $HC(NH_2)_2PbBrCl_2$, $HC(NH_2)_2PbIBr_2$, $HC(NH_2)_2PbClBr_2$, $HC(NH_2)_2PbI_2Cl$, $HC(NH_2)_2PbICl_2$, $HC(NH_2)_2SnI_3$, $HC(NH_2)_2SnBr_3$, $HC(NH_2)_2SnCl_3$, $HC(NH_2)_2SnF_3$, $HC(NH_2)_2SnBrI_2$, $HC(NH_2)_2SnBrCl_2$, $HC(NH_2)_2SnIBr_2$, $HC(NH_2)_2SnClBr_2$, $HC(NH_2)_2SnI_2Cl$, and $HC(NH_2)_2SnICl_2$.

3. The method according to claim 2, wherein the organic cation of the perovskite has a general formula of $(R_1R_2R_3R_4N_a)^+$,

where R_1 is hydrogen, unsubstituted or substituted C_1 - C_{10} alkyl;

where R_2 is hydrogen, unsubstituted or substituted C_1 - C_{10} alkyl;

where R_3 is hydrogen, unsubstituted or substituted C_1 - C_{10} alkyl;

where R_4 is hydrogen, unsubstituted or substituted C_1 - C_{10} alkyl; and

where a is a value between 1 and 10 with 1 and 10 included.

4. The method according to claim 1, wherein the flat perovskite thin film is formed by one of spin coating, thermal evaporation, and doctor blading.

5. The method according to claim 1, wherein the substrate for depositing flat perovskite thin film is rigid or flexible.

6. The method according to claim 5, wherein the rigid substrate is glass, silicon, ITO coated glass, fluorine-doped tin oxide FTO coated glass, or any of them coated with semiconductor, and wherein the flexible substrate is ITO coated polyethylene terephthalate PET, ITO coated polyethylene-naphthalate PEN, ITO coated polyimide PI, FTO coated PET, FTO coated PEN, and FTO coated PI, or any of them coated with semiconductor.

7. The method according to claim 1, wherein the mold is made from one of PDMS, PMMA, Silicon, Nickel, or Silicon dioxide; wherein the mold is dimensional periodic nanostructure with period;

wherein the mold is two dimensional hole or pillar structure with configuration;

wherein the liquid intermediate is formed at room temperature or elevated temperature;

wherein the chemical is nitrogen-containing compound, such as amines, including monoamines, diamines, triamines and polyamines, preferably including aliphatic monoamines such as methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, 2-ethylhexylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, octadecylamine, octadecylamine, eicosylamine or docosylamine, alicyclic monoamines such as cyclohexylamine or methylcyclohexylamine, aromatic monoamines such as benzylamine or β -phenylmethylamine, symmetrical secondary amines such as N,N-dimethylamine, N,N-diethylamine, N,N-dipropylamine, N,N-dibutylamine, N,N-diethylamine or N,N-dioctylamine,

and mixed secondary amines such as N-methyl-N-ethylamine, N-methyl-N-butylamine, N-methyl-N-dodecylamine, N-methyl-N-octadecylamine, N-ethyl-N-hexadecylamine, N-ethyl-N-octadecylamine, N-propyl-N-hexadecylamine or N-propyl-N-benzylamine; preferably the chemical is selected from the group consisting of ammonia, methylamine, formamidine, ethylamine, n-butylamine, tert-butylamine, and octylamine; and/or

wherein removing the introduced chemical is achieved by heating at a temperature between 25 °C and 150 °C, evacuating under a pressure between 10^{-5} Pa and 10^5 Pa, with both heating and evacuating, and/or natural volatilization at room temperature.

8. A perovskite periodic nanostructure, wherein the perovskite periodic nanostructure is fabricated using the method according to claim 1.

9. An optoelectronic device, wherein the device comprises a perovskite periodic nanostructure according to claim 8.

10. An optoelectronic device according to claim 9, wherein the device is any one selected from the group consisting of light emitting diodes, lasers, solar cells, and photodetectors.

