

Engineering of redox interfaces for enhanced photo(electro)catalysis

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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. In any photoactive system, the photogenerated charges must be not only efficiently created, but also effectively separated in order to avoid their recombination. It is important to realize that the charge separation occurs due to the gradient of electrochemical potential (quasi-Fermi levels) at well-designed *interfaces*. Therefore, to improve the charge separation normally means to tune the interfacial properties and/or to introduce new interfaces, *i.e.* to create *hybrids* or *composites*. Many applications require driving chemical reactions along multi-electron transfer pathways. This means that the coupling between charges photogenerated in the light absorber (inherently one-electron/hole process) and co-catalysts allowing for multi-electron chemical transformation is of fundamental importance in such photochemical systems. The quality of the interfacial coupling between the light absorber and the co-catalyst will be therefore of crucial importance for the *activity*, *selectivity*, and *stability* of photo(electro)catalyst.

A typical example is solar-driven splitting of water into hydrogen and oxygen which is typically mainly limited by the slow kinetics of oxygen evolution requiring complex chemistry involving four-electron transfer reactions. Accordingly, one of the main challenges consists in finding effective ways to interface light absorbers with efficient electrocatalysts for water oxidation. Our recent work has involved the development of a novel class of visible-light photoactive inorganic/organic hybrid materials (Figure 1) and interfacing these with water oxidation electrocatalysts based on metal oxides (IrO_x , CoO_x).^[1-5] Some general aspects including the influence of the absorber-electrocatalyst interfacial design of on the activity and stability of photoanodes will be discussed.

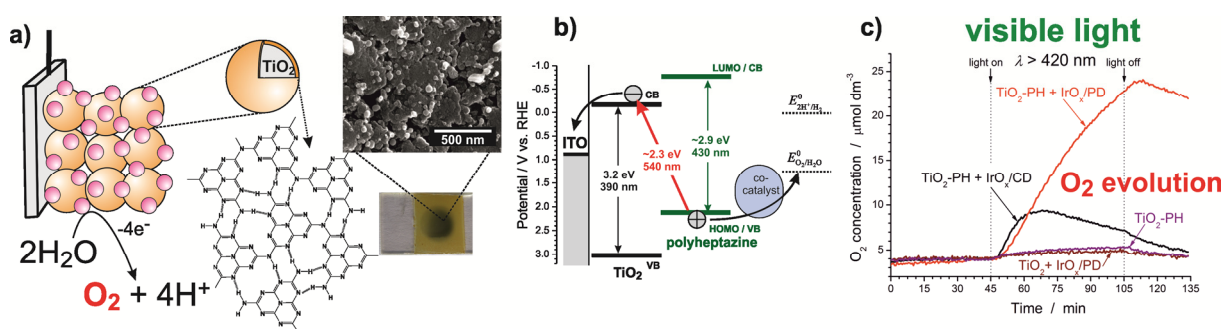


Figure 1: (a) Porous hybrid photoanodes consist of nanocrystalline TiO₂ electron collector modified at the surface with polymeric polyheptazine (melon, "graphitic carbon nitride") and IrO_x nanoparticles acting as oxygen evolution co-catalyst; (b) TiO₂ and polyheptazine form a charge-transfer complex allowing for direct optical electron transfer from the HOMO of polyheptazine to the conduction band of TiO₂; (c) hybrid photoanodes exhibit visible light induced oxygen evolution upon irradiation with visible light ($\lambda > 420$ nm).

Another example is represented by heterogeneous photocatalysis which is potentially one of the cheapest and most efficient methods for decontamination of water and air from

toxic organic pollutants. The efforts to enhance the photocatalytic activity of TiO₂-based materials have very often focused on shifting the light absorption into the visible range. An alternative – and possibly more promising – strategy is to capitalize on the intrinsic UV absorption of pristine TiO₂, and to improve the charge separation. This can be achieved by interface engineering, for example by depositing co-catalysts onto the surface of TiO₂ in order to catalyze the transfer of photogenerated electrons to oxygen molecules. An efficient reduction of oxygen is well known to be essential for achieving high degradation rates in environmental photocatalysis, and the enhancement of photocatalytic degradation efficiencies at pristine TiO₂ after deposition of small amounts of Pt nanoparticles is also well established.^[6-7] Obviously, a non-noble metal alternative is required for large scale applications. The talk will focus on our recent efforts at the development of TiO₂-based photocatalysts modified with low-cost redox co-catalysts.^[8] In particular, the advantages and drawbacks of different co-catalyst deposition routes and the role of photoelectrochemical and advanced spectroscopic techniques for elucidation of the mechanism of the photocatalytic action will be discussed in detail.

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