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A New Method for Manufacturing Nanostructured Electrodes on Plastic Substrates

Henrik Lindström, Anna Holmberg, Eva Magnusson, Sten-Eric Lindquist, Lennart Malmqvist, and Anders Hagfeldt*

Ångström Solar Center, Department of Physical Chemistry,Uppsala University, PO Box 532, 751 21, Uppsala, Sweden

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ABSTRACT

The present paper describes a new method for manufacturing a nanostructured porous layer of a semiconductor material on a conducting plastic substrate for use in an electrochemical or photoelectrochemical cell. The method involves the deposition of a layer of semiconductor particles on conducting plastic and the compression of the particle layer to form a mechanically stable, electrically conducting, porous nanostructured film at room temperature. Photoelectrochemical characteristics of the resulting nanostructured films are presented showing, for example, overall solar to electric conversion efficiencies of up to 4.9% (0.1 sun). The potential use of the new manufacturing method in future applications of nanostructured electrodes is discussed.

Introduction. In the beginning of the 90s, Grätzel and coworkers presented promising results on dye-sensitized solar cells (DSC)[1] based on nanostructured film electrodes with large internal electrode area. Nanostructured electrodes typically consist of a porous, electrically conducting network of nanosized semiconductor particles. The large inner electrode surface area of the nanostructured electrode geometry renders high amounts of adsorbed dye-molecules and concomitantly high light harvesting efficiencies. Additionally, the charge transport between interconnected nanoparticles has been shown to be very effective. Certified solar power efficiencies of 10.4%[2] and stability data with lifetime expectancies of at least 10 years for outdoor use[3] have been achieved. For a successful introduction of DSC to the market, several research groups, institutes and companies are currently looking at the manufacturability of different devices. The process technology developed by most of the workers today is based on screen-printing. The nanostructured electrodes are prepared by printing a colloidal solution of TiO_2 particles onto a conducting glass substrate. Because the colloidal solution contains organic additives, temperatures of around 450 °C are needed in order to remove these and sinter the TiO_2 particles to obtain an electrically connected network.

Due to the simple production technology, nanostructured dye-sensitized solar cells have emerged as a promising low-cost alternative to commercially available solar cells based on silicon. In order for DSC to become a competitive technology from a manufacturing point of view, we believe, however, that a batch process, including 10 to 15 steps with printing, heat treatments, coating of the dye, filling of electrolyte, and so forth, will not be fast enough to reach the very high volumes necessary to produce devices at significantly lower cost than commercial ones. We, therefore, looked into the possibility of developing a continuous roll production process. A prerequisite for such a process is to use flexible substrates (allowing roll coating of the different layers in the cell), meaning that high sintering temperature treatments must be avoided. Plastic substrates should also be advantageous in terms of flexibility, weight, overall device thickness, handling, and transport.

Recently, nanostructured TiO_2 films were prepared in a manner suitable for use with plastic substrates.[4] By removing the organic additives in the colloidal solution, these workers were able to lower the firing temperature down to 100 °C; however, only very thin films ($<1\mu$m) could be produced in this way. In another study,[5] nanostructured TiO_2 films were successfully prepared on conducting plastic substrates using a titanium dioxide paste developed for sintering at lower temperatures, 150 °C. The main purpose of this paper is essentially to introduce a new method[6] for the deposition of nanostructured electrodes on plastic conducting substrates. With the new method, the deposition can be varied and performed in a large number of ways.

Experimental Section. *Conducting Substrates.* The conducting plastic substrate was “ITO-60”, an ITO-coated PET-

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* To whom correspondence should be addressed. E-mail: anders.hagfeldt@fki.uu.se.

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based substrate supplied by IST (sheet resistance, 60 Ω/square). The plastic substrates were washed with RBS detergent (supplied by LabKemi) and rinsed with MQ water before use.

