

Electronic Supporting Information

for

**Effect of Coadsorbent Properties on the Photovoltaic
Performance of Dye-Sensitized Solar Cells**

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1. Experimental Details

UV-Vis absorption measurements. The dye-coated films were rinsed with acetonitrile and dried prior to use. UV-Vis spectrophotometry (using an Optizen POP spectrophotometer) was used to measure the amount of dye adsorbed onto the TiO₂ films, which was collected by immersing the dye-sensitized photoanode into a 0.1 M KOH aqueous solution for 20 min, followed by measuring the absorbance of the resulting solution.

ATR-FTIR measurements. The TiO₂ films were analyzed by ATR-FTIR spectrometry (Hyperion, Bruker). Spectra were derived from 64 scans, collected at a resolution of 2 cm⁻¹ by applying a reproducible mechanical force to the mesoscopic TiO₂ films using the anvil ATR Germanium accessory. To measure accurate spectra of the surfaces without contamination by weakly adsorbed molecules and moisture, the dye-adsorbed electrodes were rinsed with acetonitrile and stored in drying chambers prior to measuring the spectra at room temperature. The data reported here were collected using the 'Golden Gate' diamond anvil ATR accessory. No ATR corrections were applied to the data. It should be appreciated that the ATR technique probes the sample to a depth of at most 1 μm, depending on the sample refractive index, porosity, and other material properties.

Photoelectrochemical measurement. A 450 W xenon light source (Model No. 94022A, Oriel) was used to apply an illumination power of 100 mWcm⁻² (the equivalent of one sun at AM1.5) to the surface of the solar cell to simulate solar light irradiation. The incident light intensity was calibrated with reference to a Si solar cell equipped with an IR-cutoff filter (KG-5, Schott). Comparison of the simulated light to the true solar spectrum in the region 350–750 nm determined a spectral mismatch of less than 2%. The *I-V* characteristics were obtained by measuring the photocurrent generated by the cells (under an applied external bias) using a Keithley model 2400 digital source meter (Keithley, USA). The voltage step and delay time for the measurement were 10 mV and 40 ms, respectively.

Electrochemical impedance spectrophotometer measurements. The impedance values of devices having different co-adsorbents were measured using a computer-

controlled potentiostat (SP-200, BioLogic) under dark conditions. The frequency range examined was 0.005 Hz–100 kHz at room temperature, and the impedance spectra were recorded at potentials that varied from –0.60 to –0.80 V with a voltage amplitude set at 10 mV. The measured spectra were fit to appropriate equivalent circuits using the Z-fit software provided by BioLogic.

Preparation of the nanocrystalline TiO₂ electrodes. Contaminants were removed by washing the fluorine-doped SnO₂ (FTO) conducting glass first with detergent (Mucosol) and subsequently with DI water at 60°C for 15 min, for each wash. Organics were subsequently removed and a clean FTO glass was prepared by washing with ethanol and acetone, sequentially, at 40°C for 10 min, for each wash. The prepared FTO glass was treated with 40 mM TiCl₄ aqueous solution at 70°C for 30 min and rinsed with DI water and ethanol to support the good mechanical adhesion at the interface between the transparent TiO₂ layer and the FTO conducting glass. The nanocrystalline TiO₂ photoanode consisted of a double layered film. To improve sunlight harvesting via adsorption of large amounts of sensitizer, 20 nm TiO₂ particles were screen-printed onto the TiCl₄-treated FTO surface as a transparent and high-surface-area layer. The transparent film thickness was controlled by reapplication using a similar printing process. The second light scattering layer, consisting of 400 nm anatase particles screen-printed onto the transparent layer, reflected and scattered in the red and near-IR spectral region to enhance the absorption of the sensitizer. The thickness of the transparent layer varied from 3 μm to 16 μm, and the scattering layer thickness was held constant at 4 μm, measured using an Alpha-Step 500 Surface Profilometer (Tencor Instruments, USA). The double layer prepared on the FTO glass was sintered at 450°C for 15 min according to the programmed heating procedure. After sintering, the double layer film was treated with a 40 mM TiCl₄ aqueous solution again at 70°C for 15 min, then rinsed with water and ethanol. The nanocrystalline TiO₂ film was subsequently sintered again using the same programmed heating procedure. After

cooling to 60°C, the nanocrystalline TiO₂ electrode was immediately immersed in the dye solution to minimize moisture adsorption.

