Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 175 (2005) 165–171

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

New low-temperature preparation method of the TiO_2 porous photoelectrode for dye-sensitized solar cells using UV irradiation

David Gutiérrez-Tauste [a], Inti Zumeta [b], Elena Vigil [b], Maria Angeles Hernández-Fenollosa [c], Xavier Domènech [a], José A. Ayllón [a,*]

[a] Departamento de Química, Universidad Autónoma de Barcelona, Campus UAB, Edificio Cn, 08290 Cerdanyola del Valles, Spain
[b] Instituto de Materiales, Facultad de Física, Universidad de La Habana, Colina Universitaria, Ciudad Habana 10 400, Cuba
[c] Departament de Física Aplicada, Universitat Politècnica de València, E-46071 València, Spain

Received 20 January 2005; received in revised form 15 April 2005; accepted 25 April 2005

Abstract

Thick porous TiO_2 films have been prepared at low temperature from a mixture of a commercial TiO_2 powder (Degussa P25) and an easy-to-handle water-soluble titania precursor: titanium(IV) *bis*(ammonium lactato)dihydroxide. Films have been obtained spreading the mixture using “doctor blade” technique. UV light treatment using a medium-pressure mercury vapor lamp leads to decomposition of the titania precursor as a result of the photocatalytic activity of nanocrystalline TiO_2 present in the blend. The additional titanium oxide thus formed assures both, necking between particles and film adhesion to the substrate. Porous nano-structured TiO_2 films were fabricated by this low-temperature method (always lower than 80 °C) on transparent conducting oxide-covered glass and flexible plastic substrates (indium-tin-oxide on glass and on PET, and fluorine-doped tin oxide on glass). The photoelectrodes obtained by this method have been characterized by scanning electron microscopy, attenuated total reflection Fourier transform infrared spectroscopy, photoluminiscence, monochromatic incident photon-to-current conversion efficiency (IPCE) and *I–V* measurements. Results obtained with dye-sensitized solar cells (DSSC) built with these films are promising.

Keywords: Titanium oxide; Photocatalysis; Dye-sensitized solar cells; Low-temperature film preparation

1. Introduction

Dye-sensitized solar cells (DSSC) based on nano-structured TiO_2 photoelectrodes are intensively studied due to their low cost and promising efficiency values reached so far. At the present time, research pursues the development of this inexpensive solar cell based on a nanocrystalline TiO_2 layer deposited on a flexible plastic substrate [1–2]. This type of substrate allows a continuous-mode production process, which should lower production costs; in addition, it facilitates fabrication of light-weight and thin DSSC [3–5]. Conventional DSSC technology includes an annealing step in which temperatures as high as 400–500 °C are needed. This temperature range, adequate for glass substrates, is above the allowed temperature for possible polymer-based flexible substrates. It must also be mentioned that these temperatures increase the resistivity of the conducting substrate, particularly ITO (In_2O_3:Sn). This has favored the use of conducting SnO_2 glass (FTO) over ITO in DSSC, even though the last one has a greater availability in the market and lower price.

These relatively high temperatures normally used in the annealing step are needed for two key reasons concerning TiO_2 photoelectrodes production. The first one is to eliminate the organic substances present in the colloidal TiO_2 suspension or paste used to make the photoelectrodes. Organics are added to the TiO_2 precursor formulations to improve the quality of the film by breaking down agglomerates, to stabilize TiO_2 suspensions, and to increase the wetting capacity of the precursor mixture. Thus, more regular TiO_2 thick

---

[*] Corresponding author. Tel.: +34 935812176; fax: +34 935812920.
E-mail address: joseantonio.ayllon@uab.es (J.A. Ayllón).

1010-6030/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.jphotochem.2005.04.031

films are produced without too large pores or cracks. The second key reason is to improve the connection between the nanocrystallites that constitute the film (necking), as well as, to guarantee their adherence to the transparent conducting oxide (TCO) film acting as substrate. Annealing at high temperatures improves the diffusion coefficient of electrons, and thus the efficiency of DSSC [6,7]. It is to be expected that the quality of these contacts determines both, electrical properties of the porous thick film and also its mechanical sturdiness. Some authors [8,9] have used chemical treatment of TiO_2 porous electrodes, with titania molecular precursor solutions, followed by re-annealing to produce a freshly grown titania. Depositing TiO_2 all over the porous layer should improve the necking of the grains, and it should decrease carrier-trapping defects.

