Supporting Information

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SI Text

Experimental

Fabrication of Photoelectrodes. The SnO_2 colloidal paste used to prepare electrodes in this study was prepared using a protocol similar to that found in the literature (1). In brief, 1 mL acetic acid was added to 30 mL of 15 wt % SnO_2 colloidal dispersion in water (Alfa Aesar) and the mixture was stirred overnight at room temperature. This solution underwent hydrothermal treatment using a Parr Instruments pressure vessel at 240 °C for 60 h. The resulting solution was then sonicated and 2.5 wt % of both polyethylene oxide (mol wt 100,000) and polyethylene glycol (mol wt 12,000) was added. Stirring for 12 h yielded a homogeneous colloidal paste. Transparent thin-film electrodes were prepared by depositing the sol–gel paste onto conductive FTO glass substrates 4 cm × 2.2 cm using the doctor blade method with tape casting and sintered at 450 °C for 30 min under air.

Atomic Layer Deposition. Atomic layer deposition (ALD) was performed in a commercial reactor (Savannah S200, Cambridge Nanotech). Titanium dioxide (TiO_2) was deposited using Tetrakis (dimethylamido) titanium, $Ti(NMe_2)_4$ (TDMAT, 99.999%, Sigma-Aldrich), and water. The reactor temperature was 130 °C. The TDMAT reservoir was kept at 75 °C. The TDMAT was pulsed into the reactor for 0.3 s and then held for 10 s before opening the pump valve and purging for 10 s. ALD coating conditions were 130 °C and 20 torr of N_2 carrier gas with a sequence of 0.3-s metal precursor dose, 10-s hold, 20-s N_2 purge, 0.02-s H_2O dose, 10-s hold, 20-s N_2 purge.

The aluminum oxide (Al_2O_3) was deposited using trimethylaluminum, $Al(CH_3)_3$ (TMA, 97%, Sigma-Aldrich) The reactor temperature was 130 °C. The TMA reservoir was kept at room temperature. The TMA was pulsed into the reactor for 0.015 s and then held for 10 s before opening the pump valve and purging for 10 s. ALD coating conditions were 130 °C and 20 torr of N_2 carrier gas with a sequence of 0.15-s metal precursor dose, 10-s hold, 20-s N_2 purge, 0.015-s H_2O dose, 10-s hold, 20-s N_2 purge. The growth rate under these conditions was 0.6 Å per cycles for TiO_2 and 1.1 Å per cycles for Al_2O_3, as determined by ellipsometry on Si wafers. The quality of the TiO_2 outer layers has been confirmed by TEM (Fig. 1*B*).

Photocurrent Measurements. The mesoporous films consisting of SnO_2 nanoparticles (diameter of each individual particle ~10–20 nm) after ALD processing were annealed at 450 °C for 30 min. The assembly was surface-bound to the nanoparticle films by immersing them in assembly solutions 10^{-3}–10^{-4} M in 0.1 M HNO_3 for ~16 h. The overlayers of Al_2O_3 or TiO_2 were deposited by ALD and the slides were used without further annealing.

The fully assembled dye-sensitized photoelectrochemical cell (DSPEC) consisted of a $FTO|SnO_2\text{-}TiO_2|\text{-}[Ru_a^{II}\text{-}Ru_b^{II}\text{-}OH_2]^{4+}$ core/shell photoanode, Pt wire cathode, and a Ag/AgCl reference electrode. Current–time (i–t) measurements were recorded with an applied bias vs. Ag/AgCl and the samples were illuminated with 445-nm light (20 nm FWHM) in both pH 4.6, 0.5 M $LiClO_4$, 20 mM acetate/acetic acid buffer, and 0.1 M phosphate buffer at pH 7 with $NaClO_4$ supporting electrolyte added to give an ionic strength of 0.5 M. The photocurrent at different intensities of 445 nm (FWHM 20 nm) illumination from 15 to 86 mW cm^2 was recorded.

