Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

A Hybrid Semiconductor Electrode for Wavelength-Controlled Switching of the Photocurrent Direction

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Electrode preparation and characterization

The ITO-glass substrate (Präzision Glas & Optik, Iserlohn, Germany, sheet resistance of ~ 10 Ω/sq.) was first cut into 2.5 × 1.5 cm pieces and then subsequently degreased by sonicating in acetone and boiling NaOH (0.1 M), rinsed with demineralized water, and blown dry in a nitrogen stream. A suspension of 50 mg TiO_2 powder (Hombikat UV 100, Sachtleben, Germany, anatase, specific surface area (BET) ~ 300 m^2/g, crystallite size < 10 nm)[S1] in 1 ml of ethanol was sonicated for 20 minutes and then deposited onto the ITO glass by doctor blading using a scotch tape as frame and spacer. The electrode was then dried at 100 °C, covered with aluminum foil and a glass plate, and pressed for 3 minutes at a pressure of 200 kg/cm^2 using an IR pressing tool (Paul Weber, Stuttgart, Germany) according to a procedure similar to that described in literature.[S2] Such a procedure yields a ca. 700 nm thick porous layer of TiO_2 having an excellent mechanical stability.

The TiO_2 layer was then modified with nitrogen by a heat treatment in the presence of urea pyrolysis products.[S3,4] The electrodes were placed into a 230 ml Schlenk tube connected via an adapter with a 100 ml round bottom flask containing 1 g of urea and heated in a muffle oven for 30 minutes at 500 °C. The resulting TiO_2-N contained 11.8 % nitrogen as determined by elemental analysis (Carlo Erba, CHNSO, E.A.1108).

A saturated solution of CuI (p.a., Merck, washed with THF and ether) in acetonitrile (p.a., Acros) was prepared for CuI deposition. The solution was kept at 4 °C before the deposition and then 20 µl of the solution were dropped onto the TiO_2-N layer and let dry in air.

The electrodes were characterized using a high-resolution field-emission scanning electron microscope (FE-SEM, Hitachi S4800) equipped with energy dispersive X-ray spectroscopy (EDX, EDAX/TSL Genesis 4000). The EDX analysis was performed on three different spots.

Bandgap determination

Bandgap energies of TiO_2-N and CuI were determined using the equation

$$\alpha = A\frac{(h\nu - E_g)^n}{h\nu}$$

where α is absorption coefficient, A is a constant, $h\nu$ is the energy of light, E_g is bandgap energy and n is a constant depending on the nature of the electron transition.[S5] We assumed indirect bandgap (n = 2) for TiO_2-N[S6] and direct bandgap (n = ½) for CuI.[S7,8] Assuming wavelength-independent scattering the absorption coefficient α is proportional to Kubelka-Munk function $F(R_\infty)$ that can be obtained from diffuse reflectance data[S9,10] as

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty}$$

where R_∞ is diffuse reflectance of the sample relative to the reflectance of a standard ($BaSO_4$).

Diffuse reflectance spectra were obtained using a Shimadzu UV-2401 UV/Vis recording spectrophotometer equipped with a diffuse reflectance accessory. The samples were pressed pellets of a mixture of 2 g of $BaSO_4$ with 50 mg of TiO_2-N or 150 mg of CuI, respectively. CuI was used as purchased and washed with THF and ether. TiO_2-N was obtained from TiO_2 (Hombikat UV 100) after modification under identical conditions as described above for the electrode.

The measurements afforded bandgap energy of 2.11 eV and 2.96 eV for TiO_2-N and CuI, respectively (Fig. S1).