On the other hand, there are reports on TiO_2 film fabrication procedures that are compatible with the use of non-conducting plastic substrates, although the purpose has been to exploit TiO_2 photocatalytic or UV blocking properties [10–18]. However, they produce thin films not suitable for DSSC fabrication due to their thickness and non-porosity. Besides, deposition on TCO-covered substrates poses an extra requirement of no modification of the TCO layer, which limits the experimental conditions to be employed. For example, deposition from solution with extreme pH values is not possible because the conducting layer is damaged.

Different approaches appear in the literature to avoid high-temperature annealing of the thick porous TiO_2 layer. Pichot et al. have studied the performance of electrodes treated at temperatures as low as 100 °C, avoiding the use of organic surfactants in the formulation of the precursor paste, but the performance of the cells thus obtained is limited compared to the annealed ones [19]. A promising alternative to substitute sinterization at high temperature is to compress the particle layers using high pressure during a short time interval. Mechanically stable, electrically conducting, nano-structured porous films are thus obtained [3–5,20]. Recently, a sophisticated method that employs a shower of low-accelerating electron beams has been demonstrated as a further option to cure TiO_2 films [21].

Some authors employ a mixture containing both nanocrystalline TiO_2 and a molecular TiO_2 precursor [22–23]. Under hydrothermal treatment at low temperature (100 °C) in the solid–gas (water vapor) interphase, the molecular precursor hydrolyzes acting as glue. This method has some drawbacks, such as incomplete necking of the particles and presence of residual organics in the film [24]. These organics can be eliminated later using UV/ozone treatment [25]. A different low-temperature method proposed by De Paoli and co-workers [1] takes advantage of the photocatalytic activity of TiO_2 in order to eliminate organic substances present in the commercial TiO_2 colloidal precursor used. TiO_2 thick film fabrication is completed by a heat treatment at 140 °C during 2 h. UV treatment has also been employed by Murakami et al. [26] in order to eliminate adsorbed organic impurities in the TiO_2 obtained using an electrophoretic method and thus improves the efficiency of their DSSC.

In this paper, we propose an alternative method to prepare TiO_2 porous thick films, suitable to work as photoelectrodes in DSSC. It combines photocatalytic activity of TiO_2 with the use of a mixture of nanocrystalline TiO_2 powder and a soluble precursor of TiO_2. This precursor, after photodegradation, will produce new TiO_2 that allows necking between particles and also provides adherence to the substrate. A stable water-soluble titania precursor, titanium(IV) *bis*(ammonium lactato)dihydroxide (TALH), is used to preserve the simplicity of the method.

2. Experimental

2.1. Reagents

All chemicals mentioned hereafter were, at least, of reagent grade and used as received. All water used in the experiments was previously purified in a Millipore Milli-Q system. TiO_2 Degussa P-25 (80% anatase–20% rutile) was kindly gifted by Degussa (Spanish delegation). Titanium(IV) *bis*(ammonium lactato)dihydroxide (Aldrich) was purchased as a 50% aqueous solution and diluted with water prior to its utilization.

2.2. Substrate cleaning

The substrates used were ITO (In_2O_3:Sn)-covered glass 13–18 Ω/sq, 1.1 mm thick optical glass (Opticalfilters UK), F-doped SnO_2-covered glass 15 Ω/sq (Flabeg, Pilkington Group) and poly(ethylene terephthalate) coated with In_2O_3:Sn (PET-ITO, T-MOX 60/175, 60 Ω/sq on 175 μm thick PET)—a sample kindly supplied by Innovative Sputtering Technology N.V. Glass-based substrates were cleaned just before performing the deposition process. Samples of adequate size were subjected to 5-min ultrasonic cleaning first in acetone, then in absolute ethanol, next for 1 min in 30% nitric acid and finally for 5 min in water. After that the substrates were dried under a nitrogen flow. PET-ITO substrates, which do not support this kind of treatment (ITO films are detached from the substrate), were used as received. Maximum precautions were taken to maintain their surface clean.

