# Production of Polycrystalline *n*-$TiO_2$-Layers for Photoelectrochemical Purpose

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The preparation of highly photoactive, polycrystalline *n*-$TiO_2$-semiconductors by thermochemical oxidation of Titanium metal sheets was investigated systematically. The optimum temperature in an oxygen atmosphere was found to be between 550 °C and 650 °C for a period of 10–30 min. Careful etching of the Titanium surface prior to oxidation is a decisive step in the production process. The growth, adhesion on the substrate and photoefficiency of the $TiO_2$-crystals were studied under various experimental conditions. $TiO_2$-layers prepared under optimum conditions showed a photocurrent higher than 2 mA · cm$^{-2}$ in 0.1 mol · dm$^{-3}$ KCl as electrolyte and about 6 mA · cm$^{-2}$ in 1 mol · dm$^{-3}$ KOH, respectively. The overall energy conversion was $\eta \cong 3.5\%$.

## 1. Introduction

Since the discovery by Fujishima and Honda [1] that single crystals of *n*-$TiO_2$ (rutil) used as photoanode are able to split water under the influence of light, intensive search for other suitable semiconductors has been made [2, 3]. However, $TiO_2$ has still some special qualities to offer, i.e. its remarkable stability in aqueous electrolyte solutions and its possible use in dye sensitized photoelectrolytic cells [4–6] and for photooxidation processes [7–9]. Most of these investigations were performed with $TiO_2$ single crystals. Single crystals are, however, much too expensive to be applicable for practical purposes on a large scale. Photoactive polycrystalline films of $TiO_2$ offer the advantage to be cheaper in preparation and reliable as well. Various methods for the production of such films have been suggested, e.g. by electrochemical oxidation of Titanium metal sheets [10, 11], molecular plating [12], plasma jet spraying [13, 14], chemical vapour deposition [5, 15] and thermal oxidation of Ti-foils [12, 16, 17]. Layers of pressed and sintered $TiO_2$ powder have also been used for this purpose [17]. Although all these methods yield $TiO_2$-films with reasonable photoactivity, their mechanical adhesion on the Ti-sheet and long time stability against corrosion are still not always satisfying [11, 12]. The main interest of the work mentioned above lay in the semiconductor properties of *n*-$TiO_2$-films, while the technological and metallurgical criteria of this matter were less emphasized.

It is well known that various factors are authoritative in the production of $TiO_2$-layers of Ti-foils [18–21]: e.g. pretreatment and etching of the metal foil, temperature and duration of heating and the partial pressure of oxygen during the oxidation process. In the present paper the role of these factors in the production of photosensitive $TiO_2$-layers is examined. Furthermore, the work includes testing of representative *n*-$TiO_2$-samples with regard to their mechanical stability, photoactivity and corrosion effects during long time operation in cells. Some preliminary results of this topic have already been published [22].

## 2. Experimental

### 2.1. *Production of n-$TiO_2$ Electrodes*

The Ti-sheets (Goodfellow Metals, Cambridge, G.B.) consist of 99.7% Ti with 0.3% unspecified metallic traces. Metal foils of 0.25 mm thickness and 3 × 2 cm$^2$ size were cleaned in an ultrasonic bath with destilled water, methanol, trichloroethylene and again methanol. The samples were air dried between each washing step. If not stated otherwise, the foils were then etched with Kroll's acid (20% HF, 30% $HNO_3$, 50% $H_2O$) and rinsed with destilled water. This cleaning procedure turned out to be the most efficient one for the production of photoactive semiconductors. The cleaned sheets were then introduced into a quartz tube immediately, evacuated and heated in a

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thyristor steered oven. The gas atmosphere was created by a steady flow of air or oxygen through the tube at normal pressure. In a series of experiments the air was evacuated upto $5 \times 10^{-2}$ Torr prior to heating. The heating temperature was varied between 400 and 1100 °C, the heating time between 1 and 180 min. 4 series of samples were investigated, as presented in Table 1.

The inscriptions in the following Figures conform with the numbers of the series in Table 1. Some of the produced thicker oxide films were reduced subsequently in hydrogen atmosphere at 650 °C or 750 °C upto 4 hours in order to reduce their ohmic resistance.

