

Influence of precursors on the morphology and performance of TiO₂ photoanodes

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The preparation of TiO₂ photoanodes for dye-sensitized electrochemical devices was investigated. TiO₂ precursors with different rates of hydrolysis were used to modify the microstructures of the resulting TiO₂ photoanodes. The photoelectrochemical quantum yield for electrodes prepared from citrate remained low. Acetate precursors gave rise to electrodes with high fill factors and high open circuit voltages. Titanium isopropoxide hydrolysed very rapidly, leaving a powdery, poorly compacted deposit. Photoanodes from TiCl₄ precursors exhibit high surface roughness, which is necessary for a high degree of dye adsorption. With high hydrolysis rates, isopropoxide precursors produced powdery, poorly coherent films. A composite electrode with an acetate-based substrate and TiCl₄-based surface layers appears to be a suitable compromise.

1. Introduction

Semiconductor electrodes under illumination in contact with aqueous electrolytes operate in a very hostile environment. In consequence, those materials whose bandgaps match the solar spectrum, and therefore hold promise of efficient solar photoelectrochemical energy conversion, experience photocorrosion. Only wide bandgap materials, such as semiconducting metal oxides like TiO₂ and the titanates, are intrinsically stable under these conditions, but are relatively inefficient as energy conversion devices, being sensitive only to ultraviolet light. One response to this dilemma, the sensitization of wide bandgap semiconductors to the visible spectrum by surface-attached redox dyes, has been vigorously investigated in this laboratory. Several dye-sensitization systems, and the mechanism of operation, have been reported [1-3]. The excited state of the dye after absorption of a photon relaxes, by electron injection into the n-type semiconductor photoanode. Essential to the adsorption of a sufficient surface concentration of the dye to absorb the incident radiation effectively is the preparation of a rough or fractal semiconductor surface texture so that the effective surface is enhanced by some two orders of magnitude, compared to its geometric area. Light absorption is further promoted by the "anechoic" properties of this textured surface. The precise properties of a ceramic oxide film are of course significantly dependent on the precursors from which the material is prepared. Several such precursors and their effects on the microstructures and photoelectrochemical behaviour of TiO₂ films were investigated in the present work.

2. Ceramic precursors and preparation procedures

All semiconductor electrodes in this work were fabri-

cated on metallic titanium substrates. The metal foils were supplied by Siber Hegener Rohstoff AG, Zurich, (ASTM grade 2, thickness 0.05 cm). They were cut to size (4 cm²) and etched by boiling in 18% HCl for 30 min, rinsed with deionized water and stored under dry ethanol until use.

The precursor solutions for the preparation of TiO₂ films on the titanium substrates were prepared separately. The standard procedure in this laboratory used a titanium ethoxide synthesized from the chloride [3] and is mentioned here for comparison with the acetate, citrate and isopropyl precursors to be reported on. A solution of 4 g TiCl₄ (Fluka), freshly distilled, in 10 ml of absolute ethanol was prepared, then diluted with dry methanol to a concentration of 50 mg ml⁻¹. Applied dropwise to the substrate surface, the solution spread and as the solvent evaporated, hydrolysis of the ethoxide in an environment with a controlled humidity of 48% at 23 °C began, and TiO₂ was deposited. After a 30 min drying and hydrolysis period, the structure was heated in air for 20 min at 450 °C. The process was repeated up to 15 times to give a sufficiently thick semiconductor layer, up to 20 μm, with a highly irregular rough ("fractal") surface. The finished electrode was finally heat treated at 550 °C for 30 min in a reducing environment, under argon, so that the slight substoichiometry in oxygen which resulted would give a sufficient donor density for n-type semiconductive behaviour with low resistivity. The standard charge-transfer sensitizing dye was ruthenium tris(2,2'-bipyridyl, 4-4'-dicarboxylate) [4] which was chemisorbed by immersion of the electrode for 30 min in a 2 × 10⁻⁴ M aqueous solution of the dye at pH 3.5.

The alternative precursors for titanium dioxide deposition were prepared as follows.

1. Citrate precursor: 4 ml of titanium tetra iso-

propoxide (Aldrich) and 6.8 g of citric acid were added to 20 ml of absolute ethanol and refluxed for 45 min.

