Modified TiO₂ coatings for cathodic protection applications

Raghavan Subasri, Tadashi Shinohara, Kazuhiko Mori

Abstract

A bilayered electrode bearing the configuration SnO₂|TiO₂ over a substrate like transparent conducting Indium Tin Oxide coated glass was found to store the charge accumulated during ultraviolet illumination. Photogenerated electrons from TiO₂ are transferred to SnO₂ that store the excess charge via cation intercalation. A red shift in the absorbance of the coating was observed due to the reduction of the valence state of Sn during charging and a high capacitance in the bilayer electrode was detected by ac impedance measurements. The charge storage property of SnO₂|TiO₂ electrode makes it a candidate material to be used as an anode for improved photocathodic protection of metals and/or steels.

Keywords: TiO₂–SnO₂ composite; Cathodic protection; Charge storage; Cation intercalation; Bilayered electrodes

1. Introduction

Plain TiO₂ [1–4] and composites of TiO₂ with WO₃ [5,6], poly-tungstic acid (PWA)-TiO₂ [7] or Fe-doped TiO₂ [8] have been investigated in the recent past for cathodic protection applications in presence of ultraviolet (UV) illumination. The reason why this field has attracted considerable interest is because of the inherent advantage that TiO₂-based coatings function as non-sacrificial anodes when used for cathodic protection of metals/steels. When a metal coated with an n-type semiconductor like TiO₂ is in contact with a redox species, i.e. electrolyte, electrons will be transferred across the semiconductor–electrolyte interface until the chemical potentials of electrons in the solid and solution are equalized. This interfacial electron transfer generates a space-charge layer in the semiconductor and the band edges of the semiconductor are bent upwards at the interface deviating from their bulk values. Upon illumination of the semiconductor, the photogenerated holes migrate to the surface under the electric field of the space-charge layer, where some of them are captured by the redox couple. However, the photogenerated electrons once having migrated to the interior of the semiconductor have no possible exit. So, if these electrons could be coupled to the metal, then its electrode potential could be made sufficiently negative. Thus, a TiO₂ coating on a metal under bandgap irradiation can act as a source of electrons and provide cathodic protection. Since TiO₂ is a chemically stable material, it does not get consumed in the whole process and hence, can function as a non-sacrificial anode having an infinite life-time. Recently, Subasri and Shinohara reported on a TiO₂–SnO₂ composite electrode that showed an improved performance as photoanode [9]. Here, SnO₂ acted as a charge storage medium to save the photogenerated electrons from TiO₂ and releasing them slowly to the substrate thereby being functional even when there is little or no UV light. The present investigation reports under what conditions, such coupled photoanodes can function effectively under both illumination and dark.

2. Theoretical background

The main idea behind using a composite anode is to manifest a transfer of photogenerated electrons from TiO₂ to such a material that is capable of charge storage and from which the stored electrons can be released slowly so that a continued photoeffect can be realized. Such a phenomenon
can in principle be made possible when the conduction band edge of the material to be coupled with TiO₂ is lower than that of TiO₂. Moreover, if the coupled material is capable of exhibiting multivalence, then charge storage could be made possible. SnO₂ was identified as a candidate material that can be coupled with TiO₂ since the conduction band (CB) edge of SnO₂, \( E_{\text{CB}} \) (SnO₂) = −4.5 eV is lower than that of TiO₂, \( E_{\text{CB}} \) (TiO₂) = −4.0 eV with reference to absolute vacuum scale (AVS) (cf. Fig. 1). On illumination, excess photoexcited electrons should be transferred from TiO₂ to SnO₂. As can be seen from Fig. 1, a competing process namely reduction of oxygen also occurs due to the favorable position of the CB edge of O₂ with respect to that of TiO₂. Due to this, reduction of O₂ is highly facile on surface of TiO₂ and this process consumes most of the photogenerated electrons. However, in the absence of O₂, it can be expected that the electrons are efficiently transferred to SnO₂ that can in addition be stored in it via cation intercalation as represented below:

\[
xH^+ + \text{SnO}_2 + xe^- \rightarrow H_x\text{SnO}_2
\]  

