Electron Transfer Kinetics of Aluminum Porphyrin/ Metal Oxide Systems

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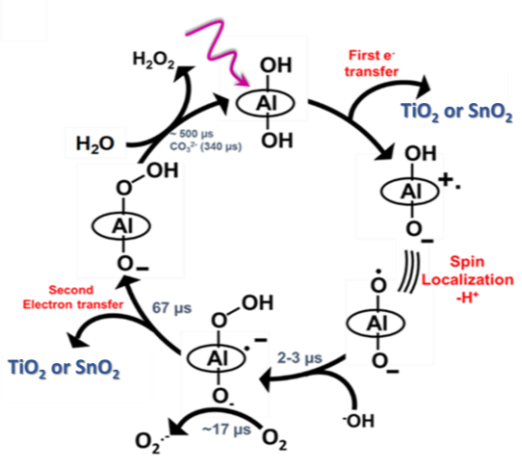
Molecular catalyst sensitized system (MCSS) for the simultaneous photocatalytic generation of hydrogen and hydrogen peroxide solely from water is a coveted, yet less explored route for sustainable energy systems. In Recent years, we probed into various earth-abundant metalloporphyrins for their potential application as two-electron water oxidation catalyst. Substantial progresses have been made from electrochemical one-electron initiated two-electron water oxidation to visible light-induced one-photon initiated water splitting.[1] These metalloporphyrin incorporated MCSS systems would be an ideal candidate for photocatalytic water splitting to hydrogen and hydrogen peroxide. Such systems have potential to solve photon flux density hurdle of artificial photosynthesis through one photon-initiated process.

Anionic 5,10,15,20-tetra(4-carboxy)phenylporphyrinatealuminum (AlTCPP) and Cationic 5,10,15,20-tetrakis(1-methylpyridin-1-ium-4-yl)porphyrinatealuminum (AlTMPyP) both show electrochemical one-electron initiated two electron water oxidation. Photocatalytic water-splitting of AlTCPP incorporated on TiO_2 served as the first exemplum to get through the above-mentioned bottle neck of artificial photosynthesis.[1] The disparity in electrochemical and photochemical activity of AlTMPyP and AlTCPP lead us to further investigate the electron transfer in one photon-initiated water splitting process by these MCSS systems. The first and second electron transfer from metalloporphyrin to the semiconductor plays a crucial role in designing an efficient photocatalytic MCSS system. How can we improve the electron transfer from molecular catalyst to semiconductor system? Here we focused our attention to the electron transfer processes in ionically adsorbed AlTCPP and AlTMPyP in titanium(IV) oxide and tin (IV) oxide. Through fluorescence lifetime and photoelectrochemical studies we compare the electron transfer of aluminum porphyrins in these two metal oxides.



1)F. Kuttassery, S. Sagawa, S. Mathew, Y. Nabetani, A. Iwase, A. Kudo, H. Tachibana, H. Inoue, *ACS Appl. Energy Mater*. **2019**, 2, 11, 8045-8051.