PHOTOINJECTION OF POLYOXOMETALLATES FOR PHOTOELECTROCHEMICAL PRODUCTION OF HYDROGEN FROM WATER

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A variety of polyoxometallates (POM) were examined for their ability to photoinject electrons into mesoporous TiO_2. Experimental cells were constructed from nanostructured TiO_2 printed onto transparent conducting oxide glass obtained from Dyesol. We determined that a Keggin lacunary type structure of a tungstosilicate POM ($H_8SiW_{11}O_{39}$) and a Dawson type structure of a tungstophosphate POM ($H_6P_2W_{18}O_{62}$) in pH 6 solution showed the greatest increase in current versus the blank pH 6 buffer solution by an average of 3-5 µA/cm^2. The effect was determined to be dependent on the pH of the solution, as no increase in photocurrent is observed when the cell currents are measured in pH 2 solutions. For the pH 6 solutions, we observed a time dependence of the response as a function of solution lifetime. We theorized that the POMs were slowly degrading into other structures from the removal of 1, 2, 3 or more tungsten oxide metal octahedrals from the given molecular structure. This was supported by UV-Vis spectroscopy of the tungstosilicate POM which revealed slow but substantial 15 nm blue shifting of the electronic absorption as the solution was allowed to sit for a period of days.