2.3. TiO_2 porous film preparation

A mixture of TiO_2 Degussa P-25 (2.0 g) and 0.416 M TALH solution (10 mL) were stirred mechanically and then introduced into an ultrasonic bath for 15 min. Then, 0.50 mL of a Tritron X-100 solution in water (1:10) was added and the mixture sonicated for 15 min. Water in the ultrasonic bath was changed periodically to avoid temperature increase. The mixture thus obtained was allowed to stand for a few minutes. With the help of Scotch (3 M) adhesive tape spacers and microscope slides, the paste was deposited using "doctor blade" technique as was described by Smestad [27]. After the films dried at room temperature, they were irradiated. Films were located at 8 cm from a medium-pressure Hg lamp (125 W, HPK Cathodeon) and no filter was placed between the lamp and the sample. For comparison, reference TiO_2 films were prepared by the conventional procedure described as method B by Nazeeruddin et al. [9].

2.4. TiO_2 films characterization techniques

The composition of TiO_2 films was analyzed by ATR-FTIR performed with a Bruker apparatus (Tensor model equipped with MKII Golden Gate). TiO_2 powder samples were obtained by scrapping off the film and pulverizing the sample in an agate mortar. To test the adhesion of TiO_2 films to the substrate, we used ultrasound disruption: the electrodes were immersed completely in a beaker with water and sonicated for different time intervals (Ultrasonic bath Selecta, 50 W). Surface characteristics of gold-covered films were further investigated by SEM, using a Hitachi S-570 electron microscope. TiO_2 film thickness was studied with SEM. TiO_2 films were easily distinguished from the substrate because of their different roughness. Low-temperature unpolarized photoluminescence (PL) experiments were performed in a backscattering geometry. Samples were placed inside a helium close-cycle cryostat and the 325.2 nm line of a 30 mW He–Cd laser was used. The emitted light was analyzed by a Jobin-Yvon HR460 spectrometer using a GaAs PMT detector optimized for the 350–650 nm range.

2.5. Sensitization of the films and photoelectrochemical measurements

The dye, *cis–bis*(isothiocyanato)*bis*(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) (Greatcell Solar S.A., Switzerland) commonly named N3, was used as sensitizer. For the purpose of eliminating water in the TiO_2, before sensitization, samples were heated for 1 h near 100 °C (80 °C in the case of ITO-PET samples). They were dipped while still warm, in a 0.5 mM solution of N3 in ethanol for 24 h and subsequently rinsed with ethanol. They were dipped in ethanol to desorb any excess dye. These films were dried in a nitrogen stream before using them as photoelectrodes. Photocurrent action spectra were measured with a Pye Unicam SP 600 UV monochromator system to which a 35 W halogen lamp for sample illumination was added. A Keithley 6487 picoammeter was coupled to this system for photocurrent measurements. For obtaining IPCE values from measured photocurrent, samples were substituted by a spectrally calibrated photodiode to measure incident light intensity at each wavelength. A two-electrode photoelectrochemical cell was used for photocurrent measurements with a Pt counter electrode. Radiation was incident on the TCO side. The redox electrolyte consisted 0.50 M LiI, 0.050 M I_2, and 0.50 mM *tert*-butylpyridine in 3-metoxy-propionitrile.

Photocurrent–voltage measurements were made in a two-electrode sandwich configuration. The active area of the cells was 1.9 cm^2. Counter electrodes were prepared by spreading a drop of 10 mM hexachloroplatinic acid solution in 2-propanol on a SnO_2:F covered glass, followed by heating at 380 °C for 30 min in air [28–29]. A spacer was placed between the two electrodes to avoid short-circuit and the previously mentioned electrolyte was used. Visible light was generated with a 50 W halogen lamp with a UV filter ($\lambda < 325$ nm). In order to decrease the temperature change caused by IR heating, a water filter (3.0 cm optical path length) was used. Lamp distance was adjusted in order to obtain a light intensity of 100 mW/cm^2. *I–V* curves were traced with the help of a simple multimeter and variable resistances.

3. Results and discussion

Our first objective was to define a good TiO_2 precursor suspension, which must contain a mixture of photoactive nanocrystalline TiO_2 and a molecular titania precursor. The first ingredient must supply the necessary photoactivity to decompose the second component, the titania precursor. The additional titanium oxide formed after TALH photodegradation must act as cement and assure electrical connection among particles, as well as, between titania and the substrate. The criteria used to find an optimal formulation was uniformity and adherence of the film obtained after UV treatment. TiO_2 Degussa P-25, easily available and with a high photocatalytic activity was chosen as the crystalline TiO_2 powder component of the mixture. TALH was chosen as titania molecular precursor because it is a stable compound even under open atmosphere and special care must not be taken during its manipulation. Besides, it is commercially available and it allows the use of water as a solvent.

