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Photooxidation reactions at nanostructured oxide photoelectrodes

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Principal obstacles to direct photosplitting of water are the corrosion of the semiconductor materials and the difficulty of matching the semiconductor band-edge energy levels with those of hydrogen and oxygen evolution reactions. Only a few n-type semiconducting oxides, such as hematite α-Fe_2O_3 and WO_3 photoanodes with band gaps of 2.1 eV, respectively, 2.5 eV, fulfil the first requirement, having demonstrated remarkable stability during long-term photoelectrolyses. However, due to the position of the conduction band edges more positive than the H_2 evolution potential, none of those materials can perform unassisted water splitting. Consequently, continuing efforts are devoted to minimize the bias voltage required to perform visible light-driven photooxidation of water. Recently, unassisted solar production of H_2 has been demonstrated in a dual-absorber tandem device combining a semitransparent WO_3 (or an α-Fe_2O_3) photoanode and the latest version of the dye sensitized solar cell providing a *ca* 1 V bias voltage to the photoelectrolyzer.[1]

Despite its photoaction range restricted to the UV and blue portions of the solar spectrum (up to 500 nm), the WO_3 photoanode reaches much larger water splitting photocurrents in the tandem cell configuration due to its less positive open-circuit photopotential (*ca* 0.45 V *vs* RHE) and the steep rise of the I_{ph}- E curve approaching the plateau at around 1 V (*vs* RHE).[2]

In this presentation we will discuss recent improvements in the photoelectrochemical performance of WO_3 photoanodes obtained through incorporation of plasmonic metal nanostructures, allowing to enhance the light capture, and by the use of electrocatalysts.

1. J. Brillet, J.-H. Yum, M. Cornuz, T. Hisatomi, R. Solarska, J. Augustynski, M. Graetzel, K. Sivula, *Nature Phot.* 2012, doi:10.1038/nphoton.2012.265

2. R. Solarska, R. Jurczakowski, J. Augustynski, *Nanoscale* 2012, *4*, 1553