Scientific paper

One Step Preparation of TiO_2 Layer for High Efficiency Dye-sensitized Solar Cell

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Abstract

A novel titanium dioxide paste based on Pechini sol-gel method and nanocrystalline TiO_2 powder has been successfully developed and tested. The paste enables the formation of sponge like structure of the TiO_2 layer *i.e.* highly porous and at the same time well connected TiO_2 network. The layers have been used to assemble dye sensitized solar cells (DSSC) with two ruthenium complex based dyes, N719 and black dye, respectively. Overall conversion efficiencies of ionic liquid electrolyte based DSSC sensitized with N719 and black dye was 6.1% and 2.0%, respectively, when determined under standard test conditions (100 mW/cm^2, AM1.5, 25 °C).

Keywords: Dye-sensitized solar cells, TiO_2 layer, Pechini method, N719, Black dye

1. Introduction

In the last decade the research in the field of dye-sensitized solar cells (DSSCs) has been focusing on development of materials which could enhance the conversion efficiency and simplify the production of DSSC while at the same time assure their long-lifetime[1,2]. The front photoactive electrode of a DSSC is a transparent conductive oxide (TCO) glass coated with nanoporous TiO_2 sensitized with a monolayer of a Ruthenium complex dye, while the counter electrode is a TCO glass coated with a thin layer of platinum. The gap between the electrodes is filled with an electrolyte containing an iodide/tri-iodide (I^-/I_3^-) redox couple[3]. Under illumination, the dye molecules are excited and initial charge separation occurs by injection of an electron from the dye into the conduction band of the TiO_2. The electron is then transported to the external load via the nanostructured TiO_2 and the front TCO. The dye molecule is regenerated (reduced) with receiving an electron from the iodide present in the electrolyte.

Nanocrystalline TiO_2 in anatase modification with a band gap of ~ 3.2 eV has been identified as the most appropriate material to use, since its conduction band lies just beneath the LUMO level of the ruthenium complex dye. In order to realize high efficient DSSC the following requirements must be met: good solar light harvesting; diminished recombination *i.e.* loss reactions of photogenerated electrons with the tri-iodide species present in the electrolyte, and good electron transport within TiO_2 layer and between TiO_2 and TCO substrate. To satisfy the requirements following characteristic apply for the TiO_2 layer: the layer thickness between 7 and 14 µm[4], high inner surface area available for dye molecules to be attached, appropriate porosity of the layer assuring electrolyte penetration through the layer, good connections of the TiO_2 grains within the TiO_2 network and good adhesion to the TCO. Therefore the optimization of the TiO_2 layer morphology according to the demands outlined above is a prerequisite for the realization of a high efficient DSSC[5–7].

The highest efficiency reported so far for a small size DSSC (~ 0.2 cm^2) using an ionic liquid (IL) electrolyte is 8.2%[8]. However, for their realization the three or fourfold layer deposition of TiO_2 was needed[9]. The TCO was firstly coated with a thin compact TiO_2 layer assuring a good mechanical contact between the following printed TiO_2 layer and the TCO substrate. In the second step a transparent layer consisting of 20 nm size TiO_2 particles was screen printed and further coated by the third screen printed layer of 400 nm light scattering TiO_2 particles. The fourth step involved treating the triple layer with an ethanol solution of $TiCl_4$ to improve the connections between the grains present in the thick nanoporous layer.The preparation procedure of fourfold TiO_2 layer is complex, since different TiO_2 precursors as well as different deposition techniques are required.

