ISSN 0027-1349, Moscow University Physics Bulletin, 2013, Vol. 68, No. 1, pp. 34–37. © Allerton Press, Inc., 2013.
Original Russian Text © N.V. Golubko, Yu.E. Roginskaya, A.E. Ozimova, D.Yu. Godovskii, D.Yu. Paraschuk, 2013, published in Vestnik Moskovskogo Universiteta. Fizika, 2013, No. 1, pp. 33–36.

Dye-Sensitized Solar Cells with Polymer Bindings Based on Titanium Dioxide

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Received July 20, 2012; in final form, October 17, 2012

Abstract—An urgent task in the field of sensitized solar cells (DSSC) is to decrease the temperature of thermal annealing of titanium dioxide photoanode. In this work, we use a titania based polymer as organic "polylinker," which allows low temperature annealing. This polylinker, which is obtained by means of partial hydrolysis of titanium polybutyltitanate or tianium 2-methoxyethoxide allowed us to decrease the annealing temperature of titanium dioxide down to 150–180°C. This permits the manufacture of DSSC on flexible polymer substrates. DSSC samples with efficiency of energy conversion up to 1% are obtained.

Keywords: solar cells, dye-sensitized solar cells, titanium dioxide, inorganic polymer binding.

10.3103/S0027134913010074

INTRODUCTION

The first high-performance thin-film solar cells that consist of percolating grids of a liquid electrolyte and dye-coated titanium dioxide nanoparticles were developed by O'Regan and Gratzel [1]. Solar cells of this type are called photoelectrochemical solar cells or dye-sensitized solar cells (DSSCs) [2, 3].

The photoanode of a DSSC is made from percolating nanoparticles of a wide-gap semiconductor (usually TiO_2), whose surface should be coated by a monolayer of an absorber (organic dye, semiconductor quantum dots, etc.). The optimal thickness of the photo anode is about 15–20 nm. The process of the preparation of a DSSC photoanode usually requires sintering at high temperature (above 400°C) to achieve structuring in the shape of percolating nanoparticles that form electric contacts between themselves and with the transparent substrate. The technology of high-temperature sintering used for DSSC preparation confines the choice of substrates for DSSCs to hard transparent materials, for example, glass.

On the other hand, the development of solar cells on thin and flexible substrates, in particular, on polymers, is of great importance due to the following circumstances. First, new structures are available, as well as applications of solar cells in the shapes of sheds, awnings, flexible mobile power supplies for portable electronics, etc. Next, replacement of a hard substrate with a flexible material can significantly decrease the weight of a DSSC, and consequently, the cost of manufacturing and mounting. Lastly, flexible substrates allow the implementation of commercial roll-to-roll production, which should significantly decrease the cost of the solar cells.

Previously, various methods were used for the deposition of TiO_2 on the surface of a polymer film, for example, on polyethylene naphthalate or polyethylene terephtalate (PETF) material coated with indium-tin oxide (ITO) at temperatures below 300°C. Thus, TiO_2 layers were deposited on ITO/PETF using spin-coating, squeegee, or electrophoresis. Performance of DSSC on a plastic substrate prepared using these techniques of TiO_2 film deposition reaches 5–6% at best. It was shown in [4] that DSSC can be obtained on flexible substrates by low temperature annealing (100°C) of colloid TiO_2 films in the absence of organic surfactants. Synthesis of TiO_2 colloid particles was performed by the method in [5] using hydrolysis of titanium isopropoxide and following autoclaving at 230°C. This method can be used to obtain titanium dioxide particles with anatase structure during sintering of the films even at 100°C. Spin-costing was used to deposit colloid solution on substrates immediately after its filtration and the following sintering was done in air during 24 hours. The drawback of this technique is production of inhomogeneous films (with a thickness about 5 μm and insufficient adhesion to the surface of the substrate), because of inability to control the homogeneous size distribution of titanium dioxide particles produced by uncontrolled hydrolysis.

A layer of semiconductor particles was deposited on conducting plastics, and the layer of particles was consolidated to obtain mechanically stable conducting porous film at room temperature [6]. The mor-

Parameters of samples

No. of sample	Linker	TiO_2 (wt %)	Annealing parameters	Color	I_{sc}, mA/cm^2	V_{oc}, V	FF, %	Efficiency, %
1	30.65 wt % $Ti(OBu)_4$	4.72	150°C (15 min) 250°C (15 min)	Ru 520 DN	0.7	0.48	56	0.19
2	$Ti(OBu)_4 + 1.2$ $Ti(OC_2H_4OCH_3)_4$	4.48	150°C (15 min) 250°C (30 min)	Ru 520 DN	2.7	0.6	59	0.96
3	30.65 wt % $Ti(OBu)_4$	5.51	150°C (15 min)	Ru 620 1H3TBA	0.2	0.33	47	0.031

phology of films that consist of TiO_2 nanoparticles, which is so important for mechanical durability of the film and for the cohesion of TiO_2 nanoparticles, can be improved by adding of a small amount of TiO_2 nanoparticles that serve as glue between coarser particles [7]. Finally, TiO_2 can be chemically bound via bridges using appropriate binding molecules [8].