The mass of TiO_2 obtained from the decomposition of the molecular precursor must be enough to assure necking among preformed nanocrystals. On the other hand, the time required for TALH decomposition increases with its concentration in the initial mixture. Besides, TALH could cover the entire catalyst surface if present in a high percentage in the mixture and this probably causes photocatalytic activity decay. Therefore, it seems reasonable that the amount of TiO_2 to be formed from the molecular precursor must be low compared to TiO_2 added as a crystalline powder. After several paste compositions were essayed, the optimized composition found contains 1 mol of TALH per 7.4 mol of TiO_2 present as powder. The qualitative criteria used for this optimization was endurance of the obtained layer with sonication time, i.e., area that remained covered after 10 min in the ultrasonic bath. The TiO_2 powder to precursor molar ratio selected is approximately half the value used by Yoshida and co-workers with their hydrothermal method [24]. A smaller percentage of TALH does not allow the production of stable films. A small amount of Triton X-100 was added to the mixture to facilitate substrate wetting and to produce uniform films using "doctor blade" technique. The organic nature of the surfactant allows its elimination after UV activation of photocalytic TiO_2. Ultrasound was used to break as much as possible the large agglomerates usually present in TiO_2 Degussa P-25 aqueous suspensions, and to facilitate the intimate mixture of the three components. It was found that additives normally employed to break TiO_2 aggregates, like acetylacetone, acetic acid, etc., lead to loosely adhered films. Probably, their presence and/or their degradation products avoid or make difficult the adsorption of the titania molecular precursor to the TiO_2 nanocrystallites. Besides, the presence of these substances, which strongly adsorb on the TiO_2 surface, can block activity center and the photodegradation processes [30–31].

The temperature attained in the film during UV irradiation was lower than 80 °C. As no UV filters are used, it must be considered that both direct photolysis and TiO_2-activated photocatalytic degradation are possible pathways for precursor decomposition. It is well known that under TiO_2 irradiation with photon energy higher than its band gap, strong oxidant species are formed that promote the complete mineralization of organic compounds. Different UV treatment times were essayed from 1 to 6 h. ATR-FTIR spectroscopy was used to assess the effect of the UV treatment, using samples representative of the whole film thickness. The reference sample was obtained simply by drying the precursor paste, i.e., prior to irradiation treatment, when all the TALH was still present. In the spectra (Fig. 1), intense peaks assignable to TALH are clearly visible (2983 and 2940 cm^{-1} C–H stretch; 1376 cm^{-1} symmetric stretch carboxylate group, 1114 and 1051 cm^{-1} methyl group skeletal vibration). After only 1 h treatment, their intensity has diminished strongly. Broadening of peaks is to be expected considering that a blend of different degradation products could be formed. The rapid elimination of the organic species could be due to the formation and diffusion of volatile intermediates. Treatment was performed for 6 h to eliminate more refractive compounds responsible of weak signals that remain and require longer treatment (Fig. 1). After this longer treatment, most of the organic substances are eliminated.

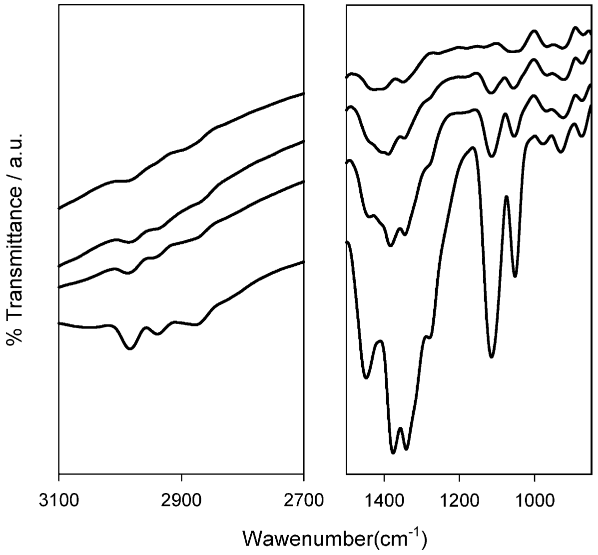

Fig. 1. ATR-FTIR spectra of the TiO_2 film after different times of irradiation (from bottom to top: 0, 1, 2, and 6 h, respectively). Spectra are representative of the whole film thickness composition as samples were obtained pulverizing film portions scrapped from the substrate.

