SUPPORTING INFORMATION

Interfacial Band Alignment for Photocatalytic Charge Separation in TiO₂

Nanotube Arrays Coated with CuPt Nanoparticles

Samira Farsinezhad $^{a\dagger},$ Himani Sharma $^{a\dagger}\,$ and Karthik Shankar $^{a,\,b*}$

^aDepartment of Electrical and Computer Engineering, University of Alberta, 9107 - 116 St,

Edmonton, Alberta, Canada T6G2 V4

^bNRC National Institute for Nanotechnology, 11421 Saskatchewan Dr NW, Edmonton, AB T6G 2M9

[‡] Both authors contributed equally to this study.

EXPERIMENTAL DETAILS

Synthesis of transparent TiO₂ nanotube arrays

Transparent TiO₂ nanotube arrays (TTNTAs) were synthesized by electrochemical anodization of thin Ti films deposited on fluorine doped tin oxide (FTO) coated glass substrates (glass:FTO) purchased from Hartford Glass Co., by direct current (DC) sputtering from a Ti target of 99.995 % purity (Kurt J. Lesker Co.); further details regarding the details of the vacuum deposition and nanotube growth processes are provided in prior work.^{1, 2} Prior to depositing Ti films, FTO substrates were cleaned in an ultrasonicated bath with soap solution, deionized water and methanol, consecutively for 10 minutes each. Electrochemical anodization of the Ti-coated glass:FTO substrates was carried out at room temperature using an organic electrolyte containing 0.3 wt % NH₄F (> 98 % purity, Fisher Chemical) and 4% deionized water in ethylene glycol (> 99 % purity, Fisher Chemical) and a graphite cathode. A constant potential of 40 V was applied across the two electrodes by using a DC power supply.

Formation of CuPt-TTNTA hybrid structures

CuPt-TTNTA hybrids were formed by photodeposition of bimetallic nanoparticles over TTNTAs. To prepare these hybrid catalysts, annealed and oxygen plasma treated TTNTAs were soaked in a methanolic solution of [Pt(acac)₂], [Cu(acac)₂] (2:1) for 60 minutes under the irradiation of a 150 W solar simulator equipped with an AM1.5 filter at an intensity of 1 sun. [Pt(acac)₂] was of 98 % purity and purchased from Strem Chemicals Inc., [Cu(acac)₂] was of 98 % purity and purchased from Acros Organics, Inc and the methanol was of 99.8 % purity and purchased from Fisher Chemical. The samples were placed in a teflon reaction cell. TTNTA samples were uniformly subjected to an oxygen plasma cleaning treatment before photodeposition to remove existing adsorbates and allow facile charge transfer to metal organic precursors in methanol solution. Pt-TTNTA hybrids were formed and subjected to UPS purely to probe the difference in band-alignment from CuPt-TTNTA hybrids; their detailed study of is outside the scope of the present work. To form Pt-TTNTA hybrids, an identical photodeposition process was used, but in a methanolic solution of [Pt(acac)₂] alone. For Sput-CuPt-TTNTA hybrids, both transparent TiO_2 nanotube samples exposed to an oxygen plasma clean and those not exposed to the plasma clean after annealing were used. The plasma cleaning process was performed in a Plasmalab Microetch reactor for 10 minutes at an oxygen partial pressure of 120 mTorr and an RF power of 225 W. To separate out the effects of photocatalytic deposition of CuPt NPs on TiO₂ nanotubes from the photochemical reduction of TiO₂ in methanol, a series of experiments were performed on TTNTA samples with conditions identical to those used for photodeposition but with no precursors present in the methanol medium. To form sputtered CuPt nanoparticles, 1.5 nm of Cu and 3.5 nm of Pt were deposited on to TTNTA samples in a DC magnetron sputtering system and subsequently annealed in Ar at 200°C.

