Electronic Supplementary Information (ESI) for

Morphology-controlled mesoporous SiO_2 nanorods for efficient scaffolds in organo-metal halide perovskite solar cells

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Experimental

Materials: Unless otherwise stated, all materials were purchased from Sigma-Aldrich and used as received. Methylamine (40% in methanol) was obtained from Junsei Chemical. Spiro-MeOTAD was purchased from Merck KGaA.

Synthesis of $mSiO_2$ nanoparticles: Three kinds of morphology-controlled $mSiO_2$ nanoparticles (spherical, short-rod, and long-rod) were synthesized using a sol-gel method.[1] The aspect ratios of the $mSiO_2$ materials were modified by controlling the amount of added water and fixing the supply of the other reagents. Spherical $mSiO_2$ particles were fabricated by mixing 27 mL of DI water, 5 mL of absolute ethyl alcohol, and 1.74 mL of ammonia solution. Then, 0.47 g of cetyltrimethylammonium bromide (CTAB) was added to the mixture and stirred for 15 min to allow micelle formation. Next, 1 mL of tetraethyl orthosilicate (TEOS) was added to the mixture and the mixture was allowed to react for 2 h. The resulting white cloudy solution was centrifuged several times with ethanol and water. The spherical $mSiO_2$ material was dried in an oven to remove residual moisture. To change the aspect ratio of $mSiO_2$ nanoparticles, different amounts of DI water were added in the first step: 120 mL for short rods and 60 mL for long rods.

Fabrication of perovskite solar cells (PSCs): The devices were fabricated on patterned, fluorine-doped tin oxide (FTO)-coated glass with a sheet resistance of 15 Ω sq^{-1} (Pilkington). FTO substrates were cleaned sequentially in DI water, acetone, and 2-propanol for 60 min. A compact TiO_2 layer (40 nm) was deposited by spin-coating a colloidal solution of TiO_2 nanoparticles and titanium diisopropoxide bis(acetylacetonate) (TiAcAc), which was

synthesized following a previously reported method[2], at 5,000 rpm and annealing at 150°C for 30 min in ambient air. Then, $mSiO_2$ nanoparticles dispersed in absolute ethanol (20 mg/mL) were spin-coated twice at 5,000 rpm and annealed at 150°C for 20 min. Methylammonium iodide (CH_3NH_3I) was prepared following a previous report.[3] A perovskite precursor solution (CH_3NH_3I:$PbCl_2$ = 3:1, 45 wt% in DMF) was prepared and stirred for 3 h at 70°C to obtain a homogeneous solution. The perovskite precursor solution was cast onto the substrate, spin-coated at 3500 rpm for 60 s under a N_2 atmosphere, and annealed at 100°C for 60 min in ambient air to form $CH_3NH_3PbI_{3-x}Cl_x$ films (humidity < 30%). The hole-transporting layer was spin-coated from a 1-mL chlorobenzene solution including 72 mg of Spiro-MeOTAD, 28.8 μL of tert-butylpyridine, and 17.5 μL of acetonitrile solution containing 520 mg/mL lithium bis(trifluoromethylsyfonyl)imide salt at 4000 rpm for 30 s. Finally, a 70-nm-thick Au top electrode was deposited by thermal evaporation. The active area of the fabricated device was 0.09 cm^2.

For fabricating $MAPbI_3$-based PSCs, $MAPbI_3$ precursor solution was prepared by mixing 461 mg of PbI_2, 159 mg of CH_3NH_3I, and 71 μL of DMSO (molar ratio 1:1:1) in 770 μL of DMF. The completely dissolved precursor solution was spin-coated on the $mSiO_2$ layer at 3000 rpm for 30 s, and 500 μL of diethyl ether was dripped onto the substrate at 10 s after starting rotation. The perovskite-precursor coated substrate was annealed on a hot plate at 100 °C for 10 m. The hole-transporting layer and Au top electrode were deposited in the same manner as described above.