If we consider the low optical transmittance of TiO_2 for λ lower than 385 nm approximately, then the upper layer of the film hinder the illumination of the material below. Nonetheless, the lactate that remains in the deeper layers, where the intensity of incoming radiation is smaller, could also be degraded because oxidizing species are able to diffuse through the pores to deeper regions of the film [32–33].

Films prepared by this new method are more opaque than those prepared by the conventional method, which are translucent. This indicates that bigger aggregates are still present in our method. In the Nazeeruddin's method [9], the use of acetylacetone helps to break the agglomerates present in P-25. As mentioned before, the use of acetylacetone or other disaggregating substances must be avoided in our method because it worsens the adherence of the films produced. SEM analysis (Fig. 2a and b) shows larger aggregates but comparable crystallite dimensions when comparing

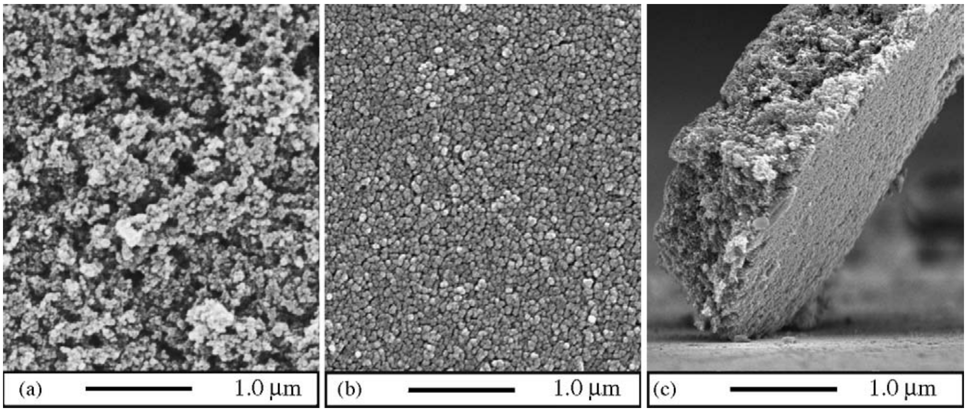

Fig. 2. SEM images of porous TiO_2 films produced by (a) the method reported in the present work, after 6 h. UV light irradiation; (b) sample obtained using Nazeeruddin method B [9]; and (c) small film fragment prepared as in (a) detached from the substrate after ultrasound treatment.

samples prepared by the present technique with samples prepared using acetylacetone for disaggregating TiO_2. The larger aggregates give rise to larger pores, since they do not pack as well as small particles. This should reduce the total real area of the device. In Fig. 2c, the typical thickness of layers obtained is shown—around 12 μm.

Adhesion to the conducting glass substrate was tested studying resistance to sonication. Tests showed that adhesion is irregular, some areas been detached while others remain firmly attached. Although the percentage of area lost after a certain time varies from sample to sample, it was possible to obtain results comparable to those obtained with the conventional method that includes an annealing step. Spots in the TiO_2 film are detached as platelets (see Fig. 2c). This shows that powder nanocrystallites hold firmly together; that a good necking among particles is obtained. It also indicates that the ITO/TiO_2 interface contact is not uniform. The same problem was found in other low-temperature sintered TiO_2 films [19]. The fact that in some areas the adhesion is much better than that in others suggests that an adequate substrate activation or pre-treatment could probably homogenize the firm adhesion of the film to the conducting glass. This aspect is under investigation. It is also possible to deposit films on ITO-PET substrates. In this case, the sonication test is not possible because the ITO layer detaches. It must be stressed, though, that the film does not peel off when the substrate is bent.

The absence of strong IR bands, as well as the fact that the hydroxides and carbonates of titanium are not stable, suggest that TiO_2 has been formed as a final TALH photodegradation byproduct. We have tried XRD to know more about the crystal structure of the generated material. The pattern is dominated by the intense signals due to the nanocrystalline TiO_2 present in the initial mixture (Degussa P-25), which constitutes most of the TiO_2 layer. One tends to think that, as it is to be expected, the deposited materials reproduces the crystalline structure on top of which it grows given the similarity between XRD of the layer obtained with “paint-on” and the one obtained with our method. The presence of a minor XRD-silent component (amorphous phase) could not be completely excluded, though.