(1)

The electrons thus stored can be slowly released in the absence of UV illumination when the reverse process of Eq. (1) occurs. Thus, if the composite electrode is coupled with a metal, its electrode potential can be maintained at sufficiently negative potentials both under illumination and in the dark. This aspect was verified in the present study by carrying out preliminary investigations on the bilayered electrode coated over conducting Indium Tin Oxide (ITO) glass substrates.

3. Experimental

3.1. Materials

A commercial 4 wt% TiO₂ sol solution (pH 7.0) supplied by Nippon Parkerizing Co. Ltd, Japan was used as the source of TiO₂. The particle size of TiO₂ in the sol was determined to be \( \sim 10 \) nm. Self-made SnO₂ powder having a mean crystallite diameter of \( \sim 100 \) nm synthesized by a modified Pechini process [10] was converted into a sol and used for further investigations. Indium Tin Oxide (ITO) coated glass plates supplied by Nippon sheet glass company, Japan were cut into pieces of dimensions 3 cm \( \times \) 2 cm and used as substrates. The ITO coating was \( \sim 450 \) Å thick and had a composition of 10% SnO₂–90% In₂O₃. SnO₂–TiO₂ bilayer electrode coatings bearing the configuration SnO₂|TiO₂ were made on the ITO substrate using the TiO₂ and SnO₂ sol by a spin coating technique so as to achieve a total thickness of \( \sim 0.2 \) μm, i.e. 0.1 μm for each layer. The coated substrate was heat treated at 200 °C in air for 20 min and used for photoelectrochemical characterization.

3.2. Characterization

3.2.1. X-ray diffraction, scanning electron microscopy and X-ray photoelectron spectroscopy

The phase analysis of all samples was carried out using a Rigaku model RINT 2500 X-ray diffractometer by employing Cu Kα as the incident radiation. The X-ray diffraction (XRD) patterns of the samples were collected over a 2 theta range from 20 to 40° at a scan rate of 5°/min. Optical micrographs of the coated ITO substrate were obtained before and after the measurements using a VH-7000 C model Keyence Digital high definition optical microscope. Scanning electron microscopic analysis was carried out on the coatings using a JEOL JSM 5400 microscope with 15 kV accelerating voltage of the electron beam at various magnifications. X-ray photoelectron spectra (XPS) were obtained using an XPS analyser model ESCA-850M supplied by M/s SHIMADZU, Japan.

3.2.2. Photoelectrochemical measurements

Photoelectrochemical measurements were carried out by first measuring the rest potential or open circuit potential (OCP) in dark with reference to a saturated calomel electrode (SCE). The electrolyte was a phosphate buffer solution with \( \text{pH} = 6.5 \). The buffer solution was made up using 0.1 M Na₂HPO₄+0.1 M Na₂SO₄ with 0.1 M Na₃HPO₄+0.1 M Na₂SO₄. A platinum strip was used as the counter electrode. ITO glass coated with the semiconductor electrode served as the working electrode. A potentiotostat/galvanostat (model 2090 HS) supplied by Toho Techniques Research, Japan was used for the rest potential measurements as well as polarization studies. For the photopotential measurements, the sample was illuminated using a 500 W High pressure Hg lamp (model UI-501C) supplied by Ushio Co., Japan. The most intense lines for a Hg lamp lie at 436 (100%), 365 (90%), 405 (80%) and 546 nm (90%) (cf. Product Catalogue of Hg lamps supplied by Ushio Corporation, Japan). In order to render possible a selective absorption of the coating, the light was first made to pass through an optical filter (UV-34, Kenko) which mostly allowed (>60%) only light of wavelength greater than 340 nm. After this light passed through a quartz window,
which absorbed the contribution of the radiation lying in the visible range, it was then made to fall on the coated side of the ITO glass substrate. Since the bandgap $E_g$ of TiO$_2$, i.e. 3.2 eV corresponds to $\lambda g = 390$ nm (cf. Fig. 1), the coating was selectively excited at $\lambda = 365$ nm. The time evolution of the OCP under illumination was followed up until it reached a stable value. This value was recorded as the photo-potential. Polarization measurements were carried out under dark as well as illumination for all samples employing a scan rate corresponding to 25 mV/min for an anodic scan of up to +1.2 V and a cathodic scan of up to −250 mV from the rest potential. In some cases, the rest potential was also measured up to several hours after stopping the source of illumination in order to monitor the rate of decline of the potential. The photoelectrochemical measurements were carried out both under aerated and deaerated conditions.