Measurement and Characterization: Transmission electron microscopy (TEM) and field-emission scanning electron microscopy (FE-SEM) images were obtained with JEM 2100 and

JSM-6701F microscopes, respectively (JEOL, Japan). Atomic force microscope (AFM) images of spin-coated $mSiO_2$ nanoparticles were acquired with an Innova SPM (Vecco, USA) and analyzed using SPMLabAnalysis software. X-ray diffraction (XRD) of $MAPbI_{3-x}Cl_x$ films was measured using Smartlab (Rigaku, Japan). UV-vis absorption and photoluminescence (PL) spectra of the $MAPbI_{3-x}Cl_x$ films were measured with a Lambda 35 and LS 45 fluorescence spectrometer, respectively (Perkin-Elmer, USA). Time-resolved PL decay curves were recorded with a compact fluorescence lifetime spectrometer (Quantaurus-Tau C11367-12, Hamamatsu). The films were photo-excited by a picosecond light pulser (PLP-10, Hamamatsu) in which the wavelength of the laser was 464 nm with a peak power of 231 mW and a pulse duration of 53 ps. The light was incident to the glass side of the sample with repetition rate of 5 MHz. The photocurrent-voltage (J-V) characteristics of the PSCs were examined using a 500-W xenon lamp and a MP-160 I-V Tracer (EKO Instruments, 5 ms delay time and 1.0 V/s scan rate). External quantum efficiency (EQE) was characterized from 350 nm to 850 nm using a K3100 IPCE Measurement System (McScience Inc., Korea; chopping frequency of 4 Hz, without bias light and 10-nm step wavelength). Electrochemical impedance spectra (EIS) of the PSCs were obtained by Zive Labs (Wonatech, Korea).

Reference

[1] H. Wang, P. V. d. Voort, H. Qu and S. Liu, *J. Nanopart. Res.*, 2013, **15**, 1-8.

[2] K. Wojciechowski, M. Saliba, T. Leijtens, A. Abate and H. J. Snaith, *Energy Environ. Sci.*, 2014, **7**, 1142-1147.

[3] J. Yun, J. Ryu, J. Lee, H. Yu and J. Jang, *J. Mater. Chem. A*, 2016, DOI: 10.1039/C5TA08250A.

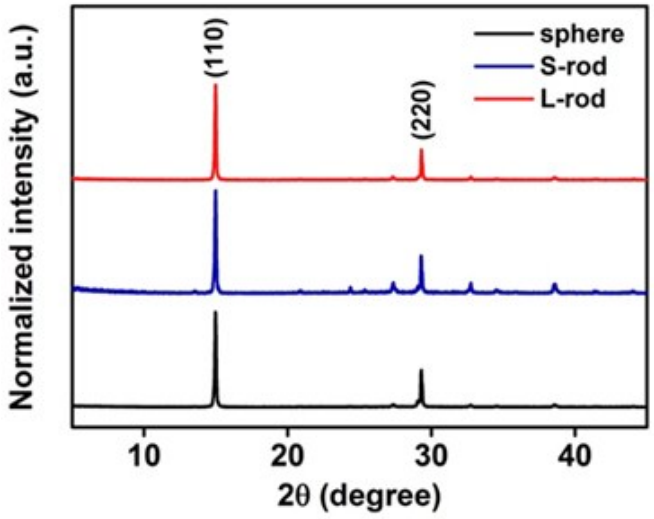

Figure S1. Normalized XRD diffractograms of $MAPbI_{3-x}Cl_x$ films spin-coated on different $mSiO_2$ nanoparticles.

