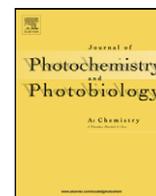




Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Electrophoretic deposition and compression of titania nanoparticle films for dye-sensitized solar cells

Larissa Grinis, Snir Dor, Ashi Ofir, Arie Zaban*

Department of Chemistry, Nano-energy Research Center, Institute of Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan 52900, Israel

ARTICLE INFO

Article history:

Received 25 December 2007
 Received in revised form 20 February 2008
 Accepted 21 February 2008
 Available online 4 March 2008

Keywords:

Dye-sensitized solar cell
 Electrophoretic deposition
 Compression

ABSTRACT

Cathodic electrophoretic deposition (EPD) of commercially available TiO₂ nanocrystals (P-25 and P-90, Degussa) for the formation of nanoporous electrodes for dye-sensitized solar cells (DSSCs) is reported. Thick, uniform, adherent TiO₂ films were obtained from alcoholic suspensions prepared in two steps: first, nanoparticles were treated in an alcoholic suspension with a small amount of acetylacetone; second, the obtained suspension was mixed with a EPD “charging solution” with small additives of iodine, acetone and water. A modified mechanical compression technique was employed to the electrophoretically deposited films to vary the porous structure and thickness of TiO₂ layers. By applying non-polar volatile organic liquids to fill the pores of dry TiO₂ films before compression, we obtained a substantial improvement in the quality of the pressed films. The fabrication of multilayer electrodes enabled us to obtain TiO₂ films with a thickness up to 25 μm and the photoelectric conversion efficiency up to 8.5% under 1 sun illumination.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Most photovoltaic solar cells currently produced are based on silicon p–n junctions. However, there is an increasing interest in dye-sensitized solar cells (DSSCs) due to the simple materials and equipment required for their manufacturing, their potentially low-cost production, and the adequate and stable conversion efficiencies currently achieved in small-area cells (11% in a DSSC smaller than 0.2 cm² and 10.1% for a cell with an active area of 1.3 cm²) [1].

DSSCs consist of a nanocrystalline, mesoporous network of a wide bandgap semiconductor (the best found is TiO₂), covered with a monolayer of dye molecules. The semiconductor is deposited onto a transparent conductive oxide (TCO) electrode, through which the cell is illuminated. The TiO₂ pores are filled with a redox mediator, which acts as an ionic conductor, connected to a counter electrode. Upon illumination, electrons are injected from the photo-excited dye into the semiconductor and move towards the transparent conductive substrate, while the electrolyte reduces the oxidized dye and transports the positive charges to the counter electrode [2].

The conventional method of preparation of porous nanocrystalline TiO₂ electrodes is based on a viscous TiO₂ paste with organic

additives that can be deposited on a substrate by screen-printing or blade-coating. Organic additives permit fabrication of crack-free thick films (10–18 μm) in one deposition. Temperatures of 450–550 °C are used to remove organic additives and sinter the nanoparticles together, in order to establish an electrically connected network.

In recent years the use of EPD for porous nanocrystalline TiO₂ electrodes fabrication has gained increased interest. In 1994, Matthews et al. [3] used electrophoretically deposited TiO₂ films for DSSC preparation. Constant current EPD from suspensions of commercially available titania nanoparticles (Degussa P-25) in 2-methoxyethanol followed by drying and annealing yielded adherent porous titania films with a thickness of 3–15 μm on electrically conducting glass.

Fujimura and Yoshikado [4] used ion-free water, without a binder, as a solvent for EPD, which has the advantages of low cost, industrial safety, environmental protection and the minimization of contamination in produced layers. However, the main problem associated with the application of water-based suspensions for EPD is the gas formation by the hydrolysis of water above a DC voltage of about 1.4 V which results in large pinholes in deposited layers, lack of film uniformity, and poor adherence [5,6].

Miyasaka et al. [7] and Murakami et al. [8] reported the EPD of commercially available TiO₂ nanoparticle powders, P-25 and F-5, from a dry mixed solvent of *tert*-butanol and acetonitrile. The distance between electrodes was only 0.3 mm. A direct current (DC) electric field of 200 V/cm was applied for 0.5–1 min. As a

* Corresponding author. Tel.: +972 3 5317876.
 E-mail address: zabana@mail.biu.ac.il (A. Zaban).

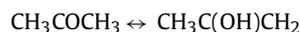
result, TiO₂ nanoporous films with a thickness of 7–13 μm were prepared, dried at 90 °C, and then used for fabrication of DSSCs. These DSSCs on conductive glass yielded a solar-to-electric conversion efficiency of 2.0% when illuminated by 100 mW/cm² white light. After post-treatment of the electrodeposited film by chemical vapor deposition (CVD) of Ti(OC₃H₇)₄, followed by exposure to UV-light, the conversion efficiency increased to 3.7%. After microwave irradiation post-treatment, the conversion efficiency reached 4.1%. Miyasaka and Kijitori [9] obtained the same 4.1% conversion efficiency at 1 sun illumination for plastic electrodes (indium-tin oxide, ITO, coated poly(ethylene terephthalate), PET).

Yum et al. [10] obtained a much lower efficiency 1.03% on ITO-PET substrates by EPD from isopropanol suspensions of P-25 titania nanoparticles. These suspensions contained small amount of magnesium nitrate and 2% of water. After a compression at 200 bar, the efficiency of the cell increased to 1.66%.

Kim et al. [11] reported anodic EPD of titanate nanotubes for DSSC preparation. A mixture of methanol with water without additives was used as the solvent. 10 μm thick films of titanate nanotubes on FTO (F-SnO₂ coated glass) were sintered at 500 °C, and then used for DSSC fabrication. The efficiency of 6.72% was obtained at 1 sun illumination. The cell prepared from the same titanate nanotubes by doctor-blade coating and annealed at 450 °C for 30 min yielded only 0.65% efficiency.

