

Supporting Information

Mg-doped TiO₂ nanorods improving open-circuit voltages of ammonium lead halide perovskite solar cells

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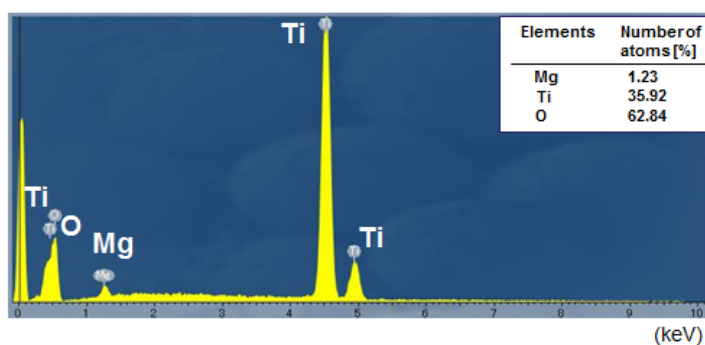


Fig. S1 EDX data for Mg-doped TiO₂ nanorods after sintering at 500°C. The synthetic condition of metal concentration is [Mg(II)]/[Ti(IV)] = 0.05.

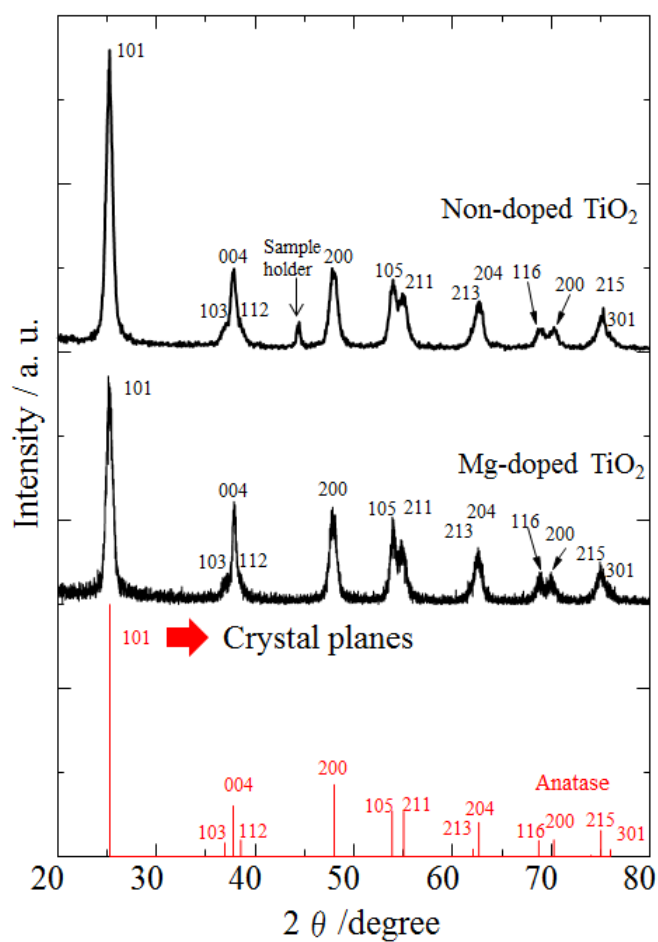


Fig. S2 XRD pattern of as-prepared TiO₂ nanorods with and without Mg doping.

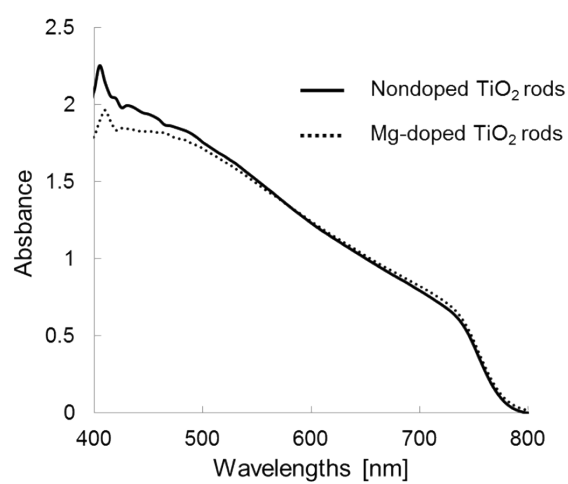


Fig. S3 UV-vis absorption spectra of CH₃NH₃PbI₃-deposited TiO₂ films.

Microwave synthesis of Mg-doped TiO₂ nanorods:

Titanium tetraisopropoxide (Wako, Purity: 95%) was used after distillation under reduced pressure in nitrogen atmosphere. 15% Aqueous solution of tetramethylammonium hydroxide (Wako) and citric acid (Kishida, Purity: 99.5%) were used as purchased from Wako. A Ti(IV) precursor of colloidal titanate dispersed in water was first prepared according to the previous report.¹ Magnesium(II) acetate tetrahydrate (Aldrich, Purity > 99%) dissolved in water was then added with stirring to the colloidal solution under the condition of [Mg(II)]/[Ti(IV)] = 0.05, followed by a hydrothermal reaction. This was carried out by a microwave-heating method using the apparatus of MicroSYNTH, Milestone, as described in our previous report.² Typically, the mixtures of titanium tetraisopropoxide of 11.4 mL and 0.05 M tetramethylammonium hydroxide of 12.4 g were diluted by 10 times. The mixtures were added with citric acid (0.01 M) as a structure directing agent (SDA) to produce desired nanorods. The 50 mL portion of mixtures in a Teflon container was then reacted under microwave hydrothermal conditions at 180 °C for 60 min. After cooling down, ethanol was then added to the mixtures and they were centrifuged at 10000 rpm for 10 min. to isolate TiO₂ nanocrystals. White powder was then dried in air overnight and thus obtained were used for paste preparation.