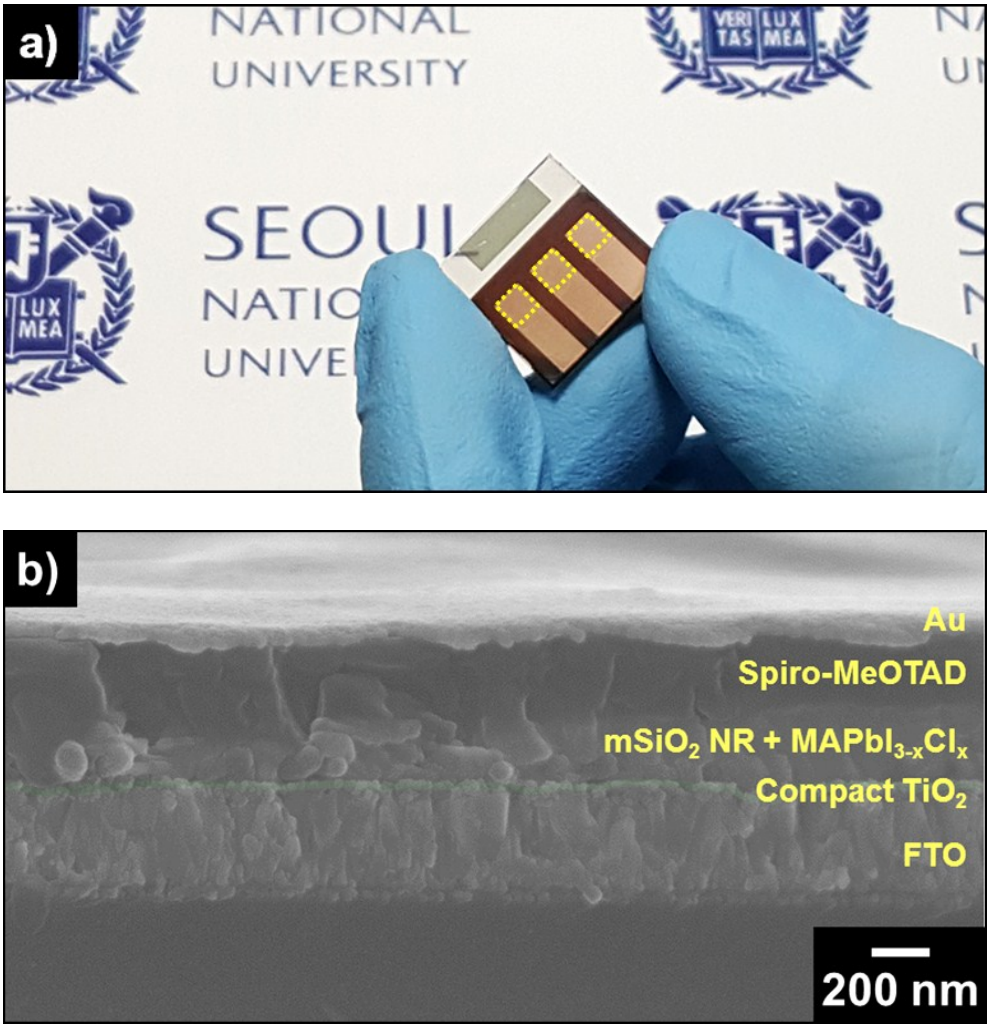

Figure S2. (a) A digital photograph of a perovskite solar cell (PSC) made with L-rod $mSiO_2$ scaffolds. The dashed yellow squares represent active areas of the cell (0.09 cm^2). (b) A cross-sectional SEM micrograph of a PSC made with L-rod $mSiO_2$ scaffolds.

