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Improved photocurrents for p-type dye-sensitized solar cells using nano-structured nickel(II) oxide microballs

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Supplementary information

NiO-NPs (NiO nanoparticle powder) were used as received from Inframat (73.22 wt% Ni) with a nominal particle size of 20 nm. All other chemicals and solvents were purchased from Sigma-Aldrich and used as received. Transmission electron microscopy (TEM) was performed on a JEOL-2100 microscope. X-ray diffraction (XRD) analyses were carried out on a Phillips powder diffractometer. The thicknesses of sintered electrodes were measured using a Veeco Dektak 6M stylus profilometer. The surface area was analyzed using Brunauer-Emmett-Teller (BET) analysis of N_2 adsorption-desorption studies (Fig. S2, ESI †) on a Micrometrics Tristar 3000 equipment. The counter electrode preparation and photocathode assembly was carried out as explained elsewhere.[2] The back filling hole was sealed using an aluminum-Surlyn sheet, which was prepared by heating aluminum foil with a 25 μm Surlyn sheet on a hot plate at 120 °C. Photocathodes were tested using an Oriel sun simulator (1,000 Wm^{-2} Xe lamp) fitted with an AM 1.5 filter. The light intensity was calibrated using a calibrated silicon reference diode equipped with a KG3 filter provided and calibrated by the Fraunhofer Institute Freiburg (Germany). Current-voltage characteristics were measured using a Keithley 2400 source meter. The spectral response (IPCE) was measured using a 300 W Xe lamp fitted with an Oriel Cornstone

monochromator and recorded on a Keithley 2400 source meter. NiO-μBs and NiO-NPs films of about one micron thickness were printed for UV-vis spectroscopic studies. NiO-μBs were crushed by low energy ball milling for 24h to get a homogeneous film for optical analysis according to Lambert-Beer's law. The absorption properties of these films were measured before and after dye absorption, using a Perkin Elmer Lambda 950 spectrophotometer with integrating sphere attachment. A 2-step process was used to achieve quantitative dye desorption of PMI-6T-TPA off the NiO surface. The dyed films were first immersed in an aqueous dipotassium monohydrogen phosphate solution (0.7 M) for 10 min, this process did not result in any observable dye desorption. The electrodes were then rinsed with H_2O and ethanol before being immersed into a phosphoric acid solution in DMF (0.6 M) for 5 min to perform the actual dye desorption. The absorption spectra of desorbed dye solutions in DMF were measured using a Perkin Elmer Lambda 950 spectrophotometer. Baseline corrections were performed with a 0.6 M phosphoric acid solution.

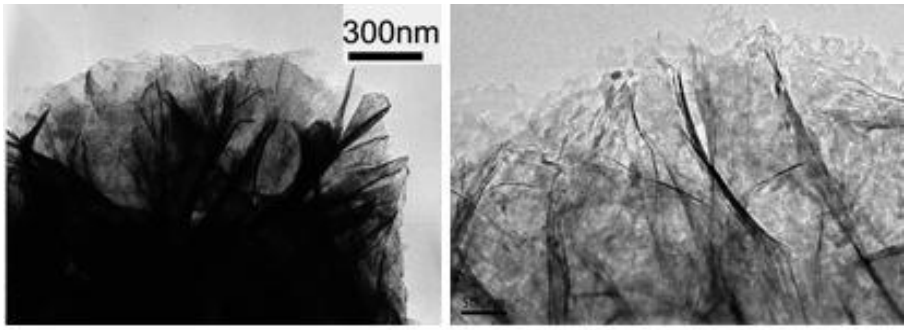

Fig.S1 TEM and HR-TEM images of synthesized NiO-μBs

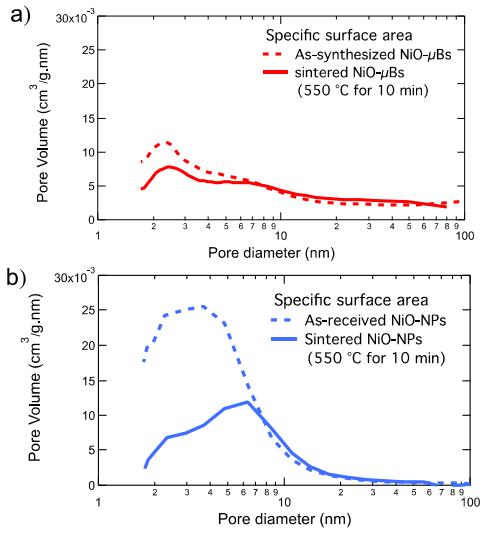

Fig.S2 Pore volume distribution for NiO powder and powder collected from NiO films sintered for 10 min at 550°C (a) NiO-μBs; and (b) NiO-NPs.

