Poster:

Elucidating Charge Transfer at Coating-Stabilized Photocatalyst/Water Interfaces

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Achieving an efficient water-splitting device is not trivial, particularly due to the instability of efficient semiconductor/liquid interfaces: despite recent demonstration of protective-coating enabled water-splitting photoelectrochemical devices at >15% solar-to-fuel efficiency, these devices consists of two electrodes and a membrane thereby costly to build. On the other hand, many efficient molecular- and material-based photocatalysts co-evolve H_2 and O_2 in near neutral conditions. However, inefficiency and instability of photocatalyst/water interfaces is the remaining challenge.

We present a general kinetics model that excited charge carriers are transferred to H^+/H_2 or O_2/H_2O redox couples as individual events. Due to the reversibility of electron-transfer process at SC/liquid junctions, net product generation does require a sufficient photon flux to overcome the backward reactions. We had constructed a semiconductor/liquid junction model involving two co-existing redox couples, by connecting individual, stochastic interfacial charge-transfer events with a statistical, net-outcome of water-splitting reactions. Our study unraveled the elementary charge-transfer kinetics of photo-excited electron transfer across SC/liquid junctions. The proposed kinetic model provided a key guidance for rational design of particle-based photocatalytic water splitting systems.

We further present the synthesis of thick $(Ti,Mn)O_x$ ternary mixed oxide films (> 20 nm) by using atomic layer deposition (ALD) to extrinsically modify the original, "leaky" TiO_2 coatings and preserve their robust chemical, electrochemical and mechanical stability in acid. We show that ALD growth can be extended to an entire class of ternary alloyed oxides, by precisely tuning compositions and crystallinity. Such an acid-stable protective coating promises many critical applications in oxidative photochemistry and earth-abundant photovoltaics. We present our outlook of combining coatings with particle semiconductors for efficient and stable particle-based water splitting.

References:

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