2. Acetate precursor: 4 ml of titanium tetra isopropoxide and 1.2 ml of glacial acetic acid were dissolved in 20 ml of absolute ethanol then refluxed for 45 min.

3. Isopropoxide precursors: 4 ml titanium tetra isopropoxide was dissolved in 20 ml of dry ethanol. As a variant, the isopropoxide was dissolved in a 20 ml mixture, equally of dry ethanol and methanol, acidified with 1 ml 18% HCl.

3. Photoelectrochemical characterization

All photoelectrochemical measurements were carried out in a single compartment three-electrode cell, with a Pt foil counter electrode and a saturated calomel reference electrode, under potentiostatic control. A 100 W tungsten-halide filament lamp was used as light source. A grating monochromator was available for investigation of the quantum efficiency of electron transfer from the photoexcited redox dye to the semiconductor substrate under a flux of monoenergetic photons in the visible region of the spectrum, normally $\lambda = 520$ nm, remote from the optical absorption edge of the semiconductor itself. Incident irradiation was measured with a silicon photodiode calibrated with reference to a radiometer (YSI Kettering model 65A) and confirmed by ferrioxalate chemical actinometry.

4. Electrode surface morphology

It is well known that the morphology of a ceramic surface is highly sensitive to the precursor and fabrication procedure employed. In the present case a high surface roughness is desirable, to chemisorb the maximum amount of redox sensitizer, yet if the structure is overly porous the permeation of the electrolyte to the interface with the metallic substrate could compromise the electronic behaviour of the device, in particular the rectifying effect at the semiconductor-electrolyte interface. The severe recombination losses normally associated with structural irregularities in photovoltaic and photoelectrochemical devices are not encountered in the visible spectrum response of the dye-sensitized system, since it functions by majority carrier injection and not as a minority carrier device like the conventional photocell.

The series of precursors for TiO_2 deposition was chosen because of the range of rates of hydrolysis, and consequently the different microstructures produced. Within the series, the citrate precursor exhibits the slowest hydrolysis, followed by the acetate. The chloride precursors, whether from TiCl_4 or acidified isopropoxide solutions are somewhat faster. Hydrolysis from the tetra isopropoxide solution in ethanol is most rapid, so that this preparation must be stored under an inert atmosphere if TiO_2 powder precipitation is to be avoided.

Citrate and acetate precursors give rise to very similar microstructures (Fig. 1). The layers are exten-

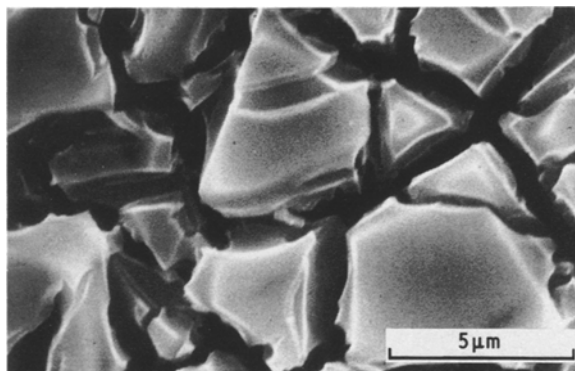


Figure 1 SEM micrograph of TiO_2 semiconductor layer deposited on a Ti substrate using an acetate precursor.

sively cracked but the individual flakes exhibit smooth surfaces. Visually these layers appear shiny, and the redox dye does not adsorb readily. As a result the quantum efficiency of the dye sensitized electrodes to visible light was low. Aluminium doping of the surface layer can, however, enhance dye adsorption. The technique for aluminium doping was a modification of the method reported by Augustynski *et al.* [5] in which 35 mg AlCl_3 was added to 5 ml of the precursor solution before use for the deposition of the last five layers. The citrate-based electrodes still gave only low quantum yields for electron transfer after dye chemisorption. With the acetate precursor, this procedure resulted in a quantum yield of 25%, with the relatively high fill factor of 75% and an open-circuit voltage of 1 V, using a Br^- - Br_2 redox couple (Fig. 2). Given the absorption spectrum of the dye, this only, however, represents a solar energy conversion efficiency of over 1% when exposed to daylight. The high open circuit voltage and low dark current demonstrate the good rectifying properties resulting from this formulation.