### 2.2. *Testing Procedures*

The produced $TiO_2$-electrodes were illuminated as anode in an irradiation vessel by means of a 300 Watt Xe-lamp (Varian Eimac R-300-2) in an electrolyte of 0.1 $mol \cdot dm^{-3}$ KCl or 1 $mol \cdot dm^{-3}$ KOH (p.A.Merck AG). The front window of the vessel was made of Pyrex glass in order to cut off light with wavelengths below 300 nm. A plastic mask was constructed to allow an illumination of an area of 1 $cm^2$. A Pt-sheet (6 $cm^2$) served as cathode and a saturated Kalomel electrode (Radiometer K 701) as reference. The voltammetric curves were registered by means of a wave generator, which superposes a triangle potential to a potentiostat (sweep 10 mV/sec) in combination with an X-Y recorder.

The light intensity ($I_0$) at 300 nm was determined by chemical actinometry [23]. The quantum efficiency ($Q_e$) of each individual $TiO_2$-electrode was measured as a function of the number of electrons ($N(e)$) flowing in the external circuit and the number of incident photons ($I_0$) [17]:

$$Q_e = N(e)/I_0 . \tag{1}$$

Table 1. Experimental conditions for the production of $n$-$TiO_2$ layers by thermal oxidation of Titanium metal foils.

| Series | Etching | Atmosphere | Temper. (°C) | Time (min) |
|---|---|---|---|---|
| 1 | yes | oxygen | 400– 800 | 10–180 |
| 2 | yes | air | 600–1000 | 1–120 |
| 3 | no | air | 600–1100 | 10–120 |
| 4 | yes | air<br>($5 \times 10^{-2}$ torr) | 600–1100 | 10–120 |

The integrated flux ($\Phi$) of the Xe-lamp was determined regularly under the same geometrical arrangement as the $TiO_2$-anode by means of a thermopile (Kipp & Zonen). Its mean value was found to be $\Phi = 11.6 \pm 1.5$ J. $cm^{-2} \cdot s^{-1}$. The energy conversion efficiency ($\eta$) [24] is defined as the ratio of electrical energy ($U\,i$) and incident light energy ($\Phi$) per unit area. The ohmic resistance (R) of the titaniumoxide film was measured in 0,1 m KCl by the method described below for thickness measurements. The current density ($i$) was taken from the voltammetric curves at zero bias:

$$\eta = U\,i/\Phi = R\,i^2/\Phi . \tag{2}$$

The thickness of the oxide films in μm was measured by a self designed phasesensitive impedance bridge and standardized by use of a step height method (Dektak, Sloane Instruments)*.

## 3. Results and Discussion

### 3.1. *Effect of Pretreatment, Heating and Temperature on the Thickness of the $TiO_2$-films*

In order to examine whether a relationship between the thickness of the $TiO_2$-layer and the photoactivity exists, it was first necessary to study the $TiO_2$-crystal growth on Ti-foils under various conditions. In Fig. 1 the Arrhenius plots of the $TiO_2$-crystal growth for typical samples produced in air or oxygen (heating time 10 or 60 min), as given in Table 1, are shown. The nonlinearity of some curves indicates a complicate oxidation mechanism. From the slope of the curves a mean value for the activation energy of about 50 kcal ($2.1 \times 10^5$ J) was calculated, which is in good agreement with previously reported data [19, 20]. This can be ascribed to the temperature dependence of the diffusion coefficient of $O_2$ in $TiO_2$ [20]. It might be mentioned that the oxide growth on Ti-metal foils has previously been investigated [18, 21], but only with respect to the mechanism of thermal oxidation. The growth of the $TiO_2$-layer is strongly dependent on the partial pressure of oxygen and heating time, as can be seen from Figure 2. In oxygen atmosphere the obtained thickness is about one order of magnitude higher than in air under else identical conditions. The growth of the oxide layer of pretreated samples follows a parabolic law in the investigated temperature region, as expected (curve 1, insert in Figure 2).

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* We thank Dr. K. Riedling for valuable help.

