## Enhanced Open-circuit Voltage of *P*-type DSC with Highly Crystalline NiO Nanoparticles

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## **Experimental detail.**

NiO octahedral nanoparticles were synthesized through a high temperature thermolysis in molten salt media. In a typical experiment, 2.0 g of nickel oxalate dihydrate (Alfa Aesar) and 8.0 g of sodium chloride (99.5%, Merck) were ground into a fine powder before being mixed with 5.0 mL of CO-630 (Aldrich). The thermolysis was carried out at 950 °C for 2 hours in an electrical muffle furnance (1200 °C laboratory muffle furnance with EUROTHERM 2100 controller, Cermic Engineering). A light green colour product was obtained and then washed with water and ethanol for several times to remove sodium chloride completely.

Field emission Scanning Electron Microscope (JEOL 7001F FEGSEM) was used for morphology observation and element analysis. Crystal structure was verified by X-ray Powder Diffraction (Phillips powder diffractometer) and Transmission Electron Microscope (FEI Tecnai F20 TEM). Standard multi-points Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area.

The colloidal solution was obtained by ball-milling the NiO in ethanol for 24 hrs. The mixture of above colloidal solution, ethyl cellulose (Aldrich) and terpinol anhydrous (≥99.5%, Fluka) was

Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2011 sonicated and magnetic stirred alternatively in order to disperse. This was made into a paste by evaporating the ethanol from the mixture on a rotary evaporator. P-type photocathode blocking layers were made by dip-coating nickel acetate (+98%, Alfa Aesar) ethanol (>99.7%, Merck) solution (0.05 M) 5 times on FTO glass (Nippon sheet glass, resistance 13  $\Omega$ /square) drying in between before screen print of NiO paste. Sintered at 500 °C for 1 hr, the color of NiO films turned slightly greyish. After cooling down, the films were soaked in a 0.2 mM dye 3 solution overnight. The resulting NiO working electrodes were assembled into devices with counter electrodes made by thermal deposition of H<sub>2</sub>PtCl<sub>6</sub> on FTO glass to produce a sandwich type cell using 25 µm Surlyn gaskets. The electrolyte, containing 0.03 M iodine, 0.5 M 4-terbutylpyridine, 0.6 M 1-butyl-3methylimidazolium iodide, and 0.1 M guanidinium thiocyanate in a mixed acetonitrile and valeronitrile (with volume ratio of 85 : 15) solution, was introduced into the cell via a vacuum filling method.

The thickness of the NiO films was measured by using a profilometer (DEKTAK 150, Veeco Instruments Inc). The sealed solar cells were shielded by a black metal mask with an aperture area of 0.36 cm<sup>2</sup>, and measured the photovoltaic properties using a Keithley 2400 Source Meter under the irradiation of simulated sunlight (100 mW/cm<sup>2</sup>) provided by an Oriel solar simulator with an AM 1.5 filter. IPCE plotted as a function of excitation wavelength was recorded on a Keithley 2400 Source Meter under the irradiation of a 300 W xenon lamp with an Oriel Cornerstone<sup>TM</sup> 2601/4m monochromator.

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Fig. S1 EDS pattern of as-synthesized NiO nanoparticles. Carbon is from carbon tape.



Fig. S2 HRTEM of lattice fringe from a NiO nanoparticle.

NiO Film	$J_{\rm sc}~({\rm mA/cm}^2)$	$V_{\rm oc}({\rm mV})$	FF (%)	η (%)
Without underlay	0.04	350	0.51	0.01
With underlay	1.32	305	0.34	0.14

**Table S1.** Performance characteristics of p-type DSCs assembled using NiO nanoparticles prepared with and without under-layer.



Fig. S3 Incident photon to current conversion efficiency (IPCE) curve of *p*-type NiO DSCs.



**Fig. S4** UV-vis absorption of dyed NiO films. Absorption was calculated from formula: A = 1 - T% - R%, where T is transmission and R is reflection.



**Fig. S5** Impedance spectra of *p*-type NiO DSCs with and without underlayer measured at 1 sun. (a) Bode phase plots; (b) Nyquist plots; and (c) enlarged Nyquist plots.