Photoluminescence spectra were also used to characterize the TiO_2 films. In Fig. 3, we can see the low-temperature spectra ($T = 15$ K) of a film made from the TiO_2 + TALH mixture before (dashed line) and after the 6 h UV treatment (solid line). For comparison, the spectrum of a film produced by Nazeeruddin method including 450 °C annealing is also showed (dotted line). Considering the same photoluminescent emission, the peak intensity depends on the concentration of other competing non-radiative recombination centers. The lower intensity of the sample prior to UV treatment (about 20% less) is due to the fact that the TiO_2 surface is covered with photodegradable substances, and the recombination process is less probable, i.e., adsorption of the TALH precursor on the crystalline TiO_2 quenches partially their PL [34–35]. The intensity of the PL signal at 550 nm of the sample after the UV treatment is very similar to that corresponding to the film prepared by thermal annealing (dotted line). This indicates that defect concentration is very similar in both samples, since non-radiative recombinations are favored at defects, e.g., those due to internal surfaces or boundaries formed by particles necking. Since the shape of the PL emission is the same for different treatments, this indicates that the kind of defects (or emissive centers) responsible of the PL signal has not changed due to the treatment.

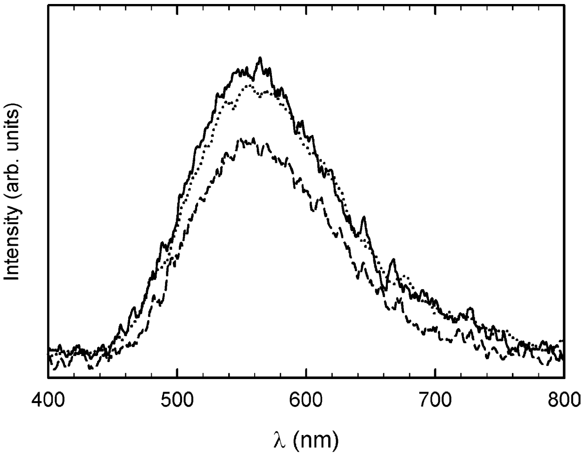

Fig. 3. PL spectra of porous thick TiO_2 films prepared by produced by (a) the method reported in the present work (dashed line) before UV light treatment and (solid line) after 6 h. UV light irradiation; (dotted line) sample obtained using Nazeeruddin’s method B [9].

The photovoltaic properties of the electrodes obtained by our method were characterized and compared to electrodes made by the more conventional method, which includes annealing at high temperature. First, we measured IPCE of N3-sensitized (Fig. 4) electrodes prepared on ITO-glass sub-

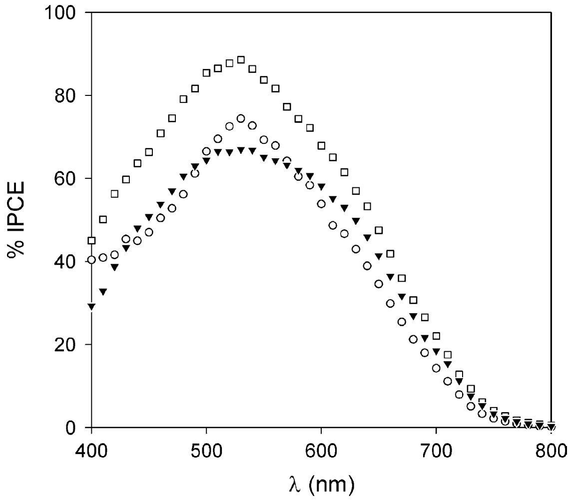

Fig. 4. Dependence of the IPCE values for N3 sensitized TiO_2 electrodes prepared on ITO-glass substrates by our UV-based method (squares); conventional method including annealing at high temperature (open circles), and photoelectrode prepared by our UV-based method on ITO-PET substrate (inverted triangles). The redox electrolyte consisted of 0.50 M LiI, 0.050 M I_2, and 0.50 mM *tert*-butylpyridine in 3-metoxy-propionitrile.