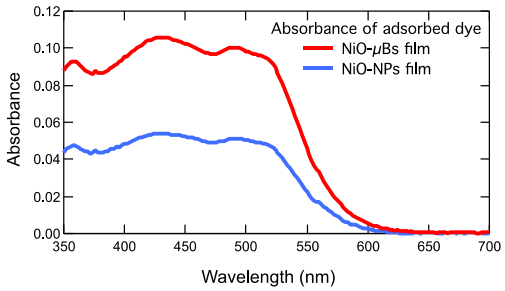

Fig.S3 Absorption spectra of desorbed dye from 1 μm thick (7 mm x 7 mm) NiO-NPs and NiO-μBs films. The amount of dye desorbed per film volume (0.049 mm^3) from the NiO-μBs film was 11 nmoles and that of a NiO-NP film was 5.2 nmoles.

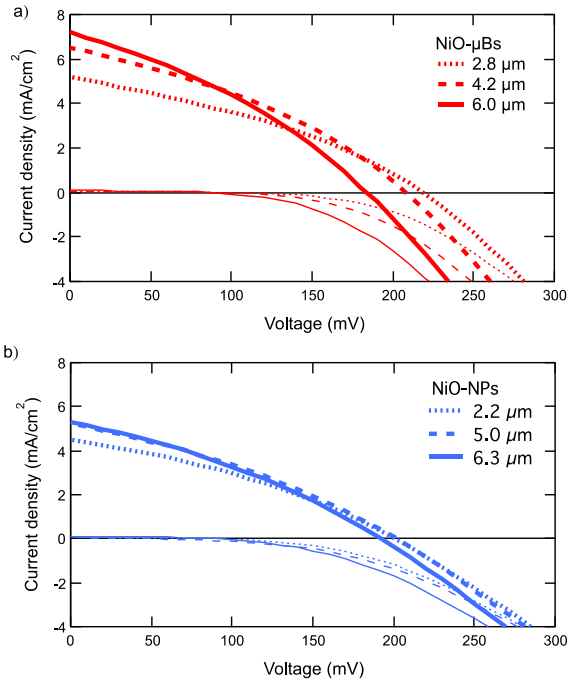

Fig.S4 Current density vs. voltage characteristics in the dark and under simulated 1 sun irradiation (1,000 W/cm^2, AM1.5) of PMI-6T-TPA sensitized (a) NiO-µBs and (b) NiO-NPs films of various thicknesses.

Table S1: Photovoltaic performance of a 6.3 µm thick NiO-NPs and 6.0 µm thick NiO-µBs photocathodes (0.16 cm^2 NiO films) sensitized with PMI-6T-TPA dye under different incident light intensities of simulated sunlight (AM 1.5, 100% sun = 1,000 W/m^2).

	NiO – NPs			***NiO – µBs***		
Light intensity	10 % sun	38.5% sun	100% Sun	10 % sun	38.5% sun	100% Sun
V_{OC} (mV)	136	166	192	136	162	184
J_{SC} (mA/cm^2)	0.90	2.54	5.32	1.07	3.28	7.21
Fill Factor	0.38	0.35	0.32	0.40	0.36	0.33
Efficiency (%)	0.45	0.38	0.33	0.56	0.5	0.44

References:

1. A. Nattestad, A. J. Mozer, M. K. R. Fischer, Y. B. Cheng, A. Mishra, P. Bäuerle and U. Bach, *Nat. Mater.*, 2010, **9**, 31-35.
2. A. Nattestad, M. Ferguson, R. Kerr, Y. B. Cheng and U. Bach, *Nanotechnology*, 2008, **19**.