TiO_2 Suspensions. The suspensions were prepared by adding TiO_2 powder to spectrograde ethanol. Ethanol was chosen as the suspending agent because its low surface tension resulted in a smooth film deposition. The TiO_2 powder was "P25" (supplied by Degussa and used as received). The "P25" consisted of 70% anatase and 30% rutile, and the particle size was 22 and 35 nm, respectively, as obtained by X-ray diffraction (Siemens D-5000 powder diffractometer). "P25" was added to an amount of 20 wt % to ethanol. The suspension was stirred with a magnetic stirrer for a period of 2 h before deposition on the conducting substrates.

Carbon Suspension. A 0.8 g portion of graphite powder (99,5%, < 325 mesh, supplied by Alfa) and 0.2 g of carbon black (Printex L, supplied by Degussa) were ground in a mortar together with 1 g of ethanol. Next, 0.36 g of P25 and 5 g of ethanol were added. The above mixture was stirred with a magnetic stirrer for 3 days before use.

SnO_2 Suspension. Sb-doped SnO_2 powder (Zelec ECP-3010-XC, supplied by Du Pont) was platinized by mixing 500 μL of 5mM H_2PtCl_6 in 2-propanol with 0.5 g of SnO_2 and heating the mixture to 375 °C for 10 min. The platinized powder was then crushed and stirred together with 1.5 g of ethanol for 12 h.

1. Suspension Deposition. In experiments where a static press was used (see below), the suspension was applied onto the conducting substrate by hand using doctor blading with scotch tape as frame and spacer. After the deposition of the particle suspension, the ethanol was allowed to evaporate to air. The resulting dry particle layer will be referred to as the "powder film".

In experiments where a roller miller was used (see below), the suspensions were applied onto the conducting layer with a K303 Multicoater from RK Print Coat Instruments.

Film Compression: 1. Static Film Compression. TiO_2^-, SnO_2^-, and carbon-film electrodes were produced on conducting plastic substrates by using a static press. A 30 μm thick film of polyethene foil was draped on each powder film, respectively. The assembly consisting of substrate, powder film and separating film was placed between two planar steel plates. Pressure was applied on the assembly via the steel plates using a 150 ton strain rod press with Anataze programmer from PHI. Pressure was applied with a speed of about 2000 kg/(cm^2 s). Pressures of 1500 kg/cm^2, 1000 kg/cm^2, and 800 kg/cm^2 were used for TiO_2-, SnO_2- and carbon films, respectively.

2. Dynamic Film Compression. Continuous deposition of a nanostructured TiO_2 film on a flexible conducting plastic substrate was performed using a roller mill (supplied by Oy Gradek AB in Finland) with two cooperative rollers. The compression was performed by allowing the substrate with the deposited powder film to pass between the rollers with a speed of about 1m/s and with a roller line pressure of 400 kN/m.

The roller temperature was 20 °C. The mechanical stability of electrodes obtained by dynamic pressing was slightly lower compared to static pressing because the maximum line pressure with the present roller equipment was not sufficiently high.

Film Characterization. The film thickness was measured with a Dektak 3 profilometer from Veeco instruments.

Dye-Sensitization and Electrolyte Preparation. The electrodes were dye-sensitized by submerging the substrate with the deposited film for 2 h in a dye-bath consisting of 0.5 mM cis-bis(isothiocyanato)bis(2,2′bipyridyl-4,4′dicarboxylato) ruthenium (II) bis-tetrabutylammonium (N719) dye in ethanol. Two different electrolytes were used. The first electrolyte consisted of 0.5 M LiI , 0.05 M I_2, and 0.5 M *tert*-butyl pyridine in methoxypropionitrile and was used at high light intensities (0.1 sun, using a sulfur lamp). The second electrolyte consisted of 0.5 M LiI, 0.01 M I_2, and 0.5 M *tert*-butyl pyridine in methoxypropionitrile and was used for low intensities (230 lux, using fluorescent lamps).

