

# Rapid Dye Adsorption *via* Surface Modification of TiO<sub>2</sub> Photoanodes for Dye-Sensitized Solar Cells

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## Experimental section

### *Preparation of TiO<sub>2</sub> photoanode*

To prepare the working electrode, pastes based on nanocrystalline TiO<sub>2</sub> particles (20 nm, synthesized) were prepared according to a previous report.<sup>1</sup> Scattering pastes containing G2 (500 nm, Showa Denko, Japan) were also prepared using the same procedure. For the construction of a compact TiO<sub>2</sub>-blocking layer, a 0.15-M 2-propanol solution of titanium diisopropoxide-bis(acetylacetonate) in 1-butanol was spin-coated onto an FTO substrate followed by sintering at 500 °C for 10 min. The porous TiO<sub>2</sub> films (thickness = 18 μm) were deposited onto the compact TiO<sub>2</sub> layer/FTO substrates using the TiO<sub>2</sub> paste doctor blade technique followed by sintering at 500 °C for 30 min (heating rate of 5 °C/min). The scattering paste was deposited on the annealed TiO<sub>2</sub> films using the doctor blade and then heated again using the same heating profile. The thickness of the light scattering film was typically 5 μm. An aqueous stock solution of 2 M TiCl<sub>4</sub> was diluted to 0.04 M. Sintered electrodes were immersed into this solution and stored in an oven at 70 °C for 30 min in a closed vessel. After flushing with demineralized water and drying, the electrodes were sintered again at 500 °C for 30 min. Dye adsorption onto the TiO<sub>2</sub> electrode was performed using an ethanol (Carlo Erba CAS No. 64-17-5) solution of cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II) (N719; Everlight (D719)) at the predefined temperature and concentration with or without nitric acid treatment.

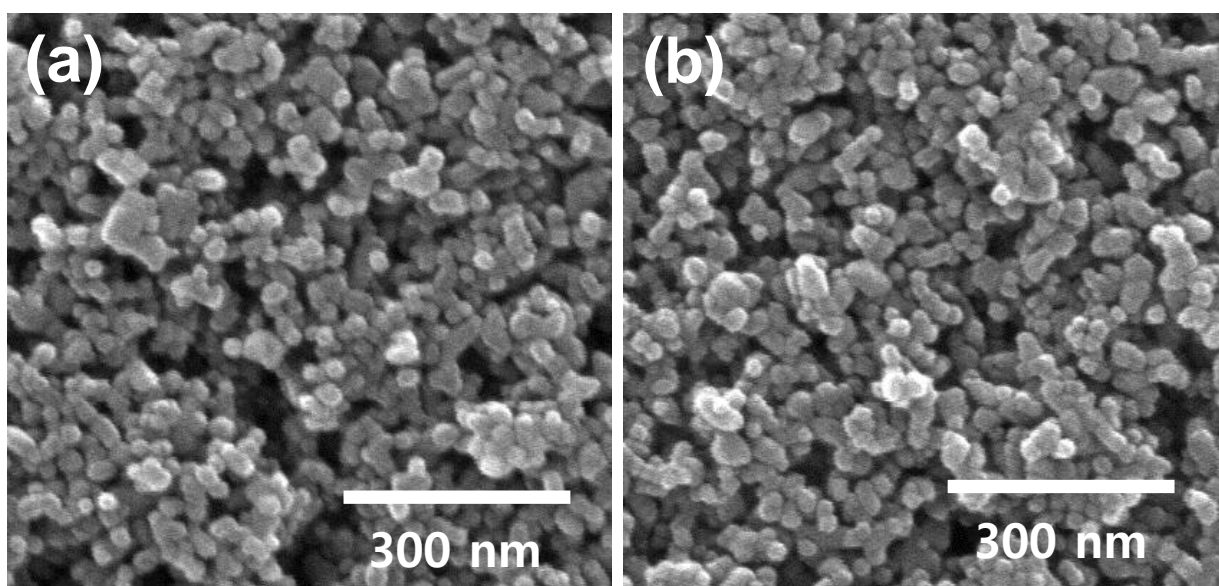
***DSSC fabrication*** The resulting working electrode and Pt counter electrode were sealed with Surllyn (60 μm, Dupont) and an electrolyte solution was then injected through the hole in the counterelectrode. The electrolyte comprised 0.7 M 1-propyl-3-methyl-imidazolium iodide (PMII, synthesized), 0.1 M guanidinium thiocyanate (Aldrich, 97%), 0.03 M I<sub>2</sub> (Aldrich, 99.8%), and 0.5 M 4-tert-butylpyridine (Aldrich) in acetonitrile. An antireflection film

(ARCTOP, ASAHI Glass) was adhered to the DSSCs when measuring the power-conversion efficiency. The active area of the DSSC dye was  $0.4 \text{ cm}^2$ , which was measured using an image analysis program equipped with a CCD camera (Moticam 1000). The  $\text{TiO}_2$  film thickness was measured using an  $\alpha$ -step surface profiler (KLA Tencor).

