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Mesoporous SnO_2 Single Crystals as an Effective Electron Collector for Perovskite Solar Cells

Zonglong Zhu†‡1, Xiaoli Zheng‡1, Yang Bai†, Teng Zhang†‡, Zilong Wang‡, Shuang Xiao†‡, Shihe Yang†‡*

†Nano Science and Technology Program, ‡Department of Chemistry, ⊥The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Experimental section

Preparation of SiO_2 colloid. Colloid silica nanospheres (diameter: ~50 nm) were synthesized by mixing 10.6 mL of H_2O (18.2 MΩ, Millipore Milli-Q), 6 mL of ammonium hydroxide (28%, VWR International S.A.S.), and 250 mL of ethanol (≥99.9%, Merck) in a 500 mL three-neck flask at room temperature. Next, 33 mL of tetraethyl orthosilicate (98%, Aldrich) was added in the flask quickly, and the mixture was stirred at 700 rpm for 24 h at room temperature. Then the product was centrifuged at 7000 rpm for 1 h, and the translucent solid was collected and sintered at 500°C for 30 min (ramping time 150 min).

Preparation of SnO_2 mesoporous single crystals. 1.4 g of $SnCl_4.5H_2O$ was added to 28 ml of ethanol/water (v/v = 1/1) mixed solvent. After the mixture was stirred for 10 min, 1.4 ml of HCl (37 wt%) was added and stirred for another 10 min. Then 0.8 g of SiO_2 was added in the autoclave and the sealed vessel was heated at 200°C for 12 h in an oven. Afterward, the vessel was cooled to room temperature naturally, and the solid particles settled at the bottom were collected. Then the solid particles were washed with a large amount of water by vacuum filtration. Finally, the silica template was removed by etching in 2 M NaOH at 80°C for 1 h. Then the remaining SnO_2 products were collected by centrifugation and washed with H_2O and ethanol several times. The SnO_2 MSC paste were deposited from suspension in the ethanol and terpineol (v/v 1:2) with the concentration 5 wt%.

Solar cell fabrication. The material synthesis and solar cell fabrication were according to a reported procedure by Michael Gratzel et al.[1] Before depositing $CH_3NH_3PbI_3$, the SnO_2 MSC paste was spin-coated onto patterned fluorine doped tin oxdie (F:SnO_2) coated glass (FTO). Then, the film was annealing at 300 °C for 30 min. For the TiO_2 coated SnO_2 MSC film, the SnO_2 films were immersed in 50 mM of $TiCl_4$ aqueous solution at 70 °C for 0.5 h and heat-treated at 500 °C for 30 min. The TiO_2 nanocyrstals (with 50 nm size diameters) paste were also spin-coated onto the FTO by 3000 rpm and annealing at 500 °C for 1 h, the films were also treated in $TiCl_4$ solution by the method above.

PbI_2 (450 mg/ml) in *N,N*-dimethylformamide (DMF) was spin-coated onto the above films, and then was dipped in a solution of CH_3NH_3I in 2-propanol (10 mg/ml) for 20 s and rinsed with 2-propanol. The hole transport layer was used by spin-coating a solution of spiro-MeOTAD, which contains chlorobenzene (130 mg/ml), 26 ul of tert-butylpyridin (TBP) solution and 35 ul of Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (170 mg/ml). For the metal electrode, 50 nm thickness of gold was deposited on the top of the HTM by a thermal evaporation through a metal shadow mask to define the active area of the devices (~7 mm^2) and to form a top anode. The cell was packaged by scribbling UV-glue on the top and covered a glass slides, then the cell was exposed to UV light radiation for 10 min to make the glue solidify. The device testing was carried out the glove box after packaging and tested within a metal mask of an aperture (7 mm^2 area).

