Using TiO2 as a Conductive Protective Layer for Photocathodic H2 Evolution - DTU Orbit (07/11/2019)

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Surface passivation is a general issue for Si-based photoelectrodes because it progressively hinders electron conduction at the semiconductor/electrolyte interface. In this work, we show that a sputtered 100 nm TiO2 layer on top of a thin Ti metal layer may be used to protect an n+p Si photocathode during photocatalytic H2 evolution. Although TiO2 is a semiconductor, we show that it behaves like a metallic conductor would under photocathodic H2 evolution conditions. This behavior is due to the fortunate alignment of the TiO2 conduction band with respect to the hydrogen evolution potential, which allows it to conduct electrons from the Si while simultaneously protecting the Si from surface passivation. By using a Pt catalyst the electrode achieves an H2 evolution onset of 520 mV vs NHE and a Tafel slope of 30 mV when illuminated by the red part (λ > 635 nm) of the AM 1.5 spectrum. The saturation photocurrent (H2 evolution) was also significantly enhanced by the antireflective properties of the TiO2 layer. It was shown that with proper annealing conditions these electrodes could run 72 h without significant degradation. An Fe2+/Fe3+ redox couple was used to help elucidate details of the band diagram.

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