Supporting Information

Light and electric field induced unusual large-scale charge separation in hybrid semiconductor objects

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1. Experimental

1.1 Chemicals

Pure TiO_2 (anatase and rutile), mixed phases (anatase+rutile) and ethanol were purchased from Alfa Aesar, with 99.9 % purity. Sintered Ta_2O_5 was obtained from Kurt J. Leshker Company. P-type silicon wafers (0.001 Ω cm resistivity, boron-doped, 275-325 µm thickness) single side polished (100 standard orientation) were purchased from Sil'tronix. Gold (III) chloride trihydrate ($HAuCl_4.3H_2O$) of 99.9 % purity was purchased from Sigma Aldrich. Millipore water (resistivity = 18 MΩ) was used for all experiments.

1.2 Instruments

A DC high voltage source (Heinzinger, PNC 10000-200POS) was used. The light source was a LC8 (Hamamatsu) 200W mercury–xenon lamp (wavelength between 300 and 450 nm, UV). Scanning Electron Microscopy (SEM) images were obtained with a Hitachi Tabletop Microscope TM-1000. High resolution SEM images were recorded with a TESCAN VEGA3 SBH instrument. X-ray diffraction (XRD) patterns were collected on a PANalitycal EMPYREAN Bragg-Brentano θ-2θ geometry diffractometer equipped with a KβNi filter over

an angular range of $2\theta = 5$ to 80° with a step of 0.02°. Each acquisition lasted for 12 minutes. The Cu-Kα radiation was generated at 45 KV and 40 mA (lambda = 0.15418 nm).
The samples were prepared on a special "zero signal" silicon wafer sample holder. A potentiostat/galvanostat (Autolab PGSTAT12) was used for the I-V curve measurements.

1.3 Preparation of PANi/PVC-carboxylated dispersion.

Polyaniline/polyvinylchloride carboxylated (PANi/PVC-carboxy) dispersions were prepared as reported previously.[1] 300 mg of PVC-carboxy were dissolved in 5 ml of tetrahydrofuran (THF). 700 mg of PANi were added to the above solution during stirring and ultrasonication for 15–30 min, followed by 6 h stirring at room temperature in a closed flask. The resulting dispersion is used for PANi/PVC-carboxy composite fabrication.

1.4 Bipolar electrodeposition of Au nanoparticles on TiO_2 or Ta_2O_5 pellets and PANi/PVC-AR-TiO_2 hybrid systems. I-V curve measurements of the PANi/PVC-AR-TiO_2 hybrid system

350 mg of TiO_2 or Ta_2O_5 in powder form was used for making pellets using a 10-mm die and applying 10-ton pressure load. Subsequently, the pellets were heated at 350 °C for 1 hr. In the case of the polymer-TiO_2 hybrid system, the PANi/PVC dispersion was casted on a glass slide. During drying of the film, a TiO_2 pellet was positioned in the partly dried PANi/PVC dispersion. The TiO_2 and Ta_2O_5 pellets and PANi/PVC-carboxy/AR-TiO_2 were used for bipolar electrodeposition. The diameter and length of the TiO_2 pellets and PANi/PVC-carboxy film were 1 and 2 cm respectively. Bipolar electrodeposition was carried out in a three-chambered glass cell under the influence of both light and electric field. The platinium feeder electrodes for generating the electric field were placed at a distance of approximately 4 cm in the two side-compartments. The bipolar electrode *i.e.* TiO_2 pellet and PANi/PVC-carboxy/AR-TiO_2 were placed in the centre compartment, exactly below the light beam created by the UV lamp. Ammonium chloride, dissolved in ethanol, was used to fill the feeder electrode compartments. $HAuCl_4$ (2mM) dissolved in D.I water containing 5% ethanol was used to fill the central chamber.[2] The feeder electrodes were separated by glass septums (2mm thickness and porosity G2) from the central chamber where the gold deposition takes place. An electric field and light with different intensities was applied to study their effect on the electrodeposition of gold (Figure S1). I-V curve measurements were carried out with the PANi/PVC-carboxy/AR-TiO_2 hybrid object in the presence and absence of light. The object was connected on the one side via the TiO_2 pellet and on the other side at the PANI/PVC section.

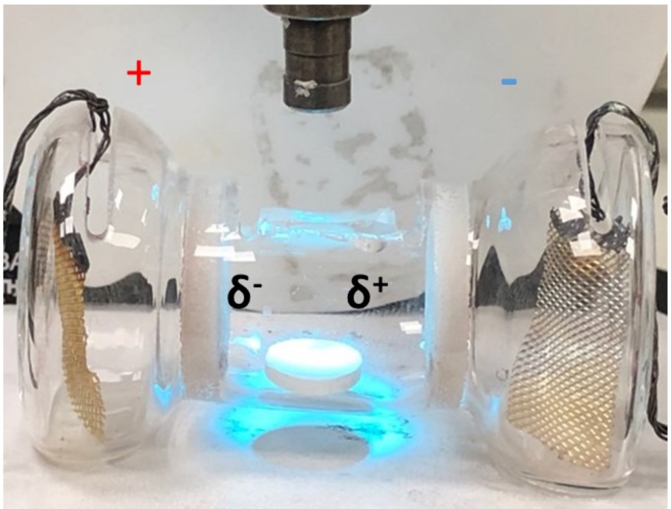

Figure S1: Bipolar electrochemistry set-up for the photoelectrodeposition of metal on TiO_2 pellets.