Therefore our aim was to simplify the preparation of TiO_2 layer in such a way that solely a deposition of a single TiO_2 paste followed by annealing of the layer would be sufficient to realize a highly efficient photoactive layer. We have focused on the development of a TiO_2 paste that would unify the requirements mentioned above. Intensive research of our group in this field has already produced relevant results[10,11] using a new paste formulation developed by applying the Pechini type sol-gel method[12]. The Pechini method is based on the preparation of a polymeric net (sol), which is achieved by mixing ethylene glycol with citric acid in which the metal alkoxide *e.g.* titanium isopropoxide is dissolved[12], while the paste was prepared with the addition of TiO_2 nanoparticles to the sol. Our previous comparison study between the "standard" TiO_2 paste based on terpineoel and methylcellulose[13] and the paste based on Pechini method has shown an improvement of DSSC efficiency for up to 190% if the Pechini based TiO_2 paste was used[10]. The main reasons were higher dye loading and improved electron transport through the TiO_2 layer.

In this paper we present study of the Pechini based TiO_2 layer using the one-step preparation procedure that have been sensitized with two ruthenium complexes (N719 and Black dye – BD). The morphology of the TiO_2 layer, characterized by scanning electron microscopy (SEM), is presented as well as the adhesion of the TiO_2 layer to the conductive substrate. The amount of the dyes adsorbed onto the TiO_2 layer was determined with UV-Vis spectroscopy. In order to evaluate the efficiency of two different dyes the DSSCs have been assembled. We compared the effectiveness of the dye molecules, the external quantum efficiency (QE) of both types of DSSCs as well as their performance under standard test conditions (100 mW/cm^2, AM1.5, 25 °C).

2. Experimental

The first step in the preparation of the TiO_2 paste was the synthesis of a polyester-based titanium sol using a precursor molar ratio of 1:6:24 [titanium isopropoxide : citric acid : ethylene glycol]. The sol was prepared by heating ethylene glycol (Riedel-de Haen) to 60 °C and during stirring the titanium isopropoxide (Fluka) was added. Finally, the corresponding amount of citric acid (Fluka) was added and the temperature increased to 90 °C. The solution was stirred at this temperature until it turned clear. The TiO_2 paste was prepared by mixing the TiO_2 powder (P25, Degussa) and sol in a mortar grinder (Retsch, RM200) for 3 hours. The molar ratio between the TiO_2 powder and titanium isopropoxide in the paste formulation was 7:1. The paste was deposited on the conduction electrode (TCO) *i.e.* a fluorine-doped SnO_2 on glass substrate, using the "*doctor blade*" technique[14]. Layers were annealed at 450 °C for one hour. Afterwards, the layer thickness was determined by surface profilometer (Taylor-Hobson Ltd.) and the thickness of a layer was 11 µm.

The particle size and the surface morphology of the TiO_2 layers were analysed with Hitachi S 4700 scanning electron microscope (SEM).

To obtain a qualitative impression of the adhesion between TiO_2 layer and the TCO substrate, the cross-cut test was applied according to the ISO 2409 standard. In the cross-cut test, two sets of cuts are made perpendicular to each other leading to a network of small squares. Then an adhesive tape is stuck on the network and pulled off by hand at a take-off angle of 60° with respect to the sample surface and almost with a constant force. Percent of squared surface crumbled from the edge of the squares, is a measure of the adhesion quality. According to ISO 2409, the quality of adhesion is ranked by different numbers ranging from 0 to 5. Ranking number of the cross-cut adhesion can vary from 0-excellent, followed by 1-very good, 2-good, 3-moderate, 4-poor and finally 5 as very poor.