EPD is a useful method for the preparation of thick binder-free particulate films on conductive substrates in a much shorter time, compared to the other coating techniques. EPD is especially attractive because of the low cost, simple equipment, formation of uniform layers of controlled thickness, and homogeneous microstructure [5,14,15]. EPD has a high potential for scaling up to large product volumes and sizes. The aim of this work was to improve the performance of DSSCs produced by EPD of commercially available TiO₂ nanoparticles P-25 and P-90 (Degussa).

EPD is a colloidal forming technique in which charged, colloidal particles from a stable suspension are deposited onto an oppositely charged substrate by the application of a DC electric field. A suspension for EPD is a complex system in which each component has a substantial effect on deposition efficiency. In such a system, it is very important to obtain well-dispersed and stable suspensions. The deposited particles should be electrically charged to permit forming by EPD. Particle charging provides two effects: coulombic repulsion for the formation of a stable suspension and charging that allows particle movement to the opposite charged electrode. Zhitomirsky reviewed methods of particles charging in suspensions [5]. One of the methods is based on a mixture of acetylacetone or acetone and iodine, sometimes with the addition of water. Koura et al. [12] proposed that the particle charging in this system is achieved via adsorption of protons, which are formed by the keto-enol reaction:



Koura et al. [12] found that the addition of small amounts of H₂O and I₂ to acetone suspensions of some metal oxide particles increased the conductivity linearly with an increase the amount of iodine. Zhitomirsky [13] showed that more stable suspensions of diamond particles could be obtained in isopropyl alcohol as a solvent, instead of acetone, with small additives of iodine, acetone and water.

We found the charging system of iodine–acetone–water promising for various metal oxide particle deposition by EPD. The advantage of these charging additives relate to their low boiling point which enables their removal at relatively low temperature; that is very important for plastic substrates.

The mechanical compression technique for the preparation of nanoporous TiO₂ films under high pressure developed by Hagfeldt and coworkers [16–20] is a useful low-temperature method for DSSCs fabrication. With this method, efficiencies of up to 3.0% on conductive glass and 2.3% on conductive plastic substrate were reported for a light intensity of 100 mW/cm². For the TiO₂ (Degussa P-25) suspension spreading onto the conductive substrates, these authors used the blade-coating method. The compression of the dry P-25 layers [16–20] was performed by using a 30 μm polyethylene foil [16] or a 50 μm aluminium foil [18] as separating films, or without any separating films at all [17,19]. In our experiments, we consistently found some transfer of TiO₂ nanopowder to the separating films or to the upper steel press plate. This transfer does not permit control of the uniformity and thickness of a TiO₂ layer and sometimes results in considerable defects in the TiO₂ films. The same phenomenon was observed also by others (see, for example [24]). We modified the compression technique by applying volatile organic liquid to fill the TiO₂ film pores, followed then by covering wet layers with a polymeric foil. This modification resulted in a significant improvement of the film quality and in a substantial increase of the compression process rate. The liquid filling pores of the TiO₂ layer transfers the applied pressure homogeneously in all directions, thus promoting uniformly pressed films.

In this paper, we study an EPD of commercially available TiO₂ nanoparticles P-25 and P-90 (Degussa) combined with the mechanical compression for producing efficient titania nanoporous electrodes for DSSC.

2. Experimental

P-25 purchased from Degussa AG (Germany), P-90 (a kind gift from Degussa), ethanol absolute anhydrous (Gadot) with maximum water content 0.1%, acetone analytical (Frutarom Ltd.), iodine 99.8% (Aldrich), acetylacetone ≥99.5% and methoxypropionitrile (Fluka), lithium iodide anhydrous and dimethylpropylimidazolium iodide bought from Merck, *tert*-butylpyridine 99% (Aldrich), acetonitrile HPLC grade (J.T.Baker) with water content 0.002% were used as received without further purification. The dye *cis*-dithiocyanato bis(4,4'-dicarboxylic acid-2,2'-bipyridine) ruthenium(II) commonly termed N3 was purchased from Dyesol (Australia).

Fluorine doped tin oxide (FTO) coated glass substrates (Pilkington, bought from Hartford Glass Co. Inc., USA) with sheet resistance 15 Ω/square were cleaned with ethanol, mild soap, thoroughly rinsed with deionized water (18.2 MΩ) and dried in a filtered air stream.

We measured the thickness of the TiO₂ films with a SurfTest SV 500 profilometer from the Mitutoyo Co. The quality of titania layers was characterized by visual inspection. The morphology of the TiO₂ films was investigated using a scanning electron microscope JEOL, JSM-840 and field emission electron microscope JEOL, JSM-7000F. X-ray diffraction was performed using a Bruker D8 X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å). The average crystallite size of the TiO₂ was calculated using the Scherrer formula. Specific surface area measurements were conducted with the use of Autosorb1 (Quantochrome, Inc.), using nitrogen as an adsorbate (BET approach). Particle size and shape were determined by HRTEM (JEOL, JEM-2010 transmission electron microscope).

2.1. Electrophoretic deposition

P-25 or P-90 titania nanoparticles suspensions for EPD were prepared by the following procedure. TiO₂ nanoparticles were mixed with 150 ml of alcohol (methanol, ethanol, or isopropanol) and a

small amount of acetylacetone. For comparison, in some experiments TiO₂ nanoparticles were mixed only with alcohol. The suspension was stirred with a magnetic stirrer for 15–72 h in a closed vessel (herein “TiO₂ suspension”). Small amounts of iodine, acetone and water were added to 100 ml of alcohol and stirred with a magnetic stirrer or sonicated with cooling the solution in an ice bath until iodine was dissolved (herein “charging solution”). Just prior to EPD, TiO₂ suspension was added to the charging solution and mixed. This was followed by sonication for 15–20 min using an ultrasound processor VCX-750 (Sonics and Materials, Inc.) to homogenize the mixture with cooling the suspension in an ice bath. The obtained suspension was applied for EPD. The electrophoretic cell contained two electrodes of F-SnO₂ conductive glass; one electrode was a cathodic substrate and the other electrode served as a counter-electrode. The electrodes were placed vertically and immersed in the suspension of 250 ml in a glass beaker. The distance between electrodes was kept 18 or 54 mm. The EPD process was performed using constant voltage or constant current modes at room temperature. The deposition area of the photoelectrodes was about 20 cm². A Keithley 2400 Source Meter was applied as a power supply. Deposit mass was obtained by weighing cathodic F-SnO₂ glass before and after EPD, and drying, first at room temperature, and then at 150 °C for 30 min.

