

Fate of the Photogenerated Electrons in Anodically Polarized Mesoporous Titanium Dioxide Films.

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Several features of mesoporous titanium dioxide films formed on electronically conducting substrates resemble those of solution suspensions of the individual TiO₂ nanoparticles. In particular, in both cases, the rates of photooxidation reactions are strongly affected by the nature of hole and also electron scavengers present in the solution. This is reflected by unusually large differences between the saturation photocurrents generated at nanocrystalline TiO₂ films in the presence of irreversibly oxidized effective hole scavengers (such as aliphatic alcohols and carboxylic acids) on the one hand, and those obtained for the oxidation of reversible redox species (e.g., I⁻, hydroquinone), on the other. Low apparent incident-photon-to-current efficiencies (IPCE's) observed in the latter cases are clearly due to the interception of a part of photogenerated electrons by the oxidized form of the redox couple (i.e., I₃⁻, quinone). Such redox cycling accounts for an effective hole-electron recombination causing a marked decrease of the net photocurrent. We observed systematically that the addition of various electron acceptors to a solution containing an efficient hole scavenger (e.g., methanol, formic acid) leads also to an abrupt drop of the saturation photocurrent at the mesoporous TiO₂ film electrodes. Importantly, the latter effect still occurs in the presence of a large anodic bias, i.e., when the potential applied to the back contact of the TiO₂ film markedly exceeds the reduction potential of the electron acceptor present in the solution.

The behavior of this kind is consistent with the absence in such films of a regular space-charge layer and raises an additional question regarding the actual distribution of the electric potential across the film, i.e., between the back contact and the outer film/solution interface.

Due to a relatively negative value of its reduction potential ($E_0 = MV_{2+}/MV_{+} = -0.446$ V) more negative than that of the conduction band edge of TiO₂ in acidic media but becoming more positive than the latter in alkaline solutions, the methyl viologen dication appears particularly suited to establish a correlation between the onset of the electron acceptor induced drop of the photocurrent and the actual conduction band potential of TiO₂. In fact, the addition of MV₂₊

to a 0.1 M aqueous solution of formic acid of pH 1 does not affect the photocurrent at the mesoporous TiO₂ photoanode but causes a strong drop of the photocurrent when the solution pH is made alkaline. In an attempt to probe the potential distribution across the mesoporous film, additional experiments were carried out employing monochromatic illumination of varying wavelengths and, consequently, penetration depths in the film. They clearly confirmed the existence of a large potential drop across the films.

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