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

Radim Beranek and Horst Kisch*
Institute of Inorganic Chemistry, University of Erlangen-Nürnberg, Egerlandstr. 1, Erlangen D-91058, Germany.

Electrode preparation and characterization

The ITO-glass substrate (Präzision Glas & Optik, Iserlohn, Germany, sheet resistance of \( \sim 10 \Omega/\text{sq.} \)) 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) \( \sim 300 \text{ m}^2/\text{g} \), crystal 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 \( \alpha \) 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.\[^5\] We assumed indirect bandgap (\( n = 2 \)) for TiO\(_2\)-N\[^6\] and direct bandgap (\( n = \frac{1}{2} \)) for Cul.\[^7,8\] Assuming wavelength-independent scattering the absorption coefficient \( \alpha \) is proportional to Kubelka-Munk function \( F(R_\infty) \) that can be obtained from diffuse reflectance data\[^9,10\] as

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

where \( R_\infty \) 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 Cul, respectively. Cul 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 Cul, respectively (Fig. S1).

![Figure S1: Bandgap determination for TiO\(_2\)-N (a) and Cul (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 Cul (\( n = 0.5 \)).](image)

**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).\[^11-13\] We determined the position of \( ^*E_{Fn} \) by the method of Roy.\[^14,15\] 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 $E_{\text{Fn}}$ coincides with the reduction potential of (DP)Br$_2$ (–0.27 V vs. NHE, pH-independent).\cite{S16-19} Assuming Nernstian shift of band edges the position of the conduction band edge $E_{\text{CB}}$ at pH 4.44 can be obtained using $pH_0 = 6.7$ from equation

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

Knowing the bandgap energy of TiO$_2$-N the position of the valence band edge $E_{\text{VB}}$ of TiO$_2$-N can be calculated as $E_{\text{VB}} = (-0.14 + 2.11)$ 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$_2$.](image)

The literature value\cite{S20} of the flatband potential was taken for the determination of the valence band edge of CuI. Assuming Nernstian behavior, $E_{\text{VB}} = 0.99$ V vs. NHE at pH 4.44. Knowing the bandgap energy of CuI the position of the conduction band edge $E_{\text{CB}}$ can be calculated as $E_{\text{CB}} = (0.99 - 2.96)$ 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$_2$EDTA (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 $-0.025 \text{ V vs. Ag/AgCl (3 M KCl)} = 0.18 \text{ V vs. NHE}$. 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

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

where $i_{ph}$ is the photocurrent density, $h$ is Planck’s constant, $c$ velocity of light, $P$ the light power density, $\lambda$ 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](image)

Figure S3: Photocurrent response of electrodes with only one component measured in LiClO$_4$ (0.1 M) containing Na$_2$EDTA (5mM) and dissolved oxygen (under equilibrium with air): (a) TiO$_2$-N; (b) CuI.
References

[S1] Manufacturer information.