3.2.3. AC impedance measurements

Impedance was measured as the current response to a superimposed ac signal of amplitude 20 mV with a frequency ranging from 0.01 up to 100 Hz at various applied potentials provided by a potentiostat. After a preliminary analysis of the impedance data as a function of frequency obtained for various applied potentials, it was found that at lower frequencies (<0.1 Hz), the system showed a capacitive behavior and this was ascertained to be arising due to the charge storage in the bilayer electrode coating. Hence, for measurement of the capacitance of the coating, the impedance was measured at potentials applied from +400 down to −1150 mV in steps of 100 mV at a low frequency of 0.01 Hz. The system was kept for 45 min at any applied potential before impedance measurement, as it was verified that a constant current state was reached at 45 min after application of potential.

4. Results and discussion

4.1. Photoelectrochemical measurements

Fig. 2 depicts the variation of the OCP as a function of time in the presence and absence of UV illumination for the ITO glass coated with the bilayer electrode under aerated and deaerated conditions. It is seen that in the presence of oxygen, the system behaves like the substrate with a plain TiO$_2$ coating, i.e. there is a rapid ennoblement of potential as soon as the illumination is stopped. However, in the absence of oxygen, after two cycles of with and without illumination, the electrode potential in absence of illumination though becomes more noble initially, slowly becomes more negative later. This behavior is indicative of a charge storage and discharge-mechanism taking place in the system, which does not become evident in presence of oxygen. Another point to be noted is that during the first two rounds of illumination under deaerated conditions, the OCP becomes positive initially (i.e. a ‘p’-type effect), exhibiting a sharp spike towards more positive potentials and then shows an n-type effect. The reasons for this instantaneous ‘p’-type effect will be discussed in Section 4.4. The ITO glass substrate observed after the photoelectrochemical experiment carried out under deaerated conditions looked red in color whereas the coating had a blue color prior to the experiment. Fig. 3 shows a comparison of the optical micrographs of the sample recorded before and after the measurements. Since the coatings were made on transparent conducting glass substrates, the change in absorbance of the coating could be discerned visually. The change in color of the coating is attributed to a charge transfer occurring from TiO$_2$ to SnO$_2$ resulting in a reduction of the valence state of Sn from Sn$^4+$ to lower states. It should be mentioned that such a color change does not occur in the case of a plain TiO$_2$ coating, which obviates the possibility of a reduction of Ti$^{4+}$ to Ti$^{3+}$ by the photogenerated electrons in the composite electrode. Such an electron transfer leads to reduction of Sn$^{4+}$ and charge storage is rendered possible via cation intercalation. Cation intercalation in SnO$_2$ has been well
proven in the literature [11,12]. A possible mechanism would be as given below

\[ \text{SnO}_2 + xe^- + xM^+ \rightarrow M_x\text{SnO}_2 \]

(2)

where \(M = \text{H, Li or Na and } x = 1 \text{ or } 2\).

The reduction of \(\text{Sn}^{4+}\) to lower valence states leads to a red shift in the absorbance of the coating.