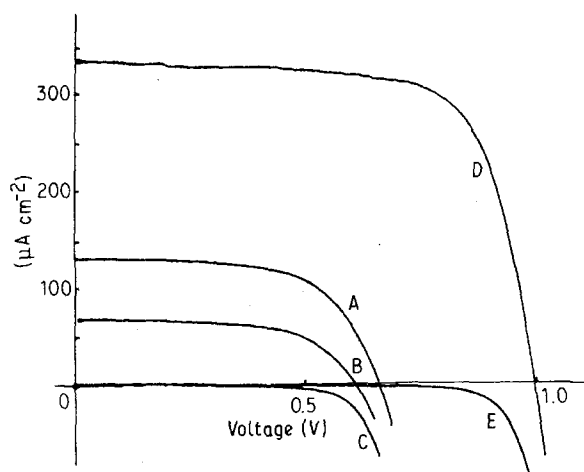


Figure 2 Current-voltage characteristics of sensitized TiO_2 anodes using a Br_2 - Br^- redox electrolyte in a regenerative photoelectrochemical cell. (a) Wide spectrum photoresponse of TiO_2 photoanode fabricated with an acetate precursor and sensitized using ruthenium tris (2,2'-bipyridyl, 4,4'-dicarboxylate). (b) Same electrode, visible (sensitized) response only: the ultraviolet component was suppressed using a 410 nm cut-off filter. (c) Same electrode, in darkness. (d) Aluminium-doped to $\frac{1}{3}$ of the layer thickness: wide spectrum photo-response. (e) Aluminium-doped electrode, in darkness.

