Supplemental Information

Low temperature Sputtered Nickel Oxide Compact Thin Film as Effective Electron Blocking Layer for Mesoscopic $NiO/CH_3NH_3PbI_3$ Perovskite Heterojunction Solar Cells

*Kuo-Chin Wang[1], Po-Shen Shen[1], Ming-Hsien, Li[1], Shi Chen[1], Ming-Wei Lin[2], Peter Chen[1,3,4,] *, Tzung-Fang Guo[1,3,4]*

[1] Department of Photonics, National Cheng Kung University, Tainan, Taiwan 701

[2] National Synchrotron Radiation Research Center, Nsrrc,

101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu, Taiwan

[3]Research Center for Energy Technology and Strategy (RCETS)

National Cheng Kung University, Tainan, Taiwan 701

[4] Advanced Optoelectronic Technology Center (AOTC)

National Cheng Kung University, Tainan, Taiwan 701

*petercyc@mail.ncku.edu.tw

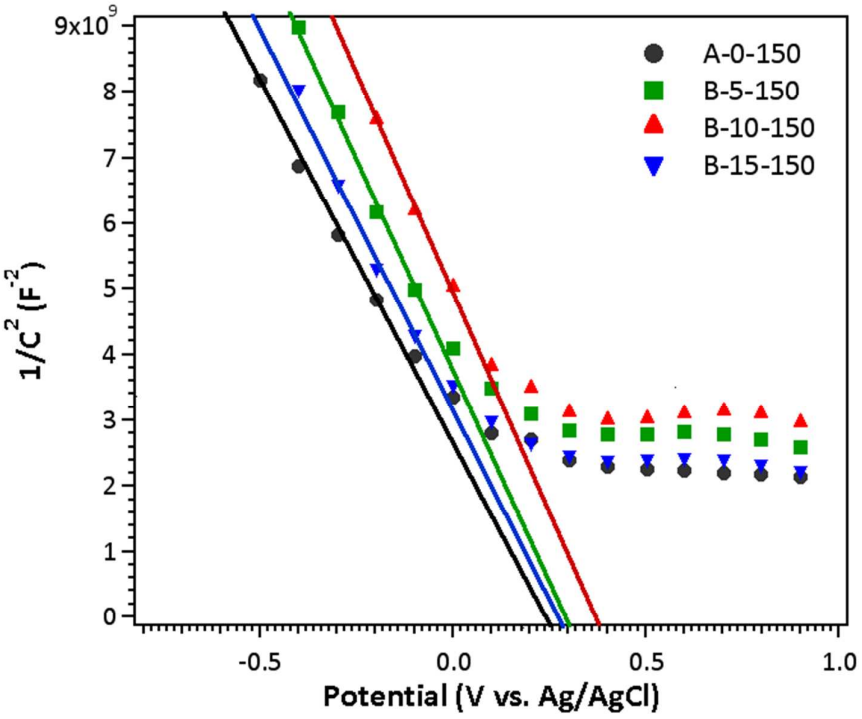

Figure S1. Mott-Schottky plots obtained from sputtered NiOx films doped with various oxygen flow ratios deposited on ITO-coated substrates.

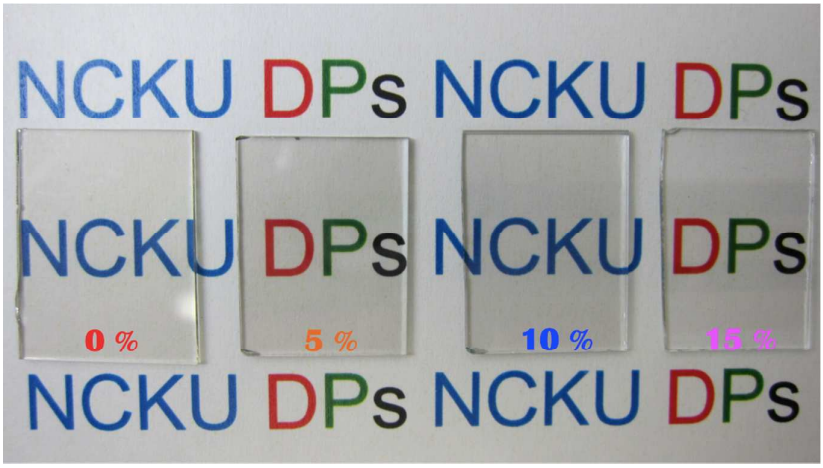

Figure S2. The photos of sputtered NiOx films doped with various oxygen flow ratios (0-15 %, from left to right) on ITO-coated substrates.

