

Photoelectrochemical Properties of Titanium Dioxide Electrodes Prepared from a Titanium-Aluminum Alloy

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ABSTRACT

Titanium dioxide electrodes, prepared from titanium-aluminum alloy on a titanium sheet, were examined for photosensitized processes using adsorbed dye molecules, and for photoanodic oxidation of water by direct bandgap excitation. For the photosensitized reactions, which employed ruthenium(II) tris(2-2'-bipyridine-4-4'-dicarboxylic acid) or the iron complex, Prussian blue, the alloy-derived electrode showed photocurrents one to two orders of magnitude higher than for an electrode prepared by oxidation of an unalloyed titanium sheet. Scanning electron micrographs suggest that the high efficiency of the alloy-derived electrode is due to the rough and cracked TiO₂ surface. However, for the water oxidation reaction, the differences were much smaller. The different behavior between the photosensitized reactions under sub-bandgap excitation and water photo-oxidation by direct bandgap excitation could be explained by the greater effectiveness of the rough electrode surface in utilization of the adsorbed dye molecules. For the alloy-derived electrodes, photosensitized currents were optimized by varying the temperature used to form the alloy and to oxidize the titanium sheet, and varying the extent of doping.

Photosensitization by electron transfer from an excited dye to a semiconductor electrode, such as titanium dioxide, has been widely studied as a method of solar energy conversion (1, 2). However, the photocurrent obtained is usually small because of the small amount of dye adsorbed on a semiconductor electrode with a low surface area (leading to poor absorption of incident light by the small number of adsorbed dye molecules). Some efforts have been made to produce oxide semiconductor electrodes with rough surfaces (3, 4). For example, Grätzel *et al.* have demonstrated highly efficient spectral sensitization of a titanium dioxide film electrode prepared by hydrolyzing titanium ethoxide (3). In the field of catalysis, high surface-area metal catalysts are prepared by first making an aluminum alloy of the metal and then leaching the aluminum in aqueous alkali solution (5). The purpose of the present work was to explore the preparation and properties of titanium dioxide layers in intimate contact with metallic titanium by using this approach.

Using visible light (sub-bandgap), we examined the photosensitized electron transfer reactions between the electrode and ruthenium(II) tris(2-2'-bipyridine-4-4'-dicarboxylic acid) or an iron complex, Prussian blue, as a function of electrode preparation conditions. The UV photoanodic oxidation of water over titanium dioxide itself (direct bandgap excitation) was also measured. The titanium dioxide electrodes were characterized by scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), energy dispersive x-ray analysis (EDX), and x-ray diffraction (XRD). The different behavior found for dye-sensitized and direct water photo-oxidation is discussed.

Experimental

Electrode preparation.—The aluminum-titanium alloy layer on the surface of a titanium sheet was prepared by heating, at selected temperatures in flowing Ar, an aluminum sheet (Johnson Matthey, purity: 99.999%; thickness: 0.5 mm) laid over a titanium sheet (Johnson Matthey, purity: 99.7%; thickness: 0.89 mm). The titanium sheet with a surface aluminum-titanium alloy or mixture was dipped in aqueous sodium hydroxide solution (2M, 500 ml) at 90°C for ca. 35h to leach the aluminum. After leaching, the resulting titanium sheet was washed with distilled water and oxidized in air at various controlled temperatures ($\pm 10^\circ\text{C}$). Al₃Ti, AlTi, AlTi₃, etc., are known alloy phases (6), and in

spatial regions rich in aluminum, Al₃Ti should be formed. By XRD (Philips, Cu K α , 35 mA, 20 kV) the formation of Al₃Ti, as well as a mixture of titanium and aluminum, was confirmed.

Attachment of sensitizing dyes.—Ruthenium(II) tris(2-2'-bipyridine-4-4'-dicarboxylic acid) (1) and Prussian blue (2) were used as photosensitizers. The ruthenium(II) tris(2-2'-bipyridine-4-4'-dicarboxylic acid) (PF₆) was synthesized according to a previous method (7). The complex was adsorbed on the titanium dioxide electrode by immersing the dried electrodes prepared as described above in an aqueous solution (5×10^{-5} M) of 1 at pH 3.5 (adjusted with hydrochloric acid) for ca. 6h. The adsorbed dye/TiO₂ electrode was then washed with aqueous HCl (pH 3). The adsorption of 1 on the TiO₂ powder has been examined in detail (8). The carboxyl group forms a strong ester-like linkage to the surface of the TiO₂ (9). The Prussian blue (2) was deposited on the surface of the TiO₂ electrode from aqueous potassium ferrocyanide solution (1×10^{-2} M) by irradiation of the electrode while scanning the electrode potential between +1.0 and -1.0V vs. standard calomel electrode (SCE). The mechanism for the deposition of 2 is unclear.

