

# Hybrid and composite photoactive materials for solar energy conversion

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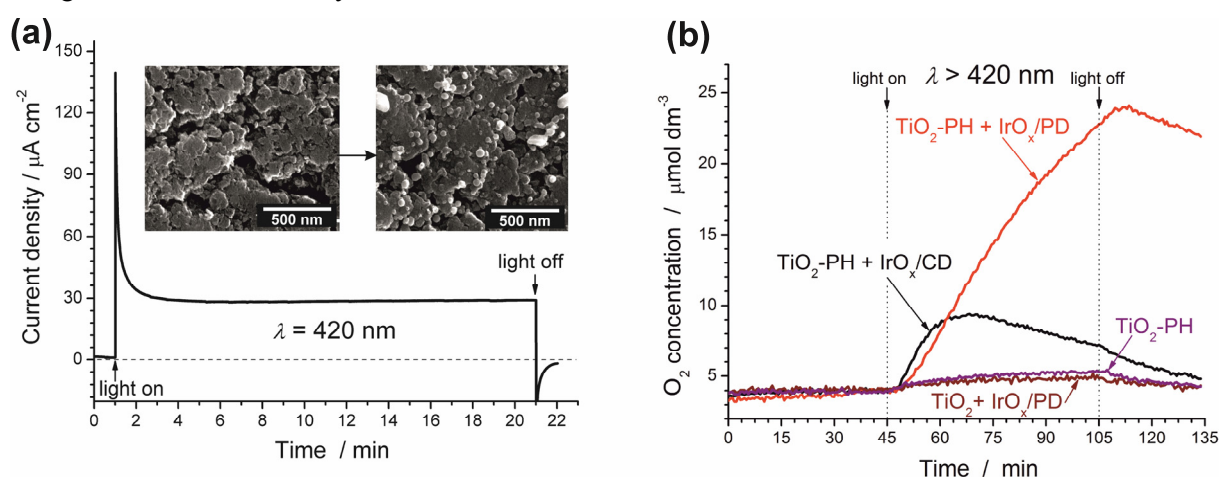
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The development of photochemical systems capable of mimicking the natural photosynthesis by driving useful chemical transformations has attracted significant interest motivated by the need to meet various environmental concerns and to secure the future 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 driving force for charge separation is the gradient of electrochemical potential (quasi-Fermi levels) established at *interfaces*. Therefore, to improve the charge separation in an absorber means to tune its interfacial properties and/or introduce new interfaces, i.e. to create *hybrid* or *composite* materials. Moreover, 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.

A typical example is solar-driven splitting of water into hydrogen and oxygen which is typically 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 photogenerated charges to efficient co-catalysts for water oxidation.

