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# **Supporting Information:**

### Efficient Perovskite Solar Cell Fabricated Using an Aqueous Lead

## **Nitrate Precursor**

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### Methods

Synthesis of MAI. Hydroiodic acid (50 g, 57 wt% in water, Wako) was added to methylamine (50 mL, 40% in ethanol, Wako) drop by drop with gentle stirring and nitrogen purging in an ice bath. After stirring for 2 hours, a white precipitate was recovered through evaporation at 50°C for 1 hour. Subsequently, the product was recrystallized using ethanol and diethyl ether sequentially in a  $-7^{\circ}$ C environment. The precipitate was recovered again through evaporation at 50°C for 1 hour. The MAI was obtained by washing with diethyl ether and then drying at 45°C in a vacuum oven overnight.

**PSC fabrication.** A piece of FTO (10  $\Omega$ /sq, NSG Group, Japan) glass was patterned using zinc powder and 3 M HCl aqueous solution, cleaned with commercial detergent (2% Hellmanex in water), deionized water, and ethanol in a sonication bath sequentially, and dried with clean air. After UV-ozone pre-treatment, a TiO<sub>2</sub> BL was spin-coated onto cleaned FTO glass by using 0.3 M titanium dissopropoxide bis-(acetylacetonate) (75 wt% in isopropanol, Sigma-Aldrich) in a 2-propanol (99.9%, Wako) solution at 1500 rpm for 30 seconds, followed by drying at 120°C for 5 minutes and annealing at 450°C for 30 minutes. After cooling to room temperature, the TiO<sub>2</sub> paste (PST 18NT, JGC&C, Japan), diluted with pure ethanol at a ratio of 1/3.5 (w/w), was spin-coated onto the BL-containing FTO glass at 5000 rpm for 30 seconds. The film was subsequently dried at 120°C for 5 minutes, annealed at 500°C for 30 minutes, and cooled to room temperature, forming an approximately 250 nmthick mesoporous TiO<sub>2</sub> layer. This layer was further treated with a bath containing 40 mM TiCl<sub>4</sub> (16%–17% solution, Wako) aqueous solution at 70°C for 30 minutes. After washing with deionized water and ethanol, the layer was dried by air and then sintered again at 450°C for 30 minutes. MAPbI<sub>3</sub> was prepared primarily according to a published sequential deposition method<sup>12</sup> and modified for the optimal condition in our system as follows: Briefly, in the Pb(NO<sub>3</sub>)<sub>2</sub>/water system, the mesoporous TiO<sub>2</sub> film was exposed to a UV-ozone atmosphere for 10 minutes before spin-coating with 1 M Pb(NO<sub>3</sub>)<sub>2</sub> (>99%, J.T. Baker) aqueous solution at 6000 rpm for 10 seconds. The Pb(NO<sub>3</sub>)<sub>2</sub> aqueous solution was maintained at 70°C and stirred during the entire spincoating process. The water was removed by drying the spin-coated Pb(NO<sub>3</sub>)<sub>2</sub> film at 70°C for 30 minutes. Subsequently, the  $Pb(NO_3)_2$ -coated TiO<sub>2</sub> film was dipped into a solution containing 98.7 mM MAI in 2-propanol (15 mg ml-1) for 700 seconds and rinsed with 2-propanol. After air drying, the film was heated at 85°C for 10 minutes to facilitate crystal growth. In the PbI<sub>2</sub>/DMF system, a solution containing 1 M PbI<sub>2</sub> (99.999%, Sigma-Aldrich) in DMF (99.8%, Sigma-Aldrich) was spin-coated onto the mesoporous TiO<sub>2</sub> layer at 6000 rpm for 10 seconds and then dried at 70°C for 30 minutes, during which time the PbI<sub>2</sub> solution was maintained at 70°C. The PbI<sub>2</sub>coated TiO<sub>2</sub> film was immersed in a 65.8 mM MAI solution in 2-propanol (10 mg ml<sup>-</sup> <sup>1</sup>) for 100 seconds, then subjected to the same drying and heating processes as that used in the Pb(NO<sub>3</sub>)<sub>2</sub>/water system. The hole transport material (HTM) was deposited