To produce the DSSC, the TiO_2 layers were immersed in an ethanol solution of the Ruthenium complex dye ($c = 1 \times 10^{-3}$ M). Two different dyes were used; *cis*-diisothiocyanato-bis(2,2'bipyridyl-4,4'dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (Solaronix) marked as N719 and triisothiocyanato-(2,2':6',6"-terpyridyl-4,4',4"-tricarboxylato) ruthenium(II) tris(tetra-butylammonium) (Solaronix) marked as black dye – BD. For a counter electrode, platinum (thickness ~ 5 nm) was sputtered onto a SnO_2 : F glass substrate. Both electrodes were sealed with a 25 µm thick polymer foil (Surlyn, DuPont) that acts also as a spacer between the electrodes. After sealing, the electrolyte was injected through two holes pre-drilled into the counter electrode. The electrolyte was a binary ionic liquid mixture of 1-propyl-3-methyl-imidazolium iodide (PMII, Merck) and 1ethyl-3-methyl-imidazolium tetracyanoborate ($EMIB(CN)_4$, Merck) mixed in volume ratio 13:7, 0.2 M iodine (Merck), 0.5 M 1-methylbenzimidazole (MBI; Aldrich) and 0.1 M guanidine thiocyanate (Fluka). For each type of the dyes, three identical samples of DSSCs each with an active area of 0.6 cm^2 were assembled. Oriel Class A solar simulator equipped with 1.5G air mass filter was used as the light source which spectrum closely matches required AM1.5 spectrum. Nevertheless, according to the IEC 60904-3 standard the short circuit current mismatch parameter was calculated and it was used in conjunction with a calibrated c-Si reference solar cell covered with KG5 glass filter. Before characterization each cell was painted on the back side with white colour as external back reflector for unabsorbed light and covered with a black mask fitting the photoactive layer[15]. To set the cell temperature to standard test conditions (25 °C), the temperature was stabilized with a cooling/heating setup based on Peltier element designed for solar cell characterization[16]. Current–voltage characteristics (*I/V*) were measured using a Keithley 238 source meter by applying voltage and measuring current. The *I/V* measurements were scanned from 0 V (short circuit condition) to 0.9 V (beyond open circuit voltage), with a step of 10 mV.

The spectral response of the assembled DSSCs was analysed with a Xenon lamp and a monochromator. The measurement were scanned in increments of 5 nm from 300 to 800 nm, while in order to obtain stable reading the 3 s delay was always applied between setting wavelength and measurement of the current.

The amount of the dye molecules adsorbed on the TiO_2 layer, which correlates with the active surface area of the TiO_2 layer, was determined with UV-Vis spectroscopy[17]. The N719 and BD were desorbed from the TiO_2 layers with 0.02 M NaOH (Merck), the dye solution was diluted with 0.02 M NaOH to 50 ml before obtaining UV-Vis spectra. In order to determine the amount of the dye adsorbed on the TiO_2 layers, firstly a calibration curves were made for different N719 and BD dye solutions varying in the dye concentration between 1.0×10^{-7} M and 1.0×10^{-4} M in 0.02 M NaOH. The measurements were scanned in decrements of 5 nm from 800 to 350 nm. In the spectra the peaks at 370 and 500 nm characteristic for the N719 and peaks at 385 and 565 nm characteristic for the BD have been identified (Fig. 1). For the calibration curve and the evaluation of the samples concentration the absorbance of the second peak *i.e.* at 500 and 565 nm, for N719 and BD, respectively, have been considered (Fig. 1).

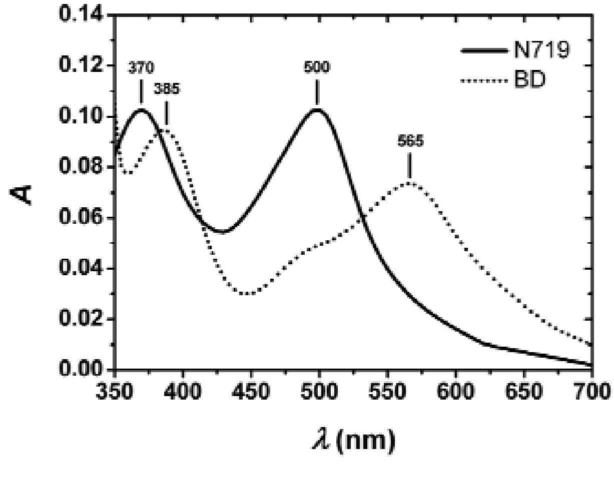

Figure 1. Absorbance spectrum of N719 and BD (dye solution in ethanol 1.0×10^{-5} M).

