

Supporting information

Light harvesting enhancement for Ti-based dye-sensitized solar cell by introducing a grooved texture underlayer

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Experiments

Ti substrate Surface treatment: Commercial Ti foil substrates (0.10 mm thickness, 99.5% purity, Nilaco Crop., Japan) were used as photoanode substrates. Two surface treatments were performed. Direct oxidation treatment was conducted using a hydrogen peroxide (H₂O₂) solution at room temperature for 1 h. Additionally, another Ti substrate was soaked in a mixed aqueous solution of 1:1 30 wt. % H₂O₂ and 28 wt. % NH₄OH at room temperature for 1 h. The Ti foil substrates were then rinsed with DI water, acetone, and ethanol.

Fabrication of DSSCs: Anatase TiO₂ nanoparticle paste was prepared according to procedures published in literature.¹ The paste was coated onto the Ti foil substrates using the screen printing method. After screen printing, the photoanodes were heated at 520 °C for 1 h in an air atmosphere. The active area of the electrode was 0.283 cm². The TiO₂ film was immersed in 0.5 mM *cis*-bis(isothiocyanato) bis-(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetra-butylammonium (Solaronix, N719) dye solution in a 1:1 mixture of acetonitrile and *tert*-butanol for 24 h. The dye-loaded TiO₂ films were then rinsed with acetone to remove the remaining dye. The counter electrode was prepared by spraying a H₂PtCl₆ (Showa) isopropanol solution on FTO glass (2.2 mm thickness, 8-10 Ω/□, Pilkington TEC glass) and heating it at 400°C for 20 min. The dye-loaded photoanodes were assembled with Pt counter electrodes by 25-μm-thick hot-melt sealant (Dupont, Surlyn). The internal space of the cell was filled with an electrolyte solution consisting of 0.6M 1, 1-methyl-3-propylimidazolium iodide (PmII, Merk), 0.01M I₂ (Sigma-Aldrich), 0.1M LiI, and 0.5M *tert*-butylpyridine (TBP, Sigma-Aldrich) in acetonitrile.

Characterization: The morphology of the Ti foil surface with different treatments, including non-treated, H₂O₂ treated, and H₂O₂/NH₄OH treated, was served by a

field-emission scanning electron microscope (FESEM) (JEOL, JSM-7000F) operating at 5 KeV and a field-emission transmission electron microscope (FETEM) (JEOL, JEM-2100F) operating at 200 KeV. Raman spectra were obtained using an Ar ion laser operating at 514.5 nm on a Jobin-Yvon T64000 microspectrometer with 1800 grooves/mm grating in a backscattering configuration. The photoanode film thicknesses were measured using a Microfigure Measuring Surfcoorder (Kosaka Laboratory, ET3000). Optical reflectance spectra were obtained using a UV-vis spectrophotometer (Hitachi, U-3010). The overall energy conversion efficiency was evaluated using a solar simulator (Yamashita Denso, YSS-100A) at a light intensity of 100 mW cm^{-2} (AM1.5). The incident light intensity was calibrated using a standard silicon photodiode (Bunko Keiki, BS-520). The incident monochromatic photon-to-current conversion efficiency (IPCE) was measured using an IPCE measurement system (C-995, PV-measurement Inc.). The evolution of the electron transport process in the cell was investigated using electrochemical impedance spectroscopy (EIS). Impedance spectroscopy was performed using an electrochemical analyzer (Autolab, PGSTAT30). Impedance measurements were conducted by applying a DC bias at an open circuit voltage (V_{OC}) and an AC voltage with an amplitude of 10 mV at a frequency range of 50 mHz to 10^5 Hz under AM1.5G illumination.

