ELSEVIER

Low temperature preparation of mesoporous TiO_2 films for efficient dye-sensitized photoelectrode by chemical vapor deposition combined with UV light irradiation

Takurou N. Murakami*, Yujiro Kijitori, Norimichi Kawashima, Tsutomu Miyasaka

Graduate School of Material Science, Toin University of Yokohama, 1614 Kurogane-cho, Aoba-ku, Yokohama City, Kanagawa 225-8502, Japan

Abstract

A new method for fabricating plastic film-based mesoporous TiO_2 electrodes for efficient dye-sensitized solar cells is described. TiO_2 nanocrystalline layers electrophoretically deposited on indium-tin-oxide (ITO)-coated polyethylene terephthalate (PET) film was post-treated with chemical vapor deposition (CVD) of Ti alkoxide followed by UV light irradiation at temperatures below 110 °C. UV-assisted CVD treatment drastically enhanced dye-sensitized photocurrent and improved photovoltage up to 750 mV. A film electrode bearing Ru complex (Ru 535-bis TBA) dye-sensitized TiO_2 on ITO–PET yielded solar energy conversion efficiency of 3.8%.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Dye; Solar cell; Flexible; Photoelectrochemical; CVD; UV

1. Introduction

As an efficient and environmentally benign alternative to silicon-based photovoltaic cells, dye-sensitized solar cells (DSSCs) have attracted increasing interest since the pioneering work of Grätzel and his co-workers [1–3]. High solar conversion efficiency up to 10.4% [3], well competing with amorphous Si p/i/n junction photocells, is realized with photoelectrochemical cells of a simple junction structure. DSSCs of highest efficiency require a combination of Ru complex dyes and mesoporous TiO_2 layer that is prepared by sintering of binder-containing nanocrystalline TiO_2 at 450–550 °C. The transparent conductive electrode commonly used for this purpose has been F-doped SnO_2-coated glass that has high stability against sintering temperatures and chemical corrosion by acidic stuffs. Use of glass substrates however limits manufacture process and industrial applications of DSSCs. Another goal of DSSCs, besides pursuing further high efficiency, is to realize film-type flexible DSSCs and roll-to-roll fabrication of the cell suited to cost reduction. To this end, low temperature methods for preparing TiO_2 mesoporous films has been attempted by various approaches. Binder-free coatings of TiO_2 nanocrystals have been studied by means of repeated spin coating [4], gas phase hydrothermal treatment for mixture of Ti alkoxides and TiO_2 nanocrystals [5], electrophoretic deposition [6], and mechanical compression [7]. The compression method achieved a relatively high efficiency level of 3% under irradiation of $100\,mW\,cm^{-2}$ [7].

What is essential to ensure sufficient efficiency in electron conduction within a non-sintered nanoparticle layer is to establish chemical and physical binding between particles, that is so-called "necking". For transparent conductive flexible films, indium-tin-oxide (ITO) has been widely used as a conductive layer of plastic supports such as polyethylene terephthalate (PET) film. ITO is much less stable than SnO_2, thermally and chemically. The glass transition temperature (T_g) of PET is 75 °C and surface electric resistance of ITO–PET is regarded only sustainable at temperatures below 150 °C. With ITO–PET electrode, it is required to introduce a necking structure into binder-free TiO_2 coatings at low temperatures without chemically damaging the ITO layer. We have studied low temperature preparation of mesoporous TiO_2 layer based on electrophoretic deposition technique combined with post thermal and chemical treatments [8]. Conversion efficiency of the cell reached 4% using F/SnO_2–glass substrate. Displacing the F/SnO_2 glass with ITO plastic substrates, however, brings about many problems leading to lowering of efficiency, which are due to instabilities of the

* Corresponding author. Tel.: +81-45-947-5055; fax: +81-45-947-5055.
E-mail addresses: murakami@edu.toin.ac.jp (T.N. Murakami), tm12b06@edu.toin.ac.jp (Y. Kijitori), kawasima@cc.toin.ac.jp (N. Kawashima), miyasaka@cc.toin.ac.jp (T. Miyasaka).