Characterization

The morphologies of the TTNTAs and CuPt-TTNTA hybrids were examined using a field emission scanning electron microscope (S-4800, Hitachi) operating at 5 kV accelerating voltage by secondary electron imaging. The internal structure of samples was imaged using high resolution transmission electron microscopy (HRTEM) (JEOL 2200FS) operating at 200 kV, equipped with scanning transmission electron microscopy (STEM) and energy dispersive X-ray facility. UV-Vis spectra were collected in a Perkin-Elmer Lambda 1050 UV-Vis-NIR spectrophotometer equipped with a 150 mm integrating sphere to measure total diffuse reflectance. TEM sample preparation of the CuPt-coated and uncoated nanotube cross sections was performed using focused ion beam etching in a SEM system (Hitachi-NB5000). X-ray photoelectron spectroscopy (XPS) measurements were conducted out using Al K_{α} , source with energy 1486.6 eV instrument (Axis-Ultra, Kratos Analytical) under UHV conditions (~10⁻⁸ Torr). The binding energies were calibrated by the C 1s peak of the surface adventitious carbon at 284.6 eV to compensate for charge shifting (see Fig. S3). There is concern expressed in some reports that the core levels of the adventitious carbon would be subject to the effects of the band bending on the semiconductor surface.³ However other reports point out that most adventitious carbon consists of adsorbed hydrocarbon polymers⁴ sufficiently external to the metalsemiconductor interface. We also used the following equation based on the Kraut method⁵ to calculate the alignment of energy levels using purely the XPS core level and valence band spectra:

$$\phi_{bi} = E_{VB}^{TTNTA}(abs) - E_{VB}^{CuPt-TTNTA}(abs) = \left[E_{VB}^{TTNTA} - E_{F}^{TTNTA}\right] - \left[\left(E_{CL}^{CuPt-TTNTA} - E_{F}^{CuPt-TTNTA}\right) - \left(E_{CL}^{TTNTA} - E_{VB}^{TTNTA}\right)\right]$$

where (abs) represents energy values on an absolute scale vs. vacuum. The subscripts CL, VB and F refer to core level, valence band and Fermi level respectively. The energy difference between the Ti $2p_{3/2}$ peak and the valence band maximum is a material constant and was found to be 456.5 eV for TiO₂ nanotube array samples in this study. Fermi level referencing was aided by a metallic Fermi edge in the XPS VB spectra exhibited both by CuPt-TTNTA hybrid samples and by Sput-CuPt-TTNTA hybrids. By this method, the upward band banding at the CuPt-TiO₂ interface was found to be 1.2-1.3 eV. However the larger escape depth of photoelectrons in XPS $(\sim 3 \text{ nm})$ as opposed to UPS $(\sim 1 \text{ nm})$ renders it less sensitive to chemical shifts at the surface and interface dipoles. Consequently, we adopted the C 1s calibration which provided us more conservative values of the Schottky barrier height. Moreover, the C 1s peak is still a standard of choice for energy referencing the XPS spectra of large bandgap semiconductors.⁶⁻¹⁰ Ultraviolet photoelectron spectroscopy studies were carried out using He lamp source with energy 21.2 eV with the sample to be probed in electrical contact with the grounded stage of the specimen holder. Time of flight-TOF depth-profiles were collected using secondary ion mass spectrometry in an ION-TOF IV instrument. Micro-Raman studies of the samples were carried out in back scattering mode (Nicolet Almega-XR). An excitation source of 532 nm with a beam spot of 2 micron was used to analyze the structure of the samples. The resolution of the XPS measurements was 0.1 eV while that of UPS was 0.02 eV.

CO₂ Photocatalytic Reduction Studies

A stainless steel reaction chamber was used to carry out the photocatalytic reaction. Samples (TNAs and Cu/Pt-TNA hybrids) were placed in the reaction chamber filled with carbon dioxide

(CO₂) gas. Before filling the chamber with the gas, it was purged by CO₂. The photoreduction experiments were carried out in a dark room using a Newport solar simulator (91160–1000) equipped with Class A filters. After photocatalytic reaction, the presence of reduced gases were quantified using gas chromatography system Varian Star (Varian, CA, USA) equipped with a Porapak QS column (12 Ft; 366 cm; 3.2 mm OD, 2 mm ID), equipped with TCD and FID detectors. The temperature of the detector was maintained at 180°C and 250°C for TCD and FID, respectively. The column temperature was held at 70°C. Helium was used as the carrier gas. H₂ and compressed air were used as the flame gases.



Fig. S1 Band-diagram of the Schottky junction at the *n*-TiO₂/CuPt interface. The direction of the built-in field in the depletion region is such as to drive photogenerated electrons toward the TiO₂ bulk and holes toward the metal-semiconductor interface.