Characterization. Morphologies of the nanomaterials and subsequent nanostructures were directly examined on JEOL6700F SEM at an accelerating voltage of 5 kV. More detailed structural examinations were carried out by transmission electron microscopy (TEM, JEOL 2010F) and high resolution TEM with an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Philips high-resolution X-ray diffraction system (model PW1830) with Cu Kα radiation (λ=1.5406 Å). The light source (Oriel solar simulator, 450 W Xe lamp, AM 1.5 global filter) was calibrated to 1 sun (100 mW cm^{-2}) using an optical power meter (Newport, model 1916-C) equipped with a Newport 818P thermopile detector. J–V characteristic curves and intensity modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS) were measured by the Zahner controlled intensity modulated photoresponse spectroscopy (C-IMPS) system. We measured the EIS spectra at open voltage and a frequency range from 1Hz and 1MHz with AC amplitude of 10 mA under illumination of simulated solar AM1.5 global light at 100mWcm^{-2}. Z-View Analyst software was used to model the Nyquist plots obtained from the impedance measurements. Incident photon to current conversion efficiencies (IPCEs) was measured on photo current spectra system of CIMPS (CIMPS-PCS) with tunable light source (TLS03).

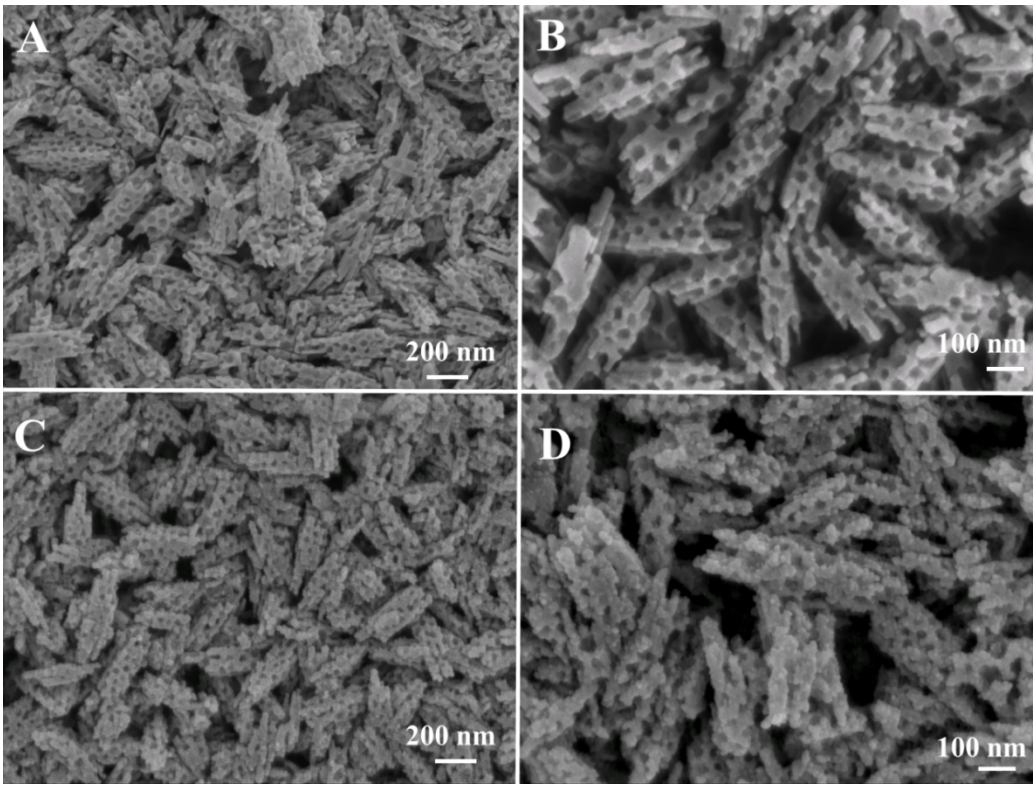
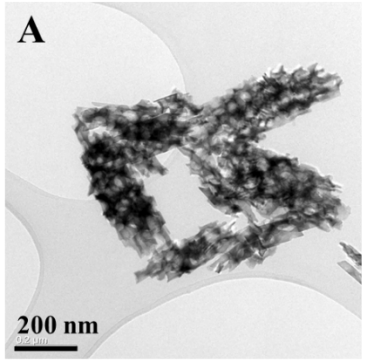


Figure S1. Top-sectional SEM images of pristine SnO_2 MSCs (A,B) and TiO_2-SnO_2 MSCs (C,D).