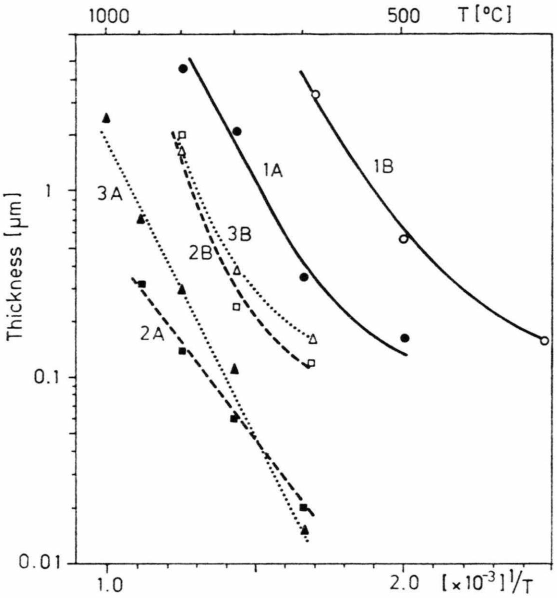

Fig. 1. Arrhenius plots of the growth of the $TiO_2$-layers under various conditions.
Curves A ... 10 min heating time;
curves B ... 60 min heating time.

For the meaning of the numbers at the curves here and in the following figures see Table 1.

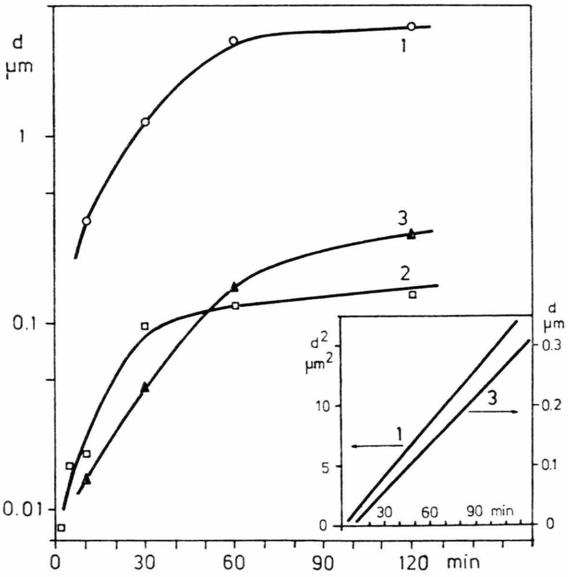

Fig. 2. Correlation between the $TiO_2$-layer thickness (*d* in µm) and the period (min) of thermal oxidation at 600 °C. *Insert:* Relationship between heating time and the square of the thickness for curve 1 and the thickness for curve 3, respectively.

Unetched probes, however, seem to follow a linear kinetic law, surprisingly (curve 3, insert in Figure 2). This behaviour was not investigated further, since these samples have proved to be not stable mechanically.

Samples oxidated in air at $5 \times 10^{-2}$ Torr have oxide layers of less than 0.05 µm and are therefore not presented in the Figures. From the data shown in Figs. 1 and 2 is obvious that the thickness of the $TiO_2$-films depends very much on the parameters of the oxidation procedure.

### *3.2. Production Parameters Affecting the Photocurrent*

The photocurrent, measured potentiostatically at zero bias, shows a remarkable dependence on heating temperature and time, as well as on the gas atmosphere, as Fig. 3 and Fig. 4 demonstrate. The highest photocurrent was achieved with samples produced from etched metal surfaces by heating in pure oxygen at 550–650 °C for about 30 min. Since the rate determining step of the oxidation process is the phase boundary reaction at the metal/oxide-interface, a variation of oxygen

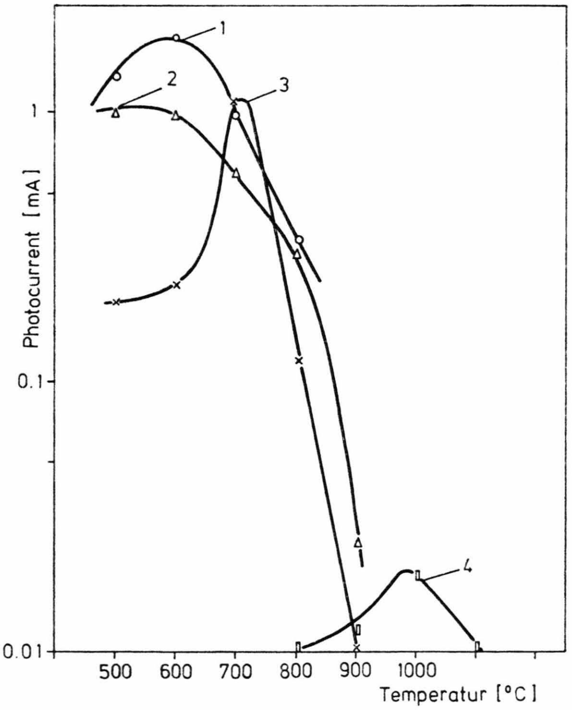

Fig. 3. Photocurrent as a function of heating temperature at 10 min heating time.