Other evidences substantiating the fact that the red coloration is only due to the reduction process are that the same phenomenon does not occur in an aerated condition. Moreover, the red color was seen to have disappeared instantaneously when a large positive potential (\(\sim +600 \text{ mV}\)) was applied to the substrate for carrying out ac impedance measurements as a function of applied potential.

Fig. 4 shows an XRD pattern of the bilayer electrode before and after the photoelectrochemical investigation under deaerated conditions. The appearance of an additional peak at a 2 theta of 31.7° is visible for the pattern recorded after the measurement. This additional peak is due to a reduced form of \(\text{Sn}^{4+}\) in the form of \(\text{Sn(OH)}_2\), i.e. \(\text{Sn}^{2+}\) or \(\text{SnO–OH}\), i.e. \(\text{Sn}^{3+}\). It should be mentioned here that the XRD pattern of the coating shows only presence of \(\text{SnO}_2\) and not \(\text{TiO}_2\) as \(\text{SnO}_2\) is more crystalline than \(\text{TiO}_2\) \((\phi_{\text{SnO}_2} = 100 \text{ nm which is greater than } \phi_{\text{TiO}_2} = 10 \text{ nm})\), so that \(\text{TiO}_2\) does not appear in the XRD pattern.

It should be noted that for an effective charge separation in the \(\text{TiO}_2\) layer and for an effective charge transfer to \(\text{SnO}_2\), it is important how close the electrons in the \(\text{TiO}_2\) film are to the \(\text{SnO}_2|\text{TiO}_2\) interface and hence, the thickness of the \(\text{TiO}_2\) layer is critical in determining this effect. In this regard, it was previously reported that for \(\text{TiO}_2\) layer thicknesses greater than 0.2 \(\mu\text{m}\), the advantageous effect of \(\text{SnO}_2\) drawing the electrons from \(\text{TiO}_2\) decreased and due to this, the desired purpose of using \(\text{SnO}_2\) in the composite was not served [13]. It was also found out from the study reported in Ref. [13] that the charge transfer from \(\text{TiO}_2\) to \(\text{SnO}_2\) took place in 20 ps, which can be understood from the position of the energy levels of \(\text{SnO}_2\) and \(\text{TiO}_2\) (cf. Fig. 1). In the present study, it was taken care that the total thickness of the bilayer coating was 0.2 \(\mu\text{m}\) (0.1 \(\mu\text{m}\) each) so that the charge transfer from \(\text{TiO}_2\) across the \(\text{SnO}_2|\text{TiO}_2\) interface was facile. Moreover, the \(\text{SnO}_2\) coating had to be maintained as porous so that a higher mobility of cations is possible in order to realize the charge storage property of \(\text{SnO}_2\) through cation intercalation.

4.2. XPS analysis

A clear picture of the valence state of Sn was obtained after performing the XPS analysis of the surface of the coated substrate. Fig. 5a depicts the spectrum obtained for the surface indicating the presence of \(\text{Ti}, \text{Sn, O, Na}\) and \(\text{P}\). The \(\text{Na}\) and \(\text{P}\) peaks can be ascribed as due to the electrolyte. In order to find out the valence state of Sn at the surface, a knowledge of the binding energies of \(\text{Sn}^{4+}\) and \(\text{Sn}^{2+}\) is essential. It is well known that the binding energies of \(\text{Sn}^{4+}\) and \(\text{Sn}^{2+}\) do not differ much (\(\Delta E_b = 0.7 \text{ eV}\)) and hence, are difficult to distinguish by XPS [14,15]. Hence, a compositional depth profile of the coating as shown in Fig. 5b was performed which revealed that the Sn 3d\(_{5/2}\) and 3d\(_{3/2}\) peaks in the inner layers have slightly shifted to lower binding energies. This indicates that there is a reduction of \(\text{Sn}^{4+}\) to lower valence states (+3 or +2) in the inner layers as any \(\text{Sn}^{2+}\) in the outer layer could have possibly got oxidized by \(\text{O}_2\) from the atmosphere during the period from after the photoelectrochemical measurement and before the XPS analysis.
4.3. AC impedance measurements