Fabrication of DSCs. The nanocrystalline TiO₂ electrode was immediately immersed in the dye solution at room temperature for 18 h. The dye solution consisted of 0.3 mM N719 sensitizer in acetonitrile and *tert*-butyl alcohol (1:1 v/v). The co-adsorbents, GBA, PPA, or SA, were introduced to the dye solution at various concentrations (0.3 mM, 1.5 mM, 3 mM) to yield a device series for each co-adsorbent. Co-adsorbents were introduced to the dye solutions by transferring appropriate volumes of a 6 mM stock solution to yield the desired final concentrations. The counter electrode was prepared by introducing two holes, using a sandblasting drill, in the FTO glass substrate. The substrate was subsequently washed using the washing method described above. The Pt paste was pasted onto the predrilled FTO glass and subsequently sintered using the programmed heating procedure. The dye-coated photoanode and counter electrode were assembled and sealed as a sandwich using a transparent 25 μm thick Surlyn spacer (DuPont) by hot pressing. The interelectrode space was filled with the electrolyte solution through the predrilled hole in the counter electrode surface, and the holes were covered with the Surlyn sheet and a thin cover glass followed by heating. The electrolyte consisted of 0.6 M BMII, 0.03 M I₂, 0.1 M guanidinium thiocyanate, 0.5 M LiI, and 0.5 M 4-*tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (85:15 v/v).

2. UV-Vis spectra

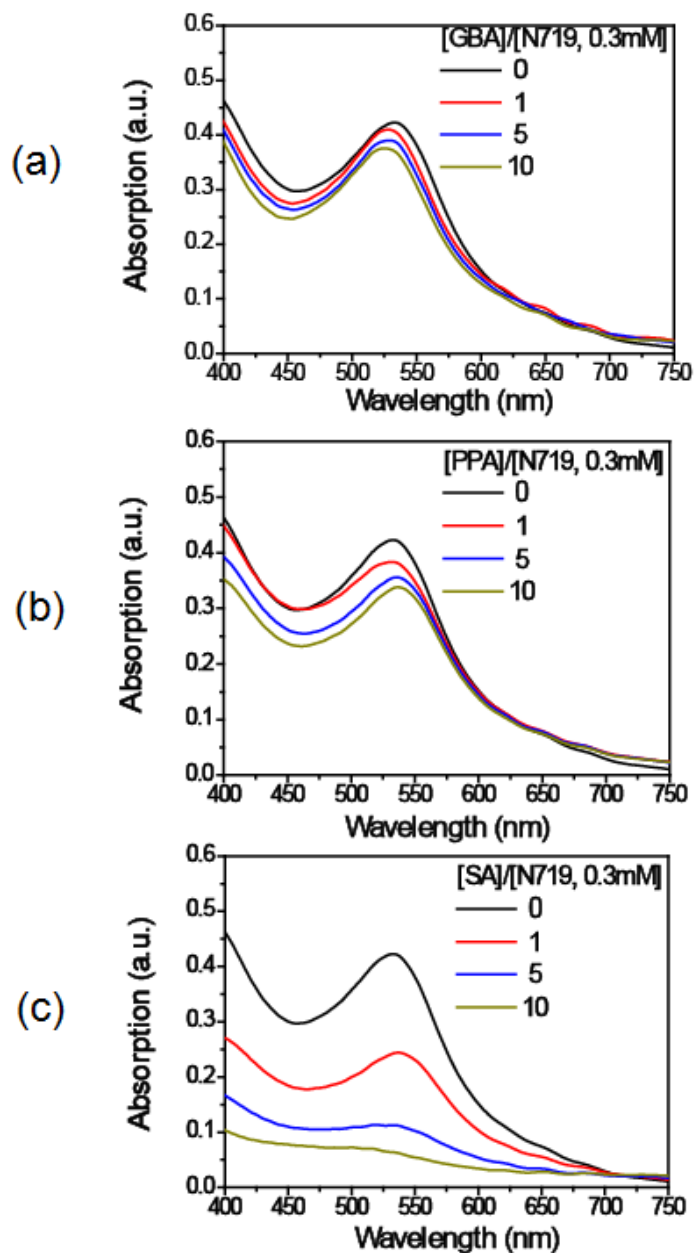


Fig. S1 Representative UV-Vis spectra of the dye (N719) detached from the TiO₂ electrodes: dye sensitized with N719 and either GBA (a), PPA (b), or SA (c) removed by immersion in a 0.1 M KOH aqueous solution.