2.2. Mechanical compression

For the compression of electrophoretically deposited films we used a hydraulic programmable press (Bivas Hydraulic Industries Ltd.). The applied pressure was delivered by 5 programmable steps. Before the compression, titania films prepared by EPD were dried at 150 °C for 30 min. After cooling the samples to room temperature, immediately before compression, the organic liquid (*n*-pentane, *n*-hexane, or *n*-heptane) was uniformly dropped on the titania film surface, and the wet layer was immediately covered with polyethylene foil (7–20 μm). A pressure was then applied.

2.3. Photoelectrochemical measurements

The porous TiO₂ electrodes were sensitized with N3-dye by immersing still warm (80–100 °C after sintering or drying) films in dye solution in ethanol (0.5 mM) and storing them overnight or longer at room temperature. The dye-covered electrodes were then rinsed with ethanol and dried under a filtered air stream. A two-electrode sandwich cell with an effective area of 0.635 cm² was employed to measure the performance of DSSCs using a Pt-coated F-doped SnO₂ layered glass as a counter-electrode. Teflon tapes with a thickness of 50 μm were positioned as spacers between the two electrodes. The composition of the electrolyte was: 0.6 M dimethylpropylimidazolium iodide, 0.1 M LiI, 0.05 M I₂, 0.5 M *tert*-butylpyridine in 1:1 acetonitrile–methoxypropionitrile. Photocurrent–voltage characteristics were performed using an Eco-Chemie Potentiostat. A 250 W xenon arc lamp (Oriel) calibrated to approximately 100 mW/cm² (AM 1.5 solar emission) served as a light source. The conversion efficiencies were not corrected for reflection and absorption losses of the conductive glass.

3. Results and discussion

The P-25 titania powder consisted of about 70% anatase and 30% rutile, with the mean particle size 22 and 35 nm, respectively, as obtained by X-ray diffraction and HRTEM. The specific surface area was about 50 m²/g. P-90 consisted, mainly, of anatase nanoparticles with a small amount of rutile (about 5%). The mean particle size was about 14 nm and the specific surface area was about 90 m²/g. The TEM images of P-25 and P-90 nanopowders are presented in Fig. 1.

These nanopowders produced by flame hydrolysis of TiCl₄ consist of aggregated TiO₂ particles.

Our experiments reveal that using only iodine, acetone, and water as additives is not enough for the preparation of stable suspensions and subsequent high quality titania films by the EPD process. We found that it is very important for these purposes to apply at least one more stage in the preparation process. When only iodine, acetone, and water additives were applied in alcoholic suspensions of P-25 or P-90, the suspensions exhibited significant settling, and post-EPD TiO₂ films were noted for their rough surface, frequently with pitting. This is apparently due to hydrogen generation from the electrolysis of a water additive.

We found that much more stable suspensions of TiO₂ particles and better quality of the electrophoretically deposited films could be obtained if we performed an additional step before using the “charging solution”. This step consists of adding a small amount of acetylacetone to the alcoholic suspension of titania particles followed by stirring for, preferably, 24–72 h. The optimal amount of acetylacetone in suspension was found to be 1.2–2.4 ml/l. Apparently acetylacetone adsorbs on the particle surface during the stirring and the subsequent sonication, thus, modifying the surface of the titania nanoparticles. Consequently, no pitting was observed after EPD, when acetylacetone was added at this step. The elucidation of the mechanism of the acetylacetone action is now in progress.

The same methodology of suspension preparation was successfully applied to other metal oxides particles (Al₂O₃, MgO, ZrO₂, ITO). These results will be reported elsewhere.

Fig. 2 shows the distribution of TiO₂ particle size in the final P-25 suspension as measured by dynamic light scattering (Zetasizer 3000 HS, Malvern Instruments Ltd., UK), 30 min after the suspension preparation. For the particle size measurements, the suspension was diluted to a concentration of 0.2 mg/cm³ suitable for light scattering measurements. The dilution was performed by “charging solution” (see Sections 2 and 2.1 and below). Three consecutive measurements (1, 2, and 3 curves in Fig. 2a and b) were carried out without stirring in the same cuvette. We observed that in the two-step suspension preparation with the addition of acetylacetone (Fig. 2a), the mean size of the particles was around 60 nm, and the suspension was highly stable. Under stirring, the prepared suspension was stable for a few days, and could be used for high quality nanoporous titania films fabrication by EPD. In the P-25 suspension prepared without acetylacetone, yet with iodine, acetone and water (Fig. 2b) during the first measurement, the mean size of the particles was around 250 nm; during the second measurement the mean particle size changed to about 170 nm, apparently, due to settling of the larger particles; and the third measurement showed the mean size of the particles around 150 nm. From these data we see that the two-step preparation of the titania nanoparticles suspension (with the acetylacetone addition in the first step) yields much smaller particles in the suspension. The two-step prepared suspension is substantially more stable than the one-step prepared suspension by the method that utilizes iodine, acetone, and water only.