Fig. S2 FESEM images display the morphological features of (a) TTNTAs, an inset image in the figure shows the cross-section of the arrays with the height of 1 micron and (b) CuPt-coated TTNTA hybrids. The scale bar refers to 500 nm for both the images.







Fig. S4 X-ray photoelectron spectra of TiO₂ nanotube arrays for C 1s



Fig. S5 Peak decomposed O1s core level spectra for transparent TiO_2 nanotube arrays (TTNTAs) with, and without, an oxygen plasma cleaning treatment.



Fig. S6 Peak decomposed O1s core level spectra for TTNTAs photodeposited with CuPt compared to TTNTAs subjected to AM1.5G illumination from a solar simulator in pure methanol.



Fig. S7 Ti 2*p* spectra for TTNTAs subjected to AM1.5G illumination from a solar simulator in pure methanol.



Fig. S8 High resolution core level spectra showing the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks for (a) TTNTA samples coated with CuPt nanoparticles by photodeposition and (b) coated with CuPt nanoparticles by sputtering.



Fig. S9 Magnified views of the low binding energy regions of the XPS spectra of TTNTAs subjected to bimetallic noble metal nanoparticle coating or ultraviolet treatment in methanol.



Fig. S10 Unlike a continuous film, a discontinuous layer of metal nanoparticles decorating a surface does not produce a planar junction. For a hemispherical Schottky point-contact with a radius of a_0 , the radius (r_0) of the hemispherical depletion region formed in the semiconductor is

given by
$$r_0 = \left(\frac{3a_0\varepsilon_r\varepsilon_0\phi_{bi}}{eN_d}\right)^{\frac{1}{3}}$$
 where *e* is the electron charge, N_d is the carrier density in the *n*-

type semiconductor, ε_r is the relative permittivity of the semiconductor, ε_0 is the permittivity of free-space and ϕ_{bi} is the built-in potential of the Schottky junction.



Fig. S11 Depletion region widths for a point-contact Schottky junction between n-type anatase TiO2 and CuPt NPs. The inset is a higher magnification view of the depletion widths obtained for the commonly observed carrier concentrations in TiO_2 nanotube arrays anodically formed in fluoride-ion containing ethylene glycol electrolytes for a band bending of 0.7 V; the depletion widths for 5 nm, 2 nm and 1 nm nanoparticles are represented by red, black and green curves respectively in the inset.



Fig. S12 (a) UPS spectra of Pt-TTNTA hybrids with the inset showing the secondary electron cutoff region and (b) Zoomed in view of the low binding energy edge in the UPS spectrum shown in (a). The valence band maximum was estimated using the intercept on the abscissa obtained by extrapolating the low binding energy edge to the baseline.

REFERENCES

- 1. S. Farsinezhad, A. N. Dalrymple and K. Shankar, *physica status solidi* (*a*), 2014, 1-9.
- 2. S. Farsinezhad, A. Mohammadpour, A. N. Dalrymple, J. Geisinger, P. Kar, M. J. Brett and K. Shankar, *Journal of Nanoscience and Nanotechnology*, 2013, **13**, 2885-2891.
- 3. D. C. Gleason-Rohrer, B. S. Brunschwig and N. S. Lewis, *The Journal of Physical Chemistry C*, 2013, **117**, 18031-18042.
- 4. T. L. Barr and S. Seal, *Journal of Vacuum Science & amp; Technology A*, 1995, **13**, 1239-1246.
- 5. E. A. Kraut, R. W. Grant, J. R. Waldrop and S. P. Kowalczyk, *Physical Review B*, 1983, **28**, 1965-1977.
- 6. J. R. Lince, D. J. Carré and P. D. Fleischauer, *Physical Review B*, 1987, **36**, 1647-1656.
- Y. Y. Tay, T. T. Tan, M. H. Liang, F. Boey and S. Li, *Phys. Chem. Chem. Phys.*, 2010, 12, 6008-6013.
- 8. H.-J. Lee, S.-Y. Jeong, C. R. Cho and C. H. Park, *Applied Physics Letters*, 2002, **81**, 4020-4022.
- 9. M. Avice, S. Diplas, A. Thogersen, J. Christensen, U. Grossner, B. Svensson, O. Nilsen, H. Fjellvag and J. Watts, *Applied Physics Letters*, 2007, **91**, ?-?
- L. Chang, C. Eng Fong and T. Leng Seow, *Semiconductor Science and Technology*, 2007, 22, 522.