

Artificial photosynthesis of fuels and other useful materials – two examples

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The development of photochemical systems capable of mimicking the natural photosynthesis by driving useful chemical transformations has attracted significant interest motivated by the need to meet various environmental concerns and to secure the future supply of clean and sustainable energy.^[1] The talk will focus on two different examples of artificial photosynthetic systems we have been investigating recently: (i) hybrid photoanodes for solar-driven water splitting,^[2] and (ii) visible-light induced synthesis of photocatalysts with enhanced performance in degradation of water pollutants.^[3]

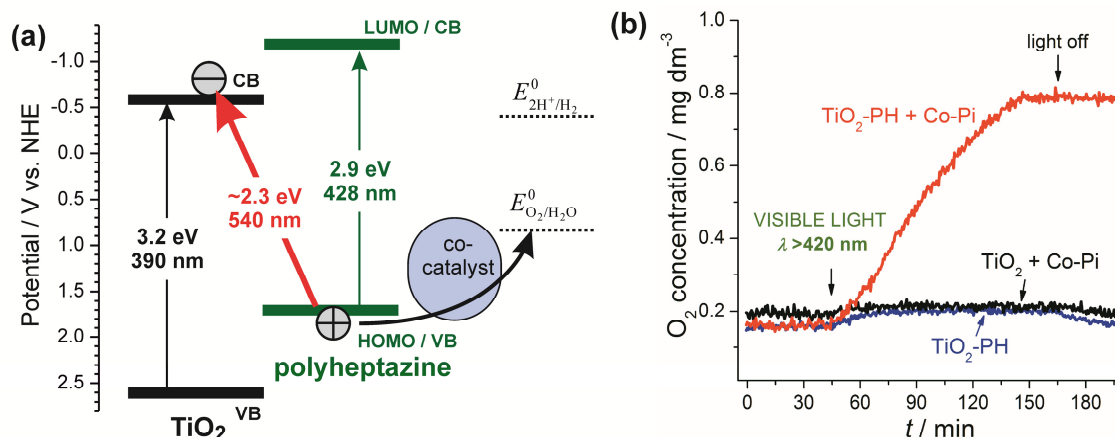


Figure 1: (a) Potential scheme (at pH 7) illustrating the visible light photoactivity of TiO₂-polyheptazine hybrids based on direct optical charge-transfer excitation of an electron from the polyheptazine HOMO (valence band) into the conduction band of TiO₂. (b) Oxygen evolution at a TiO₂-PH photoanode loaded with a CoO_x co-catalyst measured in a phosphate buffer (pH 7) at 0.5 V vs. Ag/AgCl during prolonged irradiation by polychromatic visible light ($\lambda > 420$ nm). The irradiated area was 0.5 cm², and the volume of the anode compartment was 5 mL.

In the context of solar water splitting it is important to realize that it is particularly the water *oxidation* reaction which is the major obstacle hampering the efficiency of water-splitting devices.^[4] Accordingly, one of the fundamental challenges in photoelectrochemical water splitting is the development of highly efficient and stable photoanodes with suitable optical (bandgap), photoelectrochemical (position of band edges on the energy scale), and surface catalytic properties. Recently, we have been developing photoanodes based on a novel class of visible-light photoactive inorganic/organic hybrid materials – TiO₂ modified at the surface with polyheptazine. As we have shown, the optical absorption edge of the TiO₂-PH hybrid is red-shifted into the visible (2.3 eV; ~540 nm) as compared to the bandgaps of both of the single components – TiO₂ (3.2 eV; ~390 nm) and polyheptazine (bandgap of 2.9 eV; ~428 nm), which is due to the formation of an interfacial charge-transfer complex between polyheptazine (donor) and TiO₂ (acceptor)^[2a]. In other words, the direct

optical charge transfer leads to generation of electrons with a relatively negative potential (-0.6 V vs. NHE; pH 7) in the conduction band of TiO_2 , while the estimated potential of holes photogenerated in the polyheptazine layer ($+1.7$ V vs. NHE, pH 7) allows for photooxidation of water ($+0.82$ V vs. NHE, pH 7), as evidenced by visible light-driven (wavelength > 420 nm) evolution of dioxygen on hybrid electrodes modified with iridium or cobalt oxide nanoparticles acting as oxygen evolution co-catalysts.^[2] Importantly, polyheptazine (also known as “graphitic carbon nitride”) is highly thermally stable (up to 550 °C in air), and at the same time it offers a possibility for further functionalization with transition metal-based sites enabling chemical transformations along multi-electron pathways. Our current attempts at introducing efficient catalytic sites directly into the flexible organic (and yet highly stable against oxidation) polyheptazine layer in TiO_2 -polyheptazine hybrids will be discussed.

