Dual behavior of nanostructured TiO$_2$ films.

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Several features of nanostructured oxide semiconductor films (in particular, unusually strong dependence of observed photocurrents upon the nature of the reacting redox species from the solution) situate their mode of operation as intermediate between that of a suspension of semiconductor particles and that of an ordinary compact material. We obtained a direct evidence of such a dual behavior in the case of nanostructured TiO$_2$ films by measuring faradaic efficiency of CO$_2$ formation originating from the photooxidation of formic acid. Like other small organic molecules, HCOOH has previously been shown to act as particularly efficient hole scavenger at nanostructured TiO$_2$ films [1]. The initial hole transfer

$$HCOOH + h^+ \rightarrow HCOO^{\bullet} + H^+ \qquad (1)$$

is followed, in part, by the electron injection into the conduction band of TiO$_2$

$$HCOO^{\bullet} \rightarrow CO_2 + H^+ + e^- \qquad (2)$$

as demonstrated by the quantum efficiencies of the photocurrent exceeding 100 % [1]. In the presence of a sufficiently large amount of HCOOH (> 0.1 mol/dm^3) in the solution, the photooxidation of water is virtually suppressed and CO$_2$ remains the only product of the photoanodic reaction.

Experiments consisted in monitoring simultaneously the photocurrent and the amount of formed CO$_2$ (by means of gas chromatography) as a function of the potential imposed to the conducting support of the TiO$_2$ film. The measurements were performed both in N$_2$ and air saturated solutions. Nanostructured TiO$_2$ films, ca 3 µm thick, were prepared from a commercial P25 (Degussa) photocatalyst composed of ca 75% anatase and 25 % rutile, according to the procedure described elsewhere [1]. The support acting as current collector consisted of a SnO$_2$-F coated glass. The TiO$_2$ films were illuminated from the solution side with a 150 W xenon lamp equipped with a 320 nm cut-off filter.

Measurements of the amount of CO$_2$ evolved, under illumination, at nanostructured TiO$_2$ electrodes subjected to substantial anodic bias (corresponding to the saturation of the photocurrent) gave systematically results strongly dependent on the nature of the gas dissolved in the solution. Faradaic efficiencies close to 100 %, obtained under N$_2$ bubbling through the solution, confirmed CO$_2$ as being practically the only product of the photoanodic process. On the other hand, similar experiments performed under continuous bubbling of air resulted in apparent faradaic efficiencies (based on the respective amounts of formed CO$_2$ and of the passed current) in the range of 130 - 140 %. Obviously, the extra amount of collected CO$_2$ can only be explained by the simultaneous involvement of a

reduction reaction, allowing the photooxidation of an additional portion of HCOOH without contributing to the net photocurrent. Subsequent determination of the amount of CO_2 formed at open circuit, under bubbling of air and identical illumination conditions, showed that the ¨˚excess˚¨ faradaic yields determined under anodic bias were, in fact, due to the simultaneous occurrence of the photocatalytic process. The latter involves, coupled, the hole scavenging

$$HCOOH + 2h^+ \rightarrow {}^\circ CO_2 + 2H^+ \qquad (3)$$

and the electron scavenging reaction

$$\_ O_2 + 2e^- + 2H^+ \rightarrow H_2O \qquad (4)$$
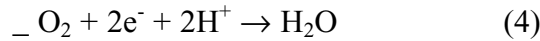
Importantly, the photocatalytic process was practically unaffected by a large anodic bias exceeding reversible potential of the oxygen electrode (i.e., 1.23 V vs. RHE). This clearly indicates that the actual potential of the illuminated region of the nanostructured film doesn t follow the anodic bias applied to the back contact. On the other hand, similar experiments performed using compact TiO_2 films, displaying a conventional, space-charge layer showed faradaic efficiencies for CO_2 formation close to 100% both in the absence and in the presence of oxygen in the solution.

References

(1) A. Wahl, J. Augustynski, *J. Phys. Chem*. **B102**˚: 7820, 1998

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