Dynamics of photogenerated electron-hole pairs in photoelectrodes for photoelectrochemical water splitting

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Abstract

With clean, renewable and abundant of sunlight convert to hydrogen has been considered an ideal solution to counter the depletion and environmental problems of fossil fuels. Photoelectrochemical (PEC) water splitting is a promising route for synthesizing hydrogen using solar energy without direct CO_2 emissions. The key to the technology is photoelectrodes (photoanodes and photocathodes) made of suitable bandgap semiconductors of photocatalytic properties. The materials should have high efficiency, high stability, and low cost. For photoanodes, the wurtzite-type of Zinc oxide (ZnO) used to produce oxygen via solar water splitting because it's earth-abundant and has a direct bandgap with favorable band edges for the water-splitting redox levels. However, ZnO has not been able to reach its optimal efficiency due to its poor optical absorption ability. Especially for PEC water splitting applications, metal oxide photoelectrodes with V_O treatment were showed to improve both light absorption and charge transport properties, leading to an enhanced PEC water splitting performance. Owing to the importance of V_O, there are several reduction methods, which have developed to generate V_O in the semiconductor-metal oxide. In 2011, Chen and Mao reported that TiO_2 powder converted by a high-pressure H_2 treatment to anatase-like ''black titania'', which improved visible and infrared optical absorption by engineering the disorder of nanophase TiO_2 with simultaneous dopant incorporation. To take advantage of H_2 treatment, the hydrogenated ZnO photoelectrodes have been synthesized in this work. For the configuration of the photoelectrodes, the hydrogenated core-shell ZnO nanorods-array can achieve high performance with current density of 4.0 mA/cm^2. For photocathodes, cuprous oxide (Cu_2O) has the potential to be a powerful material used to produce hydrogen via solar water splitting due to its abundance on earth and ideal band gap energy for solar energy harvesting. However, Cu_2O has not been able to reach its optimal efficiency due to its poor photostability and poor charge carrier density and mobility. Plasmon-assisted photocatalytic water splitting leads to lower overpotentials by unlocking unique mechanistic pathways. The strongly localized near fields at the surface of plasmonic nanoparticles can promote electron-hole pair generation in nearby semiconductors. Plasmon decay generates an excited hot electron which can be transferred to a surface molecule for direct reduction or injected into an adjacent wide band gap catalyst, effectively limiting carrier recombination through charge separation and expanding the usable portion of the solar spectrum. The electron dynamics in an irradiated plasmonic nanoparticle can alter the electronic coupling with surface adsorbed water and reaction intermediates, thereby changing the binding energy of these species and the catalytic properties of the plasmonic metals. To take advantage of plasmonic catalysis, alloy with strong plasmonic and photocatalytic behavior have been synthesized in this work. Photoelectrodes' surface chemistry, structural, optical, electrical, photoelectrochemical, dimensionality effects and interfacial electronic structure along with their efficiency have been thoroughly investigated at synchrotron radiation facilities. Therefore, this work will show how to use surface functionalized nanostructures and plasmonic nanostructures as the photosensitizers to extend the light absorption spectral range and enhancing the charge separation as the photoelectrodes to extend the light absorption spectral range and enhancing the charge separation in the semiconductor.

Keywords - Zinc Oxide, Cuprous Oxide, Photoelectrochemical Water Splitting, Synchrotron X-ray techniques.