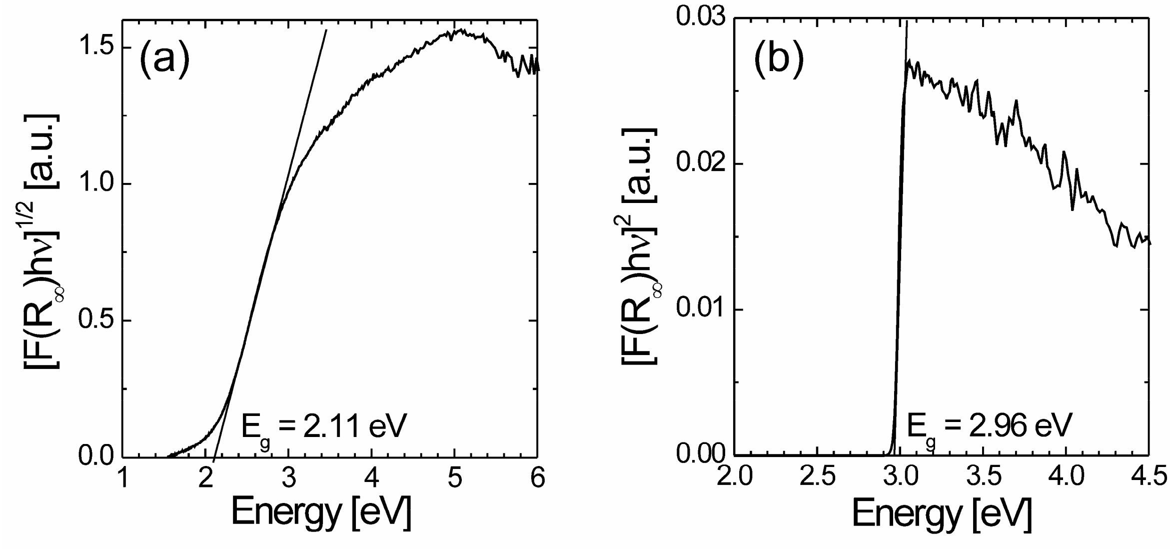

Figure S1: Bandgap determination for TiO_2-N (a) and CuI (b) using $[F(R_\infty)h\nu]^{1/n}$ vs. $h\nu$ plots assuming indirect optical bandgap of TiO_2-N (n = 2) and direct optical bandgap of CuI (n = 0.5).

Determination of band edges

For heavily doped n-type metal oxides like TiO_2, the lower conduction band edge, E_C, practically merges with the quasi-Fermi level of electrons, ${}^*E_{Fn}$, ($|E_C - {}^*E_{Fn}| < 0.1$ V).[S11-13] We determined the position of ${}^*E_{Fn}$ by the method of Roy.[S14,15] In short, we recorded the pH dependence of the potential of a Pt electrode immersed in an irradiated suspension of TiO_2-N in the presence of 4,5-dihydro-3a,5a-diaza-pyrene-dibromide, $(DP)Br_2$. The inflection point (pH_0) of the potential-pH curve (Fig. S2) determines the pH value at which ${}^*E_{Fn}$ coincides with the reduction potential of (DP)Br_2 (–0.27 V vs. NHE, pH-independent).[S16-19] Assuming Nernstian shift of band edges the position of the conduction band edge E_{CB} at pH 4.44 can be obtained using $pH_0 = 6.7$ from equation

$$E_{CB} \approx {}^*E_{Fn} = -0.27 + 0.059\,(pH_0 - 4.44) = -0.14 \text{ V vs. NHE}$$

Knowing the bandgap energy of TiO_2-N the position of the valence band edge E_{VB} of TiO_2-N can be calculated as $E_{VB} = (-0.14 + 2.11)$ V = 1.97 V vs. NHE.

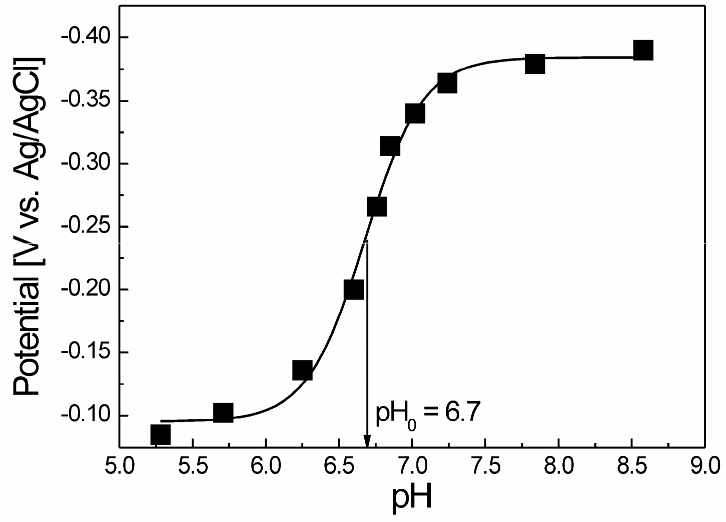

Figure S2: pH dependence of the potential of a Pt electrode immersed in an irradiated suspension of TiO_2-N in the presence of (DP)Br_2.