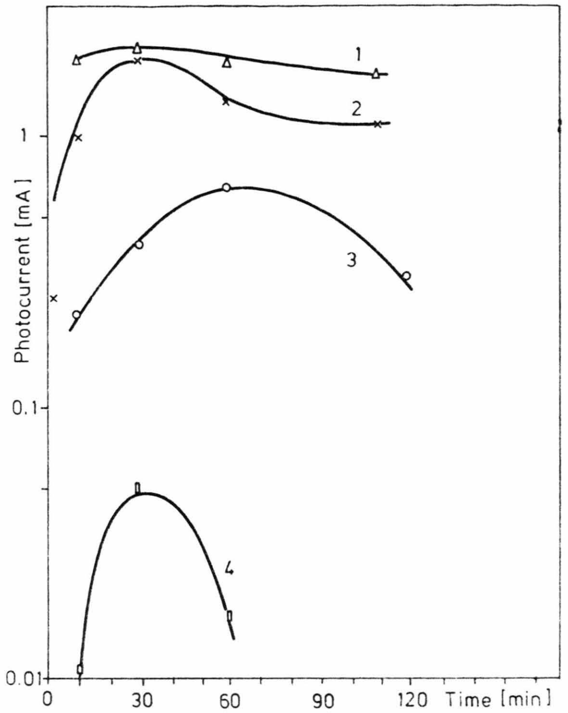

Fig. 4. Photocurrent ($i$ in mA/cm$^2$) as function of heating time (min) at 600 °C.

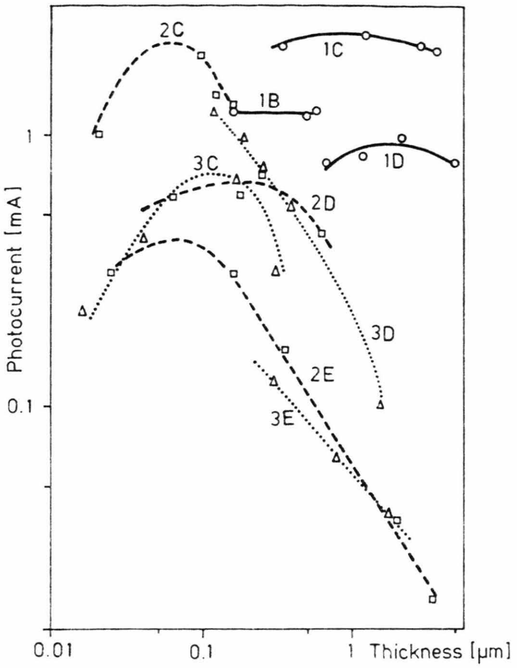

Fig. 5. Photocurrent vs. thickness of TiO$_2$-layers obtained at various temperatures: $B = 500$ °C, $C = 600$ °C, $D = 700$ °C, $E = 800$ °C.

concentration and pressure does have a remarkable effect on the growth and the properties of the TiO$_2$-layer (compare curves 1 and 4 in Figs. 3 and 4). The oxide-films obtained at reduced air pressure ($5 \times 10^{-2}$ Torr) were indeed very thin ($d < 0.05$ µm) and showed the lowest photocurrent (curve 4 in Figs. 3 and 4). They appear to get a very beautifully crystallized structure with increasing temperature which, however, consists of recrystallized Ti metal [25].

Photocurrents of thermochemically produced $n$-TiO$_2$ anodes vs. thicknesses are presented in Figure 5. Again, the oxide films obtained by etching of the metal surface and subsequent heating in oxygen at 600 °C (curve 1C, Fig. 5) showed a photocurrent of more then 2 mA in a broad thickness range ($d = 0.2-5$ µm). The unetched samples resulted in oxide layers, of which the thickness and the oxidation parameter exerted an enormous influence on their photoactivity (compare e.g. curve 2C with 3C, Figure 5).