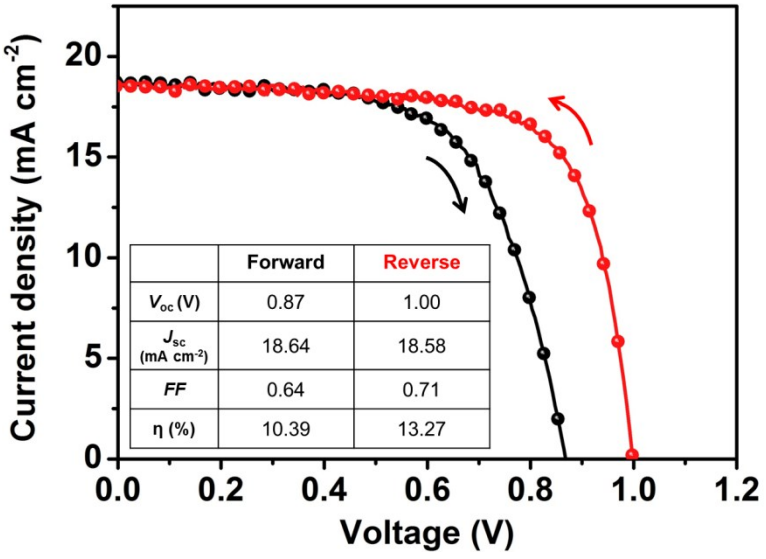

Figure S3. Hysteresis analysis of a perovskite solar cell made with L-rod $mSiO_2$ scaffolds. Photovoltaic parameters are summarized in the inset table. The scan rate of forward and reverse scan mode was 0.35 V/s.

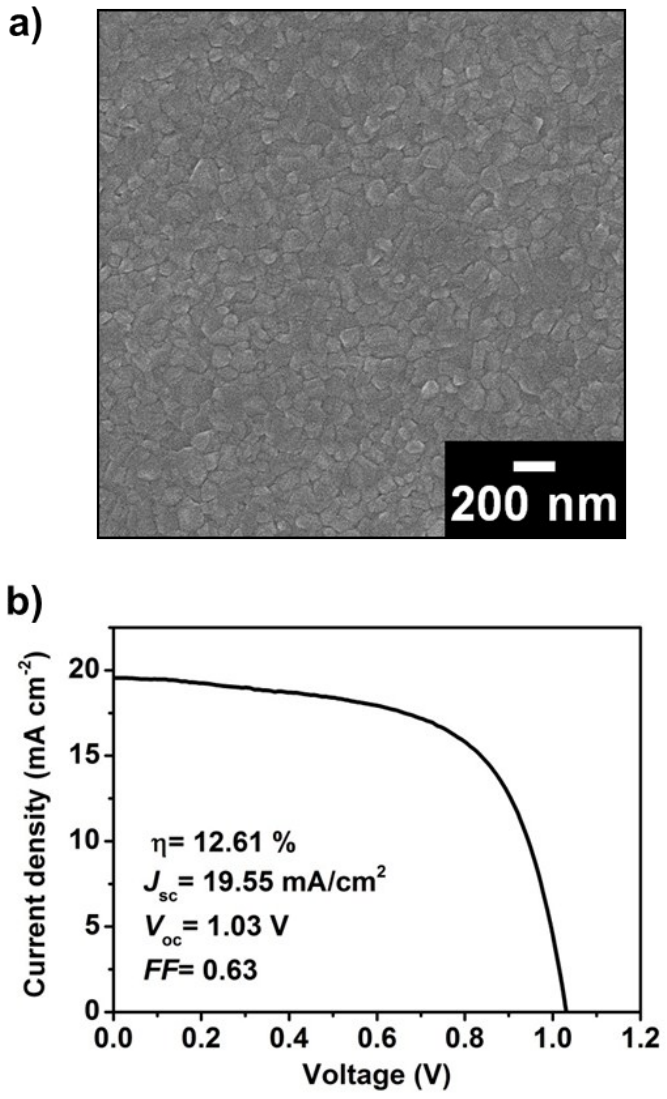

Figure S4. (a) A SEM micrograph of a spin-coated $MAPbI_3$ film on L-rod $mSiO_2$ nanoparticles. (b) *J-V* curve and photovoltaic performance parameters for the best-performing $MAPbI_3$ perovskite solar cell made with L-rod $mSiO_2$ scaffolds.

Table S1. Photovoltaic parameters of the best performing PSCs using different $mSiO_2$ nanoparticles: sphere, S-rod, and L-rod.

Sample	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	η (%)
sphere	1.06	17.22	0.68	12.36
S-rod	1.04	17.25	0.68	12.57
L-rod	1.02	19.42	0.70	13.91