Electronic Supplementary Information

Surfactant Effects on the Electrochemical-durable Lead Halide Perovskite Electro-catalysts

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1. Materials

N,*N*-Dimethylformamide (DMF, ≥ 99.8%), titanium (IV) isoproproxide (TTIP, > 98%), ethanol (EtOH, 99.5%), isopropyl alcohol (IPA, 99.5%), 2-methoxyethanol (≥ 99.5%), methylammonium iodide (MAI, 98%), 1-propyl-3-methylimidazolium iodide (PMII), and tetrahexylammonium choride (THA-Cl, 96%) were obtained from Sigma Aldrich. Lithium iodide (LiI, synthetical grade), iodine (I_2, synthetical grade), and poly(ethylene glycol) (PEG, MW~20,000) were purchased from Merck. Acetone (99%), guanidinium thiocyanate (GuSCN, ≥ 99%), 4-tert-butylpyridine (tBP, 96%), lead(II) iodide (PbI_2, 99%), tetrabutylammonium iodide (TBA-I, 98%), tetrahexylammonium bromide (THA-Br, 99%), and tert-butyl alcohol (tBA, 96%) were bought from Acros. 3-Methoxypropionitrile (MPN, 99%), cesium iodide (CsI, 99.9%), germanium(II) iodide (GeI_2, 99.99%), tetrabutylammonium hexafluorophosphate ($TBAPF_6$), and tetraethylammonium iodide (TEA-I, 98%) were procured from Alfa Aesar. 1,2-Dimethyl-3-propylimidazolium iodide (DMPII), formamidinium iodide (FAI, 99%), and tetra-*n*-octylammonium iodide (TOA-I, > 98%) were procured from Tokyo Chemical Industry Co., Ltd. Transparent TiO_2 paste (Ti–nanoxide HT/SP, average diameter of 20 nm) and cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis(tetrabutylammonium) (N719 dye) were supplied by Solaronix, S.A., Aubonne, Switzerland. Acetonitrile (MeCN, 99.99%) and dichloromethane (DCM, ≥ 99.8%) were received from J. T. Baker. The commercial light scattering TiO_2 particles, ST–41 with an averaged diameter of 200 nm, were obtained from Ishihara Sangyo, Ltd. Fluorine–doped tin oxide (FTO, TEC7, 7 Ω $sq.^{-1}$) conducting glass was purchased from NSG America, Inc., New Jersey, USA. Nickel foam (NF, 100PPI, thickness = 1.7 mm) was bought from Fucell Co., Ltd., Taiwan.

2. Fabrication of the DSSCs

Conducting substrate, FTO and carbon cloth, were cleaned with a neutral cleaner and then washed with de-ionized water, acetone, and isopropanol sequentially. A mesoporous TiO_2 photoanode (with an working area of 0.20 cm^2) was coated on a cleaned FTO by the following procedures. (1) The first TiO_2 compact layer (~100 nm) was spin-coated on FTO under 3000 rpm for 30 s using a precursor solution of TTIP/2-methoxyethanol with a weight ratio of 1/3. (2) The second TiO_2 transparent layer (~10 μm) was doctor-bladed onto the first layer using the commercial TL paste purchased from Solarnix. (3) The third TiO_2 scattering layer (~4 μm) was doctor-bladed onto the second layer using a reported home-made paste[1]. (4) Last, the TiO_2 thin film was treated by a 70 mM of $TiCl_4$ solution (with a solvent) at 70 °C for 30 min in a mixing solvent of deionc water/ethanol (v/v=9/1). The TiO_2 layer made by every step would be followed by a sintering process at 500 °C for 30 min in an ambient atmosphere. After the sintering process, the TiO_2 photoanode was immersed in a 5.0×10^{-4} M N719 dye solution using a mixed solvent of MeCN/tBA with a volume ratio of 1:1 at room temperature for 24 h. A TiO_2 photoanode was coupled with a counter electrode made by this work. And the cell gap was maintained by using a 60 μm-thick Surlyn® film as the spacer.