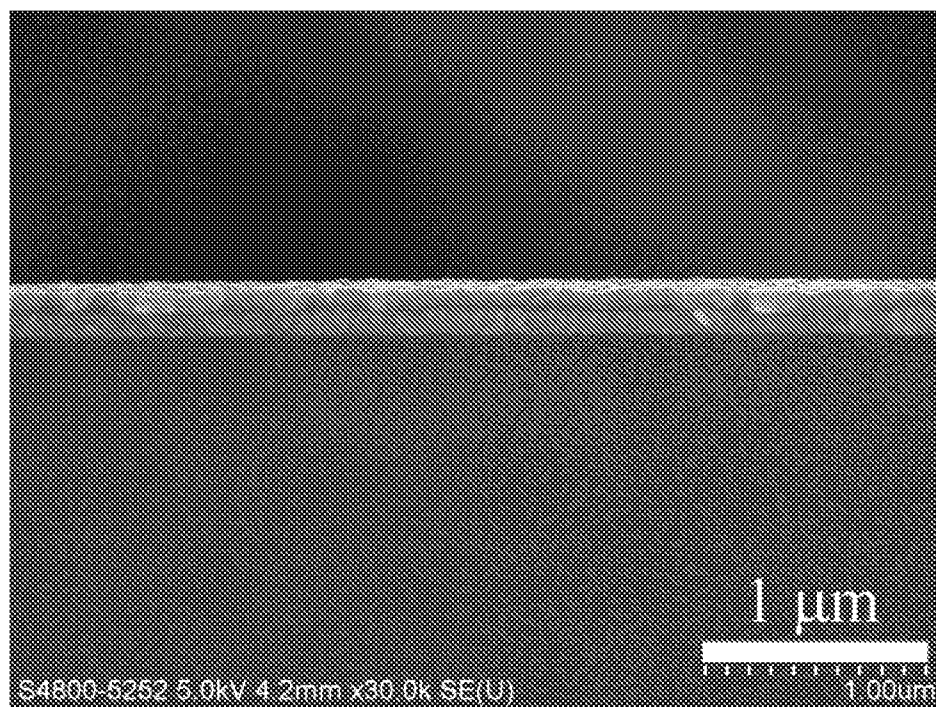


FIG. 1A

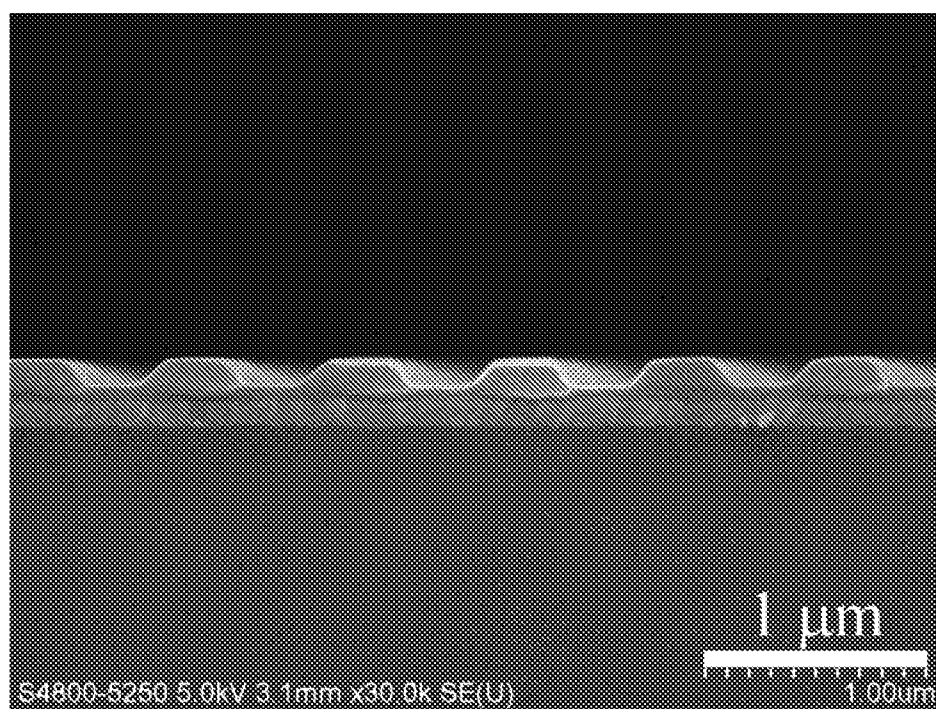


FIG. 1B

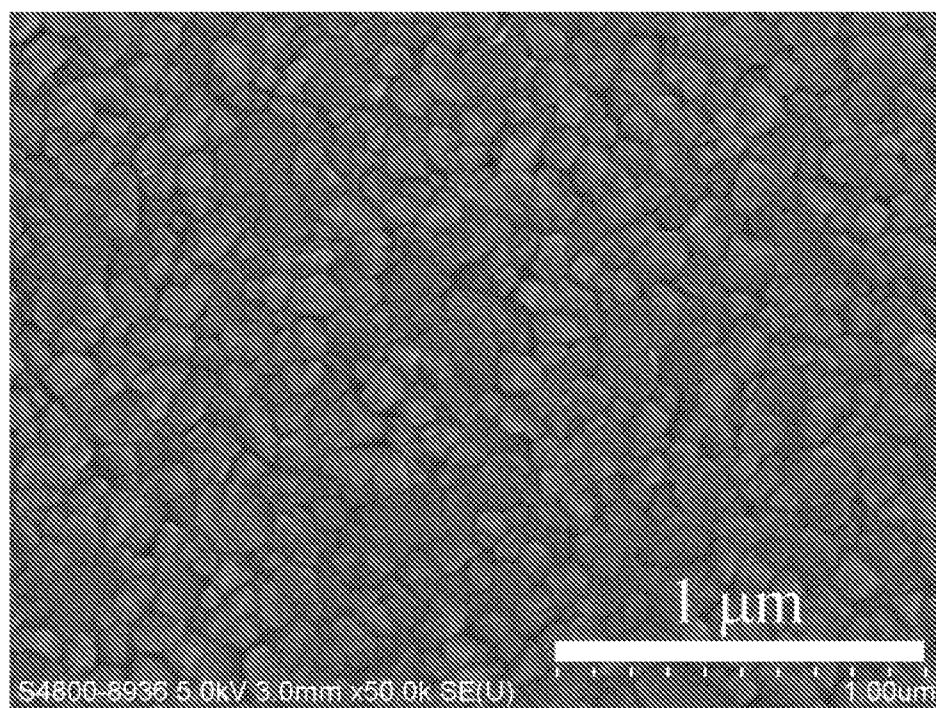


FIG. 1C

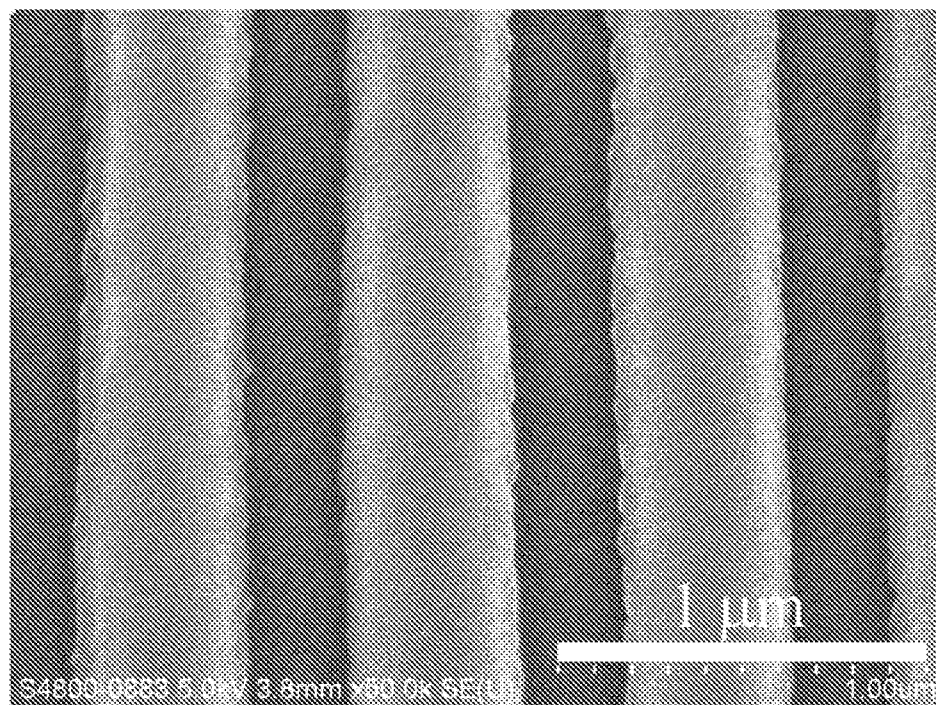


FIG. 1D

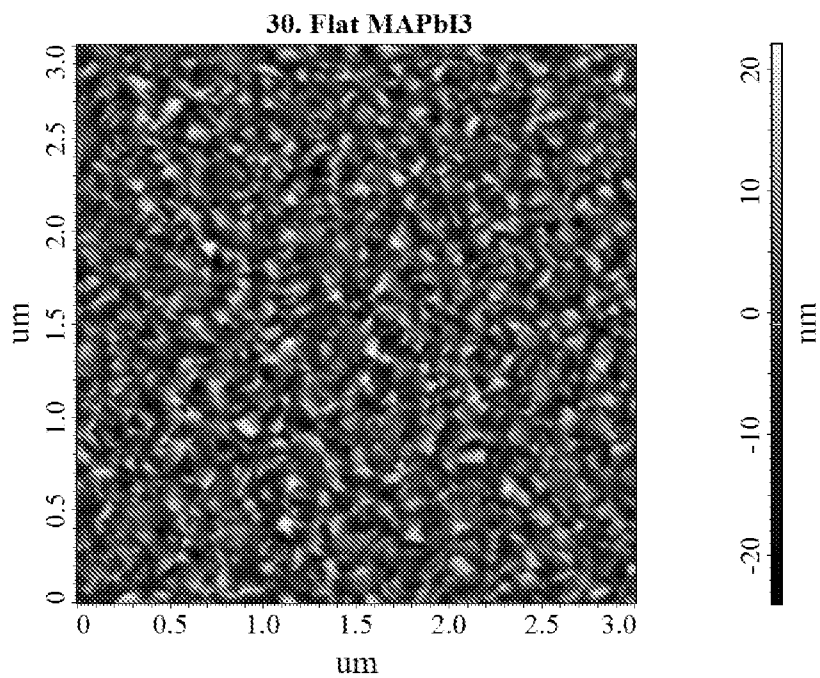


FIG. 1E

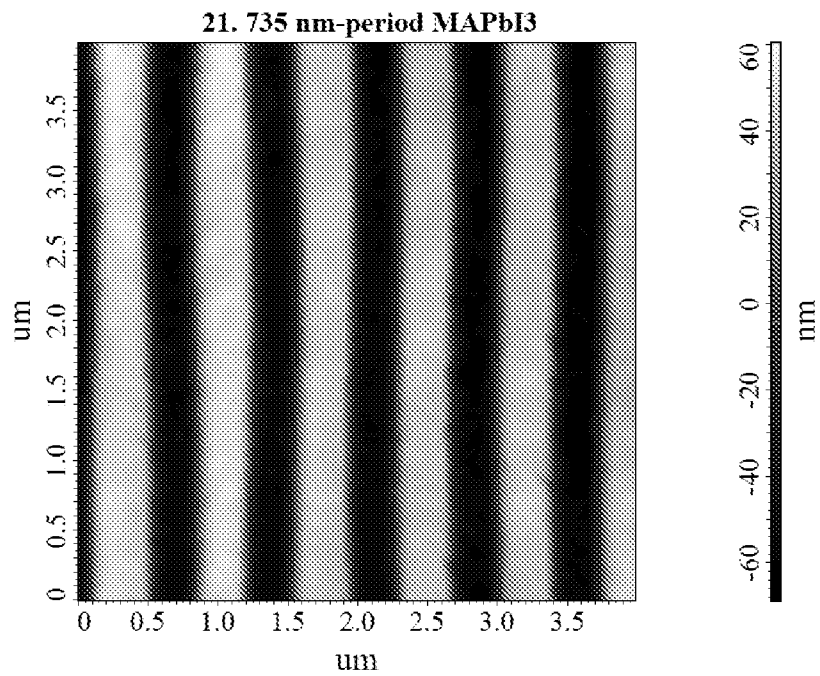


FIG. 1F

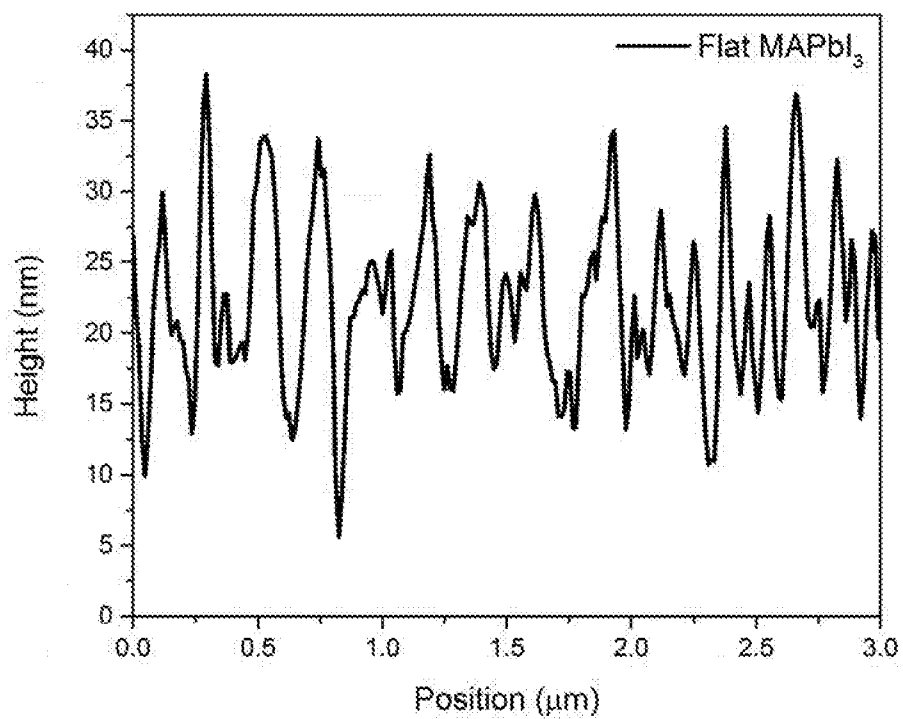


FIG. 1G

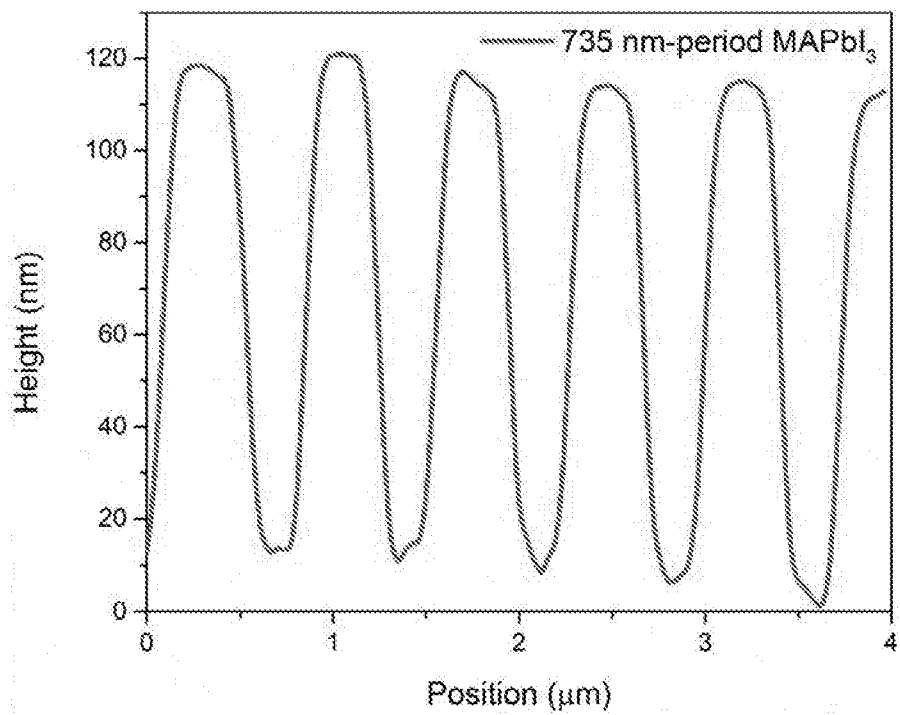


FIG. 1H