B

Element	Weight%	Atomic%
O K	18.75	33.47
Sn L	81.25	66.53
Totals	100.00	

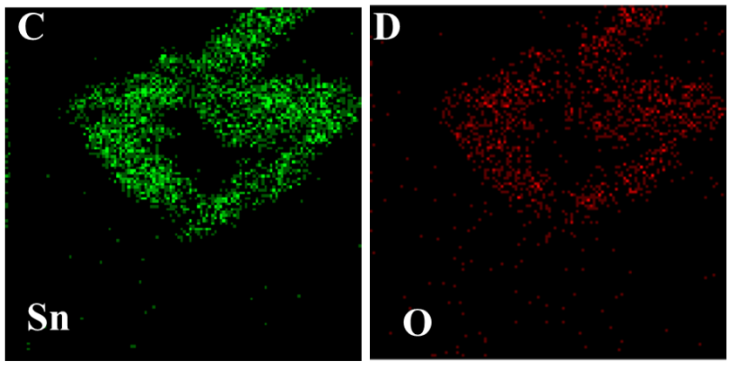
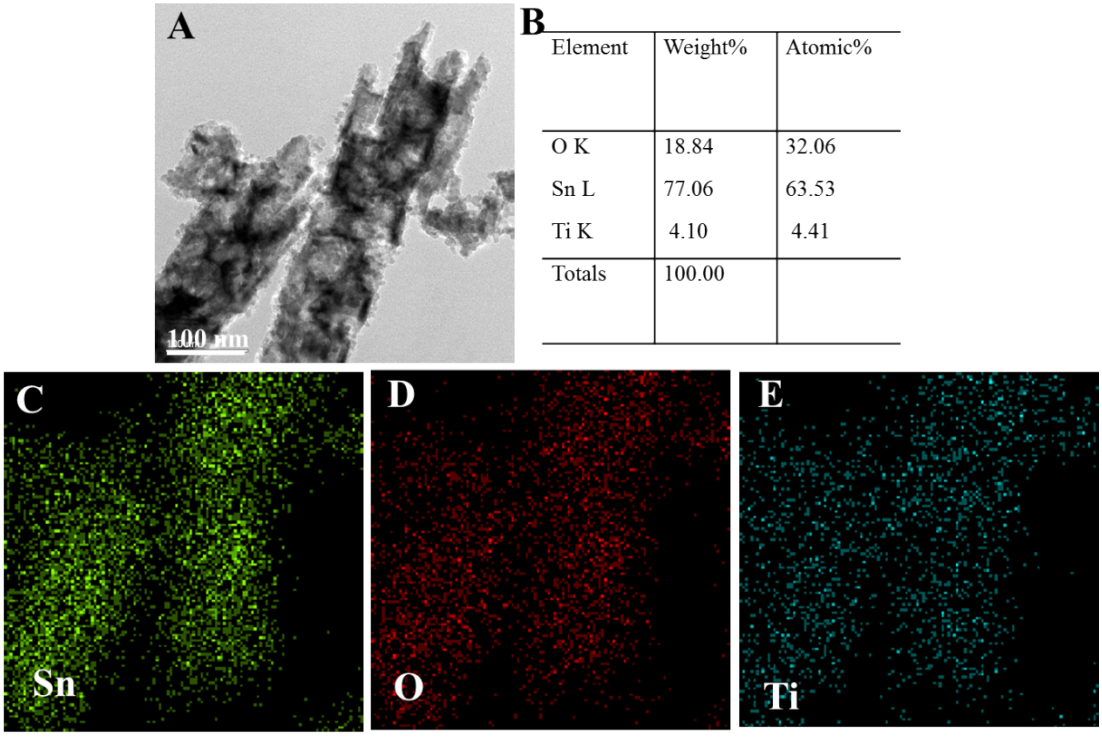


Figure S2. Element mapping analysis of (A) TEM image, (B) results of the EDX element analysis, (C) tin and (D) oxygen of pristine SnO_2 MSCs.



Element	Weight%	Atomic%
O K	18.84	32.06
Sn L	77.06	63.53
Ti K	4.10	4.41
Totals	100.00	

Figure S3. Element mapping analysis of (A) TEM image, (B) results of the EDX element analysis, (C) tin, (D) oxygen and (E) titanium of TiO_2 coated SnO_2 MSCs.