After having got the evidence for reduction of the valence state of Sn from +4 to +2 by the electrons from TiO₂ after illumination, the charge storage properties of SnO₂ by cation intercalation had to be verified. For this purpose, ac impedance measurements were carried out on the ITO coated with the bilayer electrode. A typical Bode plot obtained for \( E_{\text{app}} = -900 \text{ mV} \) is shown in Fig. 6 over the range of frequencies scanned. It is clear from the plot that the equivalent electrical circuit for the system consists of a resistor \((R)\) and capacitor \((C)\) in parallel. The same profile of plot was obtained for all the applied potentials ranging from +400 down to −1100 mV. At lower frequencies such as 0.01 Hz, the contribution to the total impedance is seen to be purely capacitive. Hence, for measurement of the capacitance of the coating, impedance measurements were carried out at 0.01 Hz as a function of applied potential and the capacitance at each \( E_{\text{app}} \) was computed from the impedance assuming the equivalent circuit corresponding to a pure capacitor at such a low frequency. A plot of the capacitance versus the applied potential is shown in Fig. 7. There is a capacitance maximum arising at \( E_{\text{app}} = -600 \text{ mV} \) followed by a sudden increase after that. The small hump with maximum at \( E = -600 \text{ mV} \) corresponds to the one electron reduction from Sn⁴⁺ to Sn³⁺ followed by subsequent reduction to Sn²⁺ as indicated by the sudden increase in the capacitance beyond \( E = -800 \text{ mV} \). The high capacitance values of \( \sim 2000 \mu\text{F/cm}^2 \) at \( E_{\text{app}} = -600 \text{ mV} \) confirm that when the electrode potential reaches the value of −600 mV
As a result, some additional investigations on plain SnO₂ coatings over ITO glass substrates were made and the results obtained are discussed here with an attempt to explain the anomalous observation. SnO₂ is a ‘n’-type semiconductor with a bandgap of \(~3.5\) eV. The electrical properties of SnO₂ depend mainly on the deviation from its stoichiometric composition. It has been widely used for gas sensing applications, the principle of which is based on the change in the electrical resistance of SnO₂ on exposure to the test gas. Generally, during its synthesis, when SnO₂ is heat-treated in an aerated atmosphere, i.e. air or pure O₂ at temperatures greater than \(640^\circ C\), a chemisorption of O₂ on SnO₂ takes place leading to an increase in its electrical resistance [16]. There is an electron transfer that is taking place in this case, from the conduction band of SnO₂ to an acceptor level introduced by the chemisorbed atoms. When a coating made of SnO₂ processed at high temperatures in air is exposed to bandgap irradiation, there are two possible interaction pathways of the photoinduced charge carriers, i.e. the electrons and holes, as given below:

\[
e^- + O_2 + SnO_2 \rightarrow O_{ads}(SnO_2) \tag{3}
\]

\[
h^+ + O_{ads}(SnO_2) \rightarrow O_2 + SnO_2 \tag{4}
\]

In a deoxygenated condition, the second reaction is thermodynamically favored according to which, a photodesorption takes place as a result of which, the free electrons that are available, increase in number on prolonged exposure to illumination [16,17].

In the present case, however, when a pure SnO₂ coating made using SnO₂ powders heat treated in air at temperatures such as \(800^\circ C\), is exposed to UV illumination under deaerated conditions, we expect that an instantaneous ‘n’-type effect to be observed indicating an increase in free electrons or in other words, the electrical conductivity of SnO₂ should increase with a simultaneous photodesorption taking place. But what we actually observe is that under aerated conditions, there is an instantaneous ‘n’-type effect during illumination (photopotential), there is a charging up of the electrode. When the source of illumination is cut-off, this stored charge is slowly discharged to the substrate such that a highly negative electrode potential of the substrate is still maintained.