3. Material characterizations

Crystallinity and molecular structure of as-synthesized Cu-MOF particle were analyzed by powder X-ray diffraction pattern spectroscopy (PXRD, Rigaku, Tokyo, Japan) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific Theta Probe, UK), respectively. The thin film morphology was observed by field–emission scanning electron microscopy (FE–SEM, Nova NanoSEM 230, FEI, Oregon, USA).

4. Photovoltaic performance measurement

Photovoltaic parameters of the DSSCs with different counter electrodes were obtained by a potentiostat/galvanostat (Metrohm Autolab PGSTAT204, Autolab, Eco-Chemie, the Netherlands) at the simulated solar irradiation (100 mW cm^{-2}, AM 1.5G) and Philip T5 lamp illumination (6000, 3000, and 1000 lux). The simulated solar irradiation was performed by a class A quality solar simulator (PEC–L11, AM1.5G, Peccell Technologies, Inc., Kanagawa, Japan). The incident light intensity was calibrated by a standard Si cell (PECSI01, Peccell Technologies, Inc.) and by an optical detector (model 818-SL, Newport, California, USA) coupled with a power meter (model 1916-R, Newport, California, USA). The DSSC device was composed of a sandwitch structure of photoanode/ electrolyte/ counter electrode; where an indentical TiO_2 film adsorbed with N719 sensitizer was the photoanode, an liquid iodide-based mixture was the electrolyte, and the different electrodes made by this work were used as the counter electrodes. Here, the iodide-based electrolyte contained 1.2 M DMPII, 0.035 M I_2, 0.1 M GuSCN, and 0.5 M tBP in MPN/MeCN (volume ratio of 1:4) and was injected into the gap between photoanode and counter electrode by capillarity.

5. Four-point probe and electrochemical measurements

Four-point probe measurement were recorded by a Keithley's instrument (Keithley 2450 – ScourceMeter Instrument, Keithley Instruments Inc., USA) by using the different electrodes made by this work. Tafel polarization plots and electrochemical impedance spectra (EIS) analysese were recorded a potentiostat/galvanostat (Metrohm Autolab PGSTAT204, Autolab, Eco-Chemie, the Netherlands) using a symmetrical cell structure of electrode/electrolyte/electrode; where an electrode made by this work was applied for both anode and cathode. The electrolyte for Tafel and EIS analyses contained 1.2 M DMPII, 0.035 M I_2, 0.1 M GuSCN, and 0.5 M tBP in MPN/MeCN (volume ratio of 1:4). For Tafel plots, linear sweep voltammetry (LSV) was performed from 1 V to –1 V at the scan rate of 50 mV s^{-1}. For EIS analysis, the data was collected using a FRA2 module between 10 mHz to 65 kHz with an AC amplitude of ±10 mV. CV analysis was executed by a potentiostat/galvanostat (Metrohm Autolab PGSTAT204, Autolab, Eco-Chemie, the Netherlands) using a three–electrode system. The sample electrode was used as the working electrode. A Pt foil and $Ag/AgNO_3$ electrodes were used as the counter and reference electrode, respectively. A dilute iodide-based electrolyte, containing 10 mM of 1-propyl-3-methylimidazolium iodide (PMII), 1 mM of iodine (I_2), and 0.1 M of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane (DCM), was used.