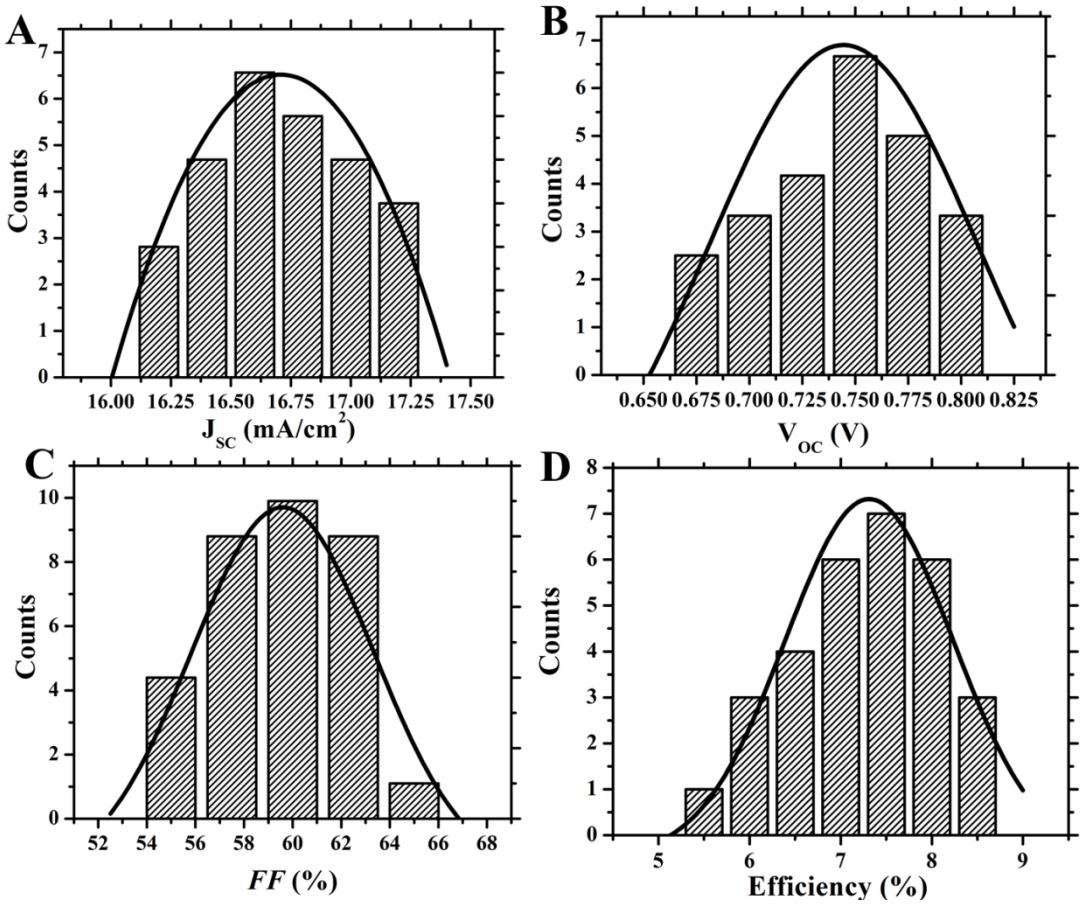


Figure S4. Histograms and related Gaussian fits of device parameters measured for 30 devices based on TiO_2-SnO_2 MSCs perovskite solar cells: (A) J_{SC}, (B) V_{OC}, (C) *FF*, (D) Efficiency.