In this paper, a method is proposed for thin-film production with high mechanical properties at relatively low temperatures [9]. Binding of TiO_2 particles at low temperatures is provided by using a polymer based on a solution of titanium butylate in butanol or by using of titanium 2-methoxyethoxide, or their mixture. These polymers, which have good film forming, binding and gluing properties, are usually called polymer bindings or polylinkers. The obtained TiO_2 films are studied in the content of DSSC samples.

MATERIALS AND METHODS

To prepare precursor solutions for deposition of a thin-film composite material, electrochemically produced titanium butylate $Ti(OC_4H_9)_4$ and titanium 2-methoxyethoxide $Ti(OC_2H_4OCH_3)_4$ were used [10]. The respective chemical purity grade alcohols containing 0.1–0.5 wt % of water were dehydrated by boiling over magnesium and aluminum alkoxides during 5–8 h to final content of moisture 0.005–0.01 wt %. Titanium alcoholates were solved in dehydrated alcohols to 30 wt % solutions. The solutions of titanium butylate and titanium 2-methoxyethoxide were mixed in an equal molar ratio. Partial hydrolysis of the alcoholates was conducted using water solutions in a respective alcohol with concentration up to 17 wt %, and the molar water/alcoholate ratio (h) was $0 \leq h \leq 1$.

Titanium dioxide containing 99.7% of TiO_2 with anatase crystal lattice and a particle size no more than 25 nm (Aldrich) was added at a concentration 3–6 wt % to the obtained titanium alcoholate and stirred using a magnetic mixer to homogeneous suspension. Operating compositions of mixtures of alcoholate solutions with TiO_2 nanoparticles are shown in the table.

The obtained suspensions were deposited on substrates that contain a conducting layer of indium-tin oxides (ITO) with a 1.5 × 1.5 cm area by spin coating of the substrate at a rotation rate of 500–3000 rpm. This method was used to deposit 10–15 layers with intermediate drying of each layer at 70°C during 5–10 min (or by annealing at 150°C for 15 min). At the end of the process, all thin-film composite materials were strengthened by annealing in air in the temperature range 150–250°C for 30–60 min.

The thickness of each layer measured by Dektak profilometer was about 1 μm, therefore, estimation of the film thickness gave 10–15 μm. The obtained films were studied by a Jeol JSM-6490 LV scanning electron microscope. Then the films were sensitized by dye solutions based on ruthenium Ru-520DN or RU-602DN-1H3TBA Solaronix in the mixture with $CH_3CH(OH)CH_3$ and CH_3CN at a volume ratio of 1 : 1 for 12 h.

The DSSC samples were prepared as follows. A platinum-based counter electrode of a DSSC was made of Platisol (Solaronix) material, which was spread with a brush. It was dried at 100°C for 10 min and then annealed at 400°C for 5 min. The main electrode (titanium dioxide film impregnated with sensitizing agent) was washed in absolute ethanol and dried with a drier. A Teflon frame was then placed between the main electrode and the counter electrode, the electrodes were pressed, and their ends were sealed by Amosil 4 (Solaronix) two-component glue. Iodyte AN-50 (Solaronix) electrolyte based on I^-/I_3^- redox-pair was then poured between the electrodes. The working area of the DSSC samples was about 1 cm^2.

Current-voltage (I/V) characteristics were measured using a Keithley 2400 precision source-detector device under radiation of a Newport 96000 solar simulator with an AM1.5G spectrum at the intensity 100 mW/cm^2. The power of the simulator was controlled using a bolometer. The performance of the samples was calculated from the product $I_{sc}U_{oc}$FF, where I_{sc} is the short circuit current, U_{oc} is the open-circuit potential, and FF is the fill factor of an I/V curve.

RESULTS AND DISCUSSION

Titanium 2-methoxyethoxide $Ti(OC_2H_4OCH_3)_4$ is more stable to hydrolysis and condensation as com-

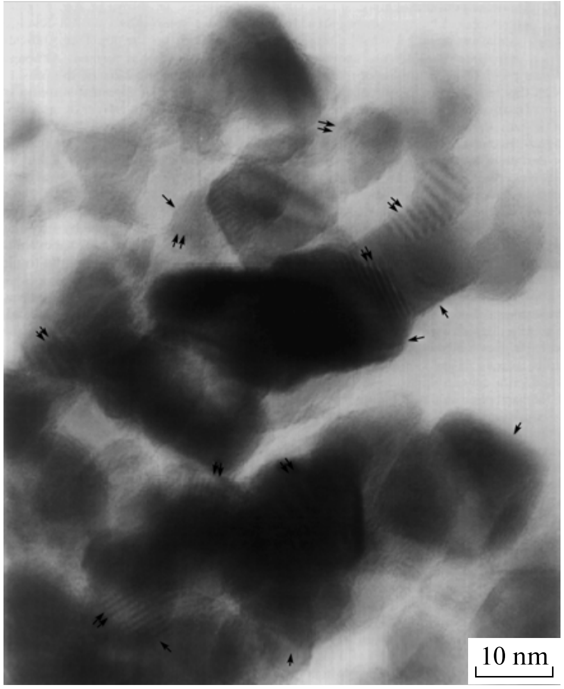

Fig. 1. SEM image of the sample 2.

pared to polybutyltitanate, which is described in the patent of the Konarka company [8]. This can be explained by the presence of chelate cycles in the molecule (formed by oxygen atoms that belong to ether groups, not only to hydroxyl oxygen atoms).