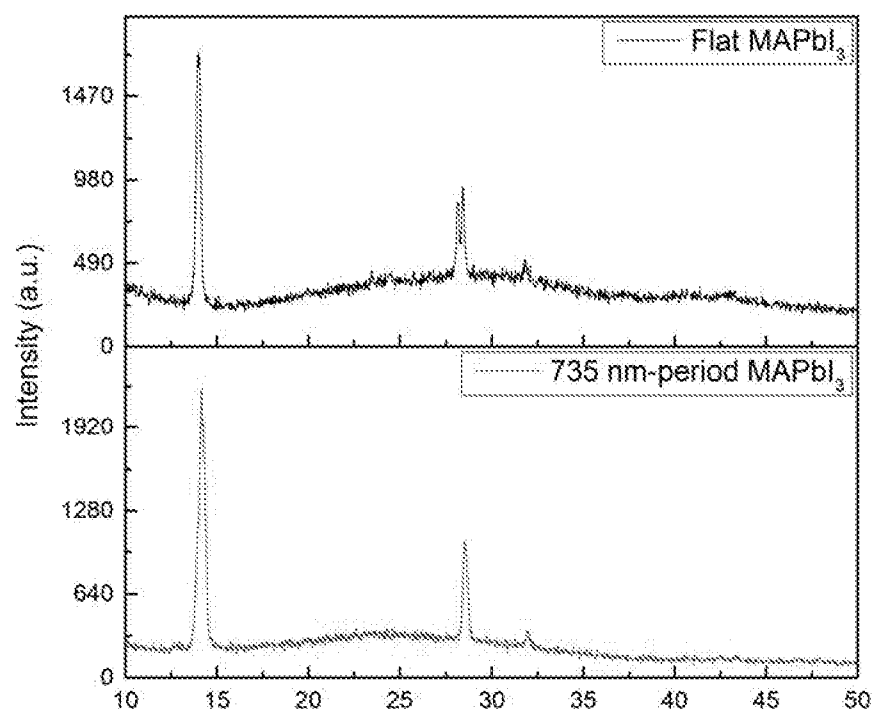


FIG. 2

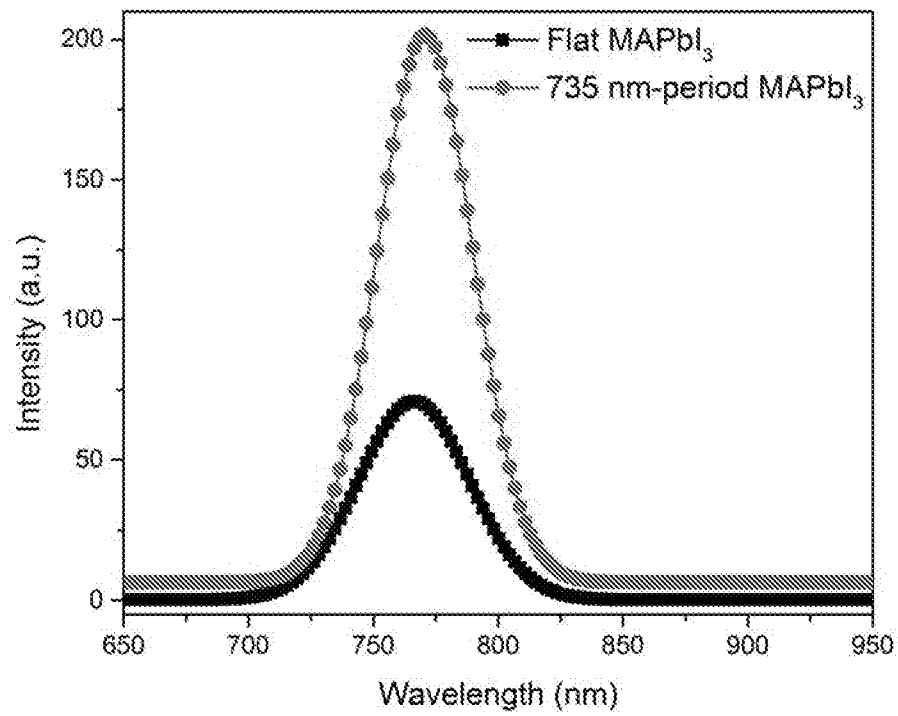


FIG. 3

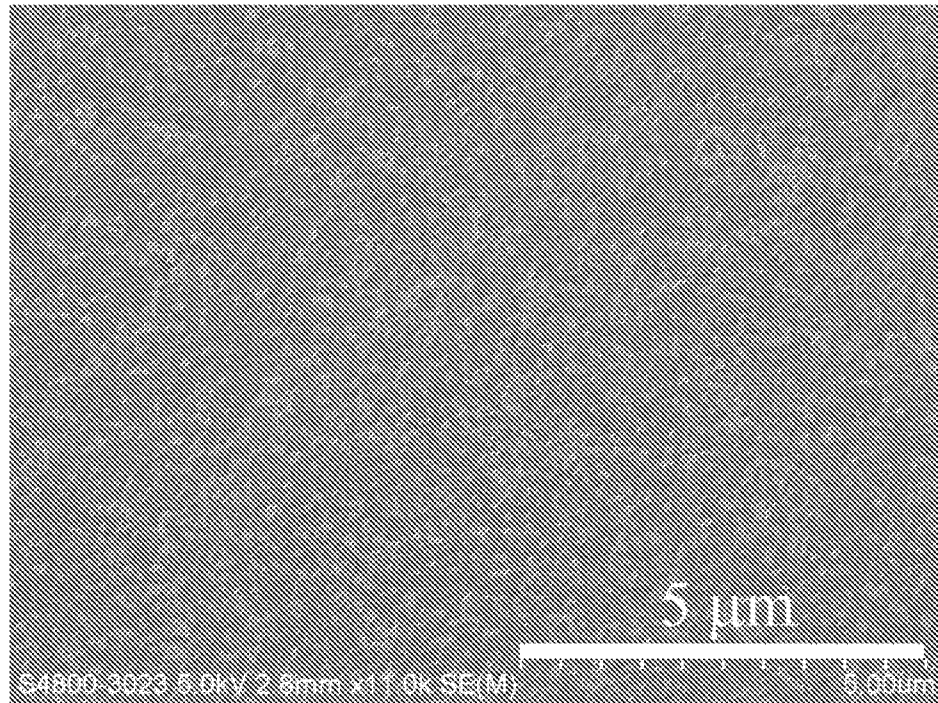


FIG. 4A

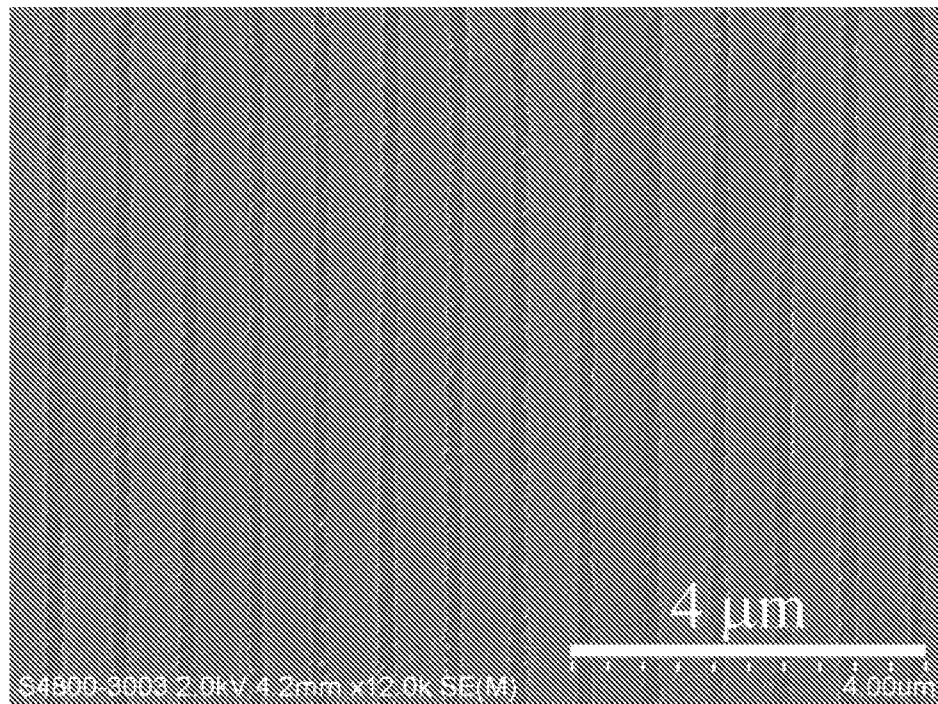


FIG. 4B

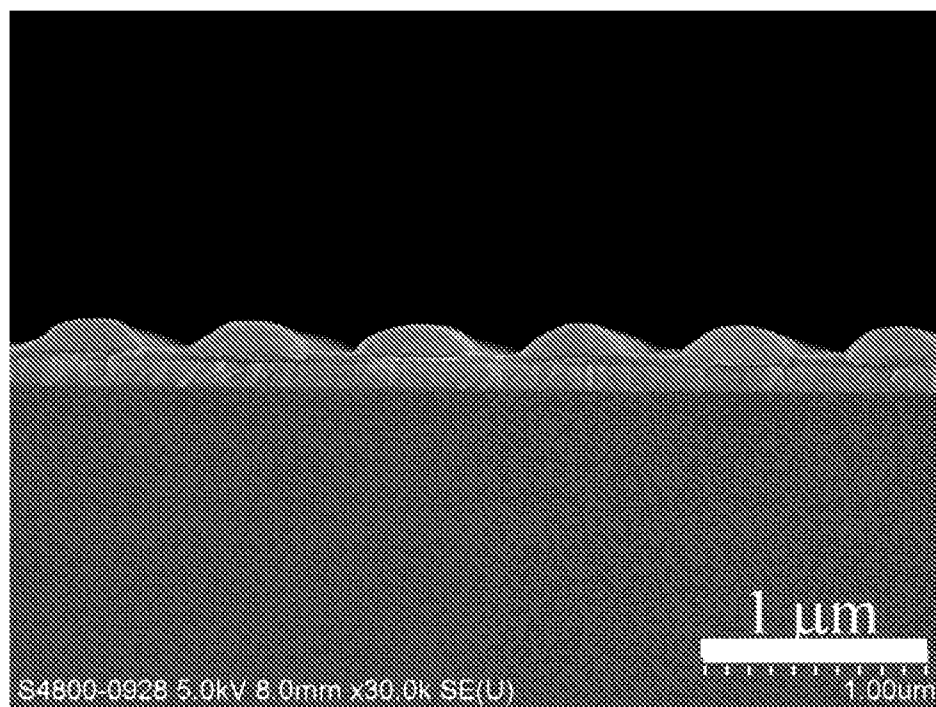


FIG. 5A

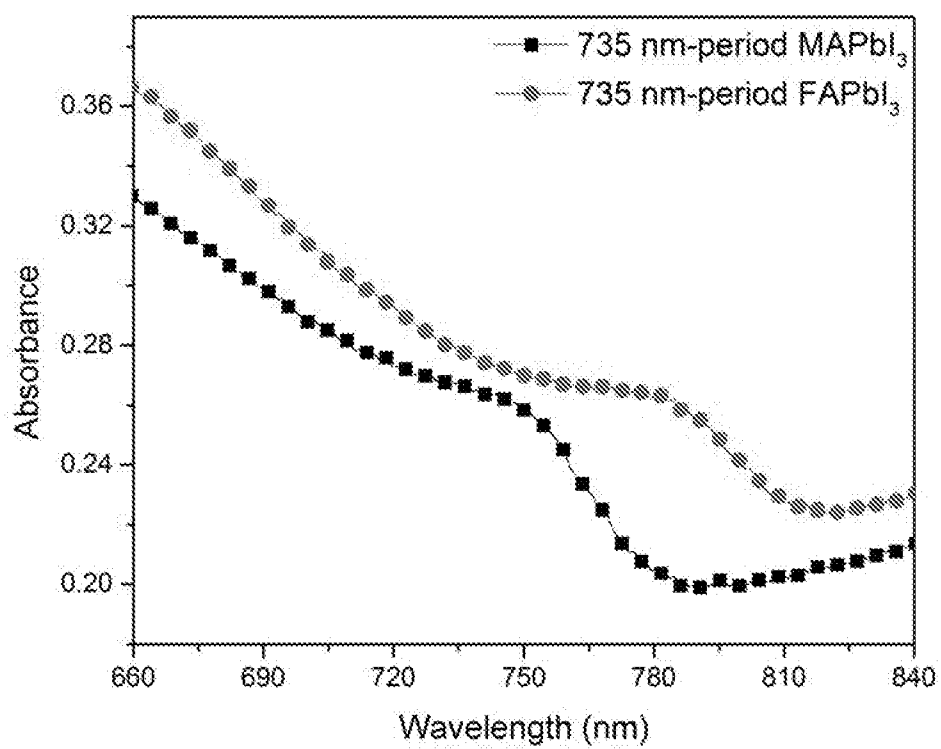


FIG. 5B

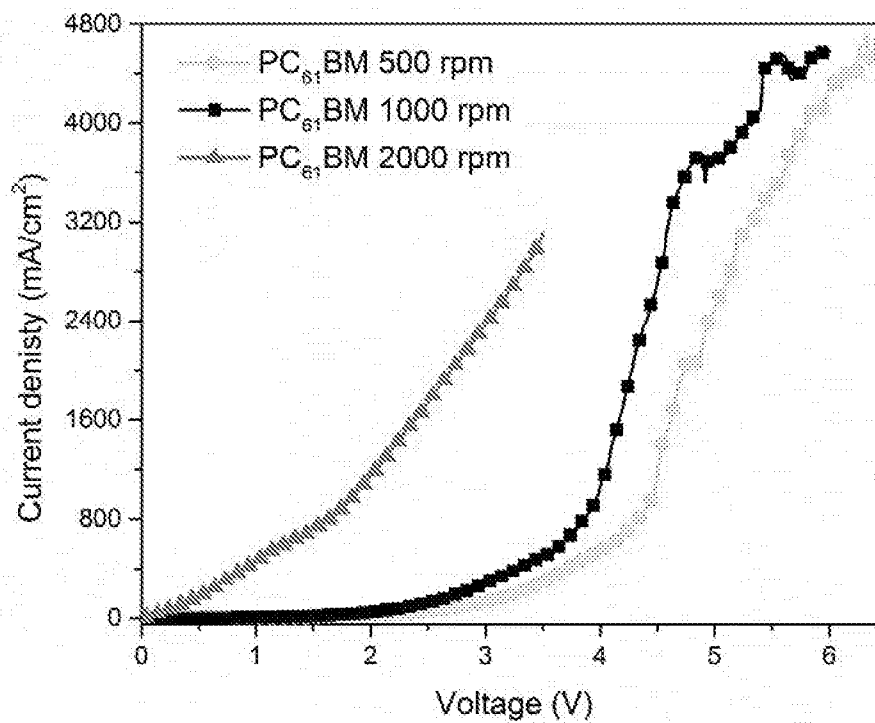


FIG. 6A

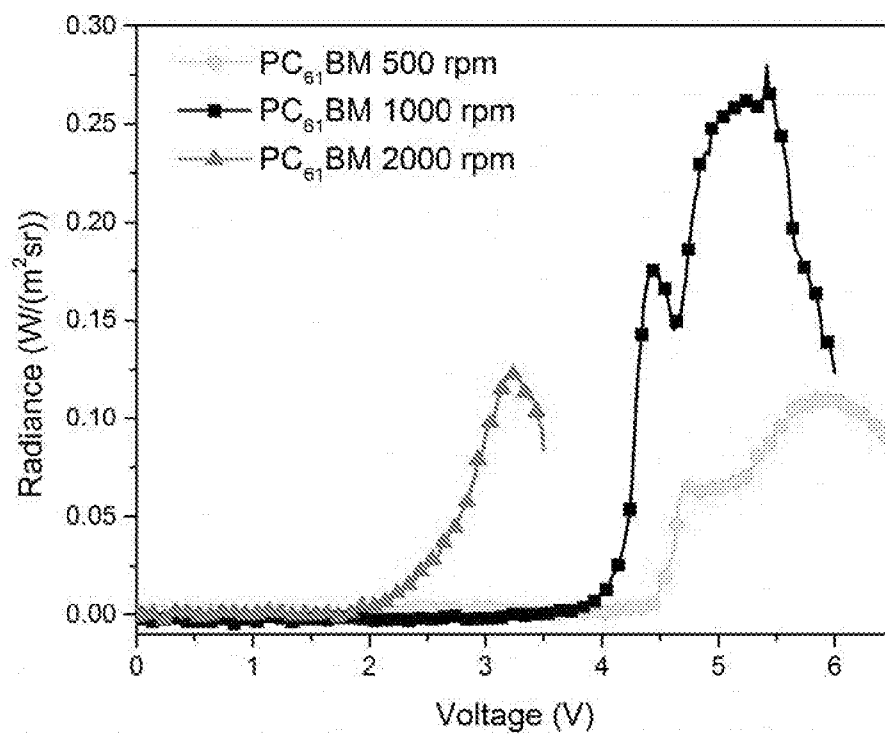