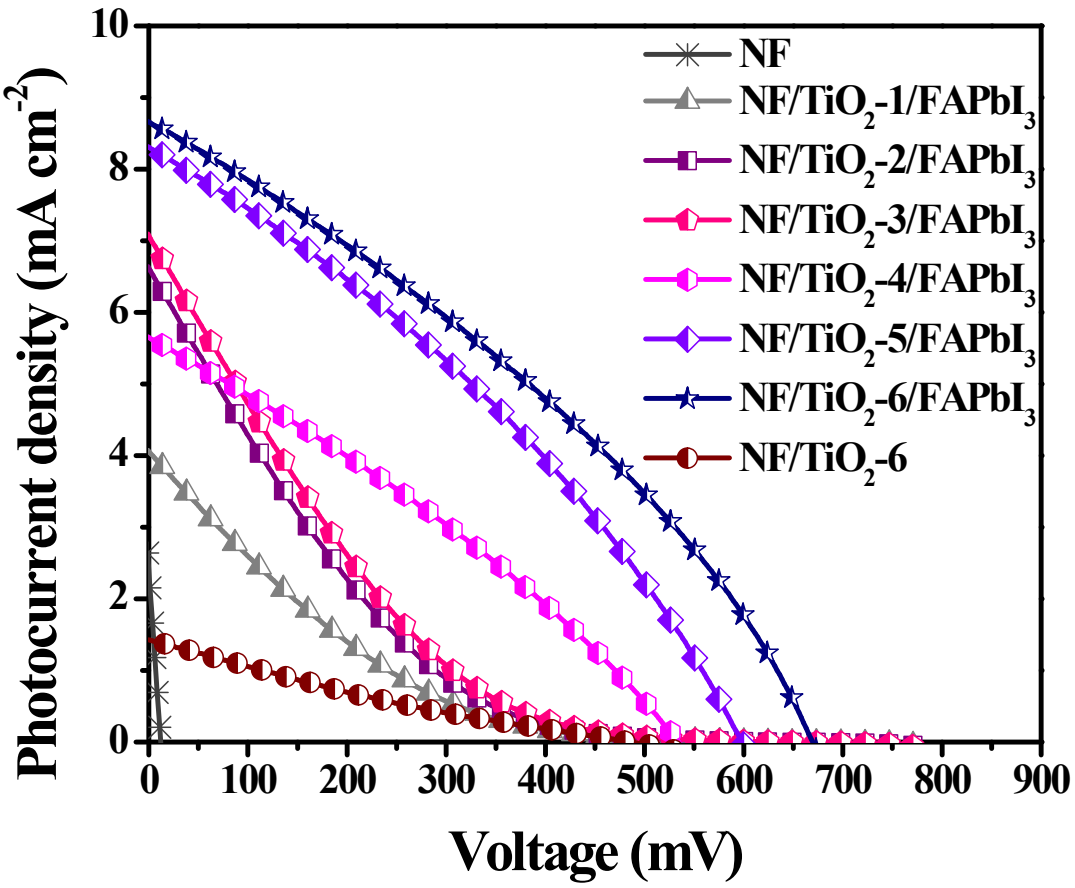

Fig. S1 Photocurrent density–voltage curves of DSSCs with counter electrodes of raw NF, different NF/TiO_2-*x*/$FAPbI_3$, (*x* = 1 to 6), and NF/TiO_2-6, measured at a simulated AM 1.5G.

Table S1 Photovoltaic parameters of the DSSCs with counter electrodes of raw NF, different NF/TiO_2-*x*/$FAPbI_3$, (*x* = 1 to 6), and NF/TiO_2-6, measured at a simulated AM 1.5G. The statistical data were based on five independent measurements.

Counter electrode	η (%)	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF*
NF	0.01±0.00	0.01±0.01	2.80±0.2	0.24±0.00
NF/TiO_2-1/$FAPbI_3$	0.29±0.05	0.61±0.06	4.10±0.2	0.12±0.00
NF/TiO_2-2/$FAPbI_3$	0.48±0.05	0.63±0.07	6.60±0.3	0.11±0.00
NF/TiO_2-3/$FAPbI_3$	0.50±0.03	0.64±0.04	6.50±0.1	0.12±0.00
NF/TiO_2-4/$FAPbI_3$	0.89±0.05	0.53±0.09	5.60±0.3	0.30±0.00
NF/TiO_2-5/$FAPbI_3$	1.62±0.04	0.60±0.05	8.00±0.2	0.34±0.00
NF/TiO_2-6/$FAPbI_3$	1.90±0.03	0.66±0.05	8.70±0.2	0.33±0.00
NF/TiO_2-6	0.13±0.01	0.49±0.07	1.40±0.3	0.20±0.01