on the perovskite layer by spin-coating a chlorobenzene (99.8%, Sigma-Aldrich) solution containing 7.5 wt% 2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'- spirobifluorene (spiro-OMeTAD, Merck), 25 mM lithium bis(trifluoromethylsulphonyl)imide (Sigma-Aldrich), and 120 mM tert-butylpyridine (>96%, Sigma-Aldrich). Finally, a gold electrode (100 nm) was thermally evaporated on the HTM to finish fabrication. All processes were conducted in ambient atmosphere with controlling environment of relative humidity in the range of  $30\pm5\%$  and temperature in the range of  $24\pm2^{\circ}$ C.

**Characterisation.** The XRD spectra of the prepared films were measured using Rigaku Ultima IV with an X-ray tube (Cu,  $K\alpha$ ,  $\lambda = 1.5418$  Å). The morphology of the prepared film was scrutinised using a Hitachi SU-8010 field-emission scanning electron microscope. HP-8453 UV-visible spectrophotometry was used to explore the absorption spectra of the prepared films. The J–V curves were characterised using a solar simulator (PEC-L15, Peccell, Japan) featuring a computer-controlled digital source meter (Keithley 2400, USA) under AM1.5, 100 mw/cm<sup>2</sup>, calibrated using a monocrystaline silicon photodiode (KG3, Oriel, USA). During measurement, a mask featuring a 0.088 cm<sup>2</sup> aperture area was attached to the incident side of all devices. Every device was measured using a forward scan (short-circuit to open-circuit) and a backward scan (open-circuit to short-circuit) with a fixed 10-mV step voltage and a 50-ms delay time.

## Supporting data



S 1 Time-dependent UV-Vis spectra of perovskite crystal growing in Pb(NO<sub>3</sub>)<sub>2</sub>/water system.

The crystal composition can be judged by on-set wavelength in UV-Vis spectrum because the bandgap changes as forming new crystals. As shown in S1, two on-set wavelength at 530 nm and 790 nm correspond to the bandgap of 2.34 eV and 1.57 eV respectively, which represents that the composition of tested samples are PbI<sub>2</sub> and MAPbI<sub>3</sub>. The phase transition occurs between 100 seconds and 200 seconds MAI incubation time indicating the slow crystal-growing rate in Pb(NO<sub>3</sub>)<sub>2</sub>/water system, which could probably be attributed to diffusion-control process and discussed in article.



S 2. SEM top-view images of MAPbI<sub>3</sub> layer based on Pb(NO<sub>3</sub>)<sub>2</sub>/water system at high magnification. (a) After 100 seconds MAI incubation. (b) After 200 seconds MAI incubation.

In Pb(NO<sub>3</sub>)<sub>2</sub> system, the crystal composition begins changing from PbI<sub>2</sub> into MAPbI<sub>3</sub> after 100 seconds MAI incubation time. As shown in S2a, sheet-like PbI<sub>2</sub> crystals possess two major faces: one is flat and the other one is rough. The rough face was adsorbed by many small particles, which were considered as nuclei. As nucleation occurs on specific face it will induce crystal growth into preferential orientation. For continuous crystal growing, they will contact to each other and change their growing direction due to spatial limitation. Finally, random-shape crystals can be formed and it will further improve the surface coverage of TiO<sub>2</sub> or even form a thin film (S2b).



S 3. Photovoltaic performance as a function of scan direction. (a) The best device based on Pb(NO<sub>3</sub>)<sub>2</sub>/water system in this study. (b) The best device based on PbI<sub>2</sub>/DMF system.

Figure S3 shows the devices measured under forward (short-circuit to open-circuit) and reverse (open-circuit to short-circuit) scans with 50 ms delay time. In  $Pb(NO_3)_2$ /water system, only small hysteresis is presented (S3a); however, the  $PbI_2$ /DMF one exhibits larger hysteresis. According to previous study, ion migration in  $PbI_2$  gives rise to the hysteresis in J-V characterization. Therefore, minor hysteresis in  $Pb(NO_3)_2$ /water system can be attributed to the higher purity of MAPbI<sub>3</sub> crystals (discussed in Fig. 1c), but the details need further study.