ITO conductive layer and the contact of TiO_2 and flexible ITO layer. In this paper, we describe a new method to improve the photoelectric performance of dye-sensitized TiO_2 layer coated on ITO–PET film electrode by applying chemical vapor deposition combined with UV light irradiation.

2. Experimental

All chemical reagents used in electrolytic composition, solvent for dye adsorption, and chemical vapor deposition (CVD) were commercial grade, including LiI (97.0%), I_2 (99.9%), acetonitrile (99.0%), t-butyl alcohol (99.0%), ethanol (99.5%) of Wako Pure Chemical Industries, 4-tert-butylpyridine (99.0%) of Lancaster, 1,2-dimethyl-3-propylimidazolium iodide of Tomiyama Pure Chemical Industries, methoxyacetonitrile (99.0%) of Aldrich, tetraiso-propyl orthotitanate ($[(CH_3)_2CHO]_4Ti$) of Tokyo Kasei Kogyo. Ru complex dye, cis-bis(isothiocyanato)bis(2,2′-bi-pyridyl-4,4′-dicarboxylato)-ruthenium(II)bis-tertabutylam-monium, was Ru 535-bisTBA available at Solaronix SA. TiO_2 particle, F-5, was supplied from Showa Titanium, which is anatase-rich (70%) particle of high crystallinity with an average size of 20–30 nm. ITO-coated polyethylene terephthalate (ITO–PET) conductive film (188 μm thick, transmittance of 76–78%, surface resistance of 15–16 $\Omega/\square$) was provided by Tobi, and was used as the plastic film substrate for dye-sensitized electrode. Binder-free TiO_2 nanoparticle layers were formed on the ITO–PET electrode by electrophoretic deposition method as reported previously [8]. A homogeneous dispersion of F-5 in t-butyl alcohol and acetonitrile (95:5) mixture (30–40 g/L) sandwiched between the ITO–PET electrode and conductive F-doped SnO_2 glass (FTO glass) counter electrode. For electrophoretic deposition, a negative DC field of amplitudes of more than 200 V/cm was applied to the ITO–PET electrode for 30 s. F-5 nanoparticles were totally deposited on the ITO surface with uniform thickness of 10 μm. After drying, the deposited layer exhibited a high porosity of 80%. Microscopic observation showed that the TiO_2 layer has a crackle-rich surface characteristic to electrophoretic deposition. Shortly after deposition, TiO_2 layer was subjected to CVD and/or UV light irradiation treatments. The CVD treatment was performed by exposure of the TiO_2 nanoparticle layer to gaseous $[(CH_3)_2CHO]_4Ti$ at 80 °C in a closed chamber for varied time of <20 min. Protection of bare ITO surfaces was made by covering with masking tape. UV treatment of TiO_2 layers was carried out independently or combined with the above CVD process as a post-CVD process. TiO_2 layer was irradiated with 254 nm light supplied by a 13 W low-pressure mercury lamp (Nippo SGL-400T4U) at 110 °C, where bare ITO surfaces were again protected with an aluminum foil. Shortly afterwards, the post-treated TiO_2 layer on ITO–PET film was dye-adsorbed with Ru 535-bisTBA by dipping the film in a 0.3 mM dye solution in a mixed solvent of acetonitrile: ethanol: t-butyl alcohol

(2:1:1) at 40 °C for 1 h. The dye-adsorbed TiO_2–ITO–PET film was combined with a platinum-deposited FTO glass counter electrode by insertion of a porous polyethylene film as a separator that prevents short circuit. Electrolytic solution comprised 0.05 M I_2, 0.1 M LiI, 0.5 M 4-tert-butylpyridine, and 0.6 M 1,2-dimethyl-3-propylimidazolium iodide in methoxyacetonitrile, which was injected between both electrodes separated by 50 μm with a spacer film.