Current–Voltage and IPCE Measurements. The i–v curve measurements were made in a two-electrode sandwich configuration. The counter electrode consisted of platinum foil, unless otherwise stated. The i–v curves were monitored and recorded using a computerized Keithley 2400 source meter. In high light intensity measurements, sunlight was simulated with a sulfur lamp (Lightdrive 1000 from Fusion Lightning). To make indoor measurements comparable with measurements performed in direct sunlight (outdoor measurement, a cloud free day at 1:00 PM in Uppsala), a pyrometer from Kipp & Zonen was calibrated. This was performed by first measuring an i–v curve of a dye-sensitized solar cell at a certain light power in sunlight. In the next step, the solar cell was exposed to simulated sunlight, and the distance to the light source was adjusted such that the same i–v characteristics that were obtained in direct sunlight were reproduced. The ratio between the light power as measured in sunlight and in simulated sunlight gave a conversion factor for the pyrometer.

Low light intensity measurements simulating indoor conditions was performed using a (70 × 50 × 40) cm^3 wooden box. The inside of the box was furnished with a coating of black paint and contained 5 fluorescent lamps (15W, 6H, Philips), and placed parallel with an internal distance of 8 cm. The distance between the solar cell and the light source was about 50 cm. The light intensity inside the box was measured with a lux meter (Lutron LX-101).

Results and Discussion. *Photoelectrochemical Measurements. 1. Static Film Compression.* The photoelectrochemical measurements were made in a two-electrode sandwich configuration using a platinum foil counter electrode. Table 1 and Table 2 show data from current–voltage measurements on statically pressed TiO_2 electrodes sensitized with N719 dye. All manufacturing parameters were kept constant; however, the electrodes in Table 1 were prepared without a heating procedure and electrodes in Table 2 were heated to 120 °C for three minutes before dye-sensitization.

The values of the fill factor, open circuit voltage, short circuit current, and overall efficiency for statically pressed

Table 1: Data Extracted from i−v Characteristics for Seven 5-μm Thick TiO_2 Films Produced with a Statical Press and Sensitized with N719[a]

ff	eff/%	V_{oc}/V	$I_{sc}/\mathrm{mAcm}^{-2}$
0.68	4.2	0.68	0.92
0.67	4.3	0.68	0.96
0.62	3.3	0.65	0.82
0.65	4.4	0.67	1.02
0.67	3.5	0.66	0.79
0.63	3.9	0.67	0.92
0.69	4.4	0.67	0.94

[a] The electrodes were *not* heated prior to dye-sensitization. The electrolyte was composed of 0.5 M LiI, 0.05 M I_2, and 0.5 M *tert*-butylpyridine in methoxypropionitrile. The light intensity was 100 W/m^2. Average values: FF, (0.66 ± 0.03); efficiency, (4.0 ± 0.5) %; V_{oc}, (0.67 ± 0.01) V; and I_{sc}, (0.91 ± 0.01) mA/cm^2.

Table 2: Data Extracted from i−v Characteristics for Six 5-μm Thick TiO_2 Films Produced with a Statical Press and Sensitized with N719[a]

ff	eff/%	V_{oc}/V	$I_{sc}/\mathrm{mAcm}^{-2}$
0.66	3.8	0.71	0.80
0.66	4.0	0.72	0.83
0.62	3.6	0.73	0.79
0.64	3.7	0.67	0.78
0.68	4.0	0.66	0.89
0.70	4.6	0.67	0.93

[a] The electrodes were heated to 120 °C for 3 min prior to dye-sensitization. The electrolyte was composed of 0.5 M LiI, 0.05 M I_2, and 0.5 M *tert*-butylpyridine in methoxypropionitrile. The light intensity was 100 W/m^2. Average values: FF, (0.66 ± 0.03); efficiency, (3.9 ± 0.4) %; V_{oc}, (0.69 ± 0.03) V; and I_{sc}, (0.84 ± 0.01) mA/cm^2.