Hydrogen and Oxygen Evolution. A custom-built, two-compartment Pyrex cell was used for the electrochemical detection of hydrogen and oxygen. In this approach, the Pt counterelectrode and photoanode compartments were separated by a Nafion sheet. The working electrode consisted of a $FTO|SnO_2/TiO_2$ (6.6 nm)|-$[Ru_a^{II}\text{-}Ru_b^{II}\text{-}OH_2]^{4+}$ electrode. This electrode was prepared with 100 ALD cycles of TiO_2 to form the core/shell layer as described previously and loaded with the surface-bound assembly **1,** and the adsorbed assembly was stabilized on the surface by an additional 10 ALD cycles of Al_2O_3. The setup used for detection of photogenerated oxygen by the chromophore–catalyst assembly **1** is shown in Fig. S3. The photoelectrochemical cell was argon-degassed for 30 min before photolysis.

1. Chappel S, Zaban A (2002) Nanoporous SnO_2 electrodes for dye-sensitized solar cells: Improved cell performance by the synthesis of 18 nm SnO_2 colloids. *Sol Energy Mater Sol Cells* 71:141–152.

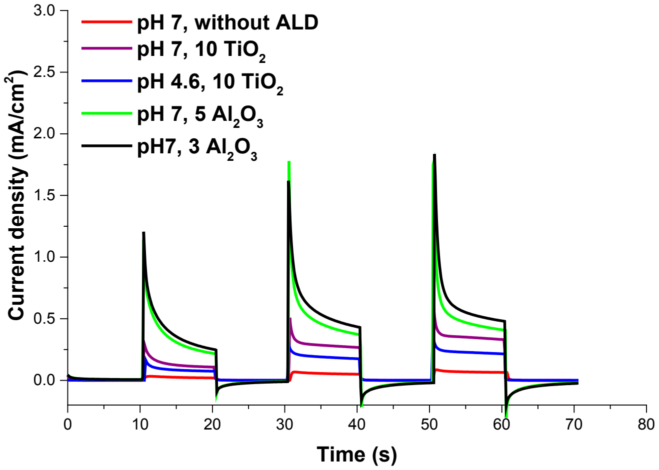

Fig. S1. Photocurrent comparisons for a FTO|SnO_2/TiO_2(6.6nm)|-[Ru_a^{II}-Ru_b^{II}-OH_2]$^{4+}$ photoanode in pH 4.6 acetate (20 mM) and pH 7 phosphate (0.1 M) buffers illustrating the effect of ALD overlayers of TiO_2 and Al_2O_3.

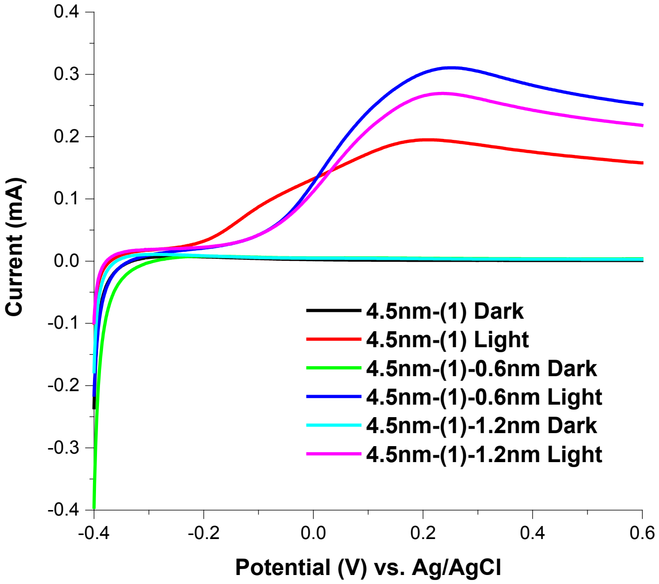

Fig. S2. Linear voltammetry measurements in pH 4.6, 0.5 M $LiClO_4$, 20 mM acetic acid/acetate buffer recorded with a FTO|SnO_2/TiO_2(4.5 nm)|-[Ru_a^{II}-Ru_b^{II}-OH_2]$^{4+}$ photoanode with no ALD overlayer (red), 10 cycles of TiO_2 ALD overlayer (blue), and 20 cycles of TiO_2 ALD (pink). Traces in light taken under continuous illumination at 445 nm (10 mW/cm^2, FWHM 20 nm).

