Photoelectrochemical Studies of Visible Light Active Surface-Modified TiO_2

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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.

This paper presents our studies[3-6] of a novel type of visible light active TiO_2 materials – TiO_2 surface-modified with nitrogen species. It is shown that both films and powders can be easily modified by a heat treatment in the presence of urea pyrolysis products. The surface modification consists in incorporation of nitrogen species containing carbon (atomic ratio N/C ~ 2) into the surface of TiO_2 and can be used for tuning its fundamental optical and photoelectrochemical properties – the optical absorption edge and the energy position of the band edges – in a systematic manner.

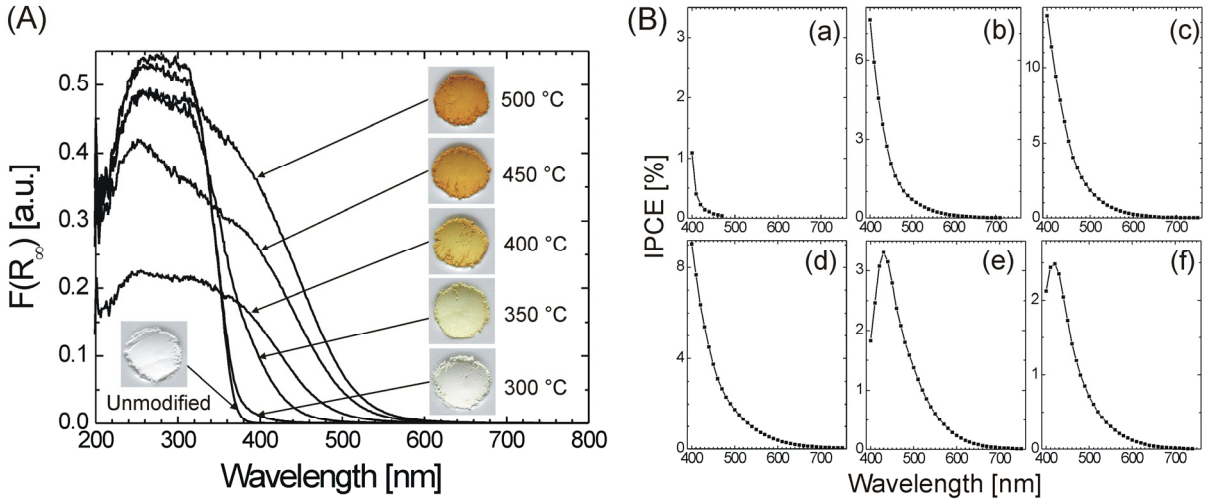

Figure 1: (A) Colors and corresponding plots of Kubelka-Munk function vs. wavelength of powders modified at different temperatures. (B) *IPCE* spectra in the visible recorded in $LiClO_4$ (0.1 M) + KI (0.1 M) electrolyte at 0.5 V vs. Ag/AgCl for ITO electrodes with pressed layers of unmodified TiO_2 (a) and TiO_2-N modified at 300 °C (b), 350 °C (c), 400 °C (d), 450 °C (e), and 500 °C (f).

In general, the modification leads to a significant red shift of the optical absorption edge (Fig. 1A). At the same time an anodic shift of the quasi-Fermi level of electrons was observed for all modified materials. The electrodes based on the surface-modified TiO_2 materials exhibited a significant photocurrent response upon visible light irradiation down to 700 nm (Fig. 1B). The efficiency of photocurrent response is also highly dependent on the redox properties of the electrolyte since the photogenerated holes are trapped in deep intra-bandgap surface states before they react with the reducing agent in the electrolyte. In aqueous electrolytes this leads to enhanced recombination unless more easily oxidizable species like iodide are present.

Furthermore, the surface-materials can be employed for fabrication of photoelectrodes exhibiting wavelength-controlled switching of photocurrent direction. The electrode is a hybrid

assembly of two simple inorganic semiconductors – TiO_2-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 (see Fig. 2). The switching mechanism is based on well-fitting electrical (n-/p-type), optical (bandgap) and photoelectrochemical (band edge positions) properties of TiO_2-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.[7]

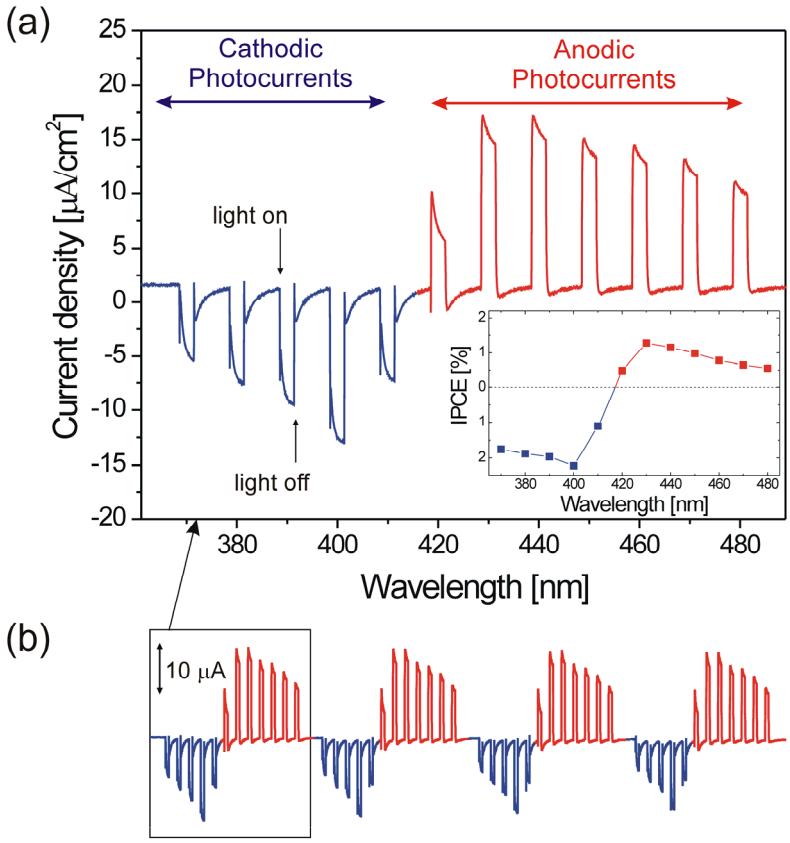

Figure 2: (a) Photocurrent response of a TiO_2-N/CuI photoelectrochemical switch measured under intermittent irradiation (5 s light, 10 s dark) as a function of irradiation wavelength (without correction for the change of light intensity) at 0.18 V vs. NHE; the inset shows corresponding IPCE values. (b) A four-cycle repetition experiment. Electrolyte: $LiClO_4$ (0.1 M) containing Na_2EDTA (5mM) and dissolved oxygen (under equilibrium with air).

In summary, surface-modification of TiO_2 materials is found to be a powerful tool for influencing its fundamental optical and photoelectrochemical properties. The photoelectrodes based on surface-modified TiO_2 exhibit visible light photocurrent response and can be utilized for fabrication of novel devices (*e.g.*, optoelectronic switches).

References

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