

# Introducing co-catalysts for multi-electron transformations into photochemical systems

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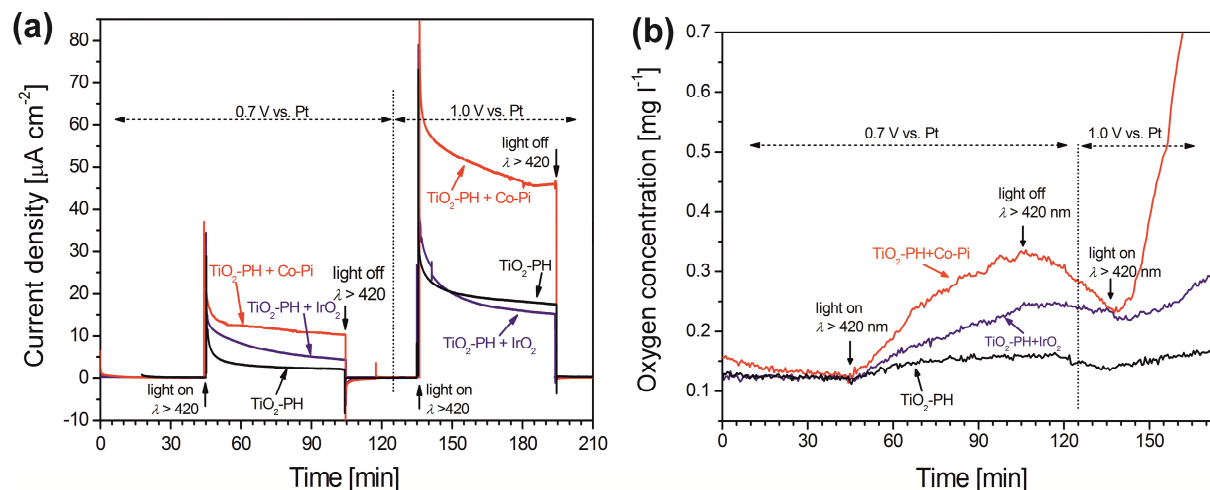
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The development of photochemical systems capable of mimicking the natural photosynthesis by driving useful chemical transformations has attracted significant interest motivated by the need to meet various environmental concerns and to secure the future supply of clean and sustainable energy.<sup>[1]</sup> Notably, 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 catalysts allowing for multi-electron chemical transformation is of fundamental importance in such photochemical systems.

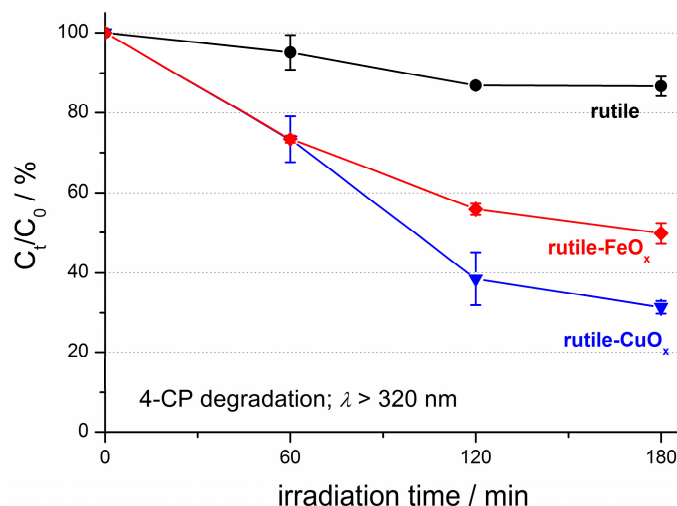
One of the chief examples is solar-driven splitting of water into hydrogen and oxygen which is typically limited by the slow kinetics of the oxygen evolution which requires complex chemistry involving four-electron transfer reactions.<sup>[2]</sup> Accordingly, the main challenge consists in finding effective ways to interface long-lived photogenerated charges to efficient co-catalysts for water oxidation.<sup>[3]</sup>



**Figure 1:** Photocurrent (a) and oxygen evolution (b) at TiO<sub>2</sub>-polyheptazine photoanodes with different co-catalysts measured in a two-electrode setup in phosphate buffer (pH 7) during prolonged irradiation by polychromatic visible light (λ > 420 nm). Working electrode was biased at 0.7 V vs. Pt in the first part (till 125 min) and at 1.0 V vs. Pt in the second part of experiment (after 125 min).<sup>[4]</sup>

Our recent work has involved the development of a novel class of visible-light photoactive inorganic/organic hybrid materials – nanocrystalline TiO<sub>2</sub> modified at the surface with polyheptazine (also known as “graphitic carbon nitride”). The most attractive feature of these inorganic/organic hybrids is the high thermal and chemical stability of polyheptazine-type compounds as compared to conventional organic dyes. The optical absorption edge of the TiO<sub>2</sub>-polyheptazine hybrids is red-shifted into the visible as compared to the bandgaps of both of the single components, which is due to the formation of an interfacial charge-transfer complex between polyheptazine (donor) and TiO<sub>2</sub> (acceptor). In other words, the direct optical charge transfer leads to generation of electrons with a relatively negative potential in the conduction band of TiO<sub>2</sub>, while the holes photogenerated in the surface polyheptazine layer can drive water photooxidation, as evidenced by visible light-driven evolution of dioxygen on hybrid electrodes modified with IrO<sub>x</sub> or CoO<sub>x</sub> nanoparticles acting as oxygen evolution co-catalysts (Figure 1).<sup>[4-5]</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.

A rather different case 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. It is important to realize that the oxygen *reduction* reaction is essential for achieving high rates in environmental photocatalysis.<sup>[6]</sup> Deposition of suitable co-catalysts able to catalyze two-electron reduction of dioxygen can render the transfer of electrons from TiO<sub>2</sub> to oxygen more efficient and thus significantly enhance charge separation and diminish recombination. Indeed, very recently some promising results on enhanced rates of photocatalytic degradation of 2-propanol in gas phase on TiO<sub>2</sub> particles decorated with small Fe<sub>2</sub>O<sub>3</sub> and CuO clusters have been reported.<sup>[7]</sup>



**Figure 2:** Photocatalytic degradation of 4-chlorophenol at pristine rutile TiO<sub>2</sub> powders and at rutile modified with FeO<sub>x</sub> and CuO<sub>x</sub> clusters.

In our own work, we impregnated rutile TiO<sub>2</sub> with FeO<sub>x</sub> and CuO<sub>x</sub> species and observed significantly enhanced rates of photocatalytic degradation of 4-chlorophenol in water (Figure 2).<sup>[8]</sup> The preparation, structural properties and mechanistic investigations of the modified materials will be discussed.

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