Photoelectrochemistry

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

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The development of molecular and nanoscale assemblies that are capable of performing logic-gate functions has attracted significant interest aimed at novel approaches to information storage and processing.[1] Among other strategies, research has focused on novel types of photoelectrochemical devices, as their output can be controlled by selective stimulation with light; photons are considered the most efficient agent for driving the communication between chemical logic gates.[2] Of particular interest are photoelectrodes that exhibit wavelength-dependent switching of the photocurrent direction, as these could be exploited for information processing controlled simply by photons of different energy.[3,4] Observations of wavelength-dependent changes in photocurrent direction have been reported for several different systems, such as metal–chlorophyll–metal sandwich cells,[5] gold electrodes covered with helical peptides containing various chromophores,[6] polymer multilayers,[3] and a ruthenium complex linked to viologen and a palladium phthalocyanine derivative.[7] Bilayers or core–shell composites of organic polymers and TiO_2,[8] as well as TiO_2 modified with Fe^{II} complexes[4,9] or with a ruthenium cluster dye also show these effects.[10]

Herein we report the fabrication and characterization of a novel photoelectrode that exhibits unusually sharp wavelength-controlled switching of photocurrent direction. The electrode is a hybrid assembly of two inorganic nanocrystalline semiconductors—nitrogen-modified TiO_2 (TiO_2-N, an n-type semiconductor) and CuI (p-type)—deposited on conducting indium–tin oxide (ITO) glass. Figure 1 shows a cross-sectional view of the electrode with CuI nanocrystals randomly distributed in the interpore space of a densely packed pressed layer of nanocrystalline TiO_2-N. The atomic ratio of Ti/Cu as measured by energy-dispersive X-ray analysis was 2.0 ± 0.1.

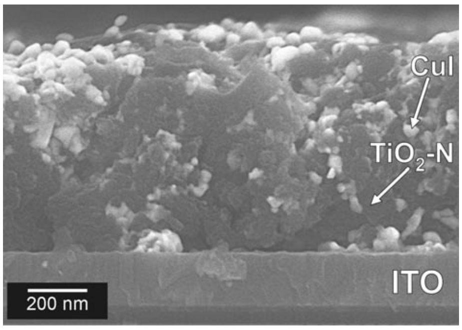

Figure 1. Scanning electron micrograph of a cross section of a 700-nm-thick layer of TiO_2-N (dark) interpenetrated with CuI crystallites (light) deposited on an ITO-glass substrate.

Figure 2a shows photocurrent transients for different wavelengths under intermittent irradiation recorded at 0.18 V vs. NHE. Whereas cathodic photocurrents are observed at wavelengths up to 410 nm, the direction of the photocurrent changes sharply to anodic above 420 nm. The incident-photon-to-current efficiencies (IPCE) exhibit cathodic and anodic maxima at 400 nm and 430 nm, respectively (Figure 2a, inset). The switching behavior was observed in the potential range from 0 to 0.25 V vs. NHE and the four-cycle repetition experiment (Figure 2b) reveals excellent stability of the photocurrent response.