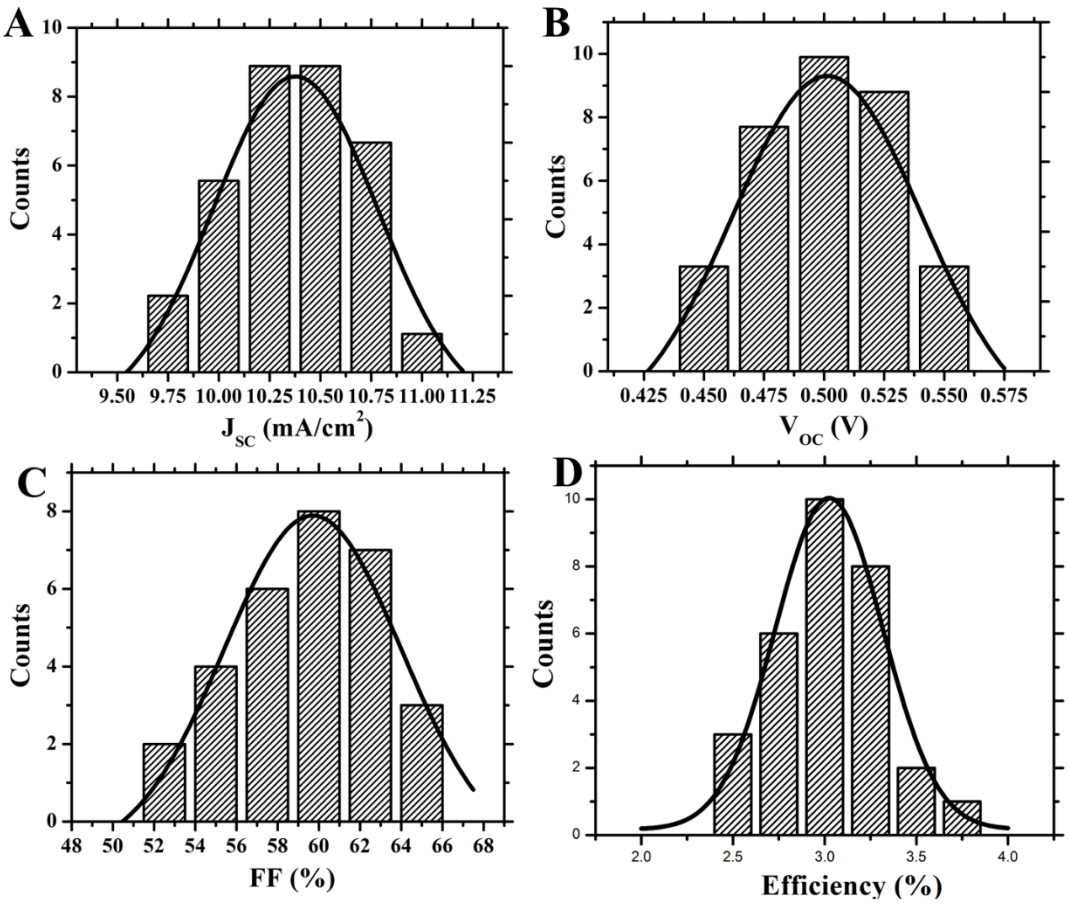


Figure S5. Histograms and related Gaussian fits of device parameters measured for 30 devices based on pristine SnO_2 MSCs perovskite solar cells: (A) J_{SC}, (B) V_{OC}, (C) *FF*, (D) Efficiency.

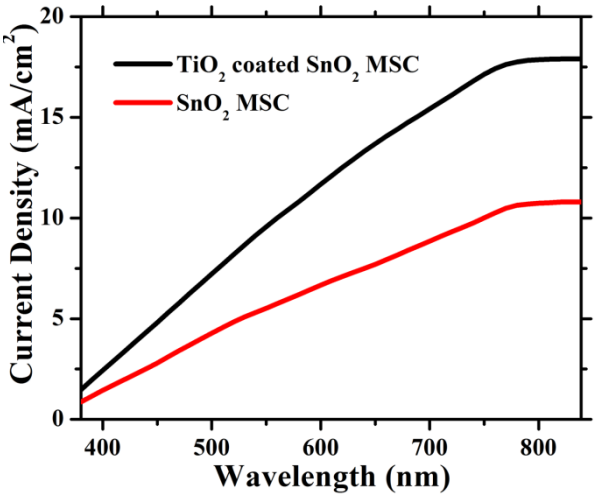


Figure S6. The integrated photocurrent densities of the IPCE spectra. SnO_2 MSCs (red line) and TiO_2-SnO_2 MSCs (black line) cells were measured under AM 1.5 G illumination at 100 mW/cm^2.