Organic solvents are preferable to water since EPD in water is accompanied by the formation of hydrogen (cathode) and oxygen (anode), resulting in bubbles in the deposit, attack on the electrodes and local heating in the electrode-deposit system [4,5]. In this work, we explored three alcohols: methanol, ethanol and isopropanol, all three being relatively cheap, non-toxic, and have low boiling points. The low boiling point of a solvent is important for low-temperature fabrication of DSSCs. We obtained well-dispersed and stable TiO₂ suspensions in all of these alcohols, however, the best results were obtained for the ethanolic suspensions: uniform, adherent, homogeneous films with controllable thickness. The amount of deposited

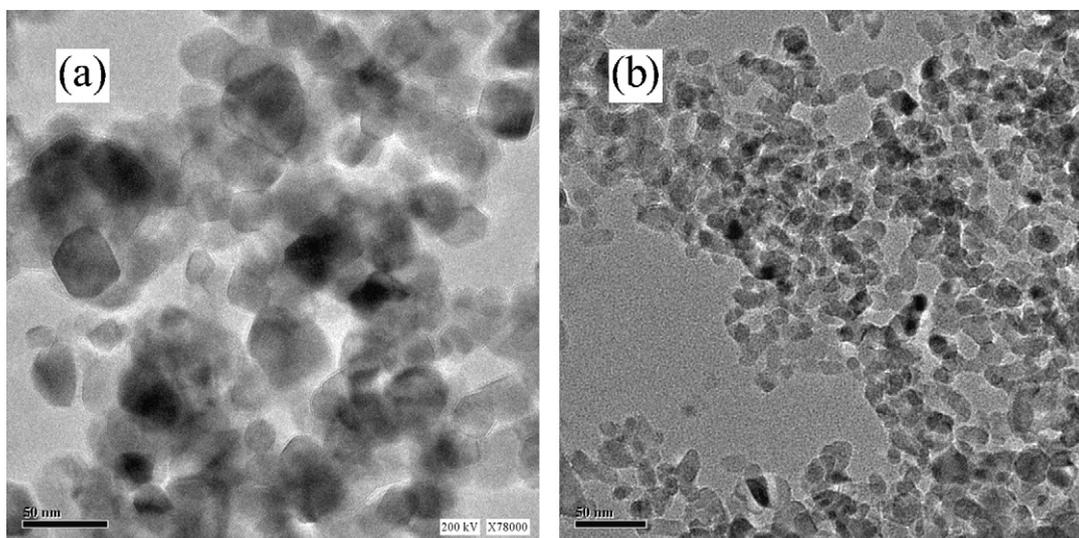


Fig. 1. The HRTEM images of TiO_2 nanopowders P-25 (a) and P-90 (b).

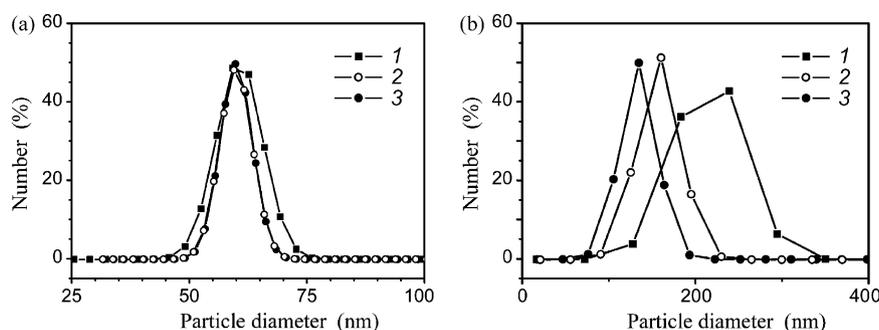


Fig. 2. The measurements of P-25 particle size distribution by Zetasizer in the suspension prepared: (a) in two steps (see text) with the additives: acetylacetone, iodine, acetone and water; (b) in one step without the acetylacetone addition. The numbers indicate the order in the consecutive measurements in the same cuvette without stirring.

material can be controlled by varying the suspension composition, deposition time, current density, or applied voltage.

The effects of the suspension composition and the EPD parameters on the performance of the DSSC were studied. The suspension composition relates to the TiO_2 and additive concentrations in the EPD suspension, while the physical parameters include the applied voltage in the constant voltage mode, the current density in the constant current mode, the distance between electrodes, and the deposition time. EPD was performed at room temperature, although some interesting results were obtained at lower temperatures [23]. Partial orientation of nanoparticles during EPD was found even at room temperature [21], but this effect was more pronounced at lower temperatures, where the effective electron diffusion coefficient increased because of a higher degree of ordering in the nanoporous TiO_2 layers formed by EPD [23].

We found, in accordance with ref. [12], that there was an increase of current at the same applied voltage when the concentration of iodine in the suspension was increased. The concentration of iodine in the suspension is a very important parameter for high-quality deposits since the addition of iodine, acetone, and water leads to the formation of free H^+ ions (see Section 1).

Our experiments, as also reported by others [5,13], showed that to obtain better quality deposited films, the amount of additives should be minimized, since only a fraction of the ions is adsorbed on the particle surface. Ions that do not adsorb on the nanocrystal surfaces increase the ionic strength of a suspension resulting in reduced thickness of the electrical double layer on the particle surface, which leads to particle agglomeration and a dete-

rioration of the quality of deposited films [5]. Furthermore, the mobility of free protons is much higher than that of charged titania particles. Consequently, the increase in free proton concentration decreases the amount of deposited titania particles. We found that the optimal concentrations of additives should be as follows: iodine 80–120 mg/l, acetone 4–48 ml/l, and water 2–24 ml/l.

Fig. 3 shows J - V characteristics of DSSCs prepared on basis of EPD from ethanolic suspensions with variable TiO_2 concentrations:

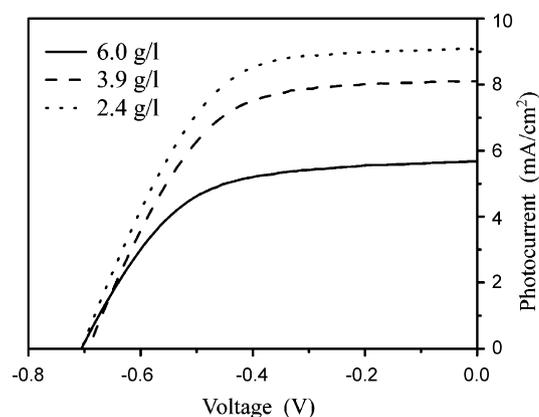


Fig. 3. J - V characteristics of DSSCs prepared by EPD in ethanolic suspensions with variable TiO_2 concentrations: (a) 6 g/l, (b) 3.9 g/l, and (c) 2.4 g/l. EPD was carried out under a constant voltage mode at 70 V, deposition time 2 min. Electrodes were sintered at 450 °C for 30 min.

