

Towards rational catalyst design?

Molecularly engineered frameworks for hydrogen evolution photocatalysis

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The conversion of sunlight into storable chemical fuels through photocatalysis has been identified as a viable strategy to alleviate future energy shortage. Although a number of potent semiconductors for solar water splitting are at hand, key features such as earth-abundance, stability and low toxicity still need to be addressed, thus calling for new material solutions for sustainable photocatalysis. While heterogeneous systems excel through their stability, homogeneous catalysts offer the potential to tune every step in the photocatalytic mechanism through molecular engineering. Combining the best of both worlds opens up new possibilities for the design of tailor-made photocatalysts.

We have recently developed a class of “soft” photocatalysts based on carbon nitrides and covalent organic frameworks (COFs),¹ which are abundant and molecularly tunable organic semiconductors. I will review our recent progress in the rational design of triazine- and heptazine-based systems for hydrogen evolution and highlight possible catalyst optimization strategies – through doping,² exfoliation,³ functionalization,⁴ and active site engineering,^{5,6} as well as hybridization with bio-inspired co-catalysts.⁷

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Hybrid charge transfer excitons at metal oxide/organic interfaces

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The talk focuses on electronic excitations formed at the interface between metal oxides and conjugated molecules and polymers. Both, ZnO as well as SnO₂ possess very large electron affinities which leads to a type-II energy level alignment with many conjugated organic materials. Such configuration facilitates exciton dissociation and charge separation at the hybrid interface which predestines them for applications where light is to be converted into electrical energy. Prior generation of free charges a coulombically bound state may form where the electron is residing on the inorganic and the hole on the organic side. Indeed, the existence of such hybrid charge transfer excitons (HCTX) at ZnO/organic, ZnMgO/organic as well as SnO₂/organic interfaces has been verified by the observation of their radiative recombination. The properties of these HCTX can be tuned by interfacial design. By doing so, their impact on photovoltaic parameters like the open circuit voltage and short circuit current has been revealed.