Supporting Information

TiO_2 Nanotube Fabrication with Highly Exposed (001) Facets for Enhanced Conversion Efficiency of Solar Cells

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EXPERIMENTAL SECTION

TiO_2 nanotubes (NTs) anodization. Highly ordered TiO_2 NTs were prepared by potentiostatic anodization in two-electrode electrochemical cells.[1] All anodization processes were carried out at 25 ^{o}C using commercial titanium foil (100 mm × 100 mm × 0.05 mm, 99.6%, Goodfellow, UK) as a working electrode and a Pt electrode 100 cm^2 in size as a counter electrode. The Ti foil was anodized in a mixed solution of ethylene glycol containing 0.25 wt% of NH_4F and 0.75 wt% of H_2O at 60 V for 3 hours. For the SC-TiO_2 NT fabrication process, 0.1 M acetic acid and 2 wt% PVP (Mw $\approx 1.3 \times 10^6$) were added into the TiO_2 NTs growing electrolyte. The mixture was then heated to 160 ^{o}C at a rate of 5 ^{o}C/min. The solution was kept at 160 ^{o}C for about 2 h in order to allow for the necessary chemical reaction to occur. The SC-TiO_2 NTs anodization process was carried out under the same conditions used for the TiO_2 NTs. After anodization, the foils were sonicated for 1-5 s, rinsed in water and ethanol, dried under an air stream, and annealed at 550 ^oC for 30 min at a ramp rate of 1 ^oC/min.

Solar cells fabrication. All TiO_2 NTs and SC-TiO_2 NTs substrates were then immersed in a 0.3 mM $(Bu_4N)_2$- ("N719", Solaronix) in ethanol for 30 min. To prepare Pt counter-electrodes, 10 mM hydrogen hexachloroplatinate (IV) hydrate (H_2PtCl_6, Aldrich, 99.9%) in a 2-propanol solution was coated on fluorine-tin-oxide (FTO, 3 mm, 10 Ω/square, Pilkington TEC8) glass, followed by heating at 450 ^oC for 30 min. The dye adsorbed TiO_2 NTs and Pt counter-electrode were assembled into a sealed sandwich-type cell by heating with a hot melt of a 50 μm thick Surlyn polymer film (Surlyn, Dupont 1702). A electrolyte solution of 0.6 M tetra-butylammonium iodide, 0.1 M lithium iodide, 0.1 M iodide and 0.5 M 4-tert-butyl pyridine in acetonitrile was introduced into holes drilled in the counter-electrode of the assembled cell, followed by sealing the holes using a microcover glass and Surlyn. The photocurrent (Jsc) and photovoltage (Voc) of the DSSCs were measured with an active area of 0.15-0.25 cm^2 using simulated solar light at AM 1.5, produced by a 1000 W xenon lamp (Oriel, 91193). Its irradiant power was adjusted with respect to Si reference solar cell (Fraunhofer Institute for Solar Energy System: Mono-Si + KG filter) to about one-sun light intensity (100 mW/cm^2). IPCE was measured using a system designed by PV measurement. A 12 W halogen lamp was applied as the light source for the monochromatic beam. For its calibration, a silicon photodiode (NIST-calibrated photodidode G425) was used. SEM images of the TiO_2 NT were obtained with a field emission scanning electron microscope (FEI, Model: Sirion, Netherlands). Field-emission transmission electron microscopy (FE-TEM) were obtained with a JEM-2100F (JEOL Ltd., Japan). XRD patterns were measured by using a D8 Discover thin-film diffractometer with Cu Kα radiation (40 kV, 30 mA, $\lambda = 1.54056$ Å) and a Ni filter plus a graphite monochromator. The XRD spectrum was recorded in a Bragg-Brentano configuration using $\theta/2\theta$ scanning and no tilt angle.

The intensity modulated photovoltage spectroscopy (IMVS) and intensity modulated photocurrent spectroscopy (IMPS) measurements: The IMVS and IMPS measurements were performed on a ZAHNER CIMPS system. A stationary DC voltage and a concurrent sinusoidal modulated AC voltage were imposed on a green LED, which gave out a green irradiance with a maximum wavelength at 525 nm. The LED was controlled by a potentiostatic feedback loop. The selected AC amplitude ranged from 5% to 15% of the stationary DC value. The transfer functions of IMPS and IMVS were determined by correlating the system response with the actual stimulation signal. The potential applied to the testing cell was controlled by a potentiostat unit. IMPS measurement was carried out under short-circuit condition while IMVS measurement was carried out under open-circuit condition. The measured short circuit photocurrent efficiency (Φext(ω)) of IMPS and the real and imaginary parts of modulated photovoltage ΔVoc of IMVS were fitted by using the Levenberg-Marquardt algorithm.

Transicient spectroscopy measurements. For transient photocurrent and photovoltage studies, the cells were probed with a weak laser pulse at 532 nm superimposed on a relatively large, back ground (bias) illumination at 680 nm.[2] The bias light was illuminated by a 0.5 W diode laser (B&W TEK Inc., Model: BWF1-670-300E/55370). The intensity of the bias light was adjusted using ND filters (neutral density filters). The 680 nm bias light is only weakly absorbed by the dye, and therefore the injected electrons are introduced into a narrow spatial region of the film, corresponding to where the probe light enters the film. A 30 mW frequency-doubled Nd:YAG laser (Laser-Export Co. Ltd, model: LCS-DTL-314QT) (λ = 532 nm, pulse duration 10 ns) was used as probe light. The photocurrent transients were obtained by using a Stanford Research Systems model SR570 low-noise current preamplifier, amplified by a Stanford Research Systems model SR560 low-noise preamplifier, and recorded on Tektronics TDS 3054B digital phosphore oscilloscope 500 MHz 5 GS s^{-1} DPO. The photovoltage transient were obtained by using a Stanford Research System model SR570 low-noise preamplifier, and then recorded on Tektronics TDS 3054B digital phosphore oscilloscope 500 MHz 5 GS s^{-1} DPO. The response time of the preamplifier at the range of photocurrent and photovoltages used was less than 1 ms. The light intensity of the probe light was adjusted so that the collected charge due to the transient photocurrent and photovoltage were less than 1% of the steady-state charge as estimated from the product of the steady-state short-circuit photocurrent/voltage, the time constant for electron collection (τ_C), and the time of electron life time (τ_R). Charge collection efficiency was estimated by the relation $\eta_{CC} = 1 - (\tau_C / \tau_R)$.[3]

References

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