The TiO$_2$-films produced at temperatures above 800 °C and long heating time are relatively thick and possess higher ohmic resistance. It was established that the observed decrease of the photocurrent of such samples corresponds to the increased resistance. An improvement upto some extent could be achieved by reduction of the oxide layer in H$_2$-atmosphere at about 600—800 °C for 4 hours.

An important factor for practical application of TiO$_2$-films as photoanode is the adhesion of the oxide layer to the Titanium sheet. For unetched probes this adhesion is rather bad, since oxide layers thicker than 0.5 µm flake off easily. After removing this "first" oxide layer of about 1 µm a "second", very thin and strongly adhesive layer ($d \simeq 0.05$ µm) is left below. The photocurrent is usually increased by this procedure from about 0.1 mA to $> 1$ mA/cm$^2$.

The etched Ti-sheets oxidized in oxygen atmosphere carried oxide layers stable upto $d = 2$ µm, which couldn't be removed by simple scratching of the surface and showed the highest photocoefficiency obtained in this work. From the results in Figs. 6 and 7 it is obvious that a comparatively wide range of heating temperatures (about 550—650 °C, Fig. 6) as well as of oxidation times exists (10—30 min, Fig. 7), where TiO$_2$-anodes with appreciable photocurrent can be produced.

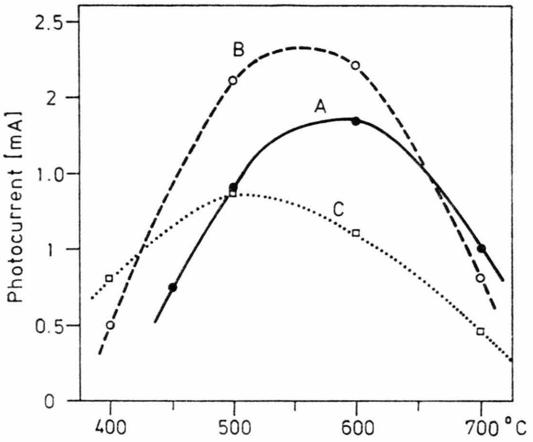

Fig. 6. Photocurrent (mA) of $TiO_2$-anodes produced by thermochemical oxidation in pure oxygen (series 1) of Titanium sheets at various temperatures for different heating times: $A = 10$ min, $B = 30$ min and $C = 120$ min. Electrolyte: 0.1 mol · $dm^{-3}$ KCl.

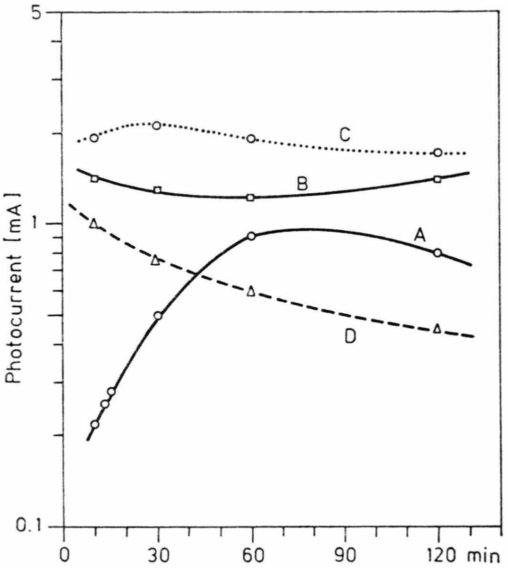

Fig. 7. Photocurrent (mA) of $TiO_2$-anodes (series 1) as a function of heating time (min) of their production at various temperatures: $A = 400$ °C, $B = 500$ °C, $C = 600$ °C and $D = 700$ °C. Electrolyte: 0.1 mol · $dm^{-3}$ KCl.