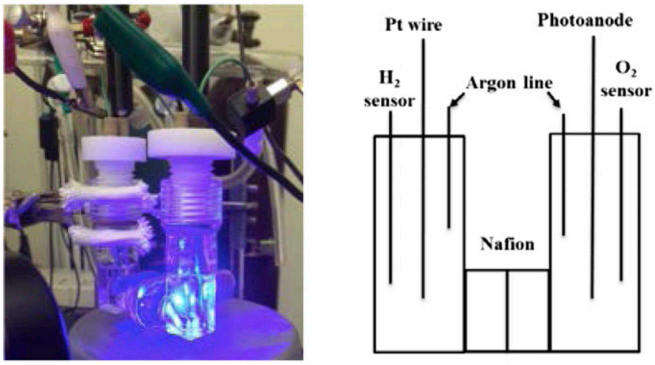

Fig. S3. Picture and schematic of the home-built DSPEC device.

Table S1. Comparisons between SnO_2 and *nano*ITO as cores with 50-cycle ALD TiO_2 shells (3.3 nm) derivatized with 1 with a Pt counterelectrode at a 200-mV vs. NHE (0 V vs. Ag/AgCl) bias at pH 4.6 in 0.5 M $LiClO_4$ with 20 mM acetate/acetic acid buffer

Light intensity at 445 nm (mW cm^{-2})	*nano*ITO/TiO_2(3.3 nm)|-$[Ru_a^{II}\text{-}Ru_b^{II}\text{-}OH_2]^{4+}$	SnO_2/TiO_2(3.3 nm)|-$[Ru_a^{II}\text{-}Ru_b^{II}\text{-}OH_2]^{4+}$	SnO_2/TiO_2(3.3 nm)|-$[Ru_a^{II}\text{-}Ru_b^{II}\text{-}OH_2]^{4+}$-(0.6 nm) TiO_2
15.1	0.10	0.48	0.79
55.6	0.12	0.54	0.78
86.0	0.12	0.59	0.85

The photocurrent densities in the table are reported in mA cm^{-2}.

Table S2. Comparisons between initial and after 10-s photocurrent densities value SnO_2 and *nano*ITO as cores with 50-cycle ALD TiO_2 shells (3.3 nm) derivatized with 1 with a Pt counterelectrode at a 200-mV vs. NHE bias at pH 4.6 in 0.5 M $LiClO_4$ with 20 mM acetate/acetic acid buffer, measured at light intensity 10% of 455 nm, 15.1 mW cm^{-2}

Time	*nano*ITO/TiO_2(3.3 nm)|-$[Ru_a^{II}\text{-}Ru_b^{II}\text{-}OH_2]^{4+}$	SnO_2/TiO_2(3.3 nm)|-$[Ru_a^{II}\text{-}Ru_b^{II}\text{-}OH_2]^{4+}$	SnO_2/TiO_2(3.3 nm)|-$[Ru_a^{II}\text{-}Ru_b^{II}\text{-}OH_2]^{4+}$-(0.6 nm) TiO_2
0	0.10	0.48	0.79
After 10 s	0.02	0.10	0.15

Table S3. Illustrating the role of variations in ALD overlayers on photocurrent densities for FTO\|SnO_2/TiO_2(6.6 nm)\|-$[Ru_a^{II}\text{-}Ru_b^{II}\text{-}OH_2]^{4+}$ as a function of incident light intensity and pH

	pH 7*				pH 4.6†
Light intensity, 445 nm (mW cm^{-2})	No overlayer	+0.55 nm Al_2O_3	+0.33 nm Al_2O_3	+0.6 nm TiO_2	+0.6 nm TiO_2
15.1	0.02	1.14	1.21	0.29	0.16
55.6	0.02	1.35	1.62	0.51	0.31
86.0	0.04	1.77	1.83	0.59	0.37

*0.1 M PO_4 buffer with the ionic strength increased to 0.5 M with $NaClO_4$.

†0.5 M $LiClO_4$ 20 mM in acetic acid/acetate buffer (HAc/OAc$^-$).