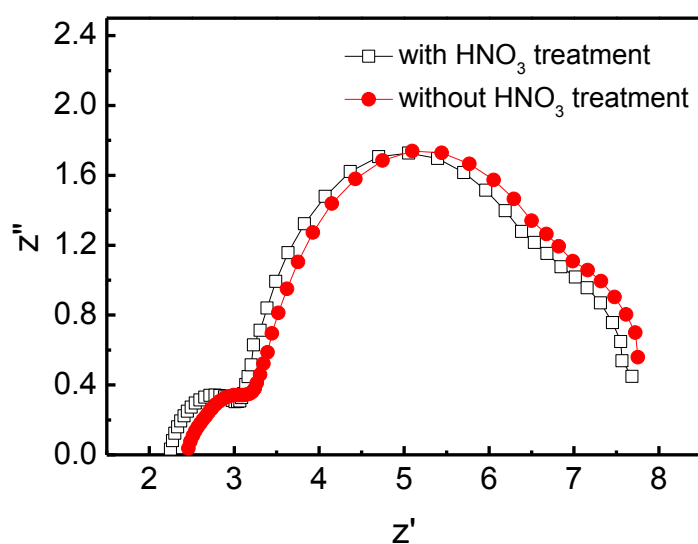
***Characterization of  $\text{TiO}_2$  nanoparticles***  $\text{TiO}_2$  nanoparticles were characterized *via* FE-SEM (Hitachi S4200), Raman spectroscopy (LabRam ARAMIS: Horiba Jobin-Yvon), and ATR-FTIR-spectroscopy (PerkinElmer Spectrum 100). The zeta potentials of  $\text{TiO}_2$  nanoparticles dispersed in an ethanol solution were measured using a zeta-potential and particle analyzer (ELS; Z Otsuka Electronics Co., Ltd).

***Photocurrent–voltage ( $J$ – $V$ ) measurements***  $J$ – $V$  measurements were performed using a Keithly model 2400 source measure unit. A class-A solar simulator (Yamashita Denso) equipped with a 150 W Xe lamp was used as the light source, and the light intensity was adjusted using an NREL-calibrated Si solar cell with KG-3 filter to approximate one sun light intensity. The  $J$ – $V$  measurement of the dye-sensitized solar cells was performed with an aperture mask to prevent extra light entering through the lateral space according to a method proposed elsewhere.

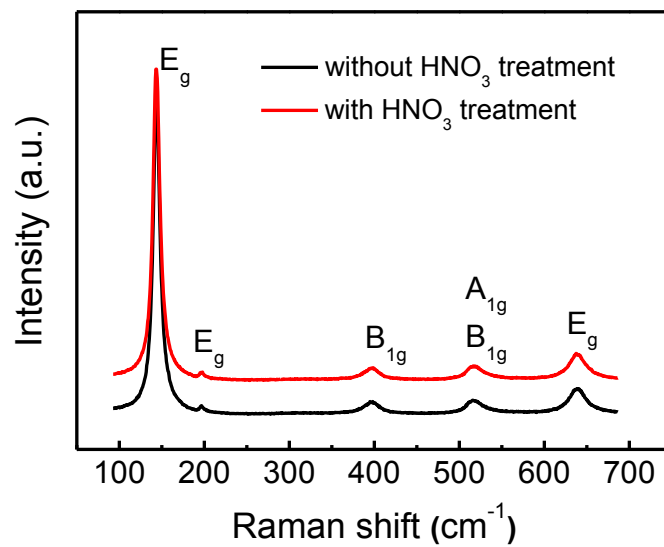
***Electrochemical Impedance measurements*** The electrochemical impedance spectra were measured under an illumination state at open-circuit potential with a Solartron 1287 potentiostat and a Solartron 1260 frequency-response detector. The sinusoidal perturbations of 10 mV were applied ranging from 0.1 Hz to 100 kHz.