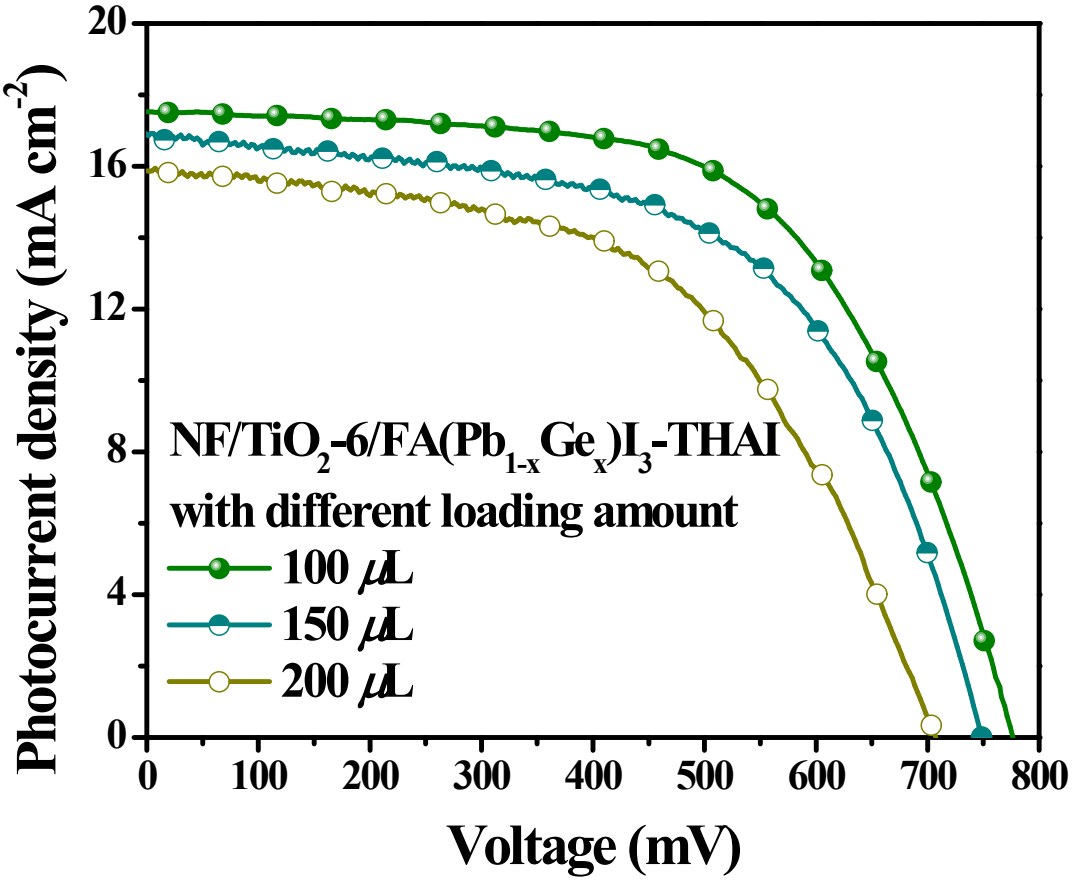

Fig. S2 Photocurrent density–voltage curves of DSSCs with the counter electrodes of different NF/TiO_2-6/FA($Pb_{1-x}Ge_x$)I_3-THAI prepared by different loading amount of precursor, measured at a simulated AM 1.5G.