Photoelectrochemical measurements.—The photoelectrochemical measurements, using a potentiostat, were carried out in a cell with a flat window made of Pyrex, following degassing of the solution with argon for more than 30 min. A platinum counterelectrode (ca. 1 cm²) and a saturated calomel reference electrode were used. A Xe lamp (Hanovia 976C1010, 1000W) with a water-jacket filter was used as a light source.

The photosensitization of 1 TiO₂ was carried out in aqueous hydroquinone (0.1M) containing NaCl (0.1M), and KBr (0.1M). The photosensitization by 2 was carried out in aqueous hydroquinone, K₄Fe(CN)₆, and KBr solutions. The pH of the solutions was adjusted to 3 with HCl or HBr to prevent the desorption of 1. A cut-off filter ($\lambda > 420$ nm) was used in the photosensitized reactions to avoid direct excitation of the TiO₂ itself. Photoanodic oxidation of water at the TiO₂ electrode was carried out in aqueous NaOH (1M) using the full Xe lamp output (no filter).

Characterization of electrode.—The surface of the electrode was observed by scanning electron microscopy (SEM) (JEOL JSM-35C, magnification: x5000). EDX (KEVEX, ANALYST8000) was used to detect the Al residue remaining in the bulk of the TiO₂ electrode after leaching. The surface composition was examined by XPS (Vacuum-Generators). The samples for SEM, EDX, and XPS

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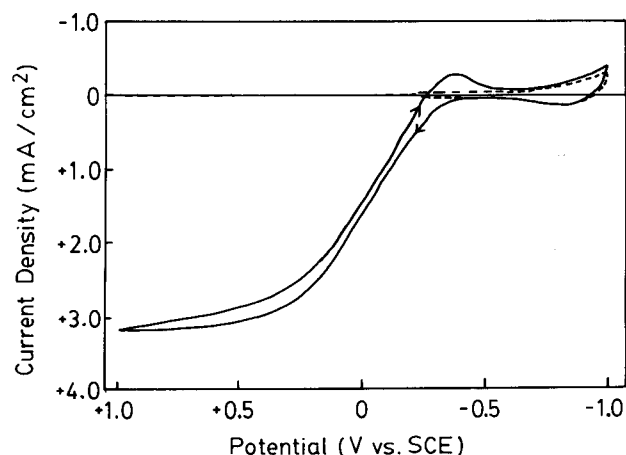


Fig. 1. Cyclic voltammogram for photosensitized process by ruthenium(II) tris(2-2'-bipyridine-4-4'-dicarboxylic acid) on titanium dioxide electrode prepared from alloy. Solid line: under irradiation; dashed line: dark; sweep rate: 25 mV/s; light source: 1 kW Xe lamp; irradiated area: 0.6 cm²; solution: HQ (10⁻¹ M) + NaCl (10⁻¹ M) + HCl (10⁻³ M); irradiated with light, $\lambda > 420$ nm.

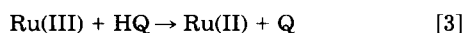
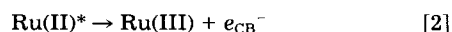
measurements were attached to the sample stage with graphite paste.

Results and Discussion

Photosensitized reactions.—An SEM photograph of the TiO₂ electrode prepared from the alloy showed a rough and cracked surface. However, the roughness factor, determined from the amount of dye adsorbed on the alloy-derived TiO₂ electrode (3), was less than 15 for every electrode, in spite of the rough appearance. No aluminum was detected by EDX, which gave information about the bulk and surface of samples, when the electrode was leached at 90°C, but significant amounts of aluminum were present for an electrode prepared by leaching at room temperature. Therefore, aluminum was leached at 90°C for all electrodes used in the experiments discussed below.

