

A plasmonic liquid junction photovoltaic cell with greatly improved power conversion efficiency

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Experimental Details

Materials: FTO-coated glass substrates (TCO22-7, 7 Ω /square) and hot melt sealing films (Meltonix 1170-60, 60 μ m thickness) were purchased from Solaronix. ITO-coated glass substrates (ITO-P001, <10 Ω /square) were purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and sodium orthovanadate (Na_3VO_4) were purchased from Sigma-Aldrich. Sulfuric acid (assay, 95.0~98.0%) and mossy zinc were purchased from EMD and Acros, respectively. A detergent solution (Deconex® 12 BASIC) was purchased from Borer Chemie AG. All reagents were used as-received.

Device fabrication: The solar cell was fabricated on an ITO glass substrate and capped with a FTO glass substrate. To prepare the anode, two small holes were drilled into the FTO glass substrate prior to its assembly to allow electrolyte injection into the assembled device. The substrates were ultrasonically cleaned for 20 min in a detergent solution, and rinsed with tap water, DI water and, ethanol. The Pt nanoparticle anode was fabricated as follows. The FTO glass was coated with a thin layer of a 5 mM solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ dissolved in isopropanol, dried at room temperature for 10 min, then promptly annealed in air by ramping the temperature at a rate of 25 $^\circ\text{C}/\text{min}$ from room temperature to 450 $^\circ\text{C}$ where it was held for 20 min.

For the cathode, 200 nm thick Au was deposited by e-beam evaporation at a deposition rate of 1 $\text{Å}/\text{s}$ on the previously cleaned ITO substrate. The nanostructured Au surface was fabricated by electrochemical double-potential step oxidation-reduction cycles using a BioLogic VMP3 potentiostat.^{1,2} The Au/ITO glass substrate was masked with adhesive tape so that only a central portion of the substrate would be in contact with the 0.1 M aqueous KCl electrolyte, and the oxidation-reduction cycles were carried out as follows: (1) -0.3 V were applied for 30 sec, and (2) linearly swept from -0.3 V to 1.2 V at a rate of 1 V/s. (3) 1.2 V were applied for 1.2 sec, and (4) linearly swept from 1.2 V to -0.3 V at a scan rate of 0.5 V/s. Typically, 45 to 55 cycles were carried out. A Pt wire was used as a counter electrode and standard calomel electrode (SCE) was used as a reference electrode. The processed Au/ITO surface was treated with O_2 plasma for 2 min at 100 W and coated with 10 nm TiO_2 by atomic layer deposition (ALD) at 120 $^\circ\text{C}$ using tetrakis(dimethylamino)titanium (TDMAT) and water in an Oxford FlexAl ALD tool. The substrate was then annealed at 400 $^\circ\text{C}$ in air for 30 min with the temperature ramped from room temperature at a rate of 25 $^\circ\text{C}/\text{min}$.

To synthesize the V^{2+} redox species, 2 mL aqueous solutions of Na_3VO_4 (0.2 M) and sulfuric acid (2.3 M) were degassed by bubbling N_2 for 30 min in an airtight vial. Excess mossy zinc was quickly added to minimize air exposure. Nitrogen was bubbled in the solution during the reduction of V^{5+} to V^{2+} . The yellow colored V^{5+} was observed to turn blue (V^{4+}), then green (V^{3+}) and finally violet (V^{2+}). The violet solution was filtered through a 0.2 μm PVDF membrane filter and a syringe in a N_2 atmosphere and the resultant solution bubbled with N_2 for 10 min. A similar procedure was carried out for the V^{3+} redox species, except that lower concentration sulfuric acid (1.2 M) was used, and the reaction stopped and the solution filtered when it had reached a green color after passing through its blue phase.

(Note that a green color also appears *before* the blue phase. It is a mixture of the yellow of the original +5 oxidation state, and the blue of the V^{4+} species, and should not be mistaken for V^{3+} .)

The cathode and an anode were sealed around their perimeters using 60 μm thick thermal melt polymer film thereby forming a 60 μm space between them on assembly. Liquid electrolyte containing V^{2+} and V^{3+} in a 10:1 volumetric ratio was injected into the space between the electrodes through one of the holes predrilled in the anode. The holes were then sealed with thermal melt polymer films and microscope cover slips. The active area of the device was 0.10 cm^2 .

Device characterization: SEM images were obtained with an FEI Thermal Field Emission SEM (Sirion) at an acceleration voltage of 5 kV. UV-Vis analysis was performed with an Agilent 8453 spectrophotometer. Photovoltaic measurements were carried out using a Newport Air Mass 1.5 Global (AM 1.5 G) full spectrum solar simulator as source at an irradiation intensity of 100 mW cm^{-2} . Current density-voltage (J-V) measurements were carried out using a Keithley 2400 Digital Source Measure Unit.

1. Z.-Q. Tian, B. Ren and D.-Y. Wu, *J. Phys. Chem. B*, 2002, **106**, 9463–9483.
2. P. Gao, M. L. Patterson, M. A. Tadayoni and M. J. Weaver, *Langmuir*, 1985, **1**, 173–176.

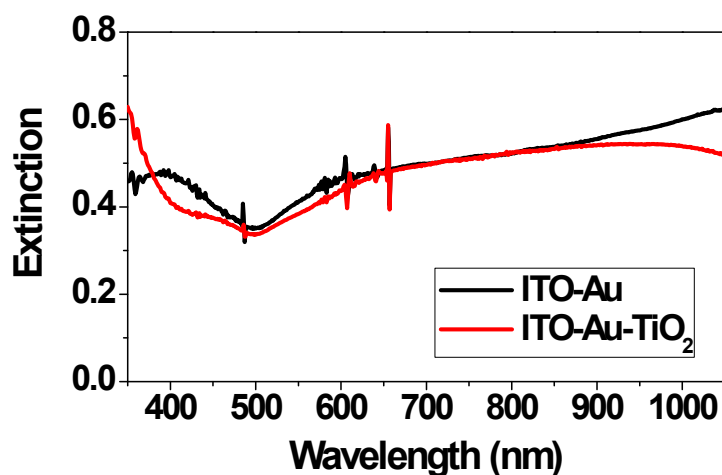


Fig. S1 UV-Vis spectra of randomly disposed Au islands on an ITO substrate before and after TiO_2 deposition (“ITO-Au” and “ITO-Au- TiO_2 ”, respectively).