Electronic Supplementary Information (ESI)

Single-molecule charge transfer dynamics in dye-sensitized p-type NiO solar cells: influences of insulating Al$_2$O$_3$ layers

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Experimental Methods

Preparation of NiO Nanoparticle Films for Steady-State and Time-Resolved Spectral Measurements. The synthesis of Ni(OH)$_2$ is the same as above, the difference is only dispersed the Ni(OH)$_2$ in 15 ml milli-Q water after centrifuged to obtain the Ni(OH)$_2$ sol. The NiO film was prepared by dip coating Ni(OH)$_2$ sol onto cleaned glass wafer, and was annealed at 500 °C for 1 h. The thickness of NiO layer is about 0.5-1 μm.

Preparation of NiO Nanoparticle Films for Photoelectrochemical Measurements. The synthesis of Ni(OH)$_2$ is the same as above, the difference is only dispersed the Ni(OH)$_2$ in 5 ml milli-Q water after centrifuged to obtain the Ni(OH)$_2$ sol. The NiO nanoparticles was obtained from the Ni(OH)$_2$ sol was annealed at 500 °C for 1 h. The NiO electrode film was prepared by spreading the NiO nanoparticle paste (NiO nanoparticles: Ni(OH)$_2$ sol (molar ratio)= 4:1) onto conducting glass substrates followed by sintering at 450 °C for 30 min. The thickness of NiO layer is about 15-25 μm.

Preparation of Al$_2$O$_3$/NiO Film for Steady-State and Time-Resolved Spectral Measurements. NiO films were dipped into a solution of 0.15 M aluminum tri-sec-butoxide (99.9%, from Aldrich) in isopropanol at 50-60 °C for 15 min. The
films were washed with isopropanol three times, hydrolyzed in water, and then annealed at 450 °C in air for 60 min.

**Preparation of Al$_2$O$_3$/NiO Film for Photoelectrochemical Measurements.** The NiO electrode film was dipped into a solution of 0.0015 M aluminum tri-sec-butoxide (99.9%, from Aldrich) in isopropanol at 50-60 °C for 15 min. The film was annealed at 450 °C in the air for 60 min.

**Sample Preparation for Steady-State and Time-Resolved Spectral Measurements.** The NiO films were soaked in an aqueous solution of WS-PDI (0.2 mM) for 24 h at room temperature.

**Sample Preparation for Photoelectrochemical Measurements.** The NiO electrode films were soaked in an aqueous solution of WS-PDI (0.2 mM) for 24 h at room temperature. After dried, the NiO electrode film was assembled face-to-face with a platinized counter electrode using a 1 mm thick silicone rubber spacer to form a chamber. The photoirradiated active area was 0.36 cm$^2$. An Ar-saturated acetonitrile electrolyte solution containing NaI (0.5 M) and I$_2$ (0.05 M) was then introduced into the chamber. IPCE spectrum was measured using Xenon light source (LAX-C100) through four bandpass filters (BP470-495 (Olympus, centered at 480 nm); BP520-550 (Olympus, centered at 535 nm); D585/20m (Chroma Technology, centered at 585 nm); D630/30m (Chroma Technology, centered at 630 nm)).

**Atomic Force Microscope (AFM) Measurements.** AFM measurements were performed using a Seiko Instruments SPA400 (DFM mode) at room temperature.

**Powder X-Ray Diffraction (XRD).** Crystallographic information of NiO nanoparticle films was analyzed using X-ray diffractometer (XRD) (Rigaku, RINT2500 XRD; Cu Kα source).

**Electrochemical Measurements.** Differential pulse voltammetry (DPV) experiments were carried out at room temperature using an electrochemical analyzer (ALS, model 660A) with a standard three-electrode configuration, which was composed of a Au gauze working electrode, a Pt wire counter electrode, and a Ag/Ag$^+$ aqueous reference electrode. All potentials were calibrated using methyl viologen (1.0 mM)
as an internal standard and are reported with respect to the normal hydrogen electrode (NHE).

Figure S1. AFM image of nanocrystalline NiO film on the glass surface.

