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PHOTO(ELECTRO)CHEMICAL PROPERTIES OF NANOPARTICULATE TITANIUM DIOXIDE ELECTRODES.

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The depollution of waste- and drinking water is a topic of utmost importance nowadays. The possibilities and the limits of photo(electro)chemical pollutant degradation in aqueous solutions based on transition metal oxide semiconductor catalysts in the form of powder suspensions, immobilized powders (paints), and massive and nanostructured thin film electrodes are discussed.

Reactions on the surface of semiconductors are always photoelectrochemical processes if photons with energies above the bandgap are used for irradiation. In the case of electrolyte suspended semiconductor particles (photocatalytic method) the global reaction is the result of local photocurrents under open circuit condition taking place at individual particles [1,2]. Here, the working point (mixed potential and local short circuit current) depends on both, the cathodic (reduction process) and the anodic (photooxidation) characteristics of the semiconductor particles.

The same holds for particles immobilized on a surface (macroscopic substrate) [1,2]. However, if this substrate is electrically conducting, the advantage is offered that an electrode potential can be imposed to the electrode with the help of an appropriate counter electrode. Thus, the working point of the photoelectrochemical reaction can be shifted to the potential range where photon flux limited (plateau) currents flow. The ratio of photocurrents (and therefore the IPCE) between this situation and the open circuit condition is 10 to 40 (depending on counter electrode polarizability) and requires an external bias of typically a few hundred mV between the two electrodes. The IPCE is mostly dependent on bulk semiconductor properties.

By contrast, nanostructured thin film electrodes are of a different nature. It is shown that very small bias can push the IPCE into the plateau region, i.e. the polarograms under light are very steep in the onset region. Therefore, operation in the open circuit mode might be envisaged, if the reduction reaction (e.g. oxygen reduction) is proceeding fast and at an optimal potential at the same electrode surface. Moreover, large differences between photocurrents in supporting electrolyte and photocurrents in the presence of organic additives (oxidizable pollutants) can be found, i.e. a very succesful competition between pollutant oxidation and water oxidation (which is an undesired side reaction).

All these specific features can be interpreted in terms of the different mechanisms of electron-hole separation and charge transport in both type of electrodes.

Here, we have measured the current-potential characteristics and the quantities IPCE, Faradaic efficiency, and quantum yield of product formation/educt degradation for TiO_2 nanoparticulate based electrodes for different additives at different concentrations and compared them to results obtained for "classical" TiO_2 electrodes investigated under the same conditions.

References.

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