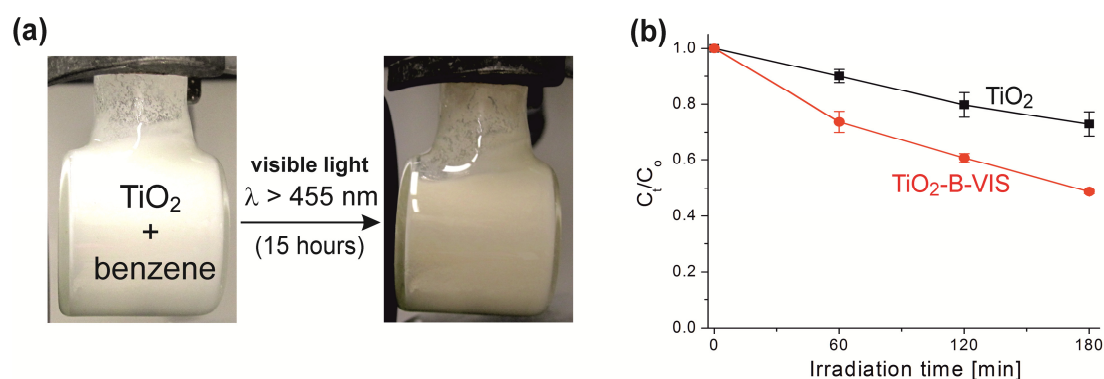


Figure 2: (a) Color change of a TiO_2 (Hombikat UV 100) suspension in benzene after irradiation with visible light ($\lambda > 455$ nm). (b) Concentration changes of 4-chlorophenol (initial concentration = 2.5×10^{-4} M) upon irradiation with visible light ($\lambda > 455$ nm) in the suspensions of TiO_2 and TiO_2 -B-VIS (20 mg photocatalyst in 20 ml solution).

Interestingly, photocatalytic reactions can be utilized also for synthesis of materials with enhanced photocatalytic properties. It is well-known that irradiation of titania by UV light in the presence of benzene leads to brownish coloration of TiO_2 due to formation of stable polymeric products of benzene photo-oxidation. This process is often reported to hamper the photo-catalytic activity through blocking the active sites on the titania surface. Surprisingly, we observed that even irradiation by *visible* light ($\lambda > 455$ nm) leads to brown coloration of titania, *i.e.*, to surface modification by products of benzene photo-conversion. Moreover, the thus prepared modified titania (TiO_2 -B-VIS) was found to be more active in visible light-induced degradation of 4-chlorophenol (4-CP) than unmodified TiO_2 . Hence, this presents one of the rare examples in which the modification of a titania photocatalyst for enhanced photo-activity is achieved *via* an artificial photosynthesis route. Some mechanistic aspects of the photochemical transformations involved will be discussed in detail.

References

- [1] a) J. A. Turner, *Science* **2004**, *305*, 972-974; b) N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729-15735; c) V. Balzani, A. Credi, M. Venturi, *ChemSusChem* **2008**, *1*, 26-58.
- [2] a) M. Bledowski, L. Wang, A. Ramakrishnan, O. V. Khavryuchenko, V. D. Khavryuchenko, P. C. Ricci, J. Strunk, T. Cremer, C. Kolbeck, R. Beranek, *Phys. Chem. Chem. Phys.* **2011**, *13*, 21511-21519; b) L. Wang, M. Bledowski, A. Ramakrishnan, R. Beranek, *ECS Trans.* **2011**, *35*, 173-182; c) L. Wang, M. Bledowski, A. Ramakrishnan, D. König, A. Ludwig, R. Beranek, *J. Electrochem. Soc.* **2012**, *submitted*; d) M. Bledowski, L. Wang, A. Ramakrishnan, A. Bétard, O. V. Khavryuchenko, R. Beranek, *ChemPhysChem* **2012**, *submitted*.
- [3] A. Ramakrishnan, L. Wang, M. Bledowski, B. Mei, M. Muhler, R. Beranek, **2012**, *in preparation*.
- [4] H. Dau, C. Limberg, T. Reier, M. Risch, S. Roggan, P. Strasser, *ChemCatChem* **2010**, *2*, 724-761.