Highly Selective Photo-oxidation Reactions at Nanocrystalline TiO_2 Film Electrodes

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Photocurrent–voltage characteristic of the junction formed between a porous nanocrystalline TiO_2 film and an electrolyte is shown to be governed by the kinetics of the interfacial hole transfer to the oxidizable species in the solution.

Kinetic limitations of photoelectrochemical reactions, due to the rate-determining charge transfer at the semiconductor–solution interface, are apparent through the influence of the nature and the concentration of the redox species on the observed photocurrent. Such limitations are expected to occur principally close to the onset potential of the photocurrent and tend to decrease with increasing band bending. Upon approaching the saturation photocurrent, the role of bulk properties of the semiconductor, which determine the width of the depletion layer and the diffusion length of minority carriers, becomes predominant. The only known exception to this rule is the so-called photocurrent-doubling, multi-step reactions. In the case of an *n*-type semiconductor, reactions of this kind involve hole transfer from the valence band to an oxidizable species in the solution, followed by injection of an electron to the conduction band of the semiconductor by the reaction intermediate.[1,2] In practice, the increase in the saturation photocurrent, upon addition to the solution of a photocurrent-doubling agent, is usually much less than twofold.

In this context, the highly selective behaviour of a new kind of TiO_2 photoanode, exhibiting a very large (generally >10) ratio of saturation photocurrents for the photo-oxidation of methanol, and the photogeneration of oxygen from an aqueous solution must appear unusual. These electrodes were prepared by attaching P25 (Degussa) TiO_2 powder to the Ti surface by means of poly(vinylidenefluoride), PVDF, and annealing at 400–500 °C. A suspension of TiO_2 in DMF containing dissolved PVDF (typical composition: 1 g P25 and 0.4 g PVDF per 10 cm^3 DMF) was deposited on a cross-section (0.28 cm^2) of Ti rods, dried in air for 30 min at 25 °C and then for 40 min at 100 °C to evaporate the solvent, and finally annealed for 1 h at 400–500 °C.

Fig. 1(*a*) shows the photocurrent–voltage curves for a conventional anatase film electrode, prepared by the sol/gel method,[3] recorded in 0.1 mol dm^{-3} aq. NaOH solution with and without addition of 0.1 mol dm^{-3} of MeOH. Band gap irradiation ($\lambda <$ *ca.* 400 nm) of the anatase film in aq. NaOH results in the oxidation of water (or, more precisely, of OH^- ions) by photogenerated valence-band holes with quantum efficiencies exceeding 40% [unbroken curve in Fig. 1(*a*)]. Addition of methanol to the electrolyte leads to quite a large shift of photocurrent onset towards negative potentials. This kind of behaviour, typical of a species undergoing rapid hole capture at a photoanode surface,[4] is consistent with the ability of methanol to compete more efficiently than OH^- ions with surface electron–hole recombination.[5] Moderate (*ca.* 20%) increase of the saturation photocurrent, observed in Fig. 1(*a*) following addition of methanol to the solution, is caused by partial occurrence of the above-mentioned photocurrent-doubling mechanism.[5]

By way of contrast, analogous photocurrent–voltage curves, obtained for a *ca.* 2 μm thick P25 (mixture of *ca.* 80% anatase and 20% rutile) TiO_2 film attached to the Ti substrate, reveal entirely different behaviour of such an electrode in the presence and absence, respectively, of methanol from the solution [Fig. 1(*b*)]. In the case of 0.1 mol dm^{-3} NaOH containing 0.1 mol dm^{-3} of MeOH, the photocurrent rises quite sharply with increasing potential in the anodic direction, reaching saturation with only 0.3 V of band bending [this rise is actually much more rapid than for the conventional sol/gel anatase electrode, Fig. 1(*a*)]. On the other hand, oxygen evolution from 0.1 mol dm^{-3} NaOH at the P25 TiO_2 electrode is strongly hindered, with the photocurrent reaching the saturation value very slowly. Surprisingly, the latter is about 20 times lower than the saturation photocurrent recorded in the presence of methanol [Fig. 1(*b*)]. This allows selective photo-oxidation of methanol from an aqueous solution, even at concentrations as low as 10^{-3} mol dm^{-3}, with virtually no photogeneration of oxygen. Other alcohols, and also formate ions, behave in an analogous way.

As both anatase[3] and rutile[6] forms of TiO_2 are known as efficient photoanodes for the oxidation of water, this observed inhibition of oxygen evolution can hardly be considered as an intrinsic property of the P25 powder material. A possible explanation might be the role played by the binder (PVDF), used for preparing powder TiO_2 electrodes, or by the residues of its decomposition, rendering the resulting films partially hydrophobic. To check this hypothesis, P25 TiO_2 films submitted to annealing treatments in air at various temperatures, were analysed by means of X-ray photoelectron spectroscopy (XPS). Decomposition of PVDF is known to start at *ca.* 375 °C and to be catalysed by TiO_2.[7]

In contrast with samples being annealed at 150 and 350 °C (in both cases for 1 h) which contained substantial amounts of