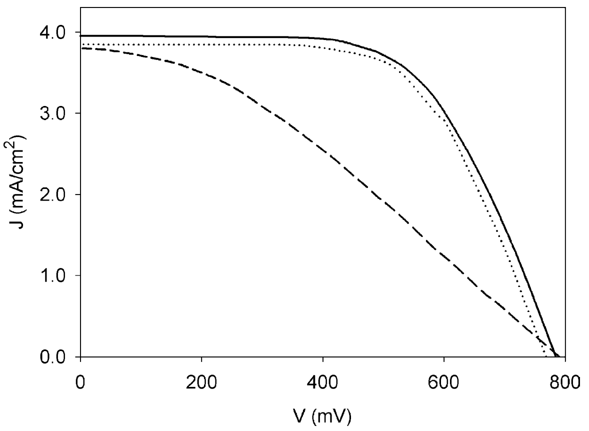

Fig. 5. Current–potential curves for N3-sensitized TiO_2 electrodes prepared on SnO_2:F glass substrates (solid line) by our method; (dotted line) conventional method including annealing at high temperature (dashed line) photoelectrode prepared by our method on ITO-PET substrate. The redox electrolyte consisted of 0.50 M LiI, 0.050 M I_2, and 0.50 mM *tert*-butylpyridine in 3-metoxy-propionitrile. The radiant power is 100 mW/cm^2. For comparative intention, in all the cases the counterelectrode was a platinized SnO_2:F glass substrate.

strates. Results indicate that the photoelectrodes prepared by the TiO_2–TALH mixture method have a satisfactory behavior comparable with electrodes prepared by the traditional method. However, it must be pointed that, since we used ITO based substrates, the traditional method is penalized as the resistivity of this oxide increases during the annealing step.

To facilitate comparison of both methods, photocurrent density (J) versus voltage (V) curves were measured for cells obtained but in this case, SnO_2:F covered glass was used, which maintains its low resistivity with temperature. As can be observed in Fig. 5, very similar results were obtained. It must be said that we have not attempted to optimize the cells contacts and geometry. Our first objective is only to compare the two methods of TiO_2 film preparation; this is why the efficiency of the cell is only around 2% and the fill factor is in the 0.60–0.65 interval. Results corresponding to electrodes prepared at low temperature are slightly better. Poorer results, though, have been obtained with electrodes prepared on plastic substrates. As known, the inverse of the slopes at points where $V = 0$ (short-circuit current I_{sc}) and where $I = 0$ (open-circuit voltage V_{oc}) give the so called, parallel resistance R_p and series resistance R_s, respectively. Ideally, the parallel resistance should be infinitely large and the series resistance 0. Therefore, for the plastic substrate, as seen in Fig. 5, the parallel resistance is too low and the series resistance too high. This must be due to the higher resistivity of the ITO layer on this flexible substrate, which is four times larger than that of the glass substrates as said before. Evidently, higher contact resistance increases series resistance; but also, high contact resistance might lower electron extraction. This could lead to electron recombination with the electrolyte at the contact, which represents a leakage current and decreases parallel resistance. Further studies are required using lower resistivity plastic substrates.

4. Conclusions

A new procedure to the preparation of porous thick TiO_2 photoelectrodes is proposed and studied. Its essence is the use of the photocatalytic properties of nanocrystalline TiO_2 to decompose a molecular titania precursor. The thus produced titania serves to neck previously crystallized TiO_2, as well as to improve TiO_2 porous layer adherence to the TCO. The highest temperature reached with this method is approximately 80 °C; therefore, it is suitable for ITO-covered plastic substrates. The use of an open-atmosphere-stable and water-soluble titania precursor is another clear advantage. A first evaluation of the performance of the films obtained as photoelectrodes for DSSC has given promising results: photoelectrodes obtained using the proposed technique show characteristics equal to or better than those obtained with the traditional method. Good mechanical properties were shown by the films obtained with the new method related to satisfactory necking among nanocrystallites and very strong adhesion in some areas (which could be made uniform for the whole area in the future). These characteristics should also favor electron transport from particle to particle and finally, to the TCO.

Acknowledgements

This work has been financed by the Spanish National Plan of Research (BQU2003-01280 project). Part of the work was conducted thanks to the grant of the Spanish Secretaría de Estado de Educación y Universidades to E. Vigil (SAB2002-0081).