Typical cyclic voltammograms of photosensitized reactions are shown in Fig. 1, 2, and 3. Anodic dark currents were negligible in all cases, whereas cathodic dark currents were observed at potentials more negative than -0.7V. Similar cathodic currents were observed under irradiation. The cathodic currents on the alloy-derived electrode were much larger than those with electrodes prepared by oxidation of a Ti sheet (not from alloy), suggesting a high surface area for the alloy-derived TiO₂ electrode.

Upon photosensitization by **1**, the observed photocurrent became saturated at ca. 0.5V (SCE), as shown in Fig. 1. The cathodic photocurrent observed at -0.40 V is attributed to the reduction of an oxidized product formed in the photosensitization process. It was not observed under dark conditions. The appearance of this peak suggests some accumulation of oxidized ruthenium complex, revealing that the reduction of the oxidized species by the electron donor (hydroquinone), Eq. [3], is slower than the electron injection from the excited complex to the semiconductor electrode, Eq. [2]. Some hysteresis of the photoanodic current was observed, with the forward photoanodic current larger than the reverse. This also suggests the accumulation of oxidized species



Photosensitization by **2** is shown in Fig. 2. The photocurrent increased initially with scan number, when the TiO₂

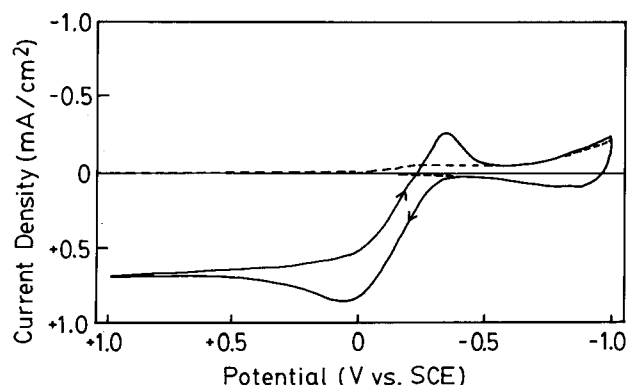
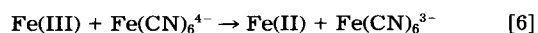
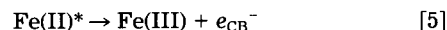


Fig. 2. Cyclic voltammogram for photosensitized process by iron complex on titanium dioxide electrode prepared from alloy. Solid line: under irradiation; dashed line: dark; sweep rate: 25 mV/s; light source: 1 kW Xe lamp; irradiated area: 0.6 cm²; solution: K₄Fe(CN)₆ (10⁻² M) + NaCl (10⁻¹ M) + HCl (10⁻³ M); irradiated with light $\lambda > 420$ nm.

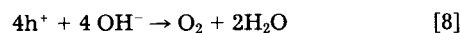
electrode was cycled in the Fe(CN)₆⁴⁻ solution, but then it stabilized. A blue material, assumed to be Prussian blue, was deposited on the TiO₂ electrode during the cycling. The sensitized photocurrents were enhanced by its deposition, suggesting that Prussian blue deposited on the TiO₂ electrode behaved as a photosensitizer. The use of Prussian blue for visible light sensitization has been reported previously (10). The electrodeposition of Prussian blue onto a Pt electrode from FeCl₃ and K₃Fe(CN)₆ at pH 2 at a bias of +0.5V (SCE) has also been reported (1). In the present work, however, the photoreaction of Fe(CN)₆⁴⁻ apparently results in the deposition of **2** on the TiO₂ electrode surface, because it did not deposit in the dark under the same electrochemical conditions. A Prussian blue-type complex is also known to form by reaction of Fe(CN)₆⁴⁻ with colloidal TiO₂ (12).

The maximum photocurrent was obtained at +0.05V (SCE) for the photosensitization by **2**. As with **1**, some hysteresis is observed. Again, the cathodic current -0.35V can be explained by the reduction of iron complex oxidized during the irradiation, with some accumulation of the oxidized species, Eq. [5]. The reduction of the oxidized iron complex by Fe(CN)₆⁴⁻, Eq. [6], is also a slow process in this case



The onset potential for the photoanodic current is ca. 0.02V more positive for the iron complex than for the ruthenium complex. Alternatively, the cathodic current observed may be caused by oxidized solution donor [Q or Fe(CN)₆³⁻] at or near the electrode surface.

