

Photoelectrochemistry with Surface-Modified TiO₂

Radim Beránek

Department of Chemistry & Pharmacy, University of Erlangen-Nürnberg, Egerlandstr. 1, Erlangen D-91058, Germany

E-mail: Radim.Beranek@chemie.uni-erlangen.de

Semiconductors enable efficient light-induced generation and separation of charges which can subsequently undergo redox reactions with substrates or induce a photocurrent.^[1,2] This opens up a route to various applications in photocatalysis, photovoltaics, sensor technology, biomedicine and optoelectronics. Obviously, in order to achieve optimal performance, semiconductors with well-tailored optical and photoelectrochemical properties are required in most applications. The development of methods allowing control of these semiconductor properties attracts therefore significant interest.

One of the most promising semiconductors for photoelectrochemical applications is titanium dioxide, particularly due to its low cost, non-toxicity, and stability against photocorrosion. However, because of its wide bandgap (for anatase 3.2 eV; ~ 390 nm) the utilization of TiO₂ typically remains confined to UV light, a tiny fraction (2-3 %) of solar radiation reaching the earth's surface. Shifting the threshold of its photoresponse into the visible would therefore enhance its potential for chemical solar energy conversion and open possibilities for further applications. Attempts to achieve this have typically focused on two different strategies: 1) bulk doping, or 2) surface modification of titania. In the former, transition metals or main group elements like carbon, nitrogen and sulfur are introduced into the lattice of titania resulting in formation of intra-bandgap donor and acceptor levels. The latter approach, surface modification, is either carried out by attaching visible light absorbing chromophores like organic dyes, transition metal complexes or quantum dots to the surface of TiO₂, or by the formation of a chromophoric surface layer through interaction between surface-bound chromogenic species and electronic states in TiO₂.^[3]

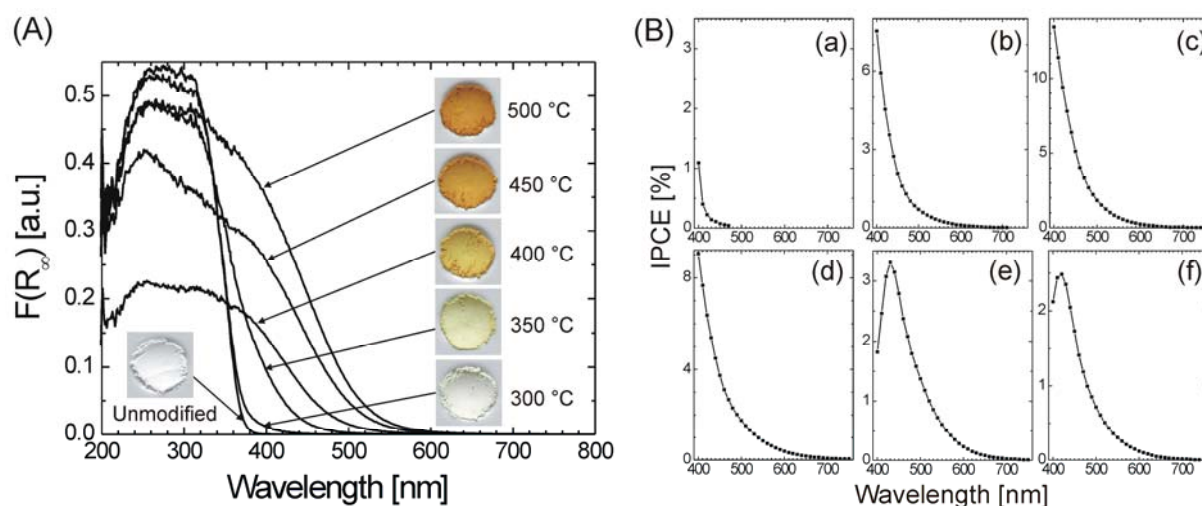


Figure 1: (A) Colors and corresponding plots of Kubelka-Munk function vs. wavelength of powders modified at different temperatures. (B) IPCE spectra in the visible recorded in LiClO₄ (0.1 M) + KI (0.1 M) electrolyte at 0.5 V vs. Ag/AgCl for ITO electrodes with pressed layers of unmodified TiO₂ (a) and TiO₂-N modified at 300 °C (b), 350 °C (c), 400 °C (d), 450 °C (e), and 500 °C (f).

Searching for a low-cost alternative, we have recently reported a novel type of surface-modified TiO₂ materials prepared by simply heating TiO₂ in a gaseous atmosphere of urea

pyrolysis products at temperatures of 300–500 °C.^[4,5] The surface of such materials was found to be modified with species containing nitrogen and carbon (atomic ratio of N/C ~ 1.9 ± 0.3).^[5] Very recently, Mitoraj et al. have identified these species as surface-bound amino-tri-*s*-triazine derivatives formed in-situ from urea pyrolysis products (isocyanic acid and cyanamide) during the heat treatment by the catalytic action of titania's surface OH-groups.^[6] Depending on the modification temperature the color of such surface-modified materials ranged from yellowish to orange and the threshold of both their visible light absorption and photocurrent response shifted down to ~ 750 nm with maximum efficiency observed for materials modified at 400 °C (see Fig. 1).^[4,5] Initial experiments using very thin (~ 75 nm) surface-modified compact anodic TiO₂ films resulted in very low incident photon-to-current efficiencies (IPCE ~ 0.56 % at 450 nm), mainly due to the poor visible light absorption in the thin surface layer.^[4] A significant improvement (IPCE ~ 3.7 % at 450 nm) was achieved when high surface area nanocrystalline TiO₂ was employed in the form of ~ 2.5 μm thick layers pressed onto ITO-glass.^[5] Further improvement was achieved when using TiO₂ nanotubes with the length of 6 – 9 μm as a substrate (IPCE ~ 4.5 % and 1.4 % at 450 nm and 550 nm, respectively).^[7]

Importantly, the reacting holes were found to be not positive enough to induce efficient one-electron oxidation of water ($E \sim 2.0$ V vs. NHE at pH = 7 for one-electron process). Therefore we have typically observed enhanced recombination in aqueous electrolytes unless a more readily oxidizable reducing agent (such as iodide, $E = 1.3$ V vs. NHE) was present.

Furthermore, the surface-modified materials can be employed for fabrication of photoelectrodes exhibiting wavelength-controlled switching of photocurrent direction.^[8] The electrode is a hybrid assembly of two simple inorganic semiconductors – TiO₂-N modified at 500 °C (n-type semiconductor) and CuI (p-type) – deposited on an ITO-glass. Under optimized conditions an unusually sharp change in photocurrent direction occurs in the range of 410 – 420 nm. The switching mechanism is based on well-fitting electrical (n-/p-type), optical (bandgap) and photoelectrochemical (band edge positions) properties of TiO₂-N and CuI. This approach opens up a route to fabrication of further optoelectronic switches of desired features by simply combining materials with optimized optical and photoredox properties.^[9]

In summary, surface-modification of TiO₂ materials is found to be a powerful tool for influencing its fundamental optical and photoelectrochemical properties. The photoelectrodes based on surface-modified TiO₂ exhibit visible light photocurrent response and can be utilized for fabrication of novel devices (e.g., optoelectronic switches). In general, we believe that the photoconversion efficiency of surface-modified TiO₂ photoelectrodes might be further enhanced by tuning the photoelectrode morphology, using alternative surface-modification procedures, or coupling with co-catalysts for water oxidation.^[10,11]

References

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