3. I-V characteristics

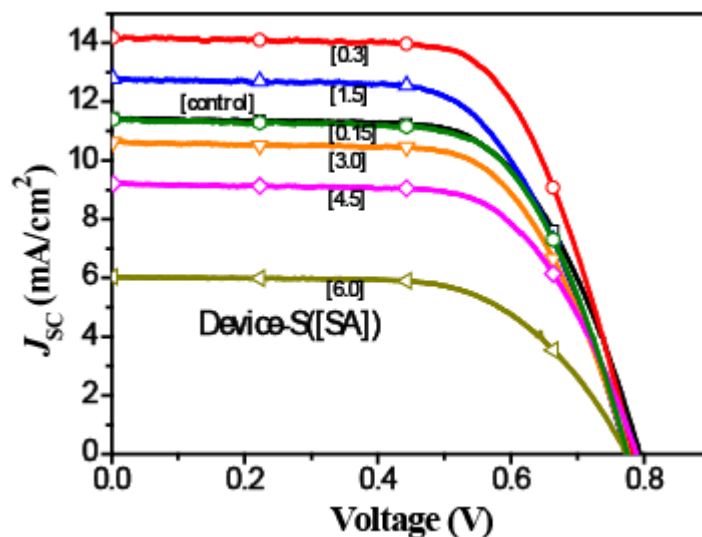


Fig. S2 Representative photocurrent–voltage curves for DSCs sensitized with N719 or N719 plus a variety of SA concentration, under AM 1.5 irradiation. The active area was 0.25 cm².

Table S1 Photocurrent–voltage characteristics^a for DSCs sensitized with N719 (control) or N719 plus SA, under AM 1.5 irradiation.

Entry	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)
Control	0.793	11.4	63.0	5.9
Device-S(0.15)	0.774	11.4	66.7	5.9
Device-S(0.3)	0.782	14.2	66.2	7.4
Device-S(1.5)	0.774	12.8	63.5	6.3
Device-S(3.0)	0.776	10.6	66.3	5.5
Device-S(4.5)	0.787	9.2	65.9	4.8
Device-S(6.0)	0.774	6.0	63.4	3.0

^a Values obtained using the average over 4 devices for each experiment

4. ATR-FTIR spectra

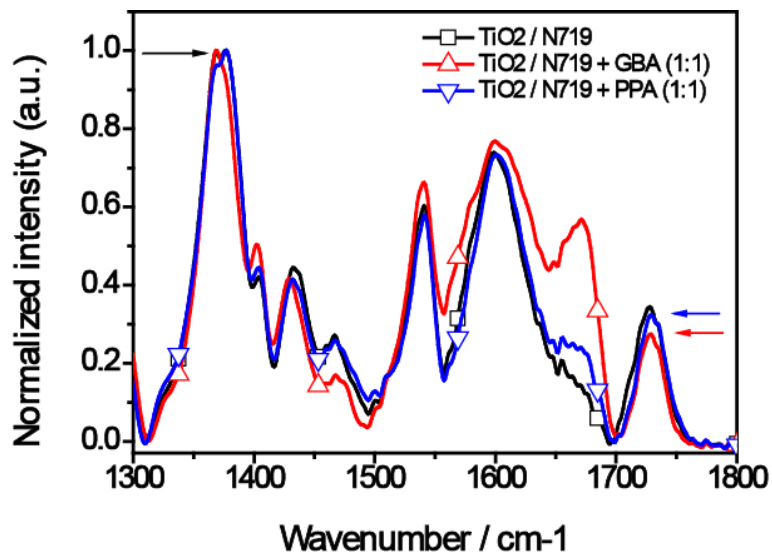


Fig. S3 Representative, normalized ATR-FTIR spectra of the TiO₂ electrodes sensitized with N719, and N719 with GBA or PPA. No difference was observed in the TiO₂ electrodes sensitized with different concentrations of GBA or PPA.

5. Cyclic Voltammograms

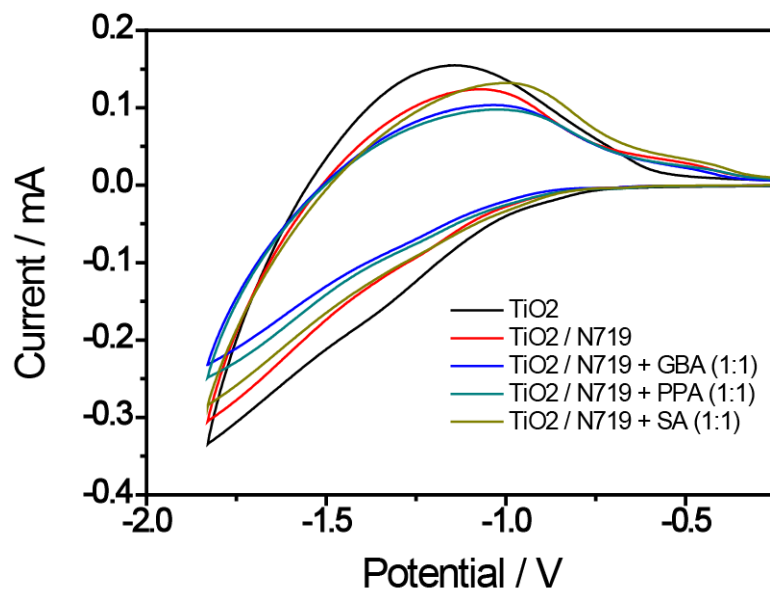


Fig. S4 Cyclic voltammograms of for TiO₂ electrodes sensitized with N719, and N719 with GBA, PPA, or SA.