4.4. Reasons for the initial ‘p’-type effect in the bilayer electrode on UV illumination

It was seen from Fig. 2 that when a ITO glass substrate coated with the composite bilayer SnO₂–TiO₂ electrode was exposed to UV illumination under deaerated conditions, instead of an ‘n’-type photoeffect, initially, a ‘p’-type effect was observed, which after two rounds of illumination exhibited the exhibited ‘n’-type effect from the next illumination onwards. It was confirmed that such a behavior was coming from only due to presence of SnO₂ in the composite and not due to TiO₂ since a plain TiO₂ coating did not show any ‘p’-type behavior on UV illumination.

As a result, some additional investigations on plain SnO₂ coatings over ITO glass substrates were made and the results obtained are discussed here with an attempt to explain the anomalous observation. SnO₂ is a ‘n’-type semiconductor with a bandgap of \(~3.5\) eV. The electrical properties of SnO₂ depend mainly on the deviation from its stoichiometric composition. It has been widely used for gas sensing applications, the principle of which is based on the change in the electrical resistance of SnO₂ on exposure to the test gas. Generally, during its synthesis, when SnO₂ is heat-treated in an aerated atmosphere, i.e. air or pure O₂ at temperatures greater than \(640^\circ C\), a chemisorption of O₂ on SnO₂ takes place leading to an increase in its electrical resistance [16]. There is an electron transfer that is taking place in this case, from the conduction band of SnO₂ to an acceptor level introduced by the chemisorbed atoms. When a coating made of SnO₂ processed at high temperatures in air is exposed to bandgap irradiation, there are two possible interaction pathways of the photoinduced charge carriers, i.e. the electrons and holes, as given below:

\[
e^- + O_2 + SnO_2 \rightarrow O_{ads}(SnO_2) \tag{3}
\]

\[
h^+ + O_{ads}(SnO_2) \rightarrow O_2 + SnO_2 \tag{4}
\]

In a deoxygenated condition, the second reaction is thermodynamically favored according to which, a photodesorption takes place as a result of which, the free electrons that are available, increase in number on prolonged exposure to illumination [16,17].

In the present case, however, when a pure SnO₂ coating made using SnO₂ powders heat treated in air at temperatures such as \(800^\circ C\), is exposed to UV illumination under deaerated conditions, we expect that an instantaneous ‘n’-type effect to be observed indicating an increase in free electrons or in other words, the electrical conductivity of SnO₂ should increase with a simultaneous photodesorption taking place. But what we actually observe is that under aerated conditions, there is an instantaneous ‘n’-type effect during illumination (photopotential), there is a charging up of the electrode. When the source of illumination is cut-off, this stored charge is slowly discharged to the substrate such that a highly negative electrode potential of the substrate is still maintained.

4.4. Reasons for the initial ‘p’-type effect in the bilayer electrode on UV illumination

It was seen from Fig. 2 that when a ITO glass substrate coated with the composite bilayer SnO₂–TiO₂ electrode was exposed to UV illumination under deaerated conditions, instead of an ‘n’-type photoeffect, initially, a ‘p’-type effect was observed, which after two rounds of illumination exhibited the exhibited ‘n’-type effect from the next illumination onwards. It was confirmed that such a behavior was coming from only due to presence of SnO₂ in the composite and not due to TiO₂ since a plain TiO₂ coating did not show any ‘p’-type behavior on UV illumination.
on UV illumination, whereas under deaerated conditions, a sharp spike towards more positive electrode potentials, i.e. a ‘p’-type effect was observed on illumination, as shown in Fig. 8. The reason for this behavior could be that when the pure SnO2 coated ITO glass substrate was initially deaerated and then exposed to UV light, the traces of O2 in the surrounding inert gas, N2 in this case, first gets adsorbed on SnO2 causing reaction (3) to occur, which means that now the number of photoinduced holes are more than electrons, eventually resulting in a ‘p’-type effect. Since the same SnO2 powder made into a sol was used for preparing the composite electrode coating with TiO2, the ‘p’-type effect arising after illumination during the first round is due to the initial adsorption of traces of O2 in the N2 stream on SnO2. The same phenomenon, however, does not happen after the second round of illumination which means that a total desorption of the chemisorbed O2 has taken place after which SnO2 shows the usual ‘n’-type behavior.