Photocurrent–voltage characteristics were measured on a Keithley 2400 source meter in combination with a solar simulator composing a 300 W xenon arc lamp (Perkin–Elmer), AM 1.5G filters (Optical Coatings, Japan), and quartz integrator lens. Incident photon to current conversion efficiency (IPCE) spectra were obtained with a Bunko Keiki action spectrum measurement system. Absorption spectra of dye-sensitized films were measured on a JASCO V-550 UV-Vis spectrometer with attachment of an integrating sphere for detecting diffuse reflectance. The X-ray diffraction (XRD) patterns of TiO_2 were obtained by using a Rigaku RINT 2500VHF diffractometer.

3. Results and discussion

3.1. Photocurrent and voltage improvement by CVD and/or UV treatments

To examine the effect of CVD and UV post treatments at electrophoretically deposited F-5 particle layers, three independent processes were conducted in which CVD treatment alone (CVD), UV irradiation alone (UV), and CVD treatment followed by UV irradiation (CVD/UV), respectively, were applied to the TiO_2-bearing ITO–PET films by varying the treatment time. Photoelectric performances of cells with these film electrodes were compared at incident power intensity of 85 mW cm^{-2}. Virgin TiO_2 layer without the treatments yielded a short circuit photocurrent density (J_{sc}) of 2.9 mA cm^{-2} and open-circuit voltage (V_{oc}) of 0.67 V. All post treatment processes, CVD, UV, and CVD/UV, were shown to improve the photocurrent. Among them, highest performance was obtained by CVD/UV process. Fig. 1 exhibits dependence of J_{sc} and V_{oc} on treating time of CVD, where the time of UV irradiation was fixed at 20 min. Plotted data were averaged for experiments of at least four times. J_{sc} increased to 6.2 mA cm^{-2} by 20 min of CVD process, which is more than twice the level of non-treated electrode. An important effect accompanying the J_{sc} improvement is substantial increase in V_{oc} reaching at values around 750 mV. This change took place for the first 10 min of CVD and remained constant afterwards. Although J_{sc} increment is generally accompanied by a slight increase in V_{oc}, the result shows that the V_{oc} increment apparently exceeds the influence of J_{sc} increase. The observed improvement may result from necking of nanocrystalline TiO_2 (F-5) particles by formation of TiO_2 introduced by CVD. Fig. 2 shows the J_{sc} and V_{oc} dependence on CVD treating time measured for
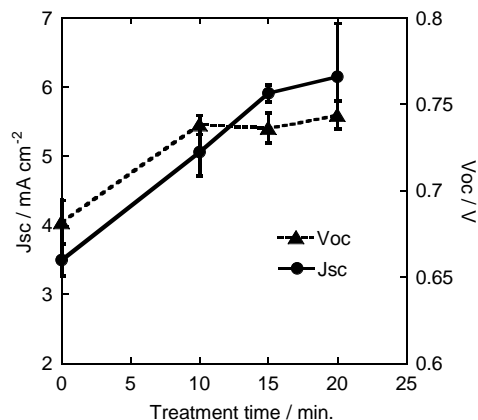
Fig. 1. Dependence of J_{sc} and V_{oc} of DSSCs on reaction time of CVD/UV treatment at TiO_2 nanocrystalline layers on ITO–PET electrode. UV light irradiation time was fixed as 20 min. Incident intensity, 85 mW/cm^2 (AM 1.5). Electrolyte composition is 0.05 M I_2, 0.1 M LiI, 0.5 M 4-*tert*-butylpyridine and 0.6 M 1,2-dimethyl-3-propylimidazolium iodide in methoxyacetonitrile.

DSSCs without undergoing the UV irradiation. The CVD process alone proved to be capable of increasing J_{sc} and V_{oc}. The resulted effects are, however, much smaller than in the above CVD/UV process. Figs. 1 and 2 indicate that the alkoxide-based CVD process is basically useful for enhancing photocurrent by necking reaction. This process is more favored over CVD treatments with acidic precursors, typically $TiCl_4$, which can chemically damage the conductive ITO coating and photoelectric performance.