References

[1] C. Longo, J. Freitas, M.-A. De Paoli, J. Photochem. Photobiol. A: Chem. 159 (2003) 33–39.
[2] A.F. Nogueira, C. Longo, M.-A. De Paoli, Coord. Chem. Rev. 248 (2004) 1455–1468.
[3] H. Lindström, E. Magnusson, A. Holmberg, S. Södergren, S.-E. Lindquist, A. Hagfeldt, Sol. Energy Mater. Sol. Cells 73 (2002) 91–101.
[4] H. Lindström, A. Holmberg, E. Magnusson, S.-E. Lindquist, L. Malmqvist, A. Hagfeldt, Nano Lett. 1 (2001) 97–100.
[5] A. Hagfeldt, G. Boschloo, H. Lindström, E. Figgemeier, A. Holmberg, V. Aranyos, E. Magnusson, L. Malmqvist, Coord. Chem. Rev. 248 (2004) 1501–1509.
[6] S. Nakade, M. Matsuda, S. Kambe, Y. Saito, T. Kitamura, T. Sakata, Y. Wada, H. Mori, S. Yanagida, J. Phys. Chem. B 106 (2002) 10004–10010.
[7] K.-J. Kim, K.D. Benkstein, J. van de Lagemaat, A.J. Frank, Chem. Mater. 14 (2002) 1042–1047.
[8] C.J. Barbe, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Gratzel, J. Am. Ceram. Soc. 80 (1997) 3157–3171.
[9] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos, M. Graetzel, J. Am. Chem. Soc. 115 (1993) 6382–6390.
[10] S. Yamabi, H. Imai, Thin Solid Films 434 (2003) 86–93.

[11] F. Bosc, A. Ayral, P.-A. Albouy, C. Guizard, Chem. Mater. 15 (2003) 2463–2468.
[12] M. Langlet, A. Kim, M. Audier, C. Guillard, J.M. Herrmann, Thin Solid Films 429 (2003) 13–21.
[13] J. Huang, I. Ichinose, T. Kunitake, A. Nakao, Langmuir 18 (2002) 9048–9053.
[14] N. Kaliwoh, J.-Y. Zhang, I.W. Boyd, Surf. Coat. Technol. 125 (2000) 424–427.
[15] K. Shimizu, H. Imai, H. Hirashima, K. Tsukuma, Thin Solid Films 351 (1999) 220–224.
[16] S. Baskaran, L. Song, J. Liu, Y.L. Chen, G.L. Graff, J. Am. Ceram. Soc. 81 (1998) 401–408.
[17] A. Dutschke, C. Diegelmann, P. Löbmann, J. Mater. Chem. 13 (2003) 1058–1063.
[18] Y. Aoi, H. Kambayashi, E. Kamijo, S. Deki, J. Mater. Res. 18 (2003) 2832–2836.
[19] F. Pichot, J.R. Pitts, B.A. Gregg, Langmuir 16 (2000) 5626–5630.
[20] G. Boschloo, H. Lindström, E. Magnusson, A. Holmberg, A. Hagfeldt, J. Photochem. Photobiol. A: Chem. 148 (2002) 11–15.
[21] T. Kado, M. Yamaguchi, Y. Yamada, S. Hayase, Chem. Lett. 32 (2003) 1056–1057.
[22] D. Zhang, T. Yoshida, H. Minoura, Adv. Mater. 15 (2003) 814–817.
[23] R. Gaudiana, J. Macromol. Sci. A39 (2002) 1259–1264.
[24] D. Zhang, T. Yoshida, K. Furuta, H. Minoura, J. Photochem. Photobiol. A: Chem. 164 (2004) 159–166.
[25] T. Oekermann, D. Zhang, T. Yoshida, H. Minoura, J. Phys. Chem. B 108 (2004) 2227–2235.
[26] T.N. Murakami, Y. Kijitori, N. Kawashima, T. Miyasaka, J. Photochem. Photobiol. A: Chem. 164 (2004) 187–191.
[27] G.P. Smestad, Sol. Energy Mater. Sol. Cells 55 (1998) 157–178.
[28] N. Papageorgiou, Coord. Chem. Rev. 248 (2004) 1421–1446.
[29] N.J. Cherepy, G.P. Smestad, M. Grätzel, J.Z. Zhang, J. Phys. Chem. B 101 (1997) 9342–9351.
[30] R. Morand, K. Noworyta, J. Augustynski, Chem. Phys. Lett. 364 (2002) 244–250.
[31] S.T. Martin, J.M. Kesselman, D.S. Park, N.S. Lewis, M.R. Hoffmann, Environ. Sci. Technol. 30 (1996) 2535–2542.
[32] W. Kubo, T. Tatsuma, A. Fujishima, H. Kobayashi, J. Phys. Chem. B 108 (2004) 3005–3009.
[33] S.-K. Lee, S. McIntyre, A. Mills, J. Photochem. Photobiol. A: Chem. 162 (2004) 203–206.
[34] F.B. Li, X.Z. Li, Chemosphere 48 (2002) 1103–1111.
[35] J.C. Yu, W. Ho, J. Yu, S.K. Hark, K. Iu, Langmuir 19 (2003) 3889–3896.