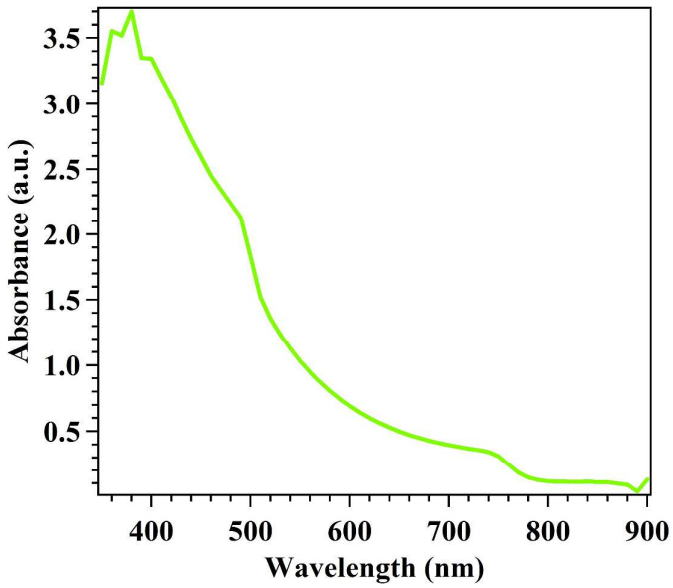

Figure S3. The absorbance of perovskite film coated on mesoscopic NiO nanocryatal layer.

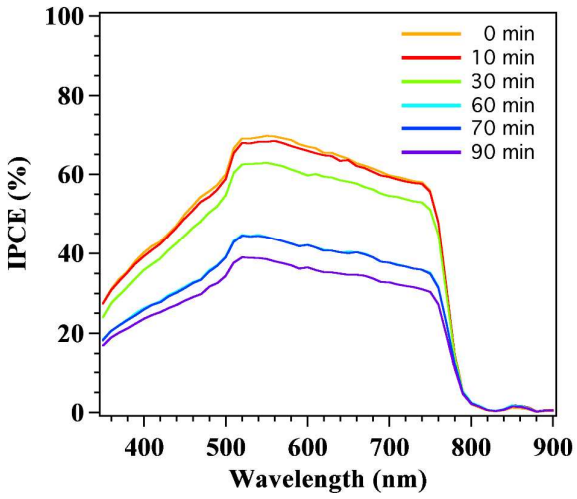

Figure S4. The evolution of IPCE as time during exposure to ambient air without encapsulation.

EXPERIMENTAL METHODS

Fabrication of Sputtered NiO_x thin films

Nickel oxide thin films were deposited on ITO-coated glass substrates (Ritek Corp., 15 Ω/sq.), which are ultrasonically cleaned with soap water, deionized water, ethanol, 2-propanol and Acetone, by an RF magnetron sputtering system from a 3 " NiO target of 3N purity. The distance between the target and the substrate was approximately 50 mm. Prior to deposition, the chamber was evacuated to the base pressure around 6×10^{-6} Torr. The RF sputtering processes were performed in pure Ar or reactive sputter method under a mixture of Ar and O_2 gas. For the following discussions, we

introduce a factor to represent the oxygen flow ratio in the gas mixture. It is defined by equation (1) below. Total pressure was maintained at 5 mTorr during sputtering. The deposition time of NiOx film varied from 100 to 200 seconds. The power applied on the target was fixed at 120 W. The substrate was not heat up with external device.

$$\phi_{O2} = \frac{f_{02}}{f_{02} + f_{Ar}} \quad (1)$$

where f_{Ar} and f_{O2} stand for argon and oxygen flows, respectively.

Fabrication of NiO_{nc} paste.

The mesoporous NiO solution applied to form mesoscopic layer by spin coating was made of NiO slurry and anhydrous ethanol in a weight ratio of 1:7. NiO slurry was prepared by making 3g of NiO nanopowder (Inframat) dissolved into 80 ml ethanol and subsequently adding with 15g of 10 wt% ethyl cellulose (in EtOH) and 10 g of terpineol. Finally, the solution was stirred and dispersed with ultrasonic horn and concentrated with rotary evaporator for ethanol removal until 23 mbar.

Synthesis of CH_3NH_3I.