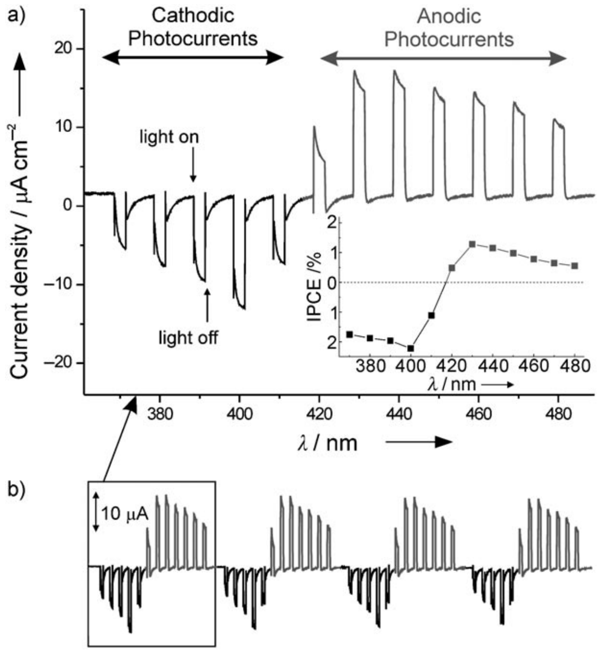

Figure 2. a) Photocurrent response measured under intermittent irradiation as a function of irradiation wavelength (without correction for the change of light intensity) at 0.18 V vs. NHE; the inset shows the corresponding IPCE values. b) A four-cycle repetition experiment.

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Supporting information for this article (details of electrode preparation, determination of band-gap energies and band edges, and photocurrent measurements) is available on the WWW under http://www.angewandte.org or from the author.

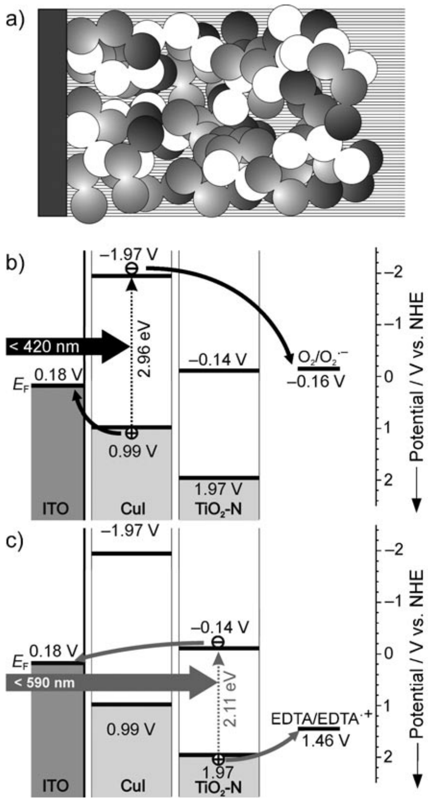

Figure 3. a) Schematic view of the electrode structure consisting of a porous network of TiO_2-N (gray) and CuI (white) deposited on ITO and permeated by electrolyte (dashed). b,c) Simplified potential diagram illustrating the mechanism of cathodic (b) and anodic (c) photocurrent generation in $LiClO_4$ (0.1 M) containing EDTA and dissolved oxygen at pH 4.44. E_F = Fermi level.

The mechanism of the switching behavior can be rationalized as depicted in Figure 3. Two points are worth mentioning. First, in contrast to compact semiconductor electrodes, the photogenerated charge separation in electrodes consisting of porous networks of particles permeated by electrolyte (Figure 3a) is not controlled by the potential gradient over the space-charge region since the crystallite size is too small for formation of a space-charge layer.[11] Instead, the photocurrent is determined by the efficiency of photogenerated electron/hole transfer at the semiconductor/electrolyte and semiconductor/ITO interface.[12] Second, the photocurrent response of a hybrid assembly of two different semiconductors will, at each wavelength, depend heavily on the difference in optical absorption of the two materials.

The optical absorption coefficients for UV light of CuI and TiO_2 are in the order of $10^6\,cm^{-1}$ and $10^5\,cm^{-1}$, respectively.[13] Accordingly, under UV irradiation CuI can be preferentially excited. Because CuI is a p-type semiconductor (higher mobility of holes than of electrons) the photogenerated holes can be transferred to the ITO layer, whereas electrons are driven to the surface of CuI and reduce the oxygen dissolved in the electrolyte to produce cathodic photocurrents (Figure 3b). As the optical band gap of CuI is 2.96 eV (corresponding to a wavelength of 419 nm), the cathodic photocurrents disappear at wavelengths above 420 nm, and, as expected, the photocurrent is dominated by TiO_2-N, which has a band gap of 2.11 eV (ca. 588 nm) and can therefore absorb visible light. Because TiO_2-N is an n-type semiconductor (higher mobility of electrons), the photogenerated electrons are transferred to the ITO layer and holes oxidize ethylenediaminetetraacetic acid (EDTA) at the TiO_2-N/electrolyte interface to produce anodic photocurrents (Figure 3c). Experiments performed under the same conditions on electrodes with single components show no switching behavior. These electrodes exhibit only anodic or only cathodic photocurrents in case of TiO_2-N and CuI, respectively, as is typically expected for n- and p-type materials, respectively (see Figure S3 in the Supporting Information).

