# Controlling the energetics and activity of nanocrystal metal oxide water splitting catalysts with potential determining ions

Rachel L. Chamousis, Frank E. Osterloh

$HCa_2Nb_3O_{10}$ nanosheets catalyze hydrogen evolution from aqueous methanol under UV light. Here we describe the effects of surface modification with potential-determining cations on the photocatalytic properties of the nanocrystals. In alkaline solution, the nanosheets are negatively charged at the surface and adsorption of cations (potassium, strontium, protons) can be achieved by simple mixing with metal salts followed by mild heating. Experimental photocatalytic rates for hydrogen evolution from aqueous methanol ranged between 230 to 550 micromol H2 h-1 (25 mg of catalyst) and increased in the order of $MCa_2Nb_3O_{10}$ (M=Sr, H, K). The photocatalytic activity was also found to decrease with increasing solution pH. The observed activity variations can be quantitatively understood with a free energy model that relates the rates to the driving force of the reaction. The latter is determined by the difference of the proton reduction potential and the Fermi potential of the electrons in the materials, as measured from photoelectrochemical onset potentials.