The literature value[S20] of the flatband potential was taken for the determination of the valence band edge of CuI. Assuming Nernstian behavior, E_{VB} = 0.99 V vs. NHE at pH 4.44. Knowing the bandgap energy of CuI the position of the conduction band edge E_{CB} can be calculated as E_{CB} = (0.99 – 2.96) V = –1.97 V vs. NHE.

Photocurrent measurements

Photocurrent experiments were performed with a tunable monochromatic light source provided with a 1000 W Xenon lamp (equipped with a water IR filter) and a universal grating monochromator Multimode 4 (AMKO, Tornesch, Germany) with a bandwidth of 10 nm. The electrochemical setup consisted of a BAS Epsilon Electrochemistry potentiostat (BAS, West Lafayette, USA) and a three-electrode cell using a platinum counter electrode and a Ag/AgCl (3 M KCl) as a reference electrode. During photoelectrochemical measurements the electrode was pressed against an O-ring of an electrochemical cell leaving a working area of 0.636 cm^2. When not denoted otherwise, the photocurrent experiments were carried out in $LiClO_4$ (0.1 M) containing Na_2EDTA (5 mM) and dissolved oxygen (under equilibrium with air). Prior to the measurements the solution was purged with air for 5 minutes. Nitrogen was passed through the solution for

15 minutes before the experiments in oxygen free electrolyte. The potential of the working electrode was kept constant at –0.025 V vs. Ag/AgCl (3 M KCl) = 0.18 V vs. NHE. Electrodes were irradiated by monochromatic light from the backside (through the ITO glass) with light and dark phases of 5 and 10 s, respectively. The incident photon-to-current efficiency (*IPCE*) was calculated according to equation

$$IPCE\,(\%) = \frac{i_{ph} hc}{\lambda P e} \times 100$$

where i_{ph} is the photocurrent density, h is Planck's constant, c velocity of light, P the light power density, λ is the irradiation wavelength, and e is the elementary charge. The spectral dependence of lamp power density was measured by the optical power meter Oriel 70260 (Oriel, Stratford, USA).

Photocurrent measurements on electrodes with single components

These electrodes exhibit no switching behavior. Their photocurrent response is anodic in case of TiO_2-N and cathodic in case of CuI, which is a typical result for n- and p-type materials, respectively.

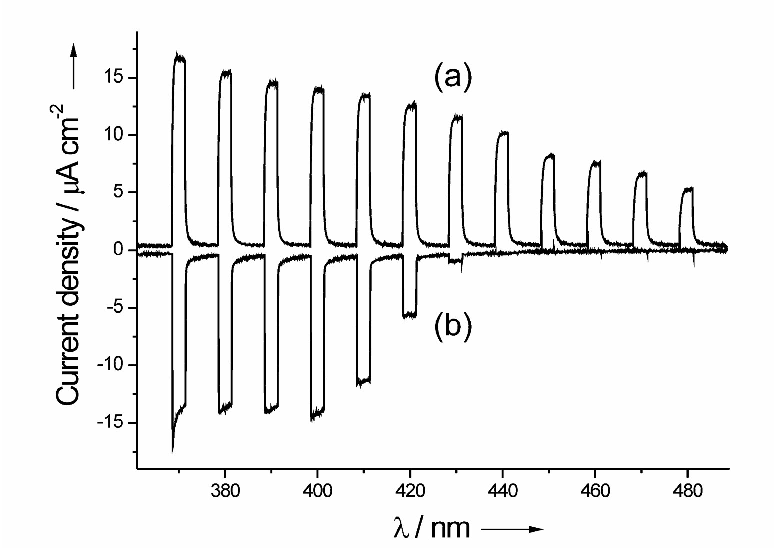

Figure S3: Photocurrent response of electrodes with only one component measured in $LiClO_4$ (0.1 M) containing Na_2EDTA (5mM) and dissolved oxygen (under equilibrium with air): (a) TiO_2-N; (b) CuI.

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