Table S2 Photovoltaic parameters of the DSSCs with the counter electrodes of different NF/TiO_2-6/FA($Pb_{1-x}Ge_x$)I_3-THAI prepared by different loading amount of precursor, measured at a simulated AM 1.5G. The statistical data were based on five independent measurements.

NF/TiO_2-6/FA($Pb_{1-x}Ge_x$)I_3-THAI Counter electrode	***η*** **(%)**	***V*$_{OC}$** **(V)**	***J*$_{SC}$** **(mA cm^{-2})**	***FF***
100 μL	8.31 ± 0.31	0.77 ± 0.01	17.69 ± 0.36	0.61 ± 0.01
150 μL	7.15 ± 0.28	0.75 ± 0.02	17.23 ± 0.11	0.57 ± 0.01
200 μL	6.27 ± 0.41	0.72 ± 0.02	15.94 ± 0.43	0.55 ± 0.02

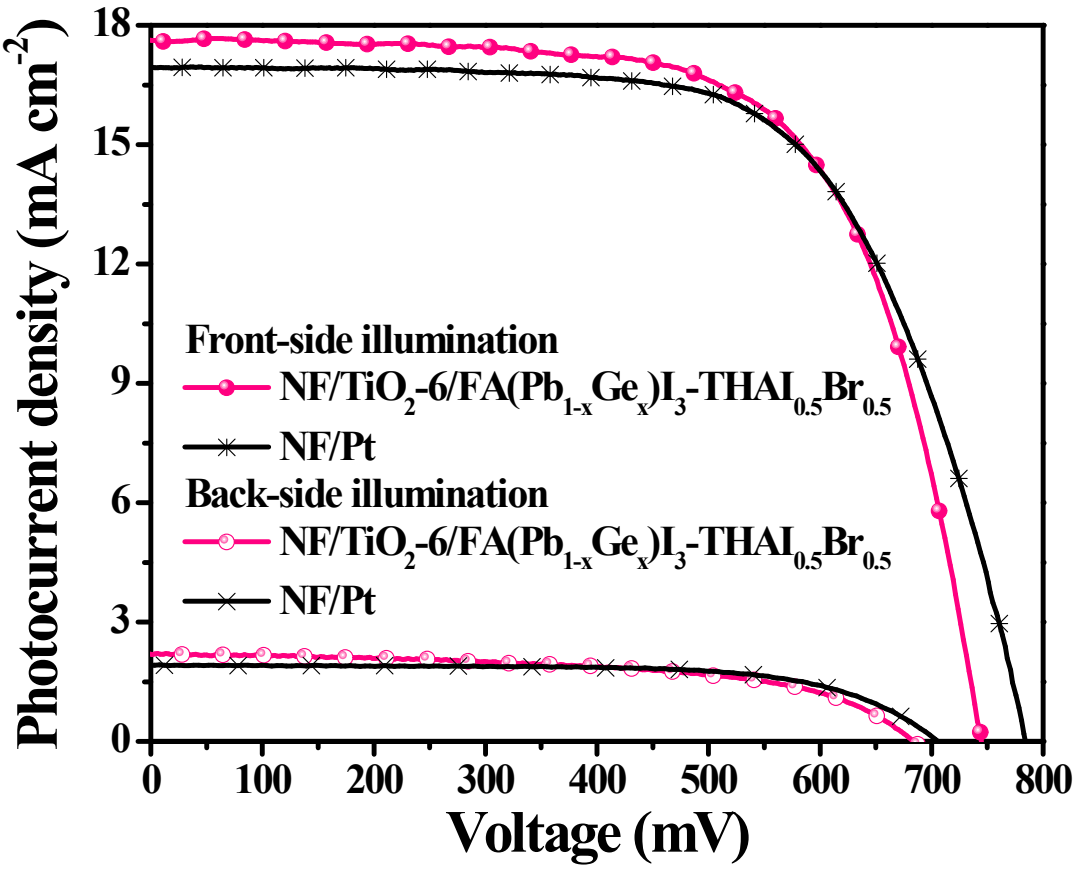

Fig. S3 Photocurrent density–voltage curves of DSSCs with the counter electrodes of NF/Pt and NF/TiO_2-6/FA($Pb_{1-x}Ge_x$)I_3-THA$I_{0.5}Br_{0.5}$, measured at a simulated AM 1.5G illumination from the front-side and back-side.