Figure S2. Powder XRD pattern of synthesized NiO nanoparticle powder.
Figure S3. Differential pulse voltammetry (DPV) of WS-PDI (0.1 mM) in Ar-saturated 0.1 M phosphate buffer (pH 7.4).

Figure S4. (a) Averaged single-molecule fluorescence spectra of WS-PDI (50 molecules) on the NiO surface in Ar-saturated acetonitrile. Inset shows a typical single-molecule fluorescence spectrum. (b) Histogram of peak wavelength of the fluorescence spectra observed during the 485-nm excitation for single WS-PDI molecules on the surface of NiO nanoparticles, together with a Gaussian function fitted to the histogram. A dominant distribution centered at the wavelength of about 585 nm with a 20 nm FWHM was observed.
**Figure S5.** Transient absorption spectrum observed at 10 ps during the laser flash photolysis of Ar-saturated 0.1 M phosphate buffer solution (pH 7.4) containing WS-PDI (0.1 mM).

**Figure S6.** Transient absorption spectrum obtained at 1 μs after an electron pulse during the pulse radiolysis of NO$_2$-saturated aqueous solution (pH 2) containing WS-PDI (0.1 mM) and HCOONa (100 mM). The molar absorption coefficient ($\epsilon$) of WS-PDI$^\bullet$ was determined to be $(5 \pm 1) \times 10^4$ M$^{-1}$ cm$^{-1}$ at 790 nm using methyl viologen (MV) as a reference ($\epsilon$(MV$^\bullet$) = 13300 M$^{-1}$ cm$^{-1}$, see J. Phys. Chem. A, 2003, 107, 5998-6006).
**Figure S7.** Transient absorption spectrum obtained at 10 ps during the laser flash photolysis of a WS-PDI-adsorbed NiO film in Ar-saturated acetonitrile.

**Figure S8.** (A) Transient absorption spectra obtained during the 532-nm laser flash photolysis (5 mJ pulse$^{-1}$, 5 ns FWHM) of WS-PDI-adsorbed NiO films in Ar-saturated acetonitrile. (B) Effect of the number of coating procedures of the Al$_2$O$_3$ layer on the charge recombination dynamics.

**Table S1.** Kinetic Parameters of Decay of WS-PDI$^+$ on NiO and Al$_2$O$_3$/NiO

<table>
<thead>
<tr>
<th>System</th>
<th>$\tau_1$ ($\mu$s)</th>
<th>$\tau_2$ ($\mu$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>3 ± 1</td>
<td>74 ± 4</td>
</tr>
<tr>
<td>Al$_2$O$_3$/NiO-1</td>
<td>6 ± 1</td>
<td>200 ± 6</td>
</tr>
</tbody>
</table>
Figure S9. Fluorescence decay profile of WS-PDI (1 nM) in Ar-saturated acetonitrile. The red line indicates a double-exponential curve fitted to the data. $\tau_1$ and $\tau_2$ correspond to the laser light scattering and fluorescence decay, respectively.

Figure S10. Histogram of the fluorescence lifetime obtained for WS-PDI molecules adsorbed on the thick Al$_2$O$_3$ layer coated on the NiO surface (NiO/Al$_2$O$_3$-2) in Ar-saturated acetonitrile. The coating procedure of the Al$_2$O$_3$ layer was repeated two times.
Figure S11. Single-molecule fluorescence polarization profiles for WS-PDI molecules adsorbed on NiO (a), NiO/Al₂O₃-1 (b, one time coating Al₂O₃ layer) and NiO/Al₂O₃-2 (c, two times coating Al₂O₃ layer) in Ar-saturated acetonitrile.
Figure S12. The relationship between the number of luminescent spots per 50 μm × 50 μm and WS-PDI concentration on different surfaces.

Figure S13. On and off time distributions for WS-PDI on NiO (a, b), Al₂O₃/NiO-1 (c, d), and Al₂O₃/NiO-2 (e, f) surfaces in Ar-saturated acetonitrile.
**Figure S14.** Photocurrent generation in WS-PDI-sensitized NiO electrochemical cells.