

# From Photocatalysis to Optoelectronic Switches: Studies of Visible Light Active Photoelectrodes Based on Surface-Modified Titanium Dioxide

by

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## Summary

Semiconductor materials play a key role in the rapid development of electronic and information processing technologies already since several decades. More recently, it has been recognized that the utilization of semiconductors represents a major challenge also for photochemistry. In this context, it is of fundamental importance that semiconductors enable efficient light-induced generation and separation of charges which can subsequently undergo redox reactions with substrates or induce a photocurrent. 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.

Whereas titanium dioxide seems to be one of the most promising semiconductors for many photoelectrochemical applications due to its low cost, chemical stability and non-toxicity, its utilization remains typically confined to UV light because of its wide bandgap (for anatase  $\sim 3.2$  eV; this corresponds to a wavelength of  $\sim 390$  nm). Shifting the threshold of its photoresponse into the visible would 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  $\text{TiO}_2$ , or by the formation of a chromophoric surface layer through interaction between surface-bound chromogenic species and electronic states in  $\text{TiO}_2$ . Particularly, the doping/modification of  $\text{TiO}_2$  with nitrogen has been found very promising since calculations suggested that this might narrow its bandgap and thereby promote also visible light photoactivity. In recent years various different preparation methods leading to different N-doped titania materials have been reported in the literature. Typically, their optical and photocatalytic properties were reported, whereas the photoelectrochemical properties have been studied relatively rarely, although these are of essential importance in understanding and controlling the photoactivity of semiconductors.

The present dissertation is a study of a novel type of N-modified  $\text{TiO}_2$  materials –  $\text{TiO}_2$  materials surface-modified with nitrogen containing species. The aim of this thesis was the

synthesis and experimental characterization of these materials with a focus on photoelectrochemical properties. The following key questions were addressed:

- What is the morphology, composition, optical, electronic, photocatalytic and photoelectrochemical properties of these modified materials and how do these relate to each other?
- How can the fundamental properties of the modified materials be tuned by varying the starting materials and/or preparation conditions, particularly in view of enhancing the visible light activity?
- How can these visible-light active materials be utilized in novel applications?

The content of this dissertation can be summarized as follows.

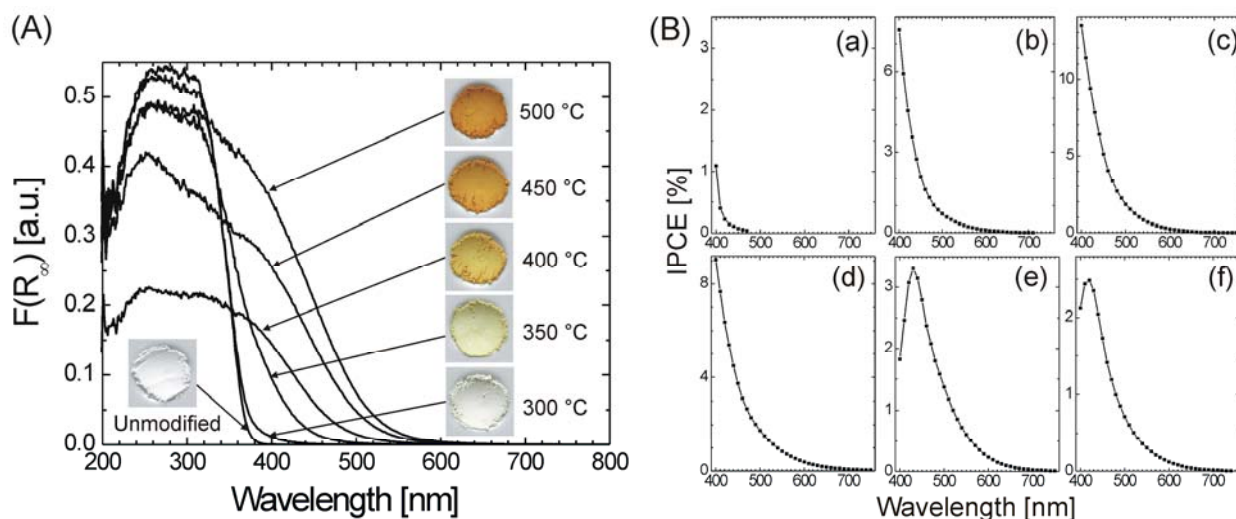
**Chapter 2** is of introductory character and brings basics of semiconductor physics and photoelectrochemistry, together with an overview of the literature on N-doped TiO<sub>2</sub> materials.