The facts that oligomerization caused by a reaction between $Ti(OC_2H_4OCH_3)_4$ and the solvent molecules has an equilibrium character and that the molecular complexity decreases significantly with respect to alcoholates can be explained by the participation of ether atoms of oxygen in the coordination of metal atoms. Oligomerization occurs as a result of chelate formation by OR groups (coordination polymerization). One example of this process is the formation of hybrid organic–inorganic materials in reactions with strong chelating agents (for example, nanoparticles of metal oxides and methacrylates) making a “hazelnut” structure, in which a core of the metal oxide is inserted in polymer organic shell.

This method is optimal for obtaining hybrid composites with the structure and texture of a polymer organic matrix (and hybrid composite) depending on the initial water/alcoholate and chelate/alcoholate ratios in the reaction [11]. Varying ratios of the agent materials can be used in the fabrication of a sewn grid of nanoparticles or core-shell structures, in which materials of a polymer binding form a shell on the surface of TiO_2 nanoparticles by changing photoelectron and mechanical properties of hybrid films based on TiO_2 nanoparticles and titanium 2-methoxyethoxide.

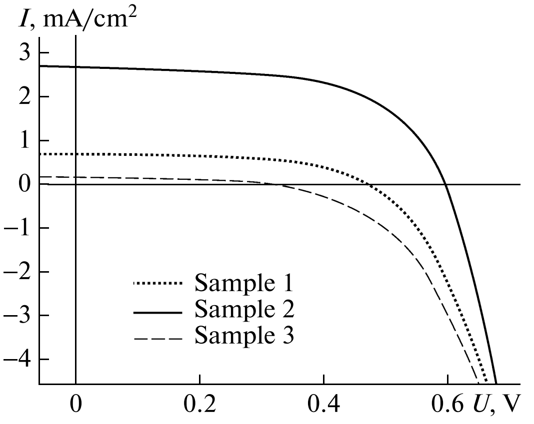

Fig. 2. Current voltage characteristics of the DSSC samples (see Table 1).

Figure 1 shows scanning-electron microscopic images of TiO_2 samples. The image shows the presence of pores on the surface with a typical size about 20–50 nm. It should be noted that impregnation of titanium dioxide layers with dye gives intensely colored layers that are comparable with similar ones that are obtained during high-temperature sintering of anatase. Consequently, it can be concluded that polymeric binding brings to formation a porous ensemble of 20–50 nm, which penetrates the entire layer of titanium dioxide at low annealing temperatures. Thus, polymer binding favors the formation of a bi-percolation grid of electrolyte, on the one hand, and titanium dioxide with a monolayer of dye, on the other hand, which is necessary for fabrication of efficient DSSCs.

It should be noted that the morphology of the layers that are formed using polymer binding is principally different from the layers that are obtained by high temperature annealing of anatase crystals. In the first case, nanocrystals are interconnected by polymer bridges formed by the –R–Ti–O–Ti–R– inorganic polymer (probably with organic side groups), while in the second case nanocrystals of anatase are connected by so-called “necks” that form during the sintering of crystallites.

A run of TiO_2 multilayered film samples sensitized with RU-520DN or RU-602DN-1H3TBA dyes was prepared. I/V curves of the best DSSC samples under radiation by a solar simulator are shown in Fig. 2. The results of measurements are shown in the table. It is seen that the highest photoelectric parameters, i.e., short-circuit current, open circuit potential, and the fill factor were found for sample 2, which was fabricated using a mixture of titanium 2-methoxyethoxide and butyltitanate as a polylinker. The open-circuit voltage is about 0.6 V, which is typical of a DSSC with an iodine electrolyte based on the I^-/I^{3-} redox pair; the rather high filling factor shows the correctness of the procedure for the preparation of the DSSC samples. The significant values of the short-circuit current point to efficient electron transport in the film structure based on titanium dioxide and formed using inorganic polymer. Consequently, electron transport along –Ti–O–Ti– chains that connect the particles of titanium dioxide can be very efficient. It should be noted that electron transport along the polymer chains should differ significantly from charge transport in the sintered titanium dioxide, where conductivity is impeded by intercrystallite barriers. The further improvement of DSSC samples by polymer binding based on titanium dioxide requires elaborated optimization of the procedure for the fabrication of multilayered TiO_2 films.

CONCLUSIONS

Thus, the polymer binding based on partially hydrolyzed titanium 2-methoxyethoxide and butyltitanate, forming inorganic (or hybride) polymer of –Ti–O–Ti– type makes it possible to sinter layers of titanium dioxide at temperatures below 200°C and to fabricate DSSC samples with performances that are comparable with conventional films made of anatase nanocrystals and annealed at temperatures of 450–500°C. These results open the prospects for the development of DSSCs on polymer substrates (polyethylene terephtalate and