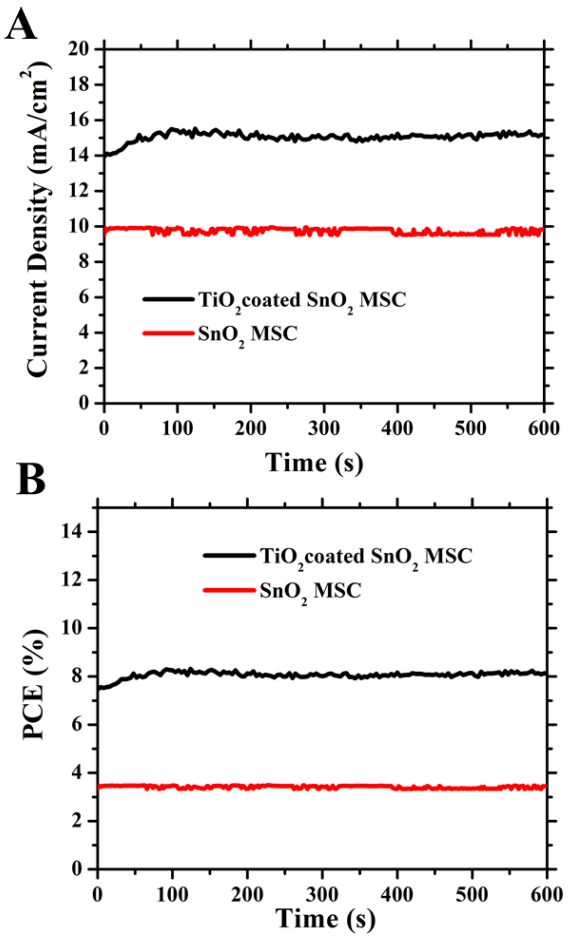


Figure S7. Stabilized photocurrent density (A) and power conversion efficiency (B) obtained while holding the solar cell near the maximum power point voltage at 0.56V for TiO_2 coated SnO_2 MSC and at 0.35 V for SnO_2 MSC, respectively.

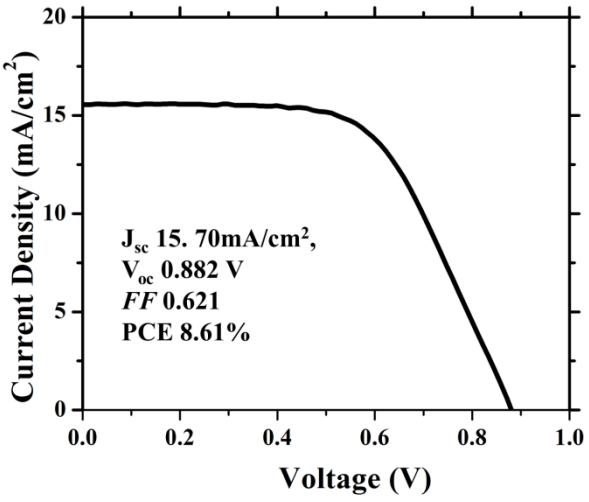


Figure S8. Typical photocurrent density versus applied voltage (J~V) curves of the TiO_2 nanocyrstals (NCs) based perovskite solar cells. Note: the TiO_2 NCs based solar

cells do not include the TiO_2 dense layer before mesoporous TiO_2 NCs coating onto FTO. After 500 ^oC annealing, the film was treated by $TiCl_4$ with the same method as SnO_2 MSCs.

Table S1. Average performance parameters of the SnO_2 MSCs and TiO_2-SnO_2 MSCs based perovskite solar cells.

Devices	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF**	**PCE (%)**
TiO_2-SnO_2 MSC	0.743 ± 0.061	16.72 ± 0.44	0.598 ± 0.023	7.31 ± 1.33
Pristine SnO_2 MSC	0.506 ± 0.041	10.33 ± 0.61	0.596 ± 0.037	3.13 ± 0.63

Table S2. Summary of the parameters of Impedance spectroscopy (Figure 4) with fitting the Nyquist plots by the equivalent circuit (inset in Figure 4).

Devices	$R_s(\Omega)$	Transport resistance (R_1)(Ω)	Recombination resistance (R_2)(Ω)
TiO_2-SnO_2 MSCs	26.1	56.3	402.1
SnO_2 MSCs	23.2	31.6	191.6
TiO_2 nanocrystals	25.9	62.5	513.2

Reference

(1) Burschka, J.; Pellet, N.; Moon, S.-J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Graetzel, M. *Nature,* **2013**, *499*, 316.