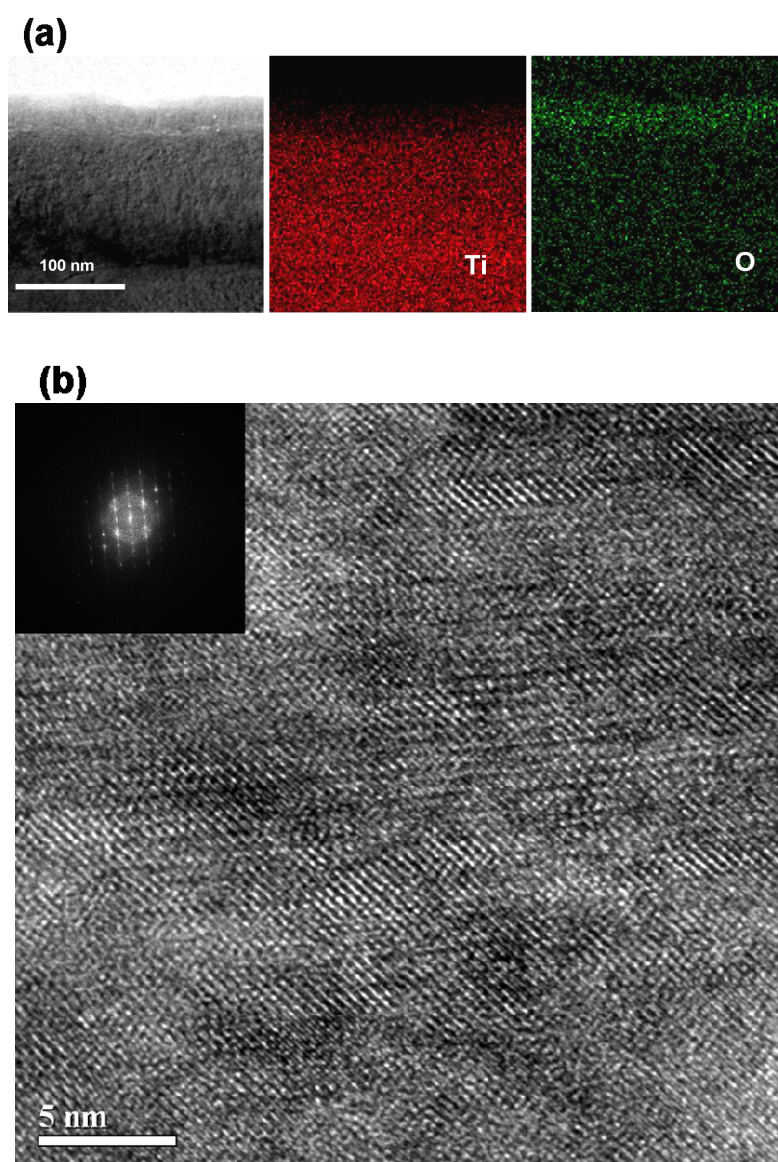


Figure S1 (a) Cross-sectional TEM image of Ti substrate with H₂O₂/NH₄OH treatment after heat annealing, and the corresponding energy-dispersive spectroscopy elemental mapping of Ti and O. (b) High-resolution TEM image with FFT diffractogram of the TiO₂ underlayer on H₂O₂/NH₄OH-treated Ti substrate.

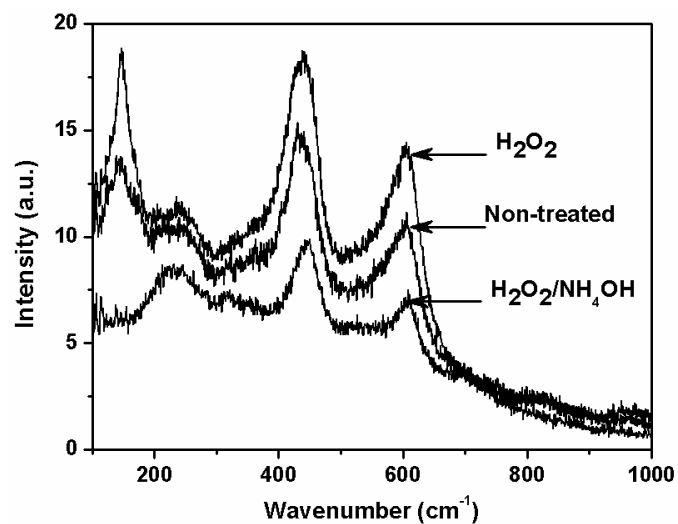


Figure S2 Raman spectra of the non-treated, H₂O₂-treated and H₂O₂/NH₄OH-treated Ti substrates after thermal annealing.