Direct bandgap excitation.—Little hysteresis was observed for the photo-oxidation of water by direct bandgap excitation, as shown in Fig. 3, because this process does not involve the reduction of oxidized sensitizers or sacrificial donors. In this case



Effect of alloy preparation conditions.—The dependence of the photocurrent on the temperature employed during the synthesis of the alloy is summarized in Table I. The photocurrent for the sensitized reaction by adsorbed dye depended strongly on the preparation temperature, while that for the photoanodic oxidation of water by direct bandgap excitation (line 6 of Table I) was less affected. For photosensitized reactions, the highest photocurrents were obtained when the alloy was formed at 670°-680°C, near the melting point of aluminum metal (660°C). This best

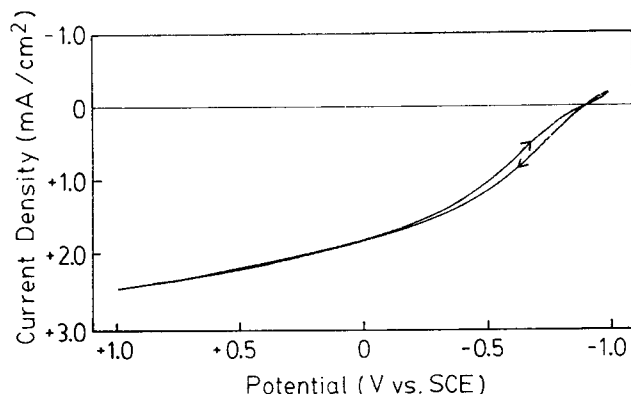


Fig. 3. Cyclic voltammogram for photo-oxidation of water by titanium dioxide electrode prepared from alloy. Sweep rate: 25 mV/s; light source: 1 kW Xe lamp; irradiated area: 0.6 cm²; solution: NaOH (1M); irradiated with full Xe lamp output (no filter).

photocurrent was 10-100 times larger than that obtained for a titanium dioxide electrode prepared by oxidation of an unalloyed Ti sheet. For example, the photocurrent with 1 on the alloy-derived electrode was 16 times higher than that on the oxidized titanium sheet (line 2 on Table I). This value corresponds well to a roughness factor of ca. 15, as determined from the amount of the ruthenium complex adsorbed. However, the surface area of the alloy-derived electrode appeared to be much larger, as observed by SEM. Thus, the ruthenium complex does not appear to have covered the whole surface. On the other hand, the photocurrent with 2 on the alloy-derived electrode was 100 times higher than that on the oxidized titanium sheet (line 1 on Table I), suggesting that the iron complex covered most of the surface. An alloy electrode prepared at 620°C did not produce good sensitized photocurrent response, because the preparation temperature was not high enough to form a sufficiently thick alloy layer. The photocurrents at this electrode were about the same as those on a non-alloy-derived one. On the other hand, for alloys prepared at very high temperatures, the photocurrent decreased with an increase in preparation temperature for the photosensitized reactions, but not for water photo-oxidation.

The preparation temperature affects the thickness of the alloy and mixture layer, and a higher preparation temperature enhances the diffusion of aluminum into the bulk of the titanium sheet. No metallic titanium was detected by XPS measurement, *i.e.*, the surface was fully oxidized to Ti(IV) (2p_{3/2}, binding energy: 458.9 eV), to a thickness sufficient (>3 nm) to remove signal from the underlying

Table I. Dependence of observed photocurrent on alloy preparation temperature

| Solution | Sensitizer | Photocurrent ^a (mA/cm ²) | Temperature to make alloy (°C) | | | |
|---|------------|---|--------------------------------|------|------|-------|
| | | | Non-alloyed ^b | 620 | 670 | 680 |
| K ₄ Fe(CN) ₆ ^c | <u>2</u> | 0.005 | 0.007 | 0.50 | 0.40 | 0.04 |
| | <u>1</u> | 0.20 | 0.15 | 3.3 | 2.3 | 0.13 |
| HQ ^d | <u>2</u> | 0.013 | 0.013 | 0.95 | 0.6 | 0.03 |
| | <u>1</u> | 0.02 | 0.03 | 1.0 | 0.3 | 0.02 |
| KBr ^e | <u>2</u> | 0.002 | 0.002 | 0.03 | 0.01 | 0.003 |
| | <u>1</u> | 0.02 | 0.03 | 1.0 | 0.3 | 0.02 |
| NaOH ^f | none | 0.6 | 0.5 | 1.8 | 2.2 | 2.3 |

^a Light source: 1 kW Xe lamp; heating time at the listed temperature: 30 min; oxidation temperature: 720°C.