Hence, the initial ‘p’-type effect gives an idea about the magnitude of traces of O2 present in the inert gas stream, which initially interacts with SnO2 on bandgap irradiation.

5. Conclusion

A modified bilayer photoanode comprising SnO2 and TiO2 was investigated for its charge storage properties. The results of the present investigations reveal that a capacitance maximum of the order of 2000 \( \mu \text{F/cm}^2 \) could be detected at an applied voltage of −600 mV, which corresponds to the photopotential of the TiO2 in the electrode. A bilayer electrode coated substrate was found to be capable of charge storage upon UV illumination and this stored charge could be released slowly on cessation of illumination thereby maintaining a sufficiently negative electrode potential. These results indicate that such bilayered photoanodes could be used for cathodic protection applications to metals even when there is a paucity of light for a few hours after illumination.

Acknowledgements

The authors are thankful to T. Otsuki, Nippon Parkerizing Ltd, Japan for performing the XPS analysis. One of the authors (R. S.) acknowledges the National Institute for Materials Science, Tsukuba, Japan for the financial support provided in the form of a fellowship.

References

[1] J. Yuan, S. Tsujikawa, J. Electrochem. Soc. 142 (1995) 3444.
[2] J. Huang, T. Shinozuka, S. Tsujikawa, Corr. Eng. 46 (1997) 789.
[3] J. Huang, T. Shinozuka, S. Tsujikawa, Zairyo-to-Kankyo 46 (1997) 651.
[4] Y. Ohko, S. Saitoh, T. Tatsuma, A. Fujishima, J. Electrochem. Soc. 148 (2001) B24.
[5] H. Park, K.Y. Kim, W. Choi, J. Phys. Chem. 106 (2002) 4775.
[6] T. Tatsuma, S. Saitoh, Y. Ohko, A. Fujishima, Chem. Mater. 13 (2001) 2838.
[7] T. Tatsuma, S. Saitoh, P. Ngaotrakanwiwat, Y. Ohko, A. Fujishima, Langmuir 18 (2002) 7777.
[8] P. Ngaotrakanwiwat, S. Saitoh, Y. Ohko, T. Tatsuma, A. Fujishima, J. Electrochem. Soc. 150 A (2003) 1405.
[9] T. Konishi, S. Tsujikawa, Meeting Abstract 97-2. The Joint International Meeting, The Electrochemical Society and The International Society of Electrochemistry, 1997, p. 500.
[10] R. Subasri, T. Shinozuka, Electrochem. Commun. 5 (2003) 897.
[11] P.A. Lessing, Ceram. Bull. 68 (1989) 1002.
[12] B.I. Lemon, J.T. Hupp, J. Phys. Chem. B 101 (1997) 2426.
[13] B. Orel, U. Lavrenčič-Stangar, K. Kalcher, J. Electrochem. Soc. 141 (1994) L127.
[14] C. Nasr, P.V. Kamat, S. Hotchandani, J. Phys. Chem. 102 (1998) 10047.
[15] J.-M. Themlin, M. Chtaib, L. Henrard, P. Lambin, J. Darville, J.-M. Gilles, Phys. Rev. B 46 (1992) 2460.
[16] Y.S. Choe, J.H. Chung, D.S. Kim, G.H. Kim, H.K. Baik, Mater. Res. Bull. 34 (1999) 1473.
[17] F. Prado, G. Meyer, J. Saura, J. Phys.: Condens. Matter 5 (1993) A351.