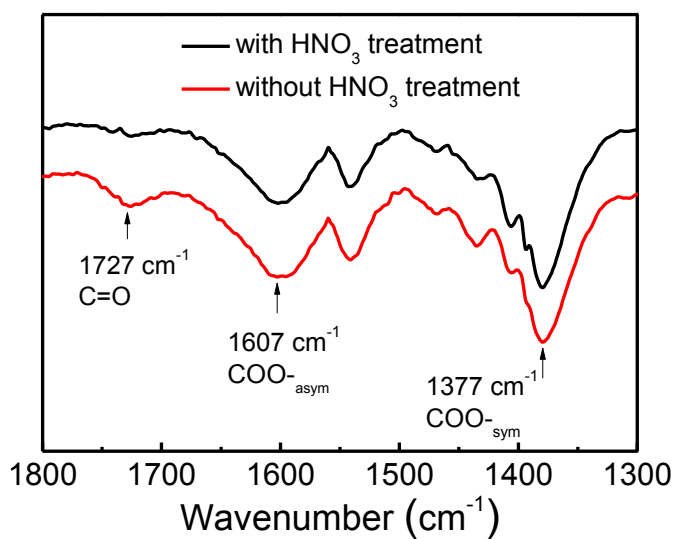
**Figure S1.** FE-SEM images of  $\text{TiO}_2$  nanoparticles deposited onto a conducting glass prepared (a) with nitric acid treatment and (b) without treatment.



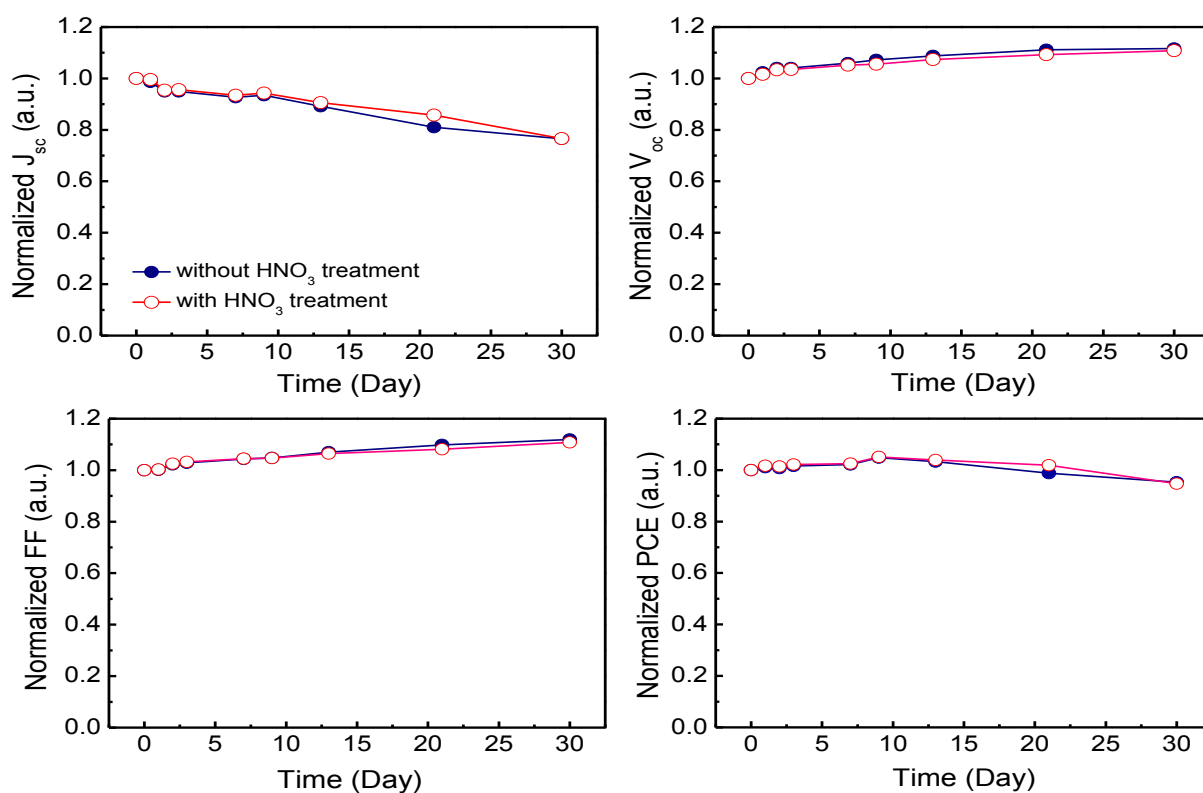
**Figure S2.** Impedance spectra of the cells measured under an illumination state at  $V_{oc}$  (Light intensity:  $100 \text{ mW/cm}^2$ , AM 1.5 G filter).



**Figure S3.** Raman spectra of the TiO<sub>2</sub> nanoparticles.



**Figure S4.** ATR-FTIR spectra of N719 dye adsorbed onto TiO<sub>2</sub> nanoparticles in a low wavenumber region.



**Figure S5.** Measurements of photovoltaic parameters of DSSCs as a function of time. The cells were stored under dark with an acetonitrile 100% condition.

## REFERENCES

- (1) Koo, H.-J.; Park, J.; Yoo, B.; Yoo, K.; Kim, K.; Park, N.-G. *Inorg. Chim. Acta* **2008**, *361*, 677-683.