

Coupling of light absorbers with cocatalysts for enhanced photo(electro)catalysis

Radim Beránek

Institute of Electrochemistry, Ulm University, Albert Einstein-Allee 47, 89069 Ulm, Germany

radim.beranek@uni-ulm.de

<http://www.rub.de/photochem>

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. The *activity*, *selectivity*, and *stability* of such systems is determined not only by the ability of materials to absorb light and create charges, but also by efficient separation of the charges and their fast and selective reaction with substrates. In this respect, the effective coupling of well-designed cocatalysts with light absorbers will play a crucial role.

The talk will focus on the problem of interfacing different light absorbers with various types of cocatalysts for water remediation,^[1] water splitting,^[2,3] or selective photocatalytic oxidations of low-cost feedstock to high-value chemicals.^[4] One of the most important features of effective cocatalysts in photo(electro)catalytic systems are their optical properties since undesired parasitic absorption of light by the catalysts should be avoided. In this respect, we have recently shown that TiO₂ powders modified with *single* Cu(II) and Fe(III) cocatalytic sites exhibit highly enhanced rates in photocatalytic degradation of organic aqueous pollutants.^[1] The results demonstrate that the single Cu(II) and Fe(III) ions act as effective cocatalytic sites, enhancing the charge separation, catalyzing "dark" redox reactions at the interface, improving thus the normally very low quantum yields of UV light-activated TiO₂ photocatalysts. The exact mechanism of the photoactivity enhancement differs depending on the nature of the cocatalyst. Cu(II)-decorated samples exhibit fast transfer of photogenerated electrons to Cu(II/I) sites, followed by enhanced catalysis of dioxygen reduction, resulting in improved charge separation and higher photocatalytic degradation rates. At Fe(III)-modified rutile the rate of dioxygen reduction is not improved and the photocatalytic enhancement is attributed to higher production of highly oxidizing hydroxyl radicals produced by alternative oxygen reduction pathways opened by the presence of catalytic Fe(III/II) sites. Importantly, it was demonstrated that excessive heat treatment (at 450 °C) of photocatalysts leads to loss

of activity due to migration of Cu(II) and Fe(III) ions from TiO₂ surface to the bulk, accompanied by formation of oxygen vacancies.

Similarly, our recent efforts in introducing efficient catalysts into porous photoanodes for water oxidation will be reviewed. The focus will be on our investigations of small cobalt hydroxide nanoclusters which outperform more conventional cobalt-based cocatalysts (Co-Pi) and exhibit interestingly different behaviour in different electrolytes. Finally, our recent research on highly selective photocatalytic transformations of low-value organic compounds into high value chemicals will be discussed. Herein I will focus on the elucidation of the distinctly hybrid nature of the metal/oxide photocatalysts, as well as its consequences for the mechanism of selective reaction.

In all parts, the role of theoretical calculation and photoelectrochemical and spectroscopic methods for elucidation of the mechanistic aspects of photo(electro)catalytic reactions will be discussed.

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