Identification of Optimal Redox Shuttle Properties for Efficient Photocatalytic Z-Scheme Solar Water Splitting Reactors

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Particle suspension reactors for solar water splitting are capable of generating hydrogen at a cost that is competitive with hydrogen produced from steam methane reforming.[1] Our team is interested in identifying guiding principles for efficient reactor designs that resemble Nature's Z-scheme. These reactors consist of two photocatalyst particle suspension beds that together drive overall solar water splitting with charge and ion transport between the beds mediated by soluble redox shuttles.[2] In my presentation I will report on our team's recent progress on a design where the photocatalyst beds are stacked vertically, leading to efficiency advantages due to serial light absorption and short redox shuttle mass transport distances. Using finite-element numerical analyses, we modelled and simulated the transient mass transport processes, light absorption, electrochemical kinetics, gas crossover, and thermal transport in the proposed reactor,[3] as well as identified the thermodynamic and kinetic limits to solar-to-hydrogen conversion efficiency.[4] We determined that redox shuttle selectivity is a key parameter that dictates overall performance. We also found that even for efficient reactor designs, operating at up to ~10% solar-to-hydrogen conversion efficiency, redox shuttle transport between the beds can be sustained with only passive diffusion,[3] and performance is enhanced with natural convection. Experimentally, we synthesized, characterized, and evaluated the photoelectrochemical and photocatalytic performance of the most promising photocatalyst nanocrystallites ($BiVO_4$, WO_3, and Rh-doped $SrTiO_3$) as particles in model reactors, and in the presence of several different redox shuttles and at various pH values. For H_2-evolving Rh-doped $SrTiO_3$, we demonstrated that introduction of Ru cocatalysts enhanced performance by increasing the rate of H_2 evolution and to a lesser extent undesired Fe(III) reduction. For O_2-evolving WO_3, we showed that O_2 does not interfere with collection of electrons and that selectivity toward Fe(III) reduction is possible at moderate concentrations of Fe(III). Collectively, our efforts represent strides toward achieving a high-level of techno-economic viability in solar water splitting reactors.

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References: [1] B. A. Pinaud, J. D. Benck, L. C. Seitz, A. J. Forman, Z. Chen, T. G. Deutsch, B. D. James, K. N. Baum, G. N. Baum, S. Ardo, H. Wang, E. Miller, and T. F. Jaramillo, *Energy & Environmental Science*, 2013, *6*, 1983–2002. [2] D. M. Fabian, S. Hu, N. Singh, F. A. Houle, T. Hisatomi, K. Domen, F. E. Osterloh, and S. Ardo, *Energy & Environmental Science*, 2015, *8*, 2825–2850. [3] R. Bala Chandran, S. Breen, Y. Shao, S. Ardo, and A. Z. Weber, *Energy & Environmental Science*, 2018, *11*, 115–135. [4] S. Keene, R. Bala Chandran, and S. Ardo, *under review*.