In Fig. 3, the effect of UV irradiation alone is shown as a function of irradiation time. UV irradiation to non-CVD-treated TiO_2 layer caused only a small increase in J_{sc} and little change in V_{oc}; the latter stayed at a low level of 670–680 mV even by prolonged irradiation. Small changes in performance indicate that necking reaction cannot be made solely by UV irradiation. In relation to the influence of UV light, Gregg and co-workers [9,10] have eluci-
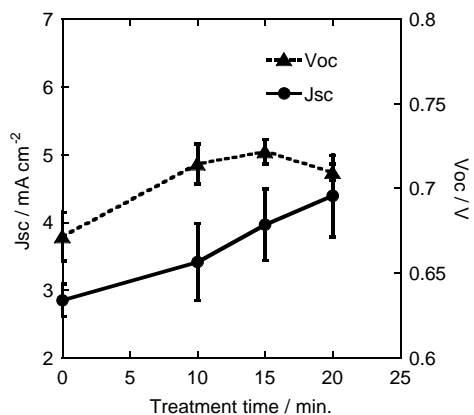

Fig. 2. Dependence of J_{sc} and V_{oc} of DSSCs on reaction time of CVD treatment at TiO_2 nanocrystalline layers on ITO–PET electrode. The electrolyte composition is same as in Fig. 1.
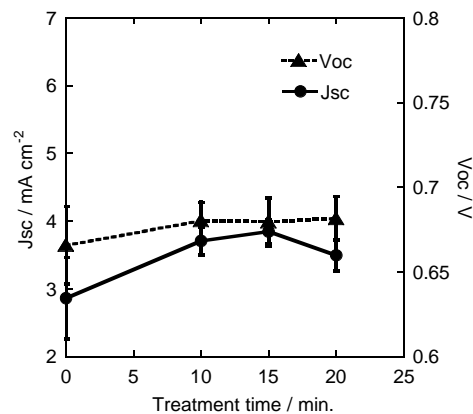

Fig. 3. Dependence of J_{sc} and V_{oc} of DSSCs on reaction time of UV irradiation treatment at TiO_2 nanocrystalline layers on ITO–PET electrode. The electrolyte composition is same as in Fig. 1.

dated that, using sintered films of TiO_2, the UV irradiation to mesoporous TiO_2 enhances J_{sc} but significantly reduces V_{oc}. They attributed the UV effect to TiO_2 surface states introduced by UV absorption. Our non-sintered TiO_2 particle layer, however, showed little of such effect except for a small increase in J_{sc}. Regarding the role of UV light in the observed improvement of J_{sc}, organic contaminants adsorbed on the TiO_2 surfaces are thought to be decomposed by UV light directly or via photocatalytic reactions of TiO_2 to give a cleaned particle surface that favors electron conduction through particles. Regarding UV light irradiated decomposition of organic compounds and surface finishing see [11].