Table 3: Data Extracted from i−v Characteristics for Four 5-μm Thick TiO_2 Films Produced with a Roller Mill and Sensitized with N719[a]

ff	eff/%	V_{oc}/V	$I_{sc}/\mathrm{mAcm}^{-2}$
0.59	2.5	0.63	0.67
0.65	2.7	0.64	0.65
0.61	3.0	0.65	0.74
0.65	2.9	0.64	0.69

[a] The electrodes were *not* heated prior to dye-sensitization. The electrolyte was composed of 0.5 M LiI, 0.05 M I_2, and 0.5 M *tert*-butylpyridine in methoxypropionitrile. The light intensity was 100 W/m^2. Average values: FF, (0.624 ± 0.029); efficiency, (2.8 ± 0.2) %; V_{oc}, (0.64 ± 0.01) V; and I_{sc}, (0.69 ± 0.04) mA/cm^2.

electrodes are very similar for both heated and nonheated electrodes. The light to electricity efficiencies of nonheated and heated electrodes were (4.0 ± 0.5) % and (3.9 ± 0.4) %, respectively.

2. Dynamic Pressing. The photoelectrochemical measurements on nanostructured TiO_2 on conducting plastic were made in a two-electrode sandwich configuration using a platinum foil counter electrode. Table 3 and Table 4 show data from current−voltage measurements on dynamically pressed TiO_2 electrodes sensitized with N719. All manufacturing parameters were kept constant. However, the electrodes in Table 3 were prepared without a heating procedure and electrodes in Table 4 were heated to 120 °C for three minutes before dye-sensitization.

Table 4: Data Extracted from i−v Characteristics for Five 5-μm Thick TiO_2 Films Produced with a Roller Mill and Sensitized with N719[a]

ff	eff/%	V_{oc}/V	$I_{sc}/\mathrm{mAcm}^{-2}$
0.66	2.7	0.65	0.63
0.70	3.4	0.66	0.74
0.61	2.7	0.64	0.68
0.67	3.3	0.64	0.76
0.70	3.4	0.65	0.76

[a] The electrodes were heated to120 °C for 3 min prior to dye-sensitization. The electrolyte was composed of 0.5 M LiI, 0.05 M I_2, and 0.5 M *tert*-butylpyridine in methoxypropionitrile. The light intensity was 100 W/m^2. Average values: FF, (0.67 ± 0.04); efficiency, (3.1 ± 0.4) %; V_{oc}, (0.65 ± 0.01) V; and I_{sc}, (0.72 ± 0.06) mA/cm^2.

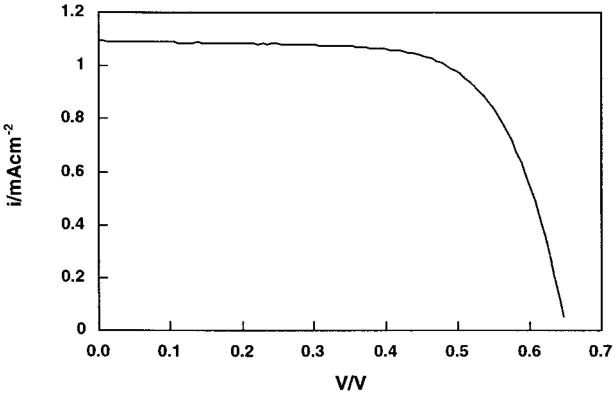

Figure 1. Current−voltage curve for a 8.3 μm thick TiO_2 film sensitized with N719. The electrode was heated to120 °C for 3 min prior to dye-sensitization. The counter electrode was a film of pressed platinized SnO_2 powder. The electrolyte was composed of 0.5 M LiI, 0.05 M I_2, and 0.5 M *tert*-butylpyridine in methoxypropionitrile. Efficiency, 4.9%; ff, 0.68; V_{oc}, 0.65 V; I_{sc}, 1.1 mA/cm^2; area, 0.19 cm^2; Int, 100 W/m^2.

The values of the fill factor, open circuit voltage, short circuit current, and overall efficiency for dynamically pressed electrodes are again very similar for both heated and nonheated electrodes. The overall light to electricity efficiencies of nonheated and heated electrodes were (2.8 ±0.2) %, and (3.1 ±0.4) %, respectively.