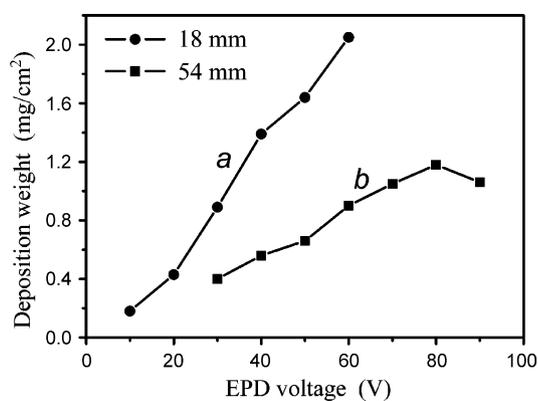


Fig. 4. Deposit weight as a function of an applied voltage for 2.4 g/l P-25 suspension in ethanol at the deposition time 2 min and the distance between the electrodes: (a) 18 mm and (b) 54 mm.

6, 3.9 and 2.4 g/l. It is evident from Fig. 3 that DSSCs fabricated from the 2.4 g/l suspension exhibit the best performance. This can be explained as follows: the intensification of titania particles agglomeration in the more concentrated suspensions apparently leads to a poor packing density of the electrophoretically deposited films. Elucidation of this phenomenon is now in progress utilizing more diluted suspensions. The lowest concentration used in this work was 2.4 g/l. This concentration promoted the formation of 6–8 similar electrodes from the same suspension since less than 10% of the TiO_2 in the suspension was consumed. For lower starting concentrations an adjusting procedure is needed.

We examined two distances between electrodes: 18 and 54 mm. This parameter hardly affected the deposited film quality in optimal conditions. Fig. 4 displays the deposit weight as a function of an applied EPD-voltage for the two working distances between the electrodes, using 2.4 g/l P-25 ethanolic suspension at 2 min of deposition. As expected, the deposit weight increased with the applied voltage (Fig. 4), and the deposition rate was higher for the smaller distance between electrodes (18 mm). For the distance of 54 mm between the electrodes, voltage higher than 80 V resulted in a decrease of the deposit weight. Independent of the distance between electrodes, when a deposit weight became more than 1.2–1.3 mg/cm², pinholes were observed in the deposits, and the DSSCs prepared from such films showed deterioration of perfor-

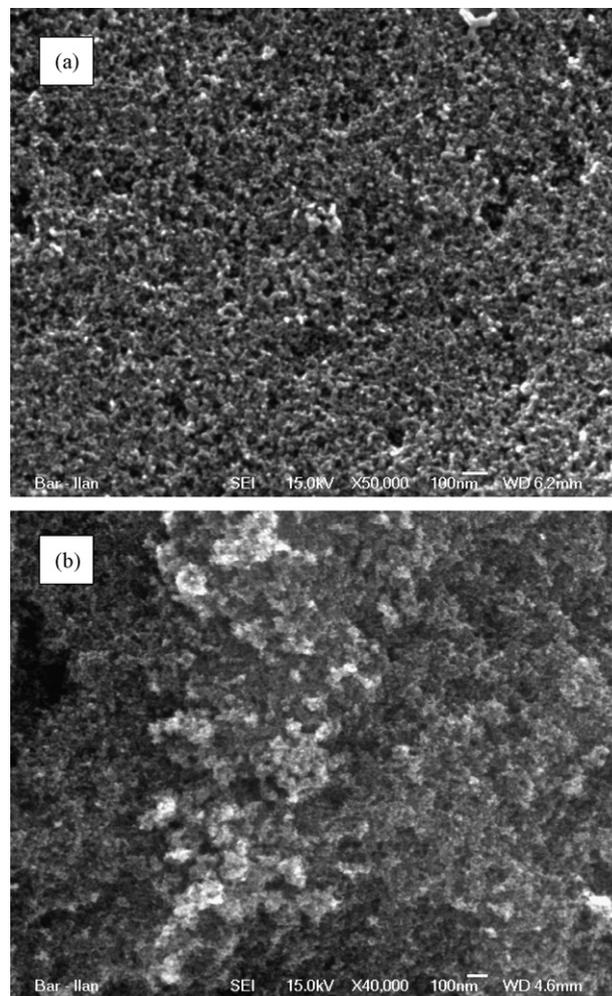


Fig. 6. The HRSEM-images of a top-view (a) and a cross-section (b) of an electrophoretically deposited TiO_2 P-90 multilayer film pressed under 1000 kg/cm².

mance. For shorter distance between the electrodes, the deposition rate was higher, and the voltage per a given current density was lower. We found a working distance of 54 mm more preferable in our setup due to better EPD stability. Consequently, subsequent experiments were performed mainly at a distance of 54 mm between the electrodes.

In the constant voltage mode, the best DSSCs performance for the 18 mm distance was achieved utilizing 40 V. Increasing the voltage to 50 and 60 V decreased the DSSC efficiency. The same dependence existed for the longer distance (54 mm), however, the optimal EPD-voltage here was less pronounced, located in the 70–90 V interval. Under optimal EPD conditions, the initial current density was, approximately, 0.4 mA/cm². The current density slowly decreased as the resistive deposit developed onto the electrode.

In accordance with other studies [14,5], we found that constant current EPD was more effective and controllable than the constant voltage mode. Considering the results obtained under the constant voltage, the suspension concentration was set at 2.4 g/l, utilizing 54 mm distance between electrodes. The optimal current density for these conditions was found to be 0.4–0.55 mA/cm². For a single step EPD, the optimum TiO_2 deposit weight was found to be 1.2–1.4 mg/cm² (approximately 2 min of deposition). The increase of the deposit weight above 1.45 mg/cm² resulted in less adherent, pinhole containing films, leading to the performance deterioration