^b The titanium dioxide electrode was prepared by oxidation of titanium sheet (no alloy).

^c Solution: K₄Fe(CN)₆ (10⁻² M) + NaCl (10⁻¹ M) + HCl (10⁻³ M); irradiated light: λ > 420 nm; photocurrent: at 0.05V vs. SCE.

^d Solution: HQ (10⁻¹ M) + NaCl (10⁻¹ M) + HCl (10⁻³ M); irradiated light: λ > 420 nm; photocurrent: at 0.3V vs. SCE.

^e Solution: KBr (10⁻¹ M) + HBr (10⁻³ M); irradiated light: λ > 420 nm; photocurrent: at 0.3V vs. SCE.

^f Solution: NaOH (1M); irradiated light: full arc (no filter); photocurrent: at 0.3V vs. SCE.

Table II. Dependence of observed photocurrent on heating time to make the alloy

| Solution | Sensitizer | Photocurrent ^a (mA/cm ²) | | |
|---|------------|---|------|------|
| | | Heating time (min) ^b | | |
| | | 10 | 30 | 60 |
| K ₄ Fe(CN) ₆ ^c | <u>2</u> | 0.85 | 0.50 | 0.17 |
| | <u>1</u> | 3.0 | 3.3 | 1.3 |
| HQ ^d | <u>2</u> | 2.2 | 0.95 | 0.20 |
| | <u>1</u> | 0.80 | 1.0 | 0.37 |
| KBr ^e | <u>2</u> | 0.05 | 0.03 | 0.01 |
| | <u>1</u> | 2.1 | 1.8 | 1.0 |
| NaOH ^f | none | | | |

^a Light source: 1 kW Xe lamp.

^b The temperature to make the alloy was 670°C and the oxidation temperature was 720°C.

^c Solution: K₄Fe(CN)₆ (10⁻² M) + NaCl (10⁻¹ M) + HCl (10⁻³ M); irradiated light: λ > 420 nm; photocurrent: at 0.05V vs. SCE.

^d Solution: HQ (10⁻¹ M) + NaCl (10⁻¹ M) + HCl (10⁻³ M); irradiated light: λ > 420 nm; photocurrent: at 0.3V vs. SCE.

^e Solution: KBr (10⁻¹ M) + HBr (10⁻³ M); irradiated light: λ > 420 nm; photocurrent: at 0.3V vs. SCE.

^f Solution: NaOH (1M); irradiated light: full arc (no filter); photocurrent: at 0.3V vs. SCE.

metal. This was the case even for samples which were not heated in air, because the surface prepared by this method is easily oxidized as soon as it is exposed to air or water. Aluminum(III) (2p, B.E.: 74.2 eV) was detected only after heat-treatment in air. We suppose that the aluminum, which had diffused into the titanium during alloying, came to the surface and formed a partial aluminum oxide coverage when the titanium sheet was oxidized in air. As the temperature of the alloy preparation increased, more aluminum diffused into the titanium sheet, and even after leaching, the ratio of Al to Ti in the sub-surface region increased. The dependence of the photocurrent on the alloy preparation temperature was generally similar for 1 and 2. However, the latter complex showed smaller photocurrents in an aqueous KBr solution, perhaps because the iron complex oxidized in the photosensitized process had an insufficiently positive potential to oxidize bromide ion to bromine.

The photocurrent increased by a factor of about 3 when the electrodes were reduced at 500°C under flowing argon or hydrogen to make them more conductive. As shown in Table II, the observed photocurrents tended to be higher when the alloy preparation involved shorter heating times at 670°C. This suggests that thick alloy layers and extensive aluminum diffusion into titanium are undesirable.