Pressed Counter Electrodes. Because of the decomposition of the plastic substrate during the heating procedure, thermal platinization at 385 °C is more or less impossible to perform on plastic substrates. However, by pressing carbon or platinized SnO_2 on conducting plastic, it is possible to produce counter electrodes at lower temperatures. The i−v curve for an all-plastic sandwich cell is shown in Figure 1. The counter electrode consisted of platinized SnO_2 powder pressed on a conducting plastic substrate (see the Experimental Section). The electrode was produced without using heat treatment. The overall cell efficiency was 4.9%.

Because of the series resistance losses in the conducting plastic layer (sheet resistance: 60 Ω/square), it was very difficult to reach high conversion efficiencies with pressed SnO_2 electrodes at higher light intensities. Nevertheless, at 1 sun intensity, we reached values for the fillfactor, open-circuit voltage, and short circuit current of 0.41 V, 0.76 V,

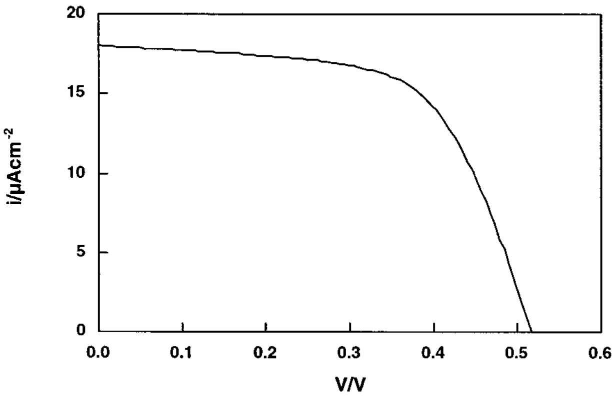

Figure 2. Current−voltage curve for an 8.3 μm thick TiO_2 film sensitized with N719. The electrode was heated to 120 °C for 3 min prior to dye-sensitization. The counter electrode was a film of pressed carbon powder on conducting plastic. The electrolyte was composed of 0.5 M LiI, 10 mM M I_2, and 0.5 M *tert*-butylpyridine in methoxypropionitrile. ff, 0.59; V_{oc}, 0.54 V; I_{sc}, 18 μA/cm^2; area, 0.39 cm^2. The intensity as measured with a blackbody and a lux meter were 660 μW/cm^2 and 230 lux, respectively.

and 7.3 mA/cm^2 (i−v data not shown). The overall conversion efficiency at 1 sun was 2.3%.

In another experiment, an alternative counter electrode was manufactured by pressing a carbon powder mixture on a conducting plastic substrate (see the Experimental Section). The electrode was heated to 120 °C for three minutes before use. Figure 2 displays the current−voltage curve recorded under indoor illumination conditions (at 230 lux). The fillfactor, open-circuit voltage, and short circuit current were, 0.59 V, 0.54 V, and 18 μAcm^{-2}, respectively.

Summary. The step of deposition is easily made using simple methods due to the low viscosity of the suspension and is well suited for automation.

The step of compressing the deposited film to achieve a thin but still porous film is also performed using simple techniques. An especially important feature is to achieve a mechanically stable and electrically conducting nanostructured film at room temperature. Therefore, it is possible to select the substrate from a wider range of materials than is possible with a conventional firing technique. This opens up the use of plastic materials that offer cheaper substrates, the possibility to manufacture large electrodes, the possibility to manufacture numerous electrodes on one large substrate to be cut at a later stage and even the possibility of easy manufacturing of nonplanar electrodes.

An important advantage with the method is the possibility of continuous manufacturing of the nanostructured porous film. This is most pronounced when the nanostructured film is attached to flexible substrates, such as plastic films, by compression in a roller mill.

Furthermore, a major advantage is that all the steps of the method are very fast, thereby allowing very high output, especially when adopted in an automated process.

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