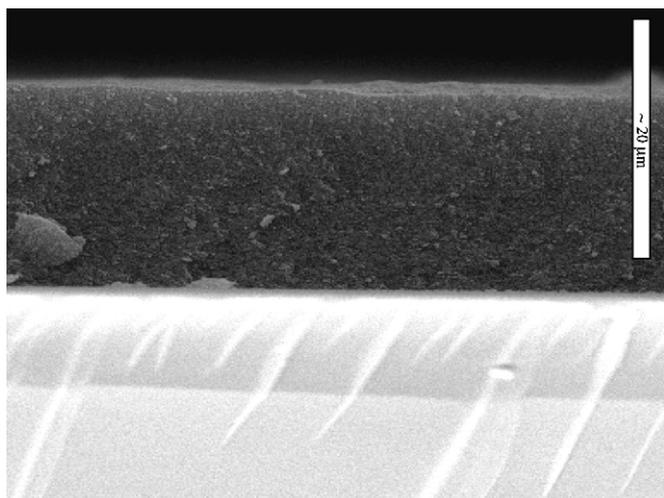


Fig. 5. The SEM-image of a cross-section of an electrophoretically deposited TiO_2 P-25 multilayer film pressed under 800 kg/cm².

of the DSSCs. Cells prepared from electrophoretically deposited in these optimal conditions, non-sintered electrodes, which were only dried at 150 °C for 4 h, yielded J_{sc} 9.29 mA/cm², V_{oc} 705 mV, fill factor (FF) 61.3% and efficiency of 4.0% (deposit weight of 1.22 mg/cm²). Electrodes sintered at 500 °C for 30 min provided J_{sc} 12 mA/cm², V_{oc} 715 mV, FF 57.1 and 4.9% conversion efficiency (deposit weight 1.39 mg/cm²).

Further improvement in the performance of DSSCs prepared by EPD required thicker, more compact films with better adherence to the FTO substrate. This was done by mechanical compression and multilayer deposition. As stated in the Introduction, unlike previous reports [16–20], our compression methodology was based on employing an organic liquid with a relatively low boiling point. We found that non-polar, low reactive saturated hydrocarbons were suited perfectly for this purpose. *n*-Pentane, *n*-hexane, and *n*-heptane were used successfully, providing homogeneously pressed TiO₂ films without visible defects. It is interesting to note that the using polar organic liquids (as, for example, ethanol) resulted in a transfer of TiO₂ layer to an upper plastic foil.

The pressure effect on both the morphology and electrical properties of the electrophoretically deposited nanoporous TiO₂ electrodes was published previously [21]. In brief, and in accordance with [16–20], after compression films became more transparent and more adherent to conductive glass substrate. The mechanical stability of pressed films improved, while irregular large pores and pronounced agglomerates disappeared. Compression provided a method to systematically decrease the porosity of electrophoretically deposited TiO₂ films and increase the effective electron diffusion coefficient in the film [21,22]. Consequently, as shown also by others [16–20], compression can, to some extent, replace the sintering process in cases where elevated temperatures cannot be used (typically, for plastic based DSSCs). Table 1 shows the pressure effect on the thickness of electrophoretically deposited TiO₂ films and the performance of DSSCs fabricated from these films for both non-sintered and sintered electrodes. The EPD in this case was performed in one step at optimal conditions. The thickness of the films decreased with an increase in pressure from an initial value of 10 to 4.2 μm subsequent to compression at 800 kg/cm². Table 1 shows that the pressure application has considerable effect on the photovoltaic performance of DSSCs containing non-sintered electrodes. Compression of non-sintered electrodes at 800 kg/cm² increased J_{sc} to 10.67 mA/cm² and the conversion efficiency up to 4.5%. The pressure effect on the V_{oc} and the fill factor was small. For sintered electrodes the effect of compression (at the given initial thickness 10 μm) is less pronounced. The most efficient DSSCs, 4.9–5.0%, were obtained using a pressure of 200–400 kg/cm². Although the performance of DSSCs from non-sintered electrodes was lower than that of sintered electrodes, the results presented in Table 1 demonstrate a potentially useful method of a low temperature DSSC manufacturing. The results obtained from the optimization of non-sintered electrodes on plastic substrates will be reported in the near future.

Comparison of results obtained with titania nanopowders P-25 and P-90 showed that for dried only, non-sintered electrodes the performance of P-25 was better. At the same time, P-90 was found more effective for sintered TiO₂ films. This can be explained by the larger size of P-25 nanoparticles and their smaller specific surface: in this case for non-sintered electrodes, where necking among particles is poor, electron transport is easier when there are fewer particle boundaries. For sintered electrodes, where the electron transport in the titania network is better, the higher surface area ensures higher dye adsorption, and also P-90 consists of almost pure anatase which is known as more effective for DSSCs than rutile [25]. It has been shown that the electron transport was slower in the rutile electrodes than in the anatase electrodes [25,26].

Table 1
Effect of an applied pressure on the thickness of the TiO₂ films and on photoelectric performance of DSSCs^a

Applied pressure (kg/cm ²)	Thickness of the films (μm)	Only dried electrodes DSSCs (150 °C, 4 h)				Sintered electrodes DSSCs (500 °C, 1 h)				
		V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	Efficiency η (%)	IPCE (%)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	Efficiency η (%)
0	10.0	—	—	—	—	695	11.93	55.7	4.6	65.6
50	9.8	675	7.76	60.2	3.15	705	13.04	51.3	4.7	67.5
150	7.3	675	7.95	63.2	3.39	715	12.60	53.5	4.8	66.7
200	6.7	690	9.06	62.7	3.92	715	12.31	56.9	5.0	75.7
400	4.9	680	9.89	61.8	4.16	725	12.15	55.9	4.9	77.0
600	4.7	690	10.07	60.8	4.22	735	12.09	54.2	4.8	74.3
800	4.2	705	10.67	59.4	4.47	735	11.53	55.3	4.68	72.1

^a EPD of TiO₂ films was carried out in a single deposition under constant current mode with current density 0.4 mA/cm² from ethanolic suspension of P-25 (concentration 2.4 g/l), deposition time 2 min, distance between electrodes 54 mm.