Figure 4 clearly shows that the presence of oxygen and EDTA is necessary for the generation of cathodic and anodic photocurrents, respectively. In the absence of oxygen (Figure 4a) no cathodic photocurrents are observed under UV light since the photogenerated electrons are not scavenged by oxygen but recombine with holes. Moreover, the fact that also anodic photocurrents are negligible up to 410 nm suggests that light with shorter wavelengths is effectively "filtered out" by CuI, so that TiO_2-N absorbs only small portion of the incident UV light. In the absence of EDTA (Figure 4b) no anodic photocurrents are observable, because, although EDTA ($E = 1.46$ V)[14] acts as an excellent electron donor for holes in TiO_2-N, water ($E > 2.0$ V) is not oxidized.[15,16]

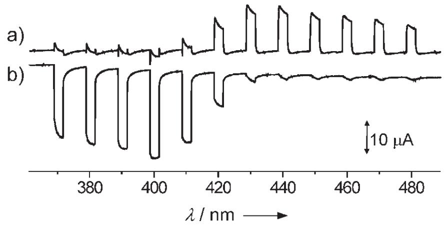

Figure 4. Photocurrent response measured under intermittent irradiation in $LiClO_4$ (0.1 M) a) in the presence of EDTA without oxygen and b) in the presence of oxygen without EDTA.

In conclusion, we have shown that a wavelength-controlled optoelectronic switch can be produced by assembling two simple semiconductor nanocrystalline materials on ITO. The switching behavior is based on the interplay of electrical (n-/p-type), optical (band gap), and photoelectrochemical (band edge positions) properties of TiO_2-N and CuI. Therefore, we believe that the present approach opens up a route to fabrication of further novel photoelectrochemical switches with desired features by simply combining materials with optimized optical and photoredox properties.

Experimental Section

The electrode was prepared by pressing an approximately 700-nm-thick porous layer of a commercial TiO_2 powder (Hombikat UV, crystallite size < 10 nm) onto ITO-glass and then heating the TiO_2 layer at 500 °C in the presence of urea pyrolysis products[15] to afford nitrogen-modified TiO_2-N. Subsequently, CuI was deposited into the porous matrix of TiO_2-N from a saturated solution in acetonitrile, and the electrode was dried in air.

The photocurrent measurements were performed in a conventional three-electrode setup with a Ag/AgCl (3 M) reference electrode[17] and a Pt counter electrode. Unless denoted otherwise, the electrolyte (pH 4.44) was $LiClO_4$ (0.1 M) containing Na_2EDTA (5 mM) and dissolved oxygen from air. Electrodes were irradiated with monochromatic light from the back side (through the ITO glass).

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[16] In our system the generation and separation of electron–hole pairs could occur also at the CuI/TiO_2-N interface (p/n junction) with the sign of the photocurrent depending on which material is in contact with the ITO layer (cathodic for CuI and anodic for TiO_2-N). However, as our electrode consists of a porous network of particles permeated by electrolyte, the dominant photocurrent generation should be expected at the CuI/electrolyte and TiO_2-N/electrolyte interfaces. Note also that the potential of the valence band edge of CuI (0.99 V) is not positive enough to induce oxidation of EDTA (1.46 V) by holes, nor is the conduction band edge of TiO_2-N (−0.14 V) negative enough for efficient oxygen reduction (−0.16 V), which is also unfavorable for the photocurrent generation by p/n junction mechanism in our system.

[17] All potential data in this paper are rescaled relative to the normal hydrogen electrode (NHE).