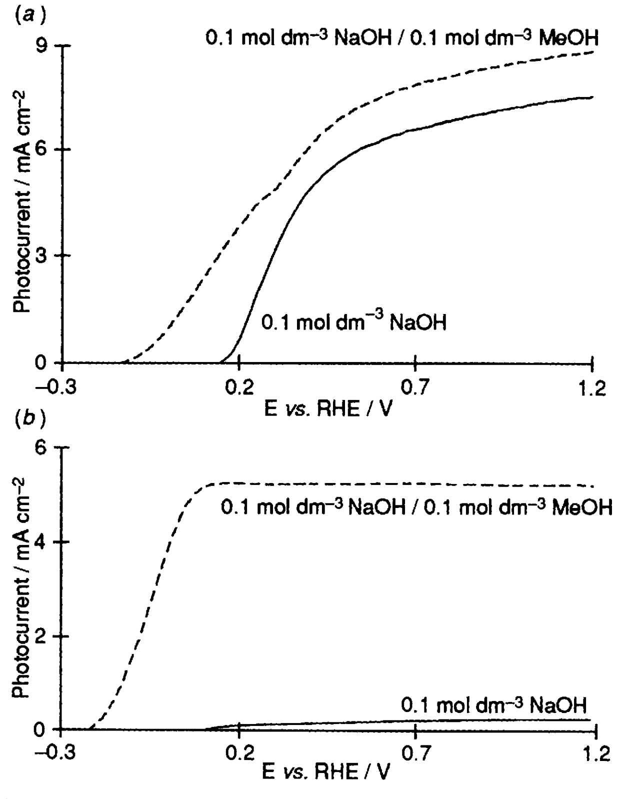

Fig. 1 Photocurrent *versus* applied potential curves for (*a*) a conventional anatase TiO_2 film and (*b*) a porous P25 TiO_2 film in 0.1 mol dm^{-3} aq. NaOH solution with and without addition of 0.1 mol dm^{-3} methanol. The electrodes were illuminated with the full output of a 150 W Xe lamp; potentials expressed *vs.* reversible hydrogen electrode (RHE) in the same solution.

fluorine (after treatment at 150 °C) and carbon (in both cases), those heated at 450 °C showed rather low concentrations of impurities. Although the surface of the sample treated at 450 °C displayed substantial carbon contamination (corresponding to C : Ti *ca.* 0.4), Ar^+ ion etching to remove a *ca.* 10 Å thick layer, decreased the C : Ti ratio to 0.02. The amount of fluorine present at the surface of this P25 TiO_2 film decreased slightly from the initial F : Ti ratio of 0.04 (before etching) to 0.03 after Ar^+ etching. However, no fluorine could be detected for the P25 TiO_2 sample being prepolarized under illumination in 0.1 mol dm^{-3} aq. NaOH, indicating possible leaching of the adsorbed HF.†

The absence of large amounts of residues from the decomposition of the PVDF binder makes it less probable that the hydrophobicity of the P25 TiO_2 films is the reason for their peculiar photoelectrochemical behaviour. In fact, as demonstrated by experiments performed with P25 TiO_2 films deposited on conducting glass substrates, the unusual selectivity of this kind of photoelectrode originates rather from differences in the interfacial charge transfer kinetics to MeOH and OH^-/H_2O species, respectively.

These measurements, carried out by illuminating consecutively both sides of the film, revealed, in the case of the 0.1 mol dm^{-3} NaOH solution, much larger photocurrents for back-wall electrode irradiation than those previously observed for front-wall irradiation. This kind of behaviour may be considered as typical of relatively thick (*i.e.* thicker than the mean penetration depth of the absorbed light) microporous nanocrystalline films[8,9] subject to large recombination losses. This is also a clear indication that the solution makes contact with individual TiO_2 particles inside the film, close to the back contact. Such a description is consistent with high resolution scanning electron micrographs of the P25 TiO_2 films showing a network of loosely packed interconnected particles *ca.* 30–40 nm in diameter. In contrast with the strong difference observed between the photocurrents recorded for back-wall and front-wall illumination of the P25 TiO_2 film in the 0.1 mol dm^{-3} NaOH solution, similar measurements performed in the presence of 0.1 mol dm^{-3} MeOH showed comparable (and still much larger than in the former case) photocurrents. These results may be explained by considering the ability of methanol to act as a particularly efficient scavanger for holes photogenerated in anatase TiO_2[5] and assuming, at the same time, a relatively slow interfacial hole transfer to OH^- ions and water molecules. Recently, Hodes *et al.*[8] postulated that, in the case of semiconductor films composed of non-sintered nanocrystals, the charge separation may occur because of differing rates of hole and electron transfer to the species in the solution, rather than a building up of conventional space-charge layer. The results presented in Fig. 1(*b*) for the nanocrystalline P25 TiO_2 film are apparently consistent with such a mechanism of charge separation, prompted to a large extent by the behaviour of colloidal suspensions of semiconductors. They also suggest a simple method for probing the activity of different photocatalysts by photocurrent measurements.

In this connection it is useful to recall that anatase-TiO_2 photocatalysts, and in particular the anatase-rich P25, display, in a large number of photo-oxidation reactions of organic compounds, much higher activity than rutile-TiO_2 powders.[10]

Experiments performed with a rutile-TiO_2 powder (Tioxide R-SM2), attached to the Ti support in the same way as described earlier for P25 TiO_2, showed practically no difference between the photocurrent–voltage curves recorded in 0.1 mol dm^{-3} NaOH solution with and without addition of methanol [the latter photocurrents were quite close to those observed under identical conditions for the P25 TiO_2 film in 0.1 mol dm^{-3} aq. NaOH, Fig. 1(*b*)]. The results obtained with the R-SM2 rutile and P25 anatase/(rutile) films, respectively, point to the fact that the photoresponse of nanocrystalline semiconductor films depends not on the kind of photooxidation (photoreduction) reaction but on the specific activity of a given photocatalyst *versus* a particular species in the solution.

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Footnote

† *Note added in proof.* Recently, similar results have been obtained using another polymer, poly(vinylidenechloride), PVDC, as a binder, instead of PVDF.

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