3.2. Properties of the CVD-treated TiO_2 film

In Fig. 1, the J_{sc} increase by CVD/UV process amply exceeds the sum of increments by CVD and UV processes. This indicates that UV irradiation participates in promoting the chemical necking reaction in CVD. Chemical vapor deposition of TiO_2 has been extensively studied using Ti alkoxide [12]. Halary et al. [12] has investigated growth of a TiO_2 film by CVD under irradiation of UV light, showing that a mixture of anatase and rutile in crystalline to amorphous states forms depending on substrate temperature. On our IR analysis, it was confirmed that $[(CH_3)_2CHO]_4Ti$ deposited in mesoporous TiO_2 was rapidly decomposed during CVD and subsequent UV irradiation. To investigate the property of resultant TiO_2 deposit, a CVD-coated TiO_2 layer prepared from $[(CH_3)_2CHO]_4Ti$ was analyzed by XRD measurement. Fig. 4 exhibits XRD patterns of the TiO_2 F-5 particle used as semiconductor layer and of a TiO_2 layer prepared by the presently used CVD process at 80–110 °C. In contrast with F-5 particle that exhibits strong diffraction peaks characteristic of anatase structure, alkoxide CVD-based TiO_2 (C12:TiO_2) gave no significant peaks, indicating an amorphous state. This is in line with the previous observation
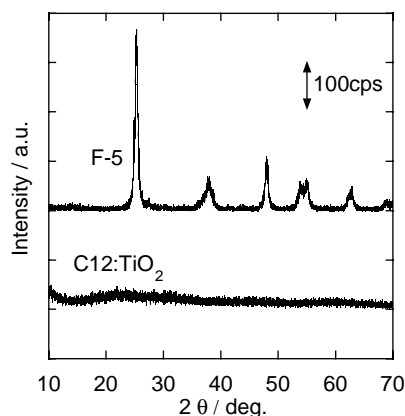
Fig. 4. X-ray diffraction patterns of TiO_2 (F-5) used as the nanocrystalline semiconductor layer and amorphous TiO_2 ($C12:TiO_2$) formed by CVD treatment.

for TiO_2 prepared by alkoxide-based low temperature CVD [12].

Influence of the CVD treatment of TiO_2 layer on dye adsorption was investigated. Fig. 5 shows spectra of optical absorbance measured by surface reflection mode for dye-sensitized TiO_2 layers with CVD/UV, CVD, and UV treatments and reference layer without the treatments. No change was observed between non-treated reference and UV-treated layer. Both CVD-treated layers (CVD/UV and CVD), however, showed a lower level of dye absorption with respect to non-treated TiO_2 layer. The result implies that the amorphous CVD-derived TiO_2 surface has a lower amount of adsorbed dye molecules than bare F-5 surfaces.

3.3. Light to electric energy conversion efficiency

The CVD/UV treatment remarkably improves photocurrent density (Fig. 1) despite the observed tendency to bring
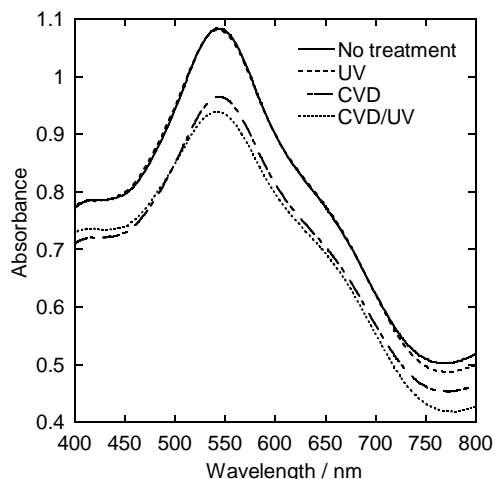

Fig. 5. Absorption spectra of Ru535-bisTBA adsorbed on CVD/UV, CVD, and UV-treated TiO_2 layers in comparison of that obtained with non-treated TiO_2 layer. Measurement was made by surface reflectance mode employing an integrating sphere.
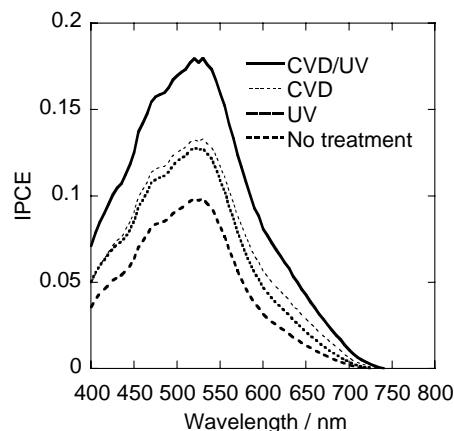

Fig. 6. IPCE action spectra of DSSCs with CVD/UV, CVD and UV-treated TiO_2 layers on ITO–PET electrodes in comparison of that obtained with non-treated TiO_2 layer. The electrolyte composition is same as in Fig. 1.