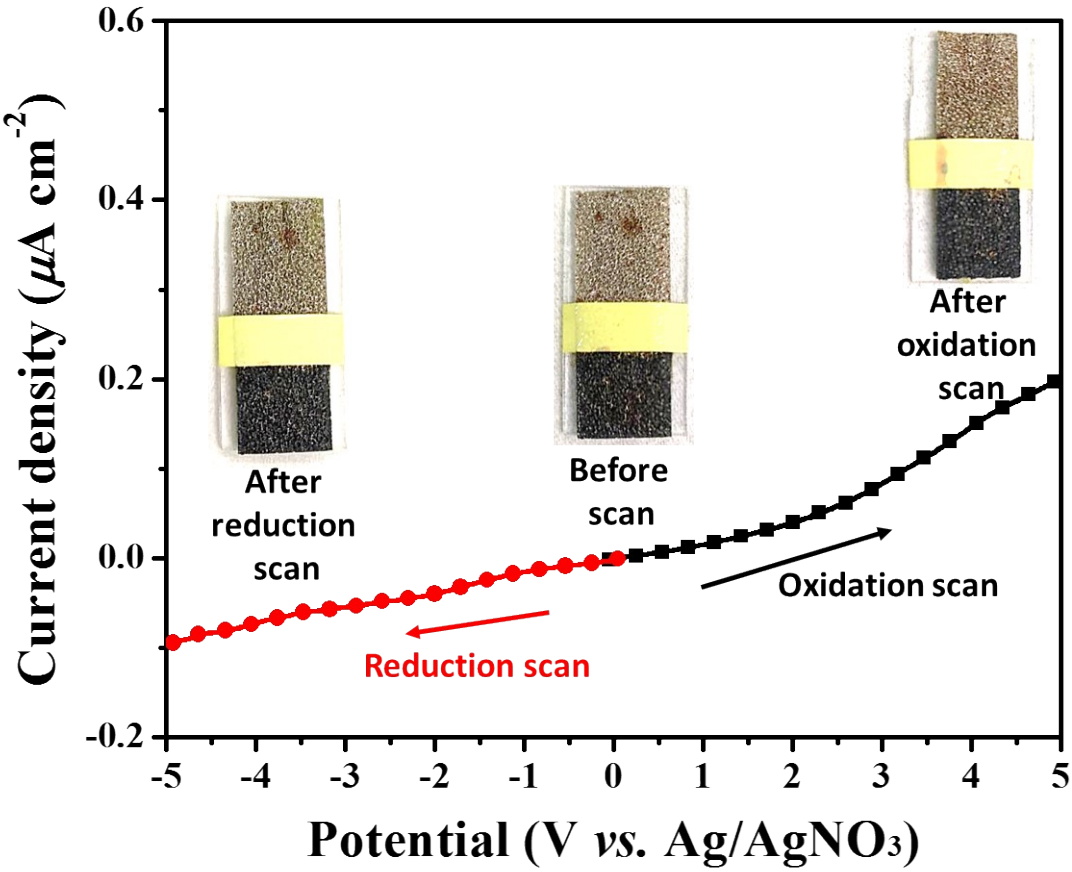

Fig. S4 Linear sweep voltammograms of NF/TiO_2-6/FA($Pb_{1-x}Ge_x$)I_3-THA$I_{0.5}Br_{0.5}$, measured under a oxidation scan (black square) and a reduction scan (red circle) at a scan rate of 10 mV s^{-1} (duration of 500 s).