CH_3NH_3I was synthesized as the method described in our previous literature[1]. Methylamine (CH_3NH_2) (13.5 mL, 40 wt% in aqueous solution, Alfa Aesar) and hydroiodic acid (HI) (15.0 mL, 57 wt% in water, Alfa Aesar) were reacted together in 250 ml round bottomed flask at 0 °C for 2 h with stirring. After the reaction, the solvent of the solution was evaporated using a rotary evaporator. The product, methyl ammonium iodide (CH_3NH_3I), was formed after the above-mentioned procedures. The precipitate was then washed with diethyl ether (Sigma–Aldrich) three times, and finally dried at 60 °C in a vacuum oven overnight[2].

Device fabrication.

The device fabrication was similar to our previous published procedure[1]. Patterned ITO-coated glass substrates (Ritek Corp., 15 Ω/sq.) are ultrasonically cleaned with soap water, deionized water and ethanol. Then, the substrates are rinsed with 2-propanol and Acetone. NiO_x compact layer is deposited on the ITO substrates using RF sputtering system in Ar (for series A samples) and a mixture atmosphere of Ar and O_2 (for series B samples) as the details mentioned above.

The mesoscopic layer of NiO(nc) was coated on the substrates by spin-coating at 4000 rpm for 30 seconds. After annealing at 400°C for 1 hour, a p-type mesoporous network was formed with thickness of 250 nm. Film thickness spin-coated with 3000 and 5000 rpm are 300 and 200 nm respectively. Sequential deposition method was adopted to fabricate NiO(nc)/$CH_3NH_3PbI_3$ layer. Prior to the deposition of PbI_2, the substrates were preheated at 70°C. PbI2 solution (1M in N,N-dimethylformamide) was spun onto the mesoporous NiO film at 6500 rpm for 90 seconds, followed by annealing at 70°C for 30 minutes. After cooling to room temperature, the resulting films were immersed into 2-propanol to pre-wet the substrates for 5 seconds and then dipped into CH_3NH_3I solution (10 mg/ml in 2-propanol) for 40 seconds at room temperature, and then annealed at 70°C for 30 minutes to complete perovskite crystallizaition. $PC_{61}BM$ (25 nm) (> 99%, Solenne, Netherlands), BCP (10 nm) (Aldrich), and Al (100 nm) were thermally deposited on the substrate inside a vacuum chamber (10^{-6} Torr). Mesoporous NiO(nc) coating was performed in the ambient atmosphere. The rest of procedures were implemented inside a nitrogen-filled glove box with oxygen and moisture levels < 1 ppm.

Materials characterization and optical measurement

The glancing angle X-ray diffraction patterns were collected on a multipurpose X-ray thin film diffractometer (D/MAX2500, Rigaku). Field-emission scanning electron microscope (XL40-FEG, Philip) was used to examine the morphology of thin films. Transmittance spectra were measured via UV-Vis spectrophotometer (U-4100, Hitachi) equipped with an integrating sphere. The current-voltage characterizations are performed in glove box with the potential scanning from short-circuit toward open-circuit direction to avoid hysteresis with scan rate of 0.06 V/sec. X-ray photoelectron spectroscopy (XPS) analysis was performed on ESCALAB 250 instrument with Al Kα radiation (1486.6 eV) under a pressure of 9×10^{-8} mbar. Detailed analysis for $Ni2p_{3/2}$ of the NiOx samples was conducted over 850-870eV. After subtraction of a linear background, the XPS spectra were fitted with mixed Gaussian-Lorentzian functions based on a nonlinear least-square algorithm. The Mott-Schotky plots were performed in 0.1 M $LiClO_4$ in acetonitrile as the procedures described in a previous report.

References:

1. Jeng, J.-Y.; Chiang, Y.-F.; Lee, M.-H.; Peng, S.-R.; Guo, T.-F.; Chen, P.; Wen, T.-C. $CH_3NH_3PbI_3$ Perovskite/Fullerene Planar-Heterojunction Hybrid Solar Cells. *Adv. Mater.* **2013,** *25*, 3727-3732.
2. Kim, H.-S.; Lee, C.-R.; Im, J.-H.; Lee, K.-B.; Moehl, T.; Marchioro, A.; Moon, S.-J.; Humphry-Baker, R.; Yum, J.-H.; Moser, J. E.; Grätzel, M.; Park, N.-G. Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. *Sci. Rep.* **2012,** *2*, 591.