a loss in optical absorption. Quantum efficiency of incident photon to electron conversion (IPCE) was measured for dye-sensitized ITO–PET film electrodes made by CVD/UV treatments and results are compared in Fig. 6. The results of IPCE well reflect the tendency of J_{sc} increase depicted in Figs. 1–3 and the CVD/UV treated electrode exhibited a twice improvement of IPCE that peaks at 530 nm. IPCE spectra show that the present TiO_2 layers lack an ample light scattering effect as judged for a longer wavelength region (550–700 nm) where IPCE value drops. This insufficient light scattering was found to be characteristic of the film of F-5 particles, which shows intrinsically high transparency compared to other commercial nano-particles like P-25. This optical property is possibly due to the crystalline shape, polyhedron, of F-5. The IPCE data further indicate that the measured IPCE values, by exposure to low-intensity monochromatic light, are too low to reflect the observed high J_{sc} value under irradiation of intense light. For this discrepancy, we speculate the existence of a path of back electron transfer either at the interface of ITO/F-5 or F-5/electrolyte (I^-), which could not be successfully eliminated by the present CVD/UV treatment. In addition, a possibility cannot be excluded that a high density of electron traps, occurred as a result of by low-temperature TiO_2 preparation, decrease the mobility of electrons and photocurrent efficiency.

Fig. 7 shows global energy conversion efficiencies of dye-sensitized TiO_2–ITO–PET electrodes as function of treating time in CVD and UV processes. The CVD/UV process realized remarkable improvement of efficiency from average 1.3% (non-treated electrophoretically deposited TiO_2 film) up to average 3.4%. Based on the photocurrent density–voltage characteristics measured at $85\,mW\,cm^{-2}$ incident power, highest efficiencies were obtained at 3.8% ($J_{sc} = 7.0\,mA\,cm^{-2}$, $V_{oc} = 750\,mV$, fill factor = 0.61) for CVD/UV treated cell and 2.7% ($J_{sc} = 5.2\,mA\,cm^{-2}$, $V_{oc} = 720\,mV$, fill factor = 0.61) for CVD-treated cell. It is worth noting that the maximum V_{oc} obtained of
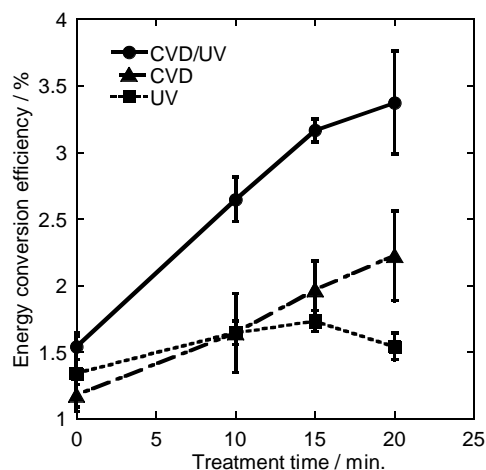
Fig. 7. Energy conversion efficiencies of the DSSCs using plastic ITO–PET electrodes with CVD/UV, CVD and UV-treated TiO$_2$ layers as a function of treatment time. The electrolyte composition is same as in Fig. 1.

740–750 mV is a level comparable with that achieved by dye-sensitized sintered TiO$_2$ electrodes of highest efficiency (10%) [1–3]. In an attempt to investigate the role of amorphous TiO$_2$ prepared by CVD, a DSSC was fabricated in which dye-sensitized photoelectrode had an undercoating of an amorphous TiO$_2$ film prepared by CVD. We found that the CVD-derived undercoating behaves like an insulating layer to block photocurrent at the interface, allowing the cell to generate only a measurable J_{sc} of <0.1 mA cm^{-2}.[1] With this condition, the cell gave a high V_{oc} of 740 mV. Based on these facts, we consider that the amorphous TiO$_2$ introduced by CVD on the surface of nanocrystalline TiO$_2$ (F-5) can functions as a thin insulating layer that suppresses the back electron transfer to electrolyte, improving V_{oc} as a result. The drastic increase in J_{sc} achieved by CVD, on the other hand, is considered due to reinforcement of inter-particle necking between F-5 particles rather than contribution of CVD-derived TiO$_2$ itself to electron conduction.