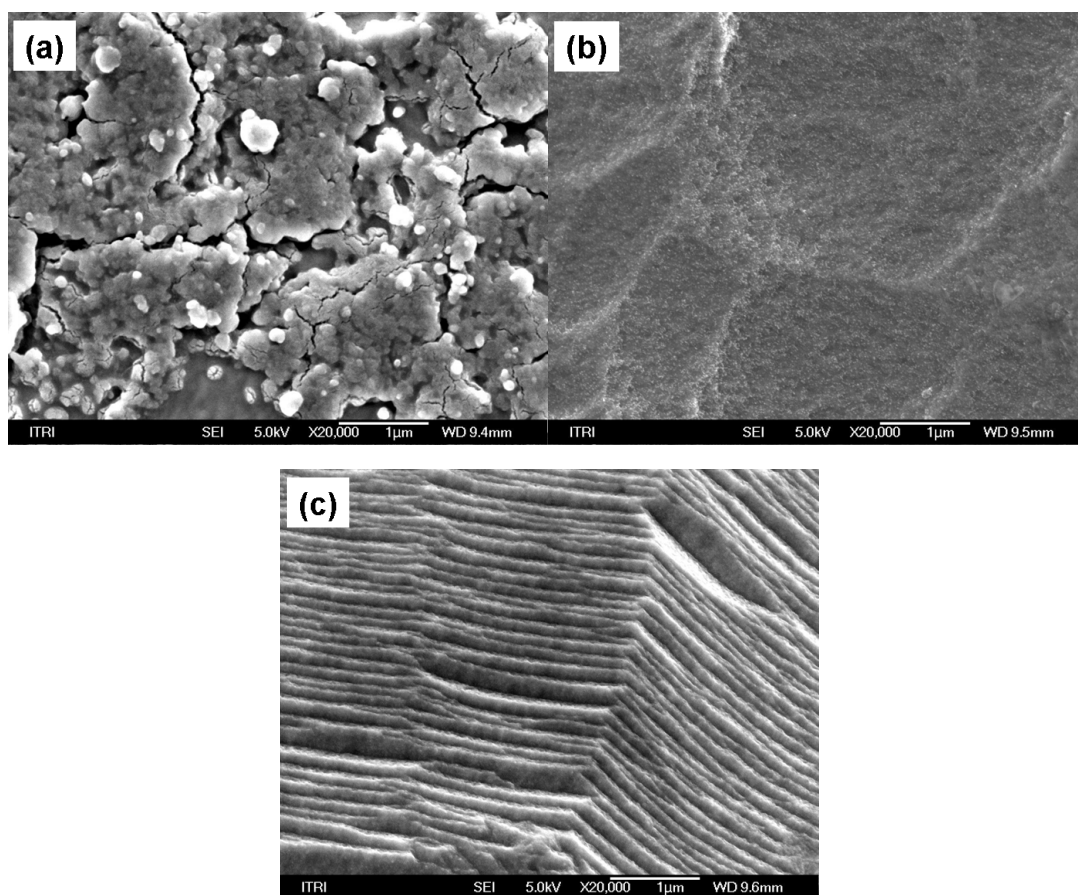


Figure S3 SEM images of Ti substrates (a) non-treated, (b) H₂O₂-treated, and (c) H₂O₂/NH₄OH-treated after thermal annealing at 520°C for 1 h.

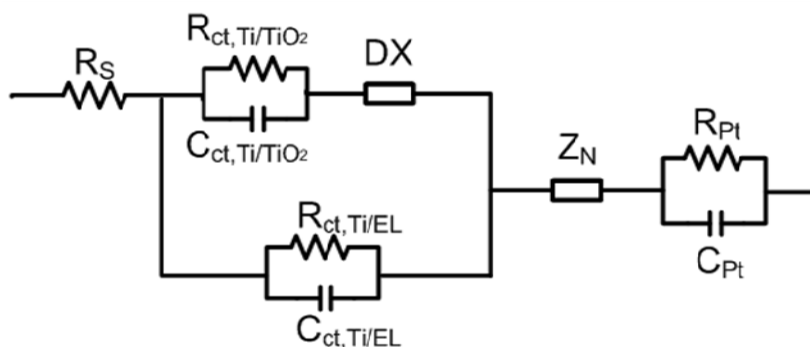


Figure S4 Equivalent circuit for the simulation of the impedance spectra of the DSSCs.² The typical transmission line model, which represents the electronic behavior in the nanocrystalline TiO₂ film and at the nanocrystalline TiO₂/electrolyte interface, was simplified as an extended element (DX), containing the parameters of charge transfer resistance at the TiO₂/electrolyte interface (R_k), the electron transport resistance (R_w) in the TiO₂ network, and the chemical capacitance of the TiO₂ photoanode (C_μ). Some circuit elements are also used, including the series resistance (R_S) related to the conductive substrates (Ti foil and FTO) and external circuits, the resistance ($R_{ct,Ti/TiO_2}$) and the capacitance ($C_{ct,Ti/TiO_2}$) at the Ti foil/TiO₂ interface, the resistance ($R_{ct,Ti/EL}$) and capacitance ($C_{ct,Ti/EL}$) at the uncovered Ti foil/electrolyte interface, the charge-transfer resistance (R_{Pt}) and the interfacial capacitance (C_{Pt}) at the Pt/electrolyte interface, and the impedance of the diffusion of I₃⁻ in the electrolyte (Z_N).

Reference to supporting information

1. S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Gratzel, M. K. Nazeeruddin and M. Gratzel, *Thin Solid Films*, 2008, **516**, 4613-4619.
2. R. Li, D. Liu, D. Zhou, Y. Shi, Y. Wang and P. Wang, *Energy Environ. Sci.*, 2010, **3**, 1765-1772.