E1-12: Photosensitization of nanocrystalline TiO_2 films by tannins

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Dye-sensitized nanocrystalline TiO_2 photoelectrochemical cell (PEC) is receiving much attention as a cheap solar energy conversion molecular electronic device. Performance of the cell largely depends on the dye used to sensitize the nanocrystallites. Sensitizers that have been used are ruthenium polypyridyl complexes with carboxylate or phosphorate ligands that facilitate charge transfer and anchorage of the sensitizer molecules. An interesting alternative to coating of a dye on TiO_2 is to look for substances that surface chelate with Ti^{4+} ions on TiO_2 to form charge transfer species. It was found that polyphenolic compounds, notably tannins surface chelate strongly with TiO_2 resulting in efficient photosensitization.

Microporous layers of TiO_2 were coated on conducting tin oxide glass (50 hm/sq). Purified commercial tannin and purified tannins obtained from black tea and gall nuts were used. Photoelectrochemical measurements were carried out in 3-electrode configuration in the KI + I_2 solution. Action spectra were recorded using a monochromator-light chopper-lock in amplifier arrangement. The absorption spectra of TiO_2 surface complexed tannins was obtained by treating a dialysed TiO_2 sol with tannin.

When the cleaned nanocrystalliine TiO_2 film was immersed in a solution o tannin, monolayer coverage of Ti^{4+}-tannin complex reddish brown in colou was formed immediately. Most tannins gave photocurrent action spectrun with peaks at 435, 485 nm. In the case of tea tannins an additional peal appeared at 585 nm due to the presence of 2 different types of tannins. A light intensities comparable to the solar intensity, PEC gave photocurrents o the order of 4-6 mA cm^{-2}. The rate of decay of the photocurrent was _0. mA $cm^{-2}n^{-1}$.

Condensed tannins have a number of hydroxyl groups attached to benzene rings and carboxylate groups. Efficient photosensitization and charge transfer originates from bonding of these groups to the TiO_2 surface. The advantage of sensitization by surface chelation is complete suppression of the desorption of the sensitizer to the solution and efficient charge transfer. Purification of tannin improves the stability of the cell, suggesting that oxidative degradation of impurities is at least partly responsible for decay of the photocurrent.