**Chapter 3** reports on the wavelength resolved surface photovoltage (SPV) and photocurrent investigations of novel N-modified TiO<sub>2</sub> photocatalysts recently developed in our group which were active in photocatalytic degradation of water pollutants under visible-light irradiation. The measurements in the presence of various reducing agents were conducted to obtain experimental evidence for the electronic structure of the valence band region in N-modified anatase powders containing different amounts of nitrogen. In the presence of air and absence of a hole scavenger only a very weak SPV signal was observable already in the visible region which completely vanished in the UV above 3.40 eV suggesting complete charge recombination. Whereas in the presence of formic acid only upon UV excitation the signal was increased, this occurred already upon visible-light irradiation when iodide was the hole scavenger. Similarly, in the photocurrent measurements visible light irradiation induced an enhancement only in the presence of iodide or hydroquinone, whereas water, thiocyanate and formate were not oxidized efficiently since their redox potential is more positive than that of holes trapped in the region of the upper valence band edge. These findings were rationalized by assuming a strong electronic coupling of N2p states with titania O2p levels that generates a novel valence band with a red-shifted band edge. It is therefore expected that holes produced in this band will efficiently relax to the band edge followed by recombination with conduction band electrons. Depending on the reduction potential of the hole scavenger, interfacial electron transfer may successfully compete with this process. The results obtained in this study also shed some light on the mechanism of visible light photocatalytic degradation of formic acid and suggest that OH radicals formed in the reductive photocatalytic pathway play a significant role in it.

In **Chapter 4** a novel modification method for surface-modification of TiO<sub>2</sub> with nitrogen species is introduced which consists in heating TiO<sub>2</sub> in the presence of gas phase urea pyrolysis products. This procedure is used for modification of ~ 75 nm thin compact TiO<sub>2</sub> films prepared by anodic oxidation of titanium sheets. The surface-modified films exhibited a significant photocurrent response upon visible light irradiation down to 700 nm, inducing an incident photon to current efficiency (*IPCE*) of 1.5 % at 400 nm. The conduction band edge as determined from flatband potential measurements was anodically shifted by 0.2 V as compared to the unmodified film. The analysis of photocurrent transients revealed that the deep intra-bandgap states above the valence band edge responsible for visible light activity induce enhanced recombination which can be partially restricted in the presence of iodide.

In **Chapter 5** the same modification method is employed for surface-modification of high surface area nanocrystalline TiO<sub>2</sub> (Hombikat UV-100). Surface-modification of TiO<sub>2</sub> at different temperatures between 300 °C and 500 °C is found to be a powerful tool for manipulating the fundamental optical and photoelectrochemical properties of TiO<sub>2</sub>. The experimental results revealed that the modification occurs through incorporation of nitrogen species containing also carbon into

the surface structure of titania. With increasing modification temperature the absorption edge shifts significantly to the visible range (see Fig. 1A).



**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  $\text{LiClO}_4$  (0.1 M) +  $\text{KI}$  (0.1 M) electrolyte at 0.5 V vs.  $\text{Ag}/\text{AgCl}$  for unmodified  $\text{TiO}_2$  (a) and  $\text{TiO}_2$ -N modified at 300 °C (b), 350 °C (c), 400 °C (d), 450 °C (e), and 500 °C (f).

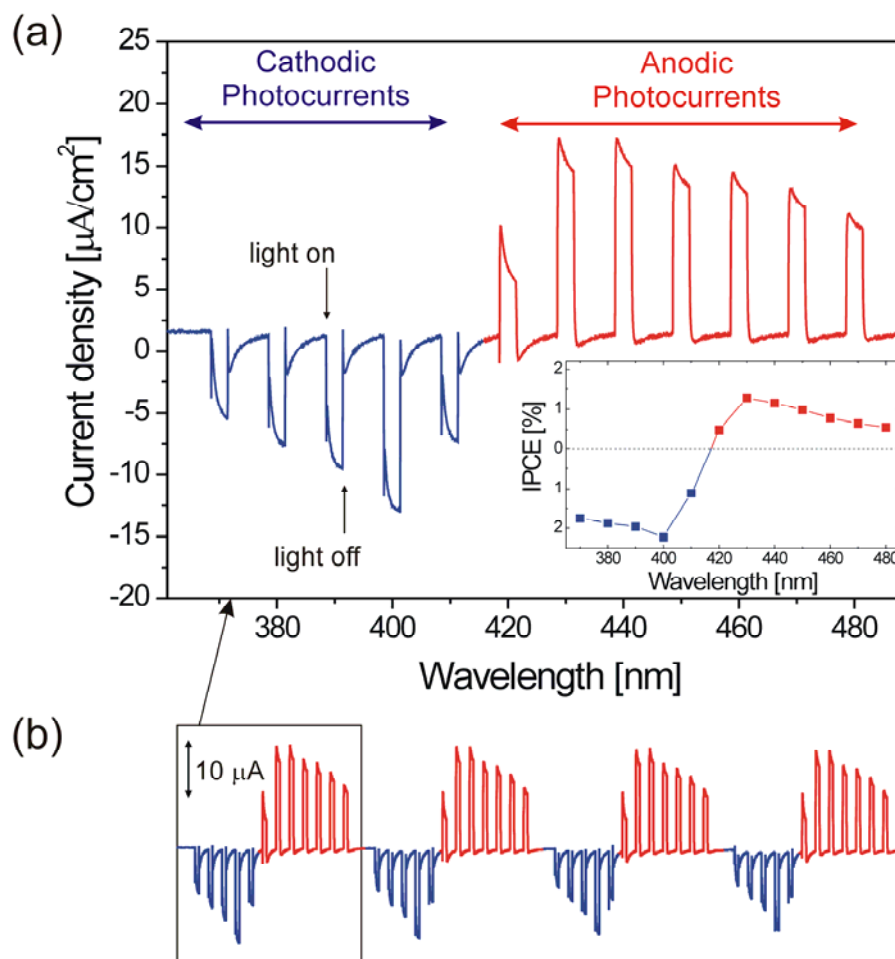
The optical bandgap of surface-modified  $\text{TiO}_2$  continuously decreases down to  $\sim 2.1$  eV and the quasi-Fermi level of electrons at pH = 7 is gradually shifted from  $-0.6$  V to  $-0.3$  V vs. NHE. The  $\text{N}1s$  XPS binding energies are 399-400 eV and decrease with increasing modification temperature whereby the  $\text{Ti}2p_{3/2}$  peak is also shifted to lower binding energies by about 0.5 eV. The surface-modified materials show enhanced sub-bandgap absorption and exhibit photocurrents in the visible down to 750 nm when deposited on the conductive glass in form of pressed opaque layers. The maximum *IPCE* values were observed for the materials modified at 350 °C and 400 °C (*IPCE*  $\sim 14$  % at 400 nm, and *IPCE*  $\sim 1$  % at 550 nm, respectively). The efficiency of photocurrent generation was found to be limited by surface recombination, which leads to a significant decrease in *IPCE* values and changes significantly the shape of the *IPCE* spectra in dependence on the optical bandgap (see Fig. 1B).