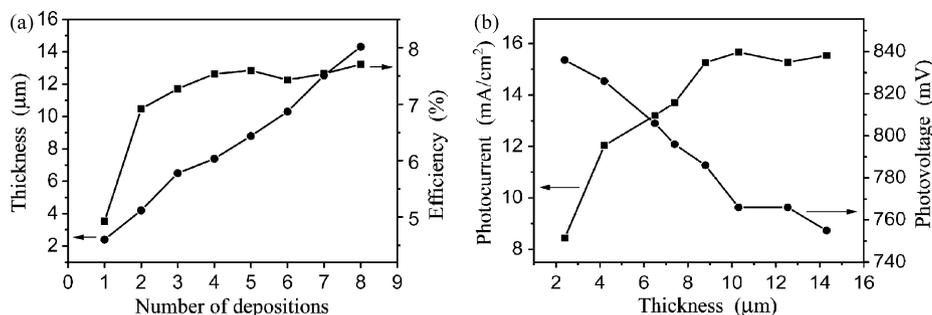


Fig. 7. The effect of a number of layers formed by EPD on the TiO_2 film thickness (a), and the thickness of the TiO_2 film on photovoltaic parameters (b). The electrodes were prepared from P-90, pressed at 800 kg/cm^2 and sintered at 550°C for 2 h.

In order to increase the thickness of the nanoporous electrodes made by EPD, we tested a multilayer approach. The fabrication of each layer involved 20–40 s of deposition at a current density of $0.4\text{--}0.55 \text{ mA/cm}^2$ followed by drying: first at room temperature and then at $60\text{--}100^\circ\text{C}$ for 1–2 min. After the successive deposition of the multilayer film, we applied mechanical compression and sintering. Using this method, the thickness of the titania nanoporous layer was increased beyond $25 \mu\text{m}$. We note that for multilayered films the optimal pressure was found to be $800\text{--}1000 \text{ kg/cm}^2$. The morphology of obtained TiO_2 films was studied by SEM and HRSEM. These data are shown in Figs. 5 and 6. Fig. 5 represents a cross-section SEM image of a pressed (800 kg/cm^2) electrophoretically deposited TiO_2 P-25 multilayer film. Fig. 6 displays HRSEM images of a top-view (a) and a cross-section (b) of electrophoretically deposited TiO_2 P-90 multilayer film pressed under 1000 kg/cm^2 . From these images we can see that the titania nanoporous structure is very homogeneous, without cracks or other defects. Fig. 7 shows the parameters of 8 DSSCs prepared from electrodes which were fabricated by the consecutive multilayer method: from one layer of titania nanoparticles to eight layers. All layers were deposited at the current density of 0.5 mA/cm^2 for 30 s with a final compression step of the multilayer film at 800 kg/cm^2 and sintering at 550°C for 2 h. Fig. 7 shows the thickness increase from $2.4 \mu\text{m}$ for a single layer to $14.3 \mu\text{m}$ for 8 layers which results in J_{sc} growth from 8.4 to 15.6 mA/cm^2 , V_{oc} decrease from 836 to 755 mV , and a conversion efficiency of 7.7% for the DSSC with 8 consecutive layers. These results were obtained after 48 h soaking in dye solution. Longer soaking periods up to 2 weeks improved the performance of the thicker electrodes (5–8 consecutive layers). The best result was obtained with the 8 layers ($15 \mu\text{m}$) sample: J_{sc} 17.3 mA/cm^2 , V_{oc} 735 mV , fill factor 66.9% and efficiency of 8.5% .

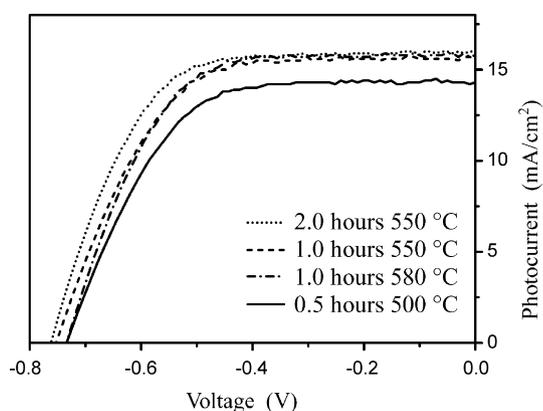


Fig. 8. The effect of the temperature and time of the sintering of P-90 electrophoretically deposited electrodes on DSSC photovoltaic parameters. The electrodes consisted of 6 consecutive deposited TiO_2 layers and were pressed at 1000 kg/cm^2 .

Finally, optimization of the sintering procedure for the multilayered electrodes was performed. The electrodes were prepared by six successive 35 s depositions of the TiO_2 nanocrystals (P-90) at the current density of 0.5 mA/cm^2 followed by 1000 kg/cm^2 compression. The electrodes were sintered at $500\text{--}580^\circ\text{C}$ for $0.5\text{--}2 \text{ h}$. The thickness of the electrodes was about $14 \mu\text{m}$. Fig. 8 shows that the optimal sintering procedure for multilayered electrophoretically deposited and pressed electrodes was 550°C for 2 h. Under these conditions, the efficiency of the prepared electrodes was 7.9% with J_{sc} 16 mA/cm^2 , V_{oc} 755 mV and fill factor 65.6% . In [21] it was found that the effective diffusion coefficient and the integrated charge were increased by increasing the sintering temperature until 550°C . This was explained by improving the necking among particles. The results of the current work agree with previous published results [21]. The decrease of the efficiency at 580°C , apparently, depends on a diminution of the pore volume due to strong sintering, and a deterioration of a DSSC electrolyte transport.

We found that the developed method is highly reproducible, because it is relatively easy to control the EPD suspension concentration, the applied current density, and the deposition time, and it is especially useful for the comparison of DSSC components: dyes, electrolytes and counter-electrodes. Using commercial TiO_2 nanocrystals (such as P-25 and P-90) makes the preparation of DSSC electrodes simpler and cheaper.

4. Conclusions

A simple, effective and highly reproducible method of nanoporous TiO_2 electrodes fabrication was developed based on EPD from suspensions of commercially available TiO_2 nanoparticles P-25 and P-90. This method is based on a two-step procedure of an EPD suspension preparation. The first step consists of nanoparticle treatment in an alcoholic suspension with a small acetylacetone addition for 15–72 h. Subsequently, the prepared suspension is mixed with a “charging solution” based on small amounts of additives: iodine, acetone, and water. The optimal concentrations of additives were experimentally found.