3. Results and Discussion

3. 1. Morphology of the TiO_2 Layer

Fig. 2 shows TiO_2 layer after the cross-cut testing. The edges of the cuts are smooth, with hardly noticeable flakes of the coating at the intersection. The layer is compact and uniform after testing which reveals that the adhesion quality of the layer is very good. According to ISO 2490, the adhesion quality of the layer is ranked by 1.

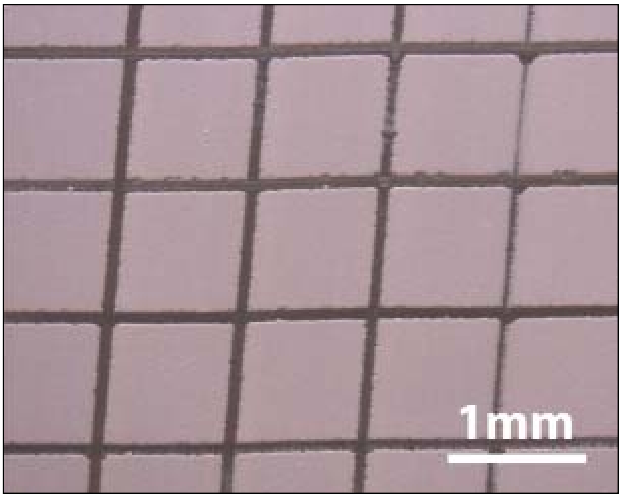

Figure 2. The photo of TiO_2 layer taken after the cross-cut test.

Additionally, the SEM micrograph (Fig. 3a) showed uniform and smooth surface of TiO_2 layer with almost no cracks. The cross-section of the active electrode consisting of TiO_2 layer deposited on TCO-coated glass substrate (from left to right: glass, TCO, TiO_2 layer) reveals that the TiO_2 layer is homogenous and well attached to the TCO layer on the glass substrate (Fig. 3b), which is in agreement with the cross-cut test (Fig. 2). The spherical TiO_2 nanoparticles are homogenously distributed within the TiO_2 layer without agglomeration (Fig. 3c). The layer exhibits high porosity *i.e.* sponge like structure. The sol, which is obtained by the Pechini sol-gel method, exothermally decomposes[18], resulting in the formation of a highly porous, but at the same time well connected, TiO_2 network.

3. 2. Dye Loading and Dye Sensitized Solar Cell

The amount of N719 and BD molecules attached to the surface of TiO_2 layers per volume of the TiO_2 layer [*n(dye)/V(layer)*] is presented in Table 1. The amount of N719 dye molecules attached to the TiO_2 layer was 1.18×10^{-4} mol/cm^3, however for the BD the value is lower for 20%.

In order to evaluate the influence of different dyes on the performance of DSSCs, the dye sensitized TiO_2 layers were used to assemble DSSCs with the N719 and BD, respectively. The performance of the DSSC was evaluated under STC (*i.e.* 100 mW/cm^2, AM1.5, 25 °C) and typical *I/V* characteristics for DSSC based on N719 and BD are shown in Fig. 4, while the values of short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and conversion efficiency (η) are gathered in Table 1. The va-