FIG. 6B

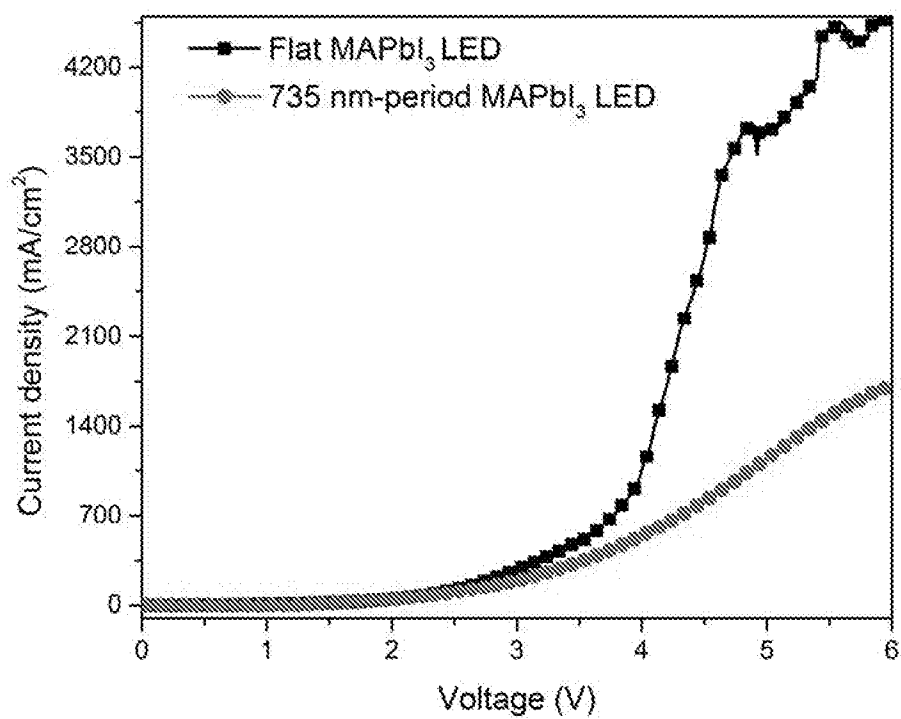


FIG. 6C

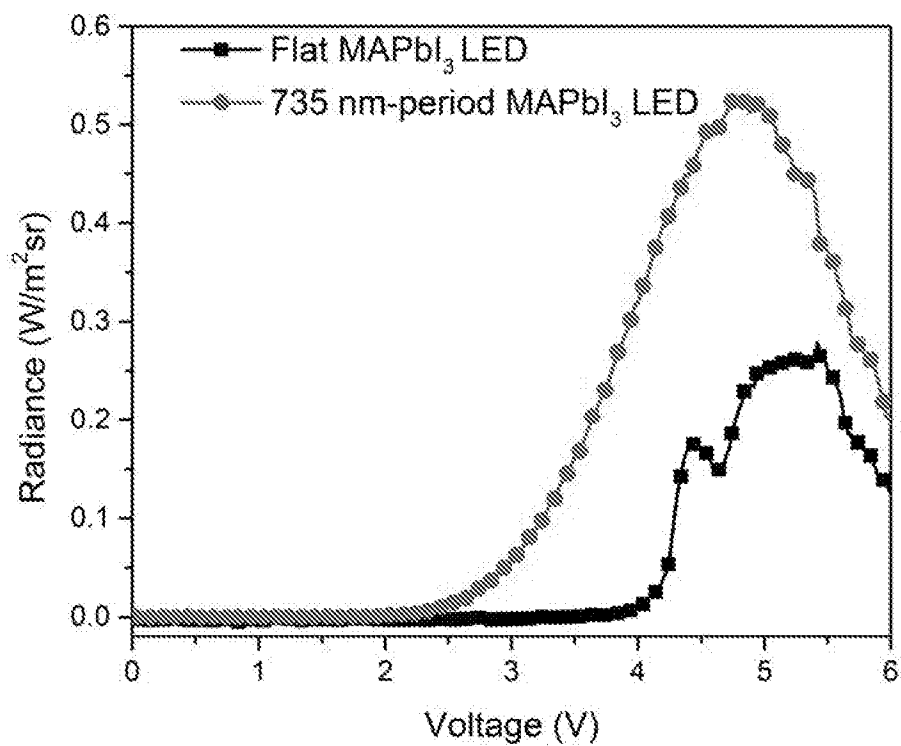


FIG. 6D

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/091992

A. CLASSIFICATION OF SUBJECT MATTER

C30B 29/12(2006.01)i; H01L 51/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C30B29/-; H01L51/-

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)

CNABS,CNKI,CNTXT,VEN:perovskite?,alkyl,periodic,mold,nanostructure,pattern,solid,liquid