Cathodic EPD from prepared suspensions was studied at constant voltage and constant current modes, and optimal parameters were found. EPD at a constant current mode appeared to be more effective and controllable than the constant voltage mode. The formation of nanoporous photoelectrodes up to $25 \mu\text{m}$ of thickness is reported. Thick, uniform, adherent TiO_2 films were obtained from ethanolic suspensions with additives in a short time and with a simple setup. Modified mechanical compression technique was employed to the electrophoretically deposited films to vary the porous structure and thickness of the TiO_2 layers. Applying non-polar volatile organic liquids to fill the pores of dry TiO_2 films before compression resulted in a substantial improvement of a pressed film quality.

The effect of multilayer deposits obtained by repeated deposition steps with the drying of each deposited layer followed by multilayer compression and sintering was studied. It was shown that such a procedure enabled us to increase the thickness of TiO₂ nanoporous layers without any deterioration of film quality and improve substantially the DSSC photovoltaic parameters. For these films, the optimal sintering temperature was found 550 °C.

DSSCs prepared by EPD of a commercial powder (Degussa P-90) followed by compression and sintering yielded up to 8.5% efficiency at 1 sun light illumination.

Acknowledgments

The authors thank the Israeli Ministry of Science for funding this research. The authors also thank Degussa AG (Germany) for the kind gift of the P-90 TiO₂ nanopowder, and Dr. Judith Grinblat for the HRTEM images.

References

- [1] J.M. Kroon, N.J. Bakker, H.J.P. Smit, P. Liska, K.R. Thampi, P. Wang, S.M. Zakeeruddin, M. Grätzel, A. Hinsch, S. Hore, U. Würfel, R. Sastrawan, J.R. Durrant, E. Palomares, H. Pettersson, T. Gruszecski, J. Walter, K. Skupien, G.E. Tulloch, *Prog. Photovolt: Res. Appl.* 15 (2007) 1–18.
- [2] B. O'Regan, M. Grätzel, *Nature* 353 (1991) 737–739.
- [3] D. Matthews, A. Kay, M. Grätzel, *Aust. J. Chem.* 47 (1994) 1869–1877.
- [4] K. Fujimura, S. Yoshikado, *Key Eng. Mater.* 248 (2003) 133–136.
- [5] I. Zhitomirsky, *Adv. Colloid Interface Sci.* 97 (2002) 279–317.
- [6] J. Tabellion, R. Clasen, *J. Mater. Sci.* 39 (2004) 803–811.
- [7] T. Miyasaka, Y. Kijitori, T.N. Murakami, M. Kimura, S. Uegusa, *Chem. Lett.* (2002) 1250–1251.
- [8] T.N. Murakami, Y. Kijitori, N. Kawashima, T. Miyasaka, *Chem. Lett.* (2003) 1076–1077.
- [9] T. Miyasaka, Y. Kijitori, *J. Electrochem. Soc.* 151 (11) (2004) A1767–A1773.
- [10] J.-H. Yum, S.-S. Kim, D.-Y. Kim, Y.-E. Sung, *J. Photochem. Photobiol. A* 173 (2005) 1–6.
- [11] G.-S. Kim, H.-K. Seo, V.P. Godble, Y.-S. Kim, O.-B. Yang, H.-S. Shin, *Electrochem. Commun.* 8 (2006) 961–966.
- [12] N. Koura, T. Tsukamoto, H. Shoji, T. Hotta, *Jpn. J. Appl. Phys.* 34 (1995) 1643–1647.
- [13] I. Zhitomirsky, *Mater. Lett.* 37 (1998) 72–78.
- [14] P. Sarkar, P.S. Nicholson, *J. Am. Ceram. Soc.* 79 (1996) 1987–2002.
- [15] A.R. Boccacini, J.A. Roether, B.J.C. Thomas, M.S.P. Shaffer, E. Chavez, E. Stoll, E.J. Minay, *J. Ceram. Soc. Jpn.* 114 (1) (2006) 1–14.
- [16] H. Lindström, A. Holmberg, E. Magnusson, S.-E. Lindquist, L. Malmqvist, A. Hagfeldt, *Nano Lett.* 1 (2001) 97–100.
- [17] H. Lindström, A. Holmberg, E. Magnusson, L. Malmqvist, A. Hagfeldt, *J. Photochem. Photobiol. A* 145 (2001) 107–112.
- [18] H. Lindström, E. Magnusson, A. Holmberg, S. Södergren, S. Lindquist, A. Hagfeldt, *Solar Energy Mater. Solar Cells* 73 (2002) 91–101.
- [19] G. Boschloo, H. Lindström, E. Magnusson, A. Holmberg, A. Hagfeldt, *J. Photochem. Photobiol. A* 148 (2002) 11–15.
- [20] A. Hagfeldt, G. Boschloo, H. Lindström, E. Figgemeier, A. Holmberg, V. Aranyos, E. Magnusson, L. Malmqvist, *Coord. Chem. Rev.* 248 (2004) 1501–1509.
- [21] A. Ofir, Th. Dittrich, S. Tirosh, L. Grinis, A. Zaban, *J. Appl. Phys.* 100 (2006) 074317.
- [22] Th. Dittrich, A. Ofir, S. Tirosh, L. Grinis, A. Zaban, *Appl. Phys. Lett.* 88 (2006) 182110.
- [23] S. Tirosh, Th. Dittrich, A. Ofir, L. Grinis, A. Zaban, *J. Phys. Chem. B* 110 (2006) 16165–16168.
- [24] B. O'Regan, F. Lenzmann, R. Muis, J. Wienke, *Chem. Mater.* 14 (2002) 5023–5029.
- [25] N.-G. Park, J. van de Lagemaat, A.J. Frank, *J. Phys. Chem. B* 104 (2000) 8989–8994.
- [26] S. Kambe, S. Nakade, Y. Wada, T. Kitamura, S. Yanagida, *J. Mater. Chem.* 12 (2002) 723–728.