Structures of TiO₂ were characterized by X-ray diffraction (XRD) patterns, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Those measurements were performed using a Rigaku RINT UltimaIII with monochromated Cu K α radiation, HITACHI S-4800, and JEM-2100, respectively.

Preparation of TiO₂ pastes and assembly of N719-sensitized solar cells:

Ethylcellulose-based pastes containing Mg-doped TiO₂ nanorods (TiO₂: 15 wt%) were prepared in the way similar to our previously reported method of the corresponding nondoped TiO₂ nanorods.² Fluorine doped SnO₂-coated glass substrates (4 mm thickness, 13 Ω \square^{-1} , Nippon Sheet Glass, Japan) were cleaned in a detergent solution using an ultrasonic bath, and then rinsed with water and ethanol. The FTO glass plates were immersed in a 40 mM TiCl₄ aqueous solution (diluted with Titanium chloride solution from Wako, 16~17% Ti) at 70 °C for 30 min. and washed with water and ethanol. The TiO₂ pastes were then doctor-bladed on the FTO glasses to create a single electrode layer (without the deposition of a light-scattering layer), where the film thickness was controlled by the thickness of adhesive tape used as the spacer. The porous TiO₂ electrodes were obtained by sintering at 500 °C for 15 min. The TiO₂ films were then treated with 40 mM TiCl₄ solution, rinsed with water and ethanol and sintered again at 500 °C for 30 min. When the TiO₂ electrodes were cooled to about 80 °C, they were immersed in a 0.5 mM N719 dye (Dyesol) solution in a mixture of acetonitrile and tert-butyl alcohol ($v : v = 1 : 1$) for 18 h. at room temperature. The dye coated TiO₂ electrode (0.30 cm² area) and a Pt-sputtered FTO glass counter electrode were assembled into a sandwich type miniature cell (0.3 cm² area), where an electrolyte composed of a solution of 0.6 M BMII (1-butyl-3-methylimidazolium iodide, Wako, Purity > 97%), 0.03 M I₂ (Wako, Purity: 99.9%), 0.1 M guanidinium thiocyanate (Wako, Purity > 99%) and 0.5 M 4-tert-butylpyridine (TBP, Aldrich, Purity: 96%) in a mixture of acetonitrile (Wako, Purity > 99%) and valeronitrile (Wako, Purity > 98%) ($v : v = 85 : 15$) was introduced into the cell. I-V curves were measured under illumination with a simulated sunlight condition at AM1.5 (100 mW/cm²) generated by a Bunko-

Keiki CEP-2000 system equipped with Xenon lamp power supply (XCS-150A) and a source meter (Keithley 2400). A mask was used to regulate the active area to 0.20 cm².

Fabrication of organo-lead halide solar cells:

A blocking layer of dense TiO₂ (thickness: 80 nm) was coated onto FTO by a spin-coating method by sintering at 500°C for 30min. The synthesized TiO₂ nanorod pastes were then deposited and calcined at 500°C as described above. TiCl₄ treatment was also conducted by the same method.

5 ml of methylamine (40% in methanol, TCI) and 5.4 ml hydroiodic acid (57 wt% in water, Aldrich) were reacted at 0°C for 2 h, with stirring under Ar. The solvent of reaction solution was evaporated under Ar atmosphere to produce yellowish powder. Thus-obtained compound was washed with diethyl ether by stirring for 30min., followed by drying at 60°C for 24 h. The CH₃NH₃I (0.395g) was then reacted with PbI₂ (1.157g, Aldrich, Purity: 99.999%) in 2ml of γ -butyrolactone (Aldrich, Purity > 99%) at 60°C for 12 h. The CH₃NH₃PbI₃ solution was then deposited onto nanorod TiO₂ electrodes by spin coating at 2000 rpm for 60sec., then at 3000 rpm for 60sec., followed by drying on a hot plate at 100°C for 2min. A regioregular poly-3-hexylthiophene (Aldrich, 99.995%, Mn: 15000~45000) dissolved in chlorobenzene (Wako, Purity > 99%) (15mg/ml), containing 12mg Li-bis(trifluoromethanesulfonyl) imide (Aldrich, Purity: 99.95%)/ acetonitrile (28 mg/ml, Wako, Purity > 99%) solution and 6mg TBP (Aldrich, Purity: 96%), was successively spin-coated on the top of CH₃NH₃PbI₃-deposited TiO₂ films. A gold electrode was finally deposited by thermal evaporation. I-V curves were measured under illumination with a simulated sunlight condition at AM1.5 (100 mW/cm²) generated by a Bunko-Keiki CEP-2000 system equipped with Xenon lamp power supply (XCS-150A) and a source meter (Keithley 2400). A mask was used to regulate the active area to 0.16 cm².

References

- 1 T. Ohya, A. Nakayama, T. Ban, Y. Ohya and Y. Takahashi, *Chem. Mater.*, 2002, **14**, 3082.
- 2 K. Manseki, Y. Kondo, T. Ban, T. Sugiura and T. Yoshida, *Dalton Trans.*, 2013, **42**, 3295.