4. Conclusion

We have demonstrated the usefulness of alkoxide-based CVD treatment combined with UV irradiation for improving the efficiency of dye-sensitized photoelectrodes with nanocrystalline TiO$_2$ deposited on ITO-coated plastic films. As a low temperature preparation of binder-free TiO$_2$ layer, our method can directly be applied to fabrication of all plastic, film-type DSSCs of sufficiently high efficiency. The TiO$_2$ layer coated on ITO–PET film showed high mechanical stability against bending of the film electrode up to curvature of 1/5 mm ($r = 5$ mm). CVD/UV

treated, dye-sensitized TiO$_2$–ITO–PET film electrode exhibited conversion efficiency of 3.8%. The efficiency is still half the level of the highest efficiency of conventional sintered TiO$_2$-based F/SnO$_2$ glass electrodes. Nevertheless, photovoltage obtained with the electrode, 750 mV, is of amply high standard as DSSC and is a characteristic advantage of this method. Further advantage of our fabrication process is emphasized in a point that total procedures from electrophoretic deposition to post treatments of TiO$_2$ are completed in fairly short time without use of sintering or annealing processes. This rapid fabrication method makes it more efficient to drive roll-to-roll continuous systems for manufacture of DSSCs that leads to cost reduction.

Acknowledgements

References

[1] (a) B. O'Regan, M. Grätzel, Nature 353 (1991) 737–740;
    (b) M. Grätzel, Nature 414 (2001) 338–344.
[2] A. Hagfelt, M. Grätzel, Acc. Chem. Res. 33 (2000) 269–277.
[3] M. K. Nazeeruddin, P. Pécky, M. Grätzel, Chem. Commun. 18 (1997) 1705–1706.
[4] F. Pichot, J.R. Pitts, B.A. Gregg, Langmuir 16 (2000) 5626–5630.
[5] (a) D. Zhang, T. Yoshida and H. Minoura, Chem. Lett. (2002) 874–875;
    (b) D. Zhang, T. Yoshida, H. Minoura, Adv. Mater. 15 (2003) 814–817.
[6] D. Matthews, A. Key, M. Grätzel, Aust. J. Chem. 47 (1994) 1869–1877.
[7] H. Lindström, A. Hormberg, E. Magnusson, L. Malmqvist, A. Hagfeldt, J. Photochem. Photobiol. A 145 (2001) 107–112.
[8] (a) T. Miyasaka, Y. Kijitori, T. N. Murakami, M. Kimura, S. Uegusa, Chem. Lett. 12 (2002) 1250–1251;
    (b) T.N. Murakami, Y. Kijitori, N. Kawashima, T. Miyasaka, Chem. Lett. 32 (2003) 1076–1077.
[9] S. Ferrere, B.A. Gregg, J. Phys. Chem. B. 105 (2001) 7602–7605.
[10] B.A. Gregg, S.-G. Chen, S. Ferrere, J. Phys. Chem. B. 107 (2003) 3019–3029.
[11] (a) T. N. Murakami, M. Takahashi, and N. Kawashima, Chem. Lett. 11 (2000) 1312–1313;
    (b) T.N. Murakami, Y. Fukushima, Y. Hirano, Y. Tokuoka, M. Takahashi, N. Kawashima, Colloids Surf. B: Biosurf. 29 (2003) 171–179.
[12] E. Halary, E. Haro-Poniatowski, G. Benvenuti, P. Hoffmann, Appl. Surf. Sci. 168 (2000) 61–65, and references therein.

---

[1] The CVD-derived film as an undercoating of dye-sensitized TiO$_2$ layer was prepared by CVD/UV treatment at 20 min for bare ITO surfaces.