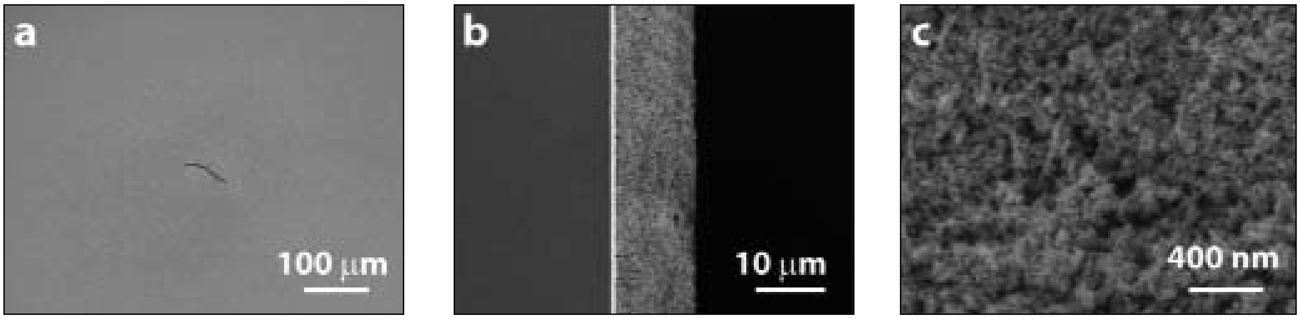

Figure 3. The SEM micrographs of (a) top view of TiO_2 layer, (b) TiO_2 layer deposited on the TCO-coated glass substrate (from left to right: glass, TCO and TiO_2) and (c) insight view of TiO_2 layer.

Table 1. The amount of the dye molecules attached to the surface of TiO_2 layers (*n(dye)/V(layer)*), short circuit current (J_{sc}), fill factor (FF), open circuit voltage (V_{oc}) and conversion efficiency (η) of the DSSCs evaluated under STC (100 mW/cm^2, AM1.5, 25 °C) and the effectiveness of the dye molecules [*n(dye)/V(layer)*]/J_{sc} attached to the TiO_2 determined for different dyes marked as N719 and BD.

	n(dye)/V(layer) [mol/cm^3]	J_{sc} [mA/cm^2]	[*n(dye)/V(layer)*]/J_{sc} [mol/mAcm]	*FF* [%]	V_{oc} [V]	η [%]
N719	1.18×10^{-4}	14.70	8.03×10^{-6}	59	0.687	6.1
BD	9.45×10^{-5}	5.37	1.76×10^{-5}	66	0.562	2.0

lue of J_{sc} for the DSSC sensitized with N719 is 14.7 mA/cm^2, while 63% smaller value of J_{sc} was noticed for the DSSC sensitized with BD, despite only 20% smaller dye loading. Another, very important parameter is the effectiveness of the dye molecules [*n(dye)/V(layer)*]/J_{sc} attached to the TiO_2 layer, which tells us the amount of dye molecules needed to be adsorbed on the layer to generate J_{sc} of 1 mA/cm^2. The results were calculated by dividing the amount of dye molecules per layer volume *n(dye)/V(layer)* with the J_{sc} for the layers sensitized with N719 and BD dyes and are presented in Table 1. They indicate that the lower amount of N719 than BD dye molecules is needed for equal generation of J_{sc} (*i.e.* 8.03×10^{-6} and 1.76×10^{-5} mol/mAcm for N719 and BD, respectively).

The external quantum efficiency (QE) measurements of the assembled DSSCs sensitized with N719 and BD are shown in Fig. 5. The measurements confirm that absorption of BD is extended to 790 nm. However, the DSSC sensitized with BD shows significantly smaller QE in the region between 300 and 710 nm when compared with N719. The *I/V* measurements of DSSCs are presented in Fig. 4, the J_{sc} was 14.7 and 5.4 mA/cm^2 for N719 and BD, respectively. The results are in accordance with the QE measuremnts. Nevertheless, a relatively small difference in dye loading could not explain the difference of J_{sc}.

