Lecture 3: Photo Meets Electrocatalysis: United we Split (. . . Water)
4:15 p.m. Wednesday, February 8, 331 Smith Hall

The cleavage of water into hydrogen and oxygen by visible light remains the Holy Grail of current photochemical research. In contrast to the “brute-force” approach using photovoltaic panels to electrolyze water, these systems employ semiconductor films or particles, which are able to perform the multi-electron transfer reactions involved in the water oxidation and reduction process. Iron oxide (α-Fe₂O₃, or hematite) is especially attractive as a photo-anode due to its abundance, stability and environmental compatibility, as well as suitable band gap and valence band edge position. However, the reported efficiencies of water oxidation at illuminated hematite electrodes are notoriously low. We have deposited silicon doped mesoscopic α-Fe₂O₃ (hematite) films on F-doped SnO₂ glass substrates by chemical vapor deposition at atmospheric pressure (APCVD). Apart from rendering the films conductive the silicon doping strongly influences the mesoscopic film morphology. The silicon-doped α-Fe₂O₃ exhibits a cauliflower-type nanostructure as shown in Figure 1 below. When used in conjunction with surface adsorbed Co(II) ions to promote water oxidation to oxygen a photocurrent of 3.5 mA/cm² was obtained. This corresponds to an overall solar to chemical conversion efficiency of about 5% in a tandem device using a dye sensitized solar cell (DSC) as a bottom electrode. The role of the DSC is to boost the potential of the cathode to enable evolution of hydrogen. A mechanistic model for water photooxidation is presented, involving stepwise accumulation of four holes by two vicinal iron or cobalt surface sites. Recent research on efficient photogeneration of hydrogen on mesoscopic Cu₂O electrodes will also be presented.

Figure 1. Scanning electron microscopy picture of a silicon doped hematite film supported on fluorine doped tin dioxide(FTO) conducting glass. Note the cauliflower-type nanostructure obtained by APCVD. Visible light induced oxygen evolution on such nanostructured hematite films.