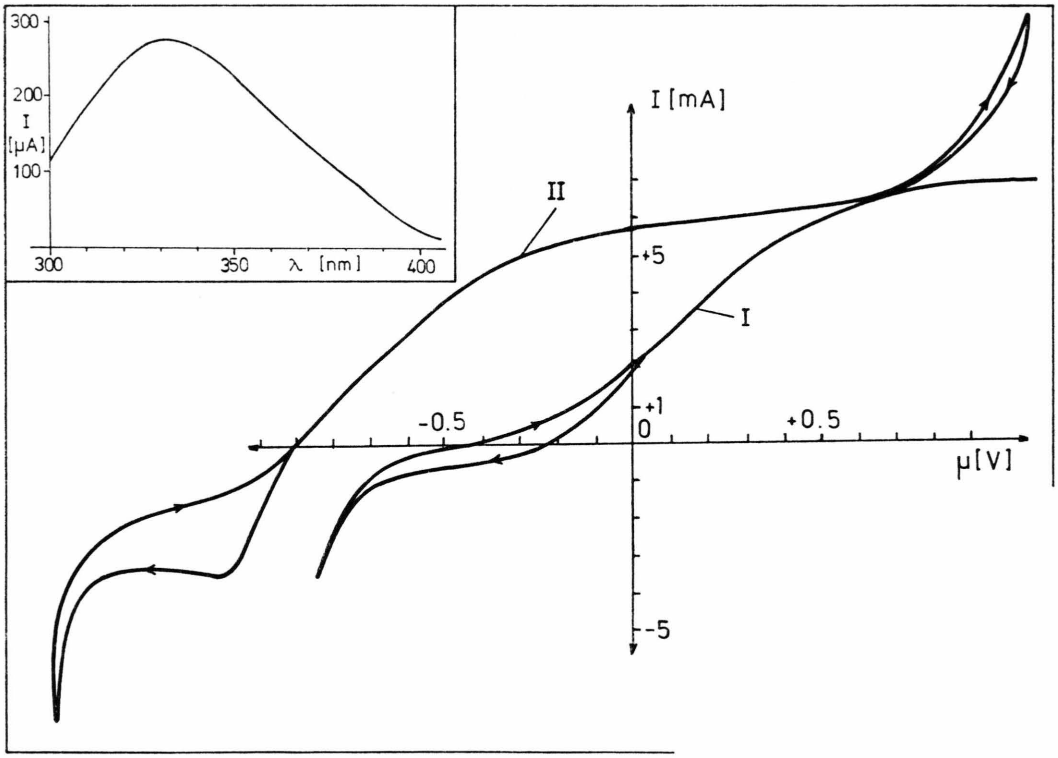

Fig. 8. Current vs. potential for a sample of series 1 (600 °C, 30 min, 02), curve I for 0.1 mol · $dm^{-3}$ KCl, curve II for 1 mol · $dm^{-3}$ KOH.

*Insert:* Current vs. wavelength of incident light for the same sample ($d = 2$ μm) in 0.1 mol · $dm^{-3}$ KCl (corrected for lamp intensity-monochromator spectral variations).

In addition to the above presented data also voltametric measurements were performed practically from each sample. A typical voltametric curve for a $TiO_2$-film, produced by careful oxidation of Ti-sheet at 600 °C (30 min, $O_2$ atmosphere) is presented in Figure 8. The photocurrent of the same samples measured in 1 mol · $dm^{-3}$ KOH is about 6 $mA/cm^2$ as compared with 2 mA in 0.1 mol · $dm^{-3}$ KCl as electrolyte. In the insert of Fig. 8 the photocurrent ($I$ in $\mu$A) of same samples is given as a function of the wavelength of the incident light. The highest $I$-value was obtained at the range of 330–340 nm.

Finally it is to be mentioned that the mean value of the quantum efficiency ($Q_e$) for the samples of series 1 was about 0.55 (not corrected for reflection of incident light). The overall energy conversion efficiency was calculated to be $\eta \simeq 3.5\%$, similar to previously reported values [26, 27].

### *3.3. Long Time Stability*

The long time stability test of various $TiO_2$-samples, produced in oxygen at 500–700 °C (heating times 10, 30 and 60 min) was performed with and without additional bias. No aging or altering of the photocharacteristics and no corrosion could be observed for an operation under steady state conditions for 120–150 hours, in contrast to electrochemically produced samples [11, 12].

## 4. Conclusion

a) The production of photoactive, polycrystalline $n$-$TiO_2$-semiconductors by simple thermochemical oxidation of Titanium metal sheets is possible.

b) For the formation and growth of highly photosensitive $TiO_2$-crystal by thermochemical oxidation of Titanium metal sheets an optimum temperature of about 550 °C–650 °C in pure oxygen atmosphere for about 10–30 min is required.

c) The treatment of the Titanium sheet surface prior to oxidation is of crucial importance for a good adhesion of the $TiO_2$-film, its photoactivity and for a satisfactory stability of the photocurrent of the photoanode during long time operation.

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