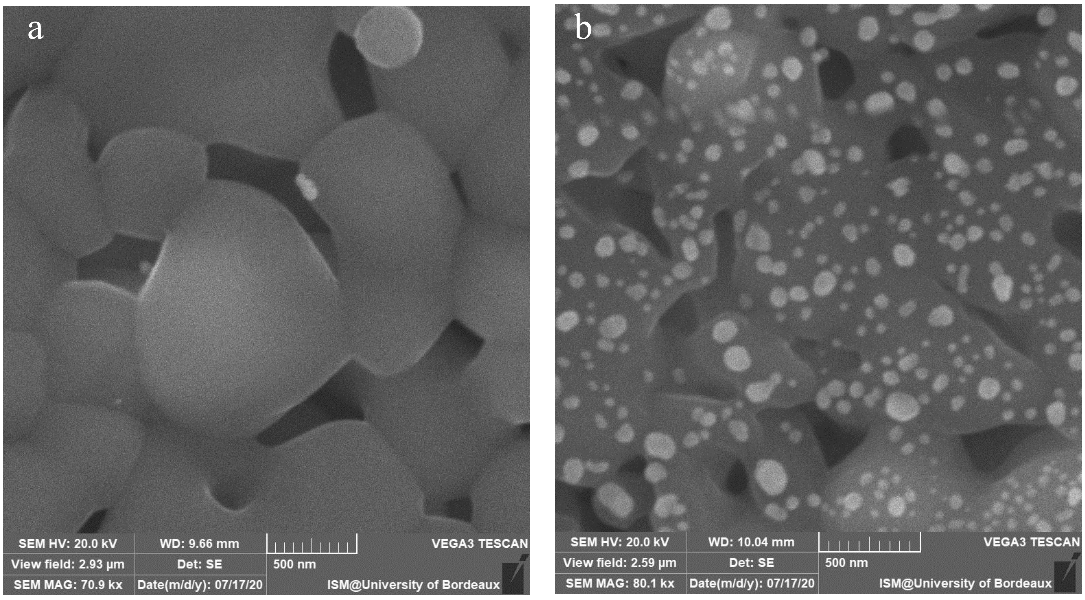

Figure S2: High resolution SEM images taken at the a) δ^- and b) δ^+ site of a TiO_2 pellet.

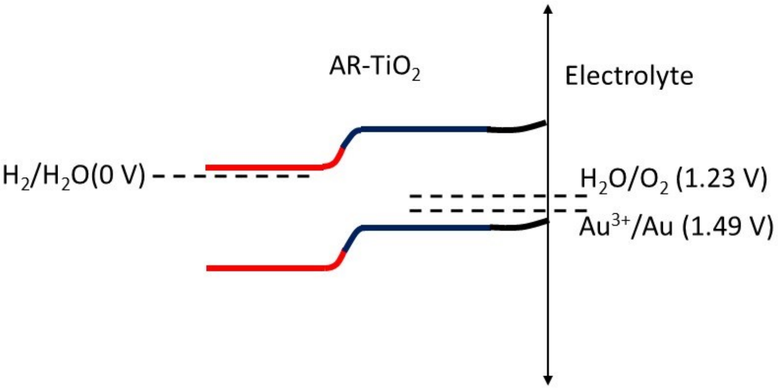

Figure S3: Energy level of TiO_2, water redox reaction and Au^{3+} reduction.

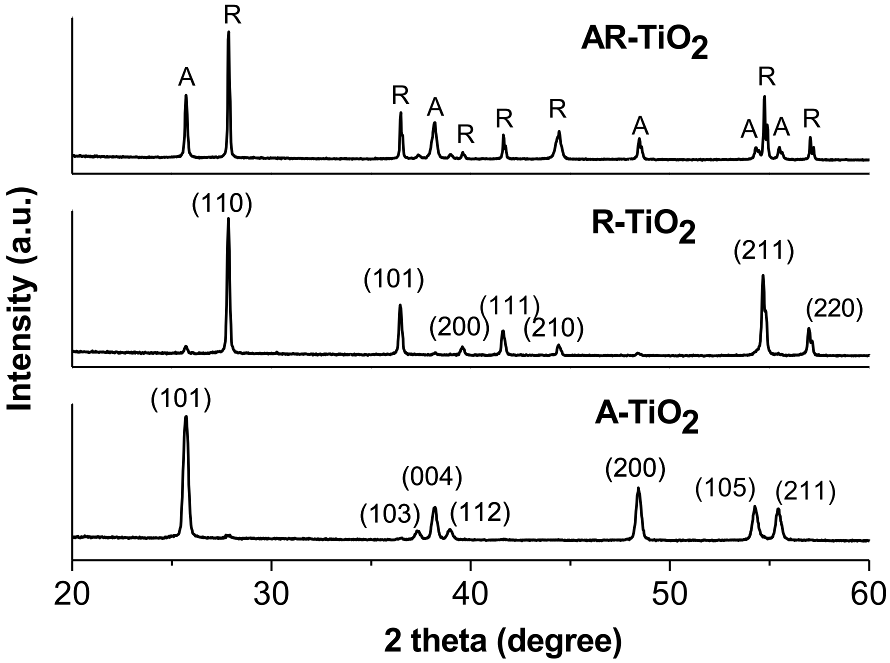

Figure S4: XRD of TiO_2 pellets with different crystallographic structures.