The effect of oxidation temperature is shown in Table III. The oxidation temperature affects the formation rate, morphology, and thickness of the TiO₂ layer. The best sensitized photocurrents were obtained with an electrode oxidized at 650°C, and the best rate for the unsensitized ox-

Table III. Dependence of observed photocurrent on oxidation temperature

| Solution | Sensitizer | Photocurrent ^a (mA/cm ²) | | | | | |
|---|------------|---|-------|------|------|------|-------|
| | | Oxidation temperature (°C) ^b | | | | | |
| | | 25 | 300 | 500 | 650 | 700 | 750 |
| K ₄ Fe(CN) ₆ ^c | <u>2</u> | 0 | 0.002 | 0.01 | 0.35 | 0.30 | 0.035 |
| | <u>1</u> | 0.01 | 0.01 | 2.0 | 2.5 | 1.3 | 0.23 |
| HQ ^d | <u>2</u> | 0.004 | 0.003 | 0.2 | 0.8 | 0.26 | 0.05 |
| | <u>1</u> | 0.05 | 0.1 | 0.4 | 1.4 | 3.0 | 0.73 |
| KBr ^e | <u>1</u> | | | | | | |
| NaOH ^f | none | | | | | | |

^a Light source: 1 kW Xe lamp.

^b The temperature and the heating time to make the alloy were 670°C and 10 min, respectively. The oxidation time was 30 min.

^c Solution: K₄Fe(CN)₆ (10⁻² M) + NaCl (10⁻¹ M) + HCl (10⁻³ M); irradiated light: λ > 420 nm; photocurrent: at 0.05V vs. SCE.

^d Solution: HQ (10⁻¹ M) + NaCl (10⁻¹ M) + HCl (10⁻³ M); irradiated light: λ > 420 nm; photocurrent: at 0.3V vs. SCE.

^e Solution: KBr (10⁻¹ M) + HBr (10⁻³ M); irradiated light: λ > 420 nm; photocurrent: at 0.3V vs. SCE.

^f Solution: NaOH (1M); irradiated light: full arc (no filter); photocurrent: at 0.3V vs. SCE.

idation of water was obtained for an electrode oxidized at 700°C. When the electrode was oxidized at low temperatures (<300°C), the photocurrents were very small for all reactions, showing that such temperatures are insufficient to form a TiO₂ layer with sufficient thickness and crystallinity. If the oxide layer is too thin, charge separation will not be rapid enough to compete with recombination (or quenching by oxidized dye), because the space charge layer will be too thin and the band bending too small. On the other hand, oxidation at high temperatures is detrimental, presumably because the resistive oxide layer becomes too thick and because morphological fine structures, such as small pores, which produce a rough surface area, are destroyed by sintering and crystallization. Moreover, high temperatures also enhance the segregation of aluminum and the formation of aluminum oxide at the surface.

The development of a high-surface-area electrode is clearly more important for the sensitized oxidation of ferrocyanide, bromide, and hydroquinone than it is for the oxidation of hydroxide using bandgap light. This is so because the high-surface-area electrodes accommodate more sensitizer molecules per unit area and can therefore absorb a greater fraction of the incident visible light. Table I shows that the efficiency of the sensitized reaction is strongly dependent on alloy preparation temperature and that the best alloy composition represents a ca. sixteenfold improvement over a non-alloy electrode.

On the other hand, the ratio of photocurrents (best alloy vs. non-alloy) is only about 4 for the non-sensitized oxidation of hydroxide ion. For direct excitation the surface area is less important, since the total number of electron-hole pairs generated by the light beam depends only on beam intensity. A greater surface area will generate a larger number of carriers near the interface with the liquid, thus causing a small increase in photocurrent, but not to the extent of a photosensitized reaction, where there is a large increase in the number of excitation centers within the light beam.

Summary

In an effort to increase the effective surface area of photoelectrodes, a TiO₂ electrode was prepared from a titanium-aluminum alloy on a titanium sheet. Photosensitized currents, using ruthenium(II) tris(2-2'-bipyridine-4-4'-dicarboxylic acid) and the iron complex, Prussian blue, and the photoanodic oxidation of water, were measured using the electrode. For the photosensitized reactions, the alloy-derived electrode showed photocurrents one to two orders of magnitude higher than a lower surface-area electrode prepared by oxidation of the titanium sheet, although these were smaller than those found with

the TiO₂ preparation of Grätzel *et al.* (3). For the water oxidation reaction via direct bandgap excitation, the differences were much less. For the photosensitized process, alloying near the melting point of aluminum (670°C) and subsequent oxidation at 650°C, for times no longer than 30 min, gave the best results. Doping with Ti³⁺, by partial surface reduction in hydrogen and argon, at 500°C, was beneficial.

Acknowledgments

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