Title

Interrogating charge-transfer mechanisms during photoacid dye-sensitization of ion-exchange membranes for light-to-ionic energy conversion

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Abstract

Recently, the Ardo Group pioneered the development of dye-sensitized ion-exchange membranes that pump ions when illuminated with visible light. Dye sensitization is achieved using photoacids, which are typically organic molecules that contain a protic group whose bond is weakened in the electronically excited state.

In my presentation, I will share recent important discoveries that follow-up from our original report (*JACS* **2017** *139* 11726) of light-driven ion pumping using photoacids covalently bound to Nafion ion-exchange membranes separating two aqueous electrolytes of largely different pH value. Unique to my work is that I replaced the previously reported large acid–*base* differences with smaller acid–*acid* differences, which essentially eliminate ion leakage crossover. Then, by introducing several means to measure photo-responses using reference electrodes that exhibit little-to-no ion leakage, I show that there are several distinct responses depending on whether a transient gradient in ion concentration is present at the membrane|solution interface. By examining photo-responses under systematically controlled conditions of fluence, electrolyte gradient, and photoacid species, my work is beginning to unravel the complex underlying causes of this observed function in this new class of functional materials. In addition, using time-resolved pulsed-laser spectroscopies that probe from the ultraviolet to the radio-frequency regime, I am characterizing the various sensitization pathways available to covalently bound photoacids based on photoacid reprotonation kinetics and mobile charge generation. Collectively, this suite of studies represents the Ardo Group's efforts to understand the fundamental limitations to using single-membrane ion pumps for applications such as solar desalination of salt water and further the mechanistic understanding of photoacid-modified polymers.