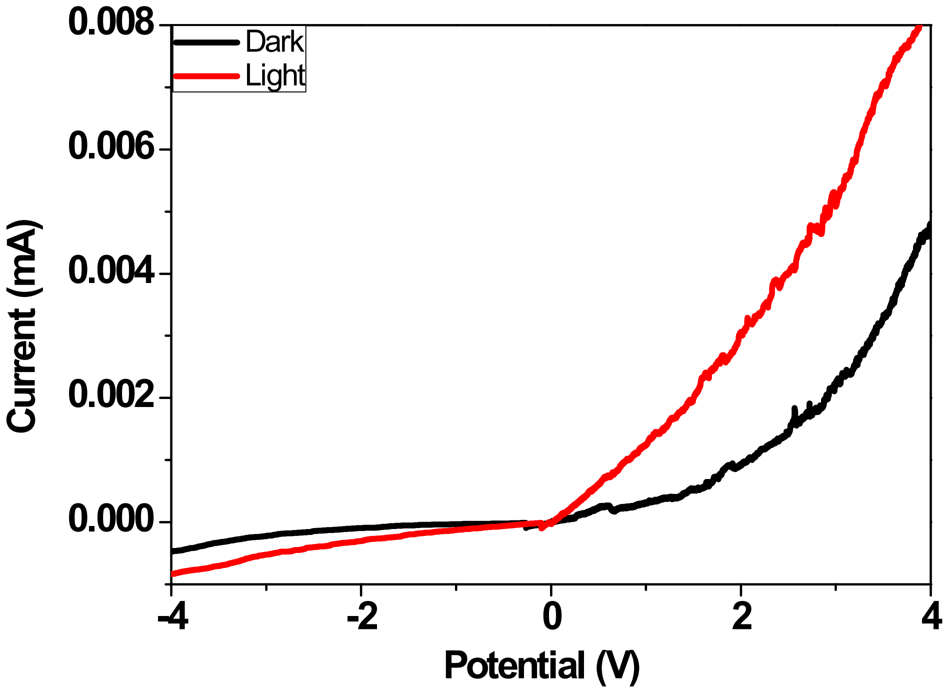

Figure S5: I-V curve of the PANi/PVC-carboxy-AR-TiO_2 hybrid system in the dark and under irradiation with UV light.

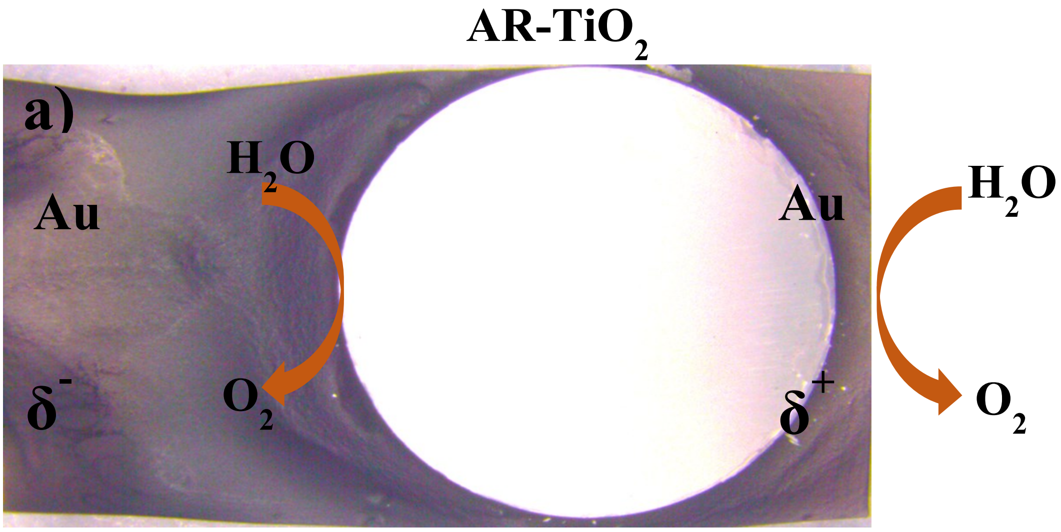

Figure S6: Schematic illustration of the spatial distribution of the different redox reactions involved in the bipolar photoelectrochemical process.

8. References

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2. S. Tiewcharoen, C. Warakulwit, V. Lapeyre, P. Garrigue, L. Fourier, C. Elissalde, S. Buffière, P. Legros, M. Gayot, J. Limtrakul, A. Kuhn, Angew. Chem. Int. Ed. 2017, 56, 11431-11435.