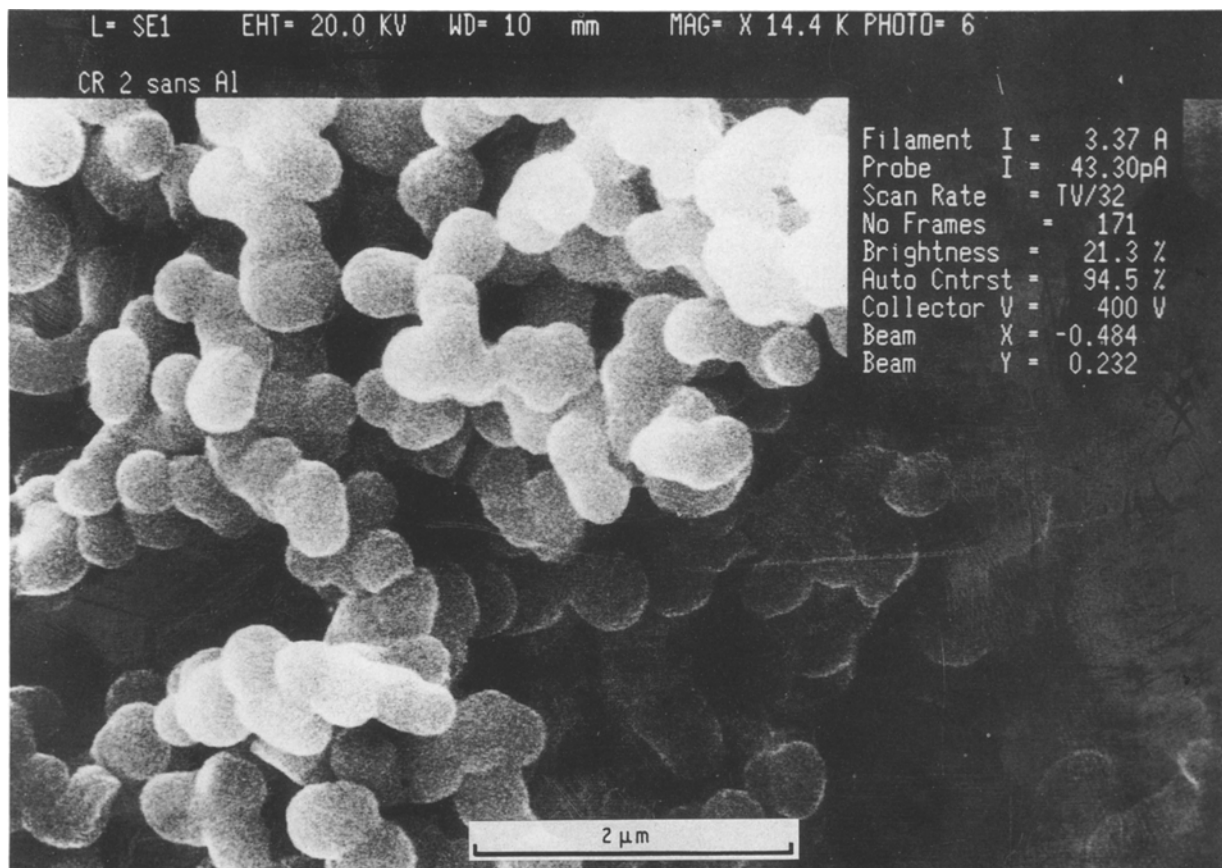


Figure 3 SEM micrograph of TiO_2 layer formed on a Ti substrate using a tetra isopropoxide precursor.

TiO_2 layers prepared from the standard TiCl_4 -based precursor differ from these already described in that, though cracked, the individual flakes are rough and the surface is visually matt. Dye absorption is enhanced in comparison with the undoped citrate or acetate-derived material, and quantum yields up to 75% have been observed [3].

The tendency of the tetra isopropoxide solution to hydrolyse rapidly, precipitating TiO_2 , is responsible for the morphology shown in Fig. 3. The structure evolved on the titanium substrate is powdery, loose and weakly interconnected, unsuitable for photoelectrochemical applications. In an attempt to produce a system with an intermediate rate of hydrolysis, the tetra isopropoxide was dissolved in a dry ethanol-methanol mixture and acidified with HCl. It was not surprising that the surface which resulted was very similar to that obtained with TiCl_4 in the same solvent mixture.

In all cases, the films are extensively cracked as a result of stresses generated during drying. Interestingly, this crack pattern is similar to the one reported for the drying of polymer particles on a glass plate shown by modelling to exhibit a fractal nature [6]. Under our preparation conditions, the hydrolysis-polymerization processes and the drying of the film are carried out concurrently. The resulting microstructure will be influenced by the relative kinetics of the drying and the hydrolysis-condensation processes. The structure derived from the acetate precursor (slow hydrolysis rate) can be likened to the one

obtained in the case of a gel, whereas the structure derived from the isopropoxide precursor (fast hydrolysis rate) resembles that of drying of a particulate film. An increase in the rate of hydrolysis resulted in a rougher microstructure as can be seen in the sequence, acetate, TiCl_4 in methanol-ethanol and isopropoxide in ethanol.

The particulate TiO_2 obtained in the case of the isopropoxide is reported to be constituted of aggregates of colloidal size particles and therefore their high surface area seemed amenable to good dye adsorption [7]. The extremely low processing temperatures used here, however, precluded their use as electrode materials. Longer sintering times at 550°C (up to 12 h), applied to acetate precursors, predictably led to smoother structures with good rectifying properties but with poor dye adsorbing properties.

5. Graded electrode structure

To exploit the advantages of each precursor, the electronic behaviour of the material derived from acetate and the high dye adsorptivity on a TiO_2 surface hydrolysed from a chloride solution, a graded multilayer device was fabricated. On a titanium substrate the first five layers were deposited from acetate, followed by seven from chloride (5%) precursors, the last of which was doped with aluminium in a ratio of one part to two of titanium. With this system a quantum efficiency for electron transfer from the dye to the electrolyte for $\lambda = 520$ nm photons was 45%.

Ongoing work can determine optimum temperatures for calcination and burnoff of organic residues and other processing parameters for each precursor, and ameliorate the fabrication of those graded structures.

The present task of optimizing the semiconducting ceramic film is paralleled by a similar effort to improve the absorption spectrum band width [8], chemisorption properties and quantum efficiency for charge injection [9] of the dyes. In particular, Enea *et al.* [9] report a quantum efficiency of 83% for the laser dye coumarin 343 (Kodak Co.) chemisorbed on TiO₂.

6. Conclusions

Precursors for the preparation of TiO₂ electrode structures with different rates of hydrolysis can give rise to widely different semiconductor morphologies. From an acetate precursor a semiconductor with superior electronic properties, high open-circuit voltage and fill factor with low dark current, is produced, but its photoelectrochemical performance was limited by poor adsorption of the dye sensitizer. Materials obtained from chloride precursors, also with aluminium doping, are more adsorbent. Graded structures to exploit these different advantages are possible.

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