In **Chapter 6** transparent nanocrystalline titania films were modified by the same method at different temperatures between 300 °C and 500 °C and investigated by optical, spectroelectrochemical and photoelectrochemical methods. The modification lead again to narrowing of the optical bandgap but the shift was not so pronounced as for corresponding samples obtained with another starting material in Chapter 5. This seems to corroborate the suggestion made in Chapter 5 that the properties of the starting material play an essential role in the surface modification process. The modified films exhibited again an anodic shift of the conduction band edge as evidenced by spectroelectrochemical measurements. When compared to opaque nanocrystalline electrodes of Chapter 5, although the efficiency of photocurrent generation in transparent electrodes is comparable in UV, it shows significantly lower efficiencies in the visible. This can be explained by larger bandgap values of the transparent samples.

**Chapter 7** brings a short comparative discussion of the results obtained in Chapters 3, 4, 5, and 6.

Finally, in **Chapter 8** the materials investigated in Chapter 5 are employed for fabrication of a photoelectrode exhibiting wavelength-controlled switching of photocurrent direction. The electrode is a hybrid assembly of two simple inorganic semiconductors –  $\text{TiO}_2$ -N modified at 500 °C (n-type semiconductor) and  $\text{CuI}$  (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 (see Fig. 2).

The switching mechanism is discussed and found to be based on well-fitting electrical (n-/p-type), optical (bandgap) and photoelectrochemical (band edge positions) properties of  $\text{TiO}_2\text{-N}$  and  $\text{CuI}$ . It is likely that the present approach opens up a route to fabrication of further photoelectrochemical switches of desired features by simply combining materials with optimized optical and photoredox properties.



**Figure 2:** (a) Photocurrent response of a  $\text{TiO}_2\text{-N}/\text{CuI}$  photoelectrochemical switch measured under intermittent irradiation (5 s light, 10 s dark) as a function of irradiation wavelength (without correction for the change of light intensity) at 0.18 V vs. NHE; the inset shows corresponding IPCE values. (b) A four-cycle repetition experiment.

**In summary**, this thesis presents investigations of novel visible light active  $\text{TiO}_2$  materials surface-modified with nitrogen species. Its focus is on photoelectrochemical characterization of these materials. It was found that the modification procedure can be used for influencing the fundamental optical and photoelectrochemical properties of the materials in a systematic manner. In general, the modification leads to a significant shift of both the absorption edge and the photocurrent response into the visible. At the same time an anodic shift of the conduction band edge was observed for all modified materials, which has been in this thesis confirmed by three different methods. In view of improvements of the photoactivity, it is important that the findings of this thesis indicate that the structural and surface properties of the starting material play a crucial role in the modification process and that the efficiency of photocurrent response is also highly dependent on the redox properties of the electrolyte. Moreover, it has been shown that the photoelectrodes based on surface-modified  $\text{TiO}_2$  can be utilized for fabrication of optoelectronic switches that exhibit an unusually sharp wavelength-controlled switching of the photocurrent direction. All these and other aspects surely offer plenty of room for future research leading to further developments and novel applications.