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2015139082 A1 (UNIV. MONASH) 24 September 2015 (2015-09-24) page12, line 20-line 30	1-10
A	EP 1419814 A1 (AIR LIQUIDE) 19 May 2004 (2004-05-19) paragraph[0031]	1-10
A	US 5246898 A (MATSUSHITA ELECTRIC IND. CO., LTD) 21 September 1993 (1993-09-21) claim 1-claim 18, abstract	1-10
A	CN 105350078 A (UNIV. JINAN) 24 February 2016 (2016-02-24) claim1-claim10, abstract	1-10
A	CN 105552236 A (CHINA ELECTRONIC TECH. GROUP CORP. NO. 18 RES. INST.) 04 May 2016 (2016-05-04) claim 1, abstract	1-10
A	CN 102241967 A (UNIV. NANJING SCIENCE & TECH.) 16 November 2011 (2011-11-16) claim 3, abstract	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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“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

10 April 2017

Date of mailing of the international search report

08 May 2017

Name and mailing address of the ISA/CN

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Telephone No. (86-10)82245714

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2016/091992

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
WO	2015139082	A1	24 September 2015	CN	106457063	A	22 February 2017
				EP	3131653	A1	22 February 2017
				AU	2015234231	A1	22 September 2016
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				US	2004127351	A1	01 July 2004
				JP	4505208	B2	21 July 2010
				JP	2004167485	A	17 June 2004
				US	7329691	B2	12 February 2008
US	5246898	A	21 September 1993	None			
CN	105350078	A	24 February 2016	None			
CN	105552236	A	04 May 2016	None			
CN	102241967	A	16 November 2011	None			