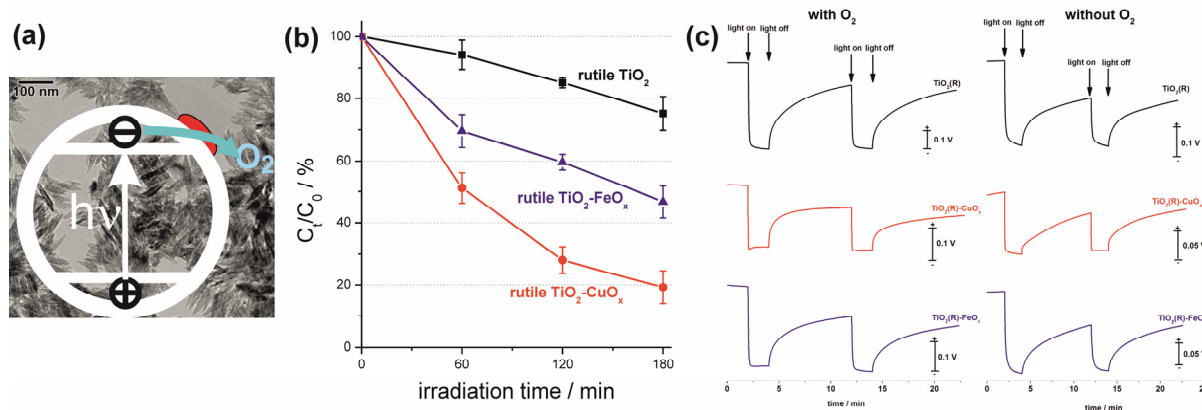


**Figure 1:** (a) Photocurrent transient recorded at a  $\text{TiO}_2\text{-PH}$  hybrid photoelectrode during photoelectrochemical deposition of  $\text{IrO}_x$  nanoparticles from an  $[\text{Ir}(\text{OH})_6]^{2-}$  solution. The electrode was irradiated with monochromatic visible light ( $\lambda = 420 \text{ nm}$ ) at 0.5 V vs.  $\text{Ag}/\text{AgCl}$  (pH 8.5). SEM pictures show the surface of the hybrid photoelectrode before (left) and after (right) the photodeposition process. (b) Improved oxygen evolution at hybrid photoanodes with *photodeposited*  $\text{IrO}_x$  ( $\text{TiO}_2\text{-PH} + \text{IrO}_x/\text{PD}$ ) as compared to hybrid photoanodes with a co-catalyst deposited by colloidal deposition ( $\text{TiO}_2\text{-PH} + \text{IrO}_x/\text{CD}$ ) during prolonged irradiation by polychromatic visible light (cut-off filter  $\lambda > 420 \text{ nm}$ ) in a phosphate buffer solution (0.1 M; pH 7) at 1.12 V vs. RHE.

Our recent work has involved the development of a novel class of visible-light photoactive inorganic/organic hybrid materials and interfacing these with co-catalysts for water oxidation based on metal oxides ( $\text{IrO}_x$ ,  $\text{CoO}_x$ ).<sup>[1]</sup> We have found that particularly the photoelectrochemical in-situ deposition of metal oxide co-catalysts is highly beneficial in terms of establishing a good coupling between the absorber and the co-catalyst (Figure 1). Some mechanistic aspects including the influence of solution chemistry on the activity and stability of photoanodes will be discussed.

Another example is represented by conventional 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  $\text{TiO}_2$ -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  $\text{TiO}_2$ , and to improve the charge separation. This can be achieved by interface engineering, for example by depositing co-catalysts onto the surface of  $\text{TiO}_2$  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  $\text{TiO}_2$  after deposition of small amounts of Pt nanoparticles is also well established.<sup>[2]</sup> Obviously, a non-noble metal alternative is required for large scale applications. Hashimoto et al. recently reported on enhanced activity of rutile  $\text{TiO}_2$  powders modified with small  $\text{CuO}_x$  and  $\text{FeO}_x$  clusters in photocatalytic decomposition of isopropanol in the gas phase.<sup>[3]</sup> The enhanced activity was ascribed mainly to visible-light photoactivity through direct optical charge transfer from the valence band of  $\text{TiO}_2$  to energy levels in the  $\text{MO}_x$  clusters.



**Figure 2:** (a) Metal oxide-based co-catalysts can be deposited onto the surface of a  $\text{TiO}_2$  photocatalyst in order to catalyze the reduction of oxygen and enhance charge separation; (b) the co-catalyst modified  $\text{TiO}_2$  photocatalysts show enhanced degradation rates of 4-chlorophenol as compared to unmodified  $\text{TiO}_2$ ; (c) photopotential transients confirm that the enhancement is due to more efficient catalysis of oxygen reduction at the photocatalyst surface.

In our recent work, rutile  $\text{TiO}_2$  powders were modified with small amounts of  $\text{CuO}_x$  and  $\text{FeO}_x$  clusters by impregnation and drying. The photocatalytic properties of modified rutile samples were investigated in the aqueous phase, and exhibited drastically enhanced photocatalytic degradation of 4-chlorophenol under UV+Vis ( $\lambda > 320$  nm) irradiation.<sup>[4]</sup> The visible light ( $\lambda > 455$  nm) activity in 4-CP degradation was negligible, which suggests that the visible light induced charge transfer transitions do not play a significant role in the enhancement. Photopotential transient measurements have confirmed that  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  co-catalytic sites at the surface of rutile  $\text{TiO}_2$  act as efficient co-catalysts for oxygen reduction by photogenerated electrons, which leads to improved charge separation and diminished recombination. Further developments will be presented, including mechanistic investigations of co-catalyzed photocatalytic reactions.

## Acknowledgements

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