In general, DSSC using BD tend to exhibit lower open circuit voltage (V_{OC}) than that using N719[19,20], which was also observed in our measurements. The difference

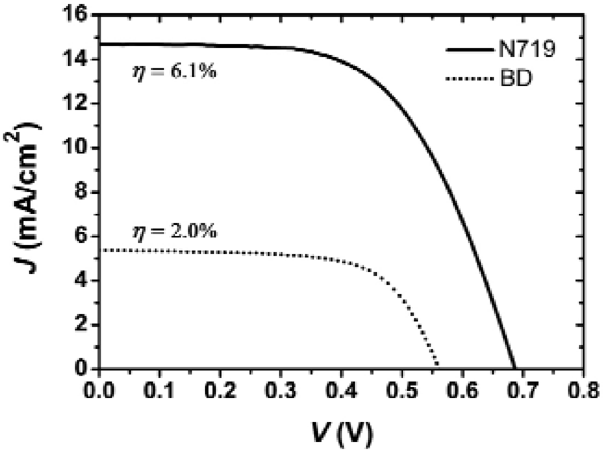

Figure 4. Current to voltage characteristics of DSSCs (IL based electrolyte) assembled with N719 and BD.

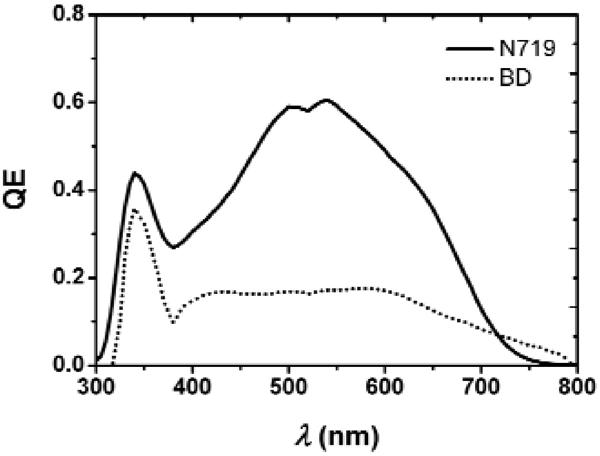

Figure 5. The quantum efficiency (QE) of the DSSCs sensitized with N719 or BD.

was up to 0.12 V (Fig. 4). The TiO_2 layer was optimized for N719, therefore this layer is not necessary expected to be optimal also for BD. The reasons for diminished performance of DSSC assembled with BD and a future optimization of TiO_2 layer for BD are under study.

As evident from this study, the layer, which was sensitized with N719 dye, posses the highest dye loading and achieves the highest performance in DSSC with the efficiency of 6.1%. However, with this kind of cell (but smaller active area ~ 0.2 cm^2) the efficiency of 7.3% has been achieved[11].

4. Conclusions

The TiO_2 paste based on the Pechini sol-gel method and commercial TiO_2 nanopowder allows a single step deposition of sponge like TiO_2 layers. The layers made with this paste show good adhesion with the conductive substrate, and exhibit higher dye-loading with N719 compared to BD. In general, the QE response of DSSC sensitized with BD is extended to higher wavelengths, but the values for N719 are much higher, which is reflected also in better performance of DSSCs sensitized with N719. In this study, the highest efficiency of DSSC sensitized with N719 was 6.1% (photoactive area of 0.6 cm^2, ionic liquid electrolyte) measured under STC (100 mW/cm^2, AM1.5, 25 °C).

5. Acknowledgements

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Povzetek

Članek obravnava nov postopek izdelave TiO_2-paste, ki temelji na solu pripravljenem po Pechinijevi metodi z dodanimi TiO_2-nanodelci. Rezultati kažejo, da nova metoda izdelave TiO_2-paste omogoča pripravo plasti gobaste strukture, ki se odlikuje po veliki poroznosti in sočasno dobri medsebojni povezavi TiO_2-nanodelcev. Plasti so bile oplaščene z dvema barviloma osnovanima na rutenijevem kompleksu (N719 in »black dye«) ter preizkušene v elektrokemijskih sončnih celicah ob uporabi elektrolita na osnovi ionskih tekočin. Učinkovitost pretvorbe sončne celice pri standardnih tesnih pogojih (100 mW/cm^2, AM1.5, 25 °C) je 6.1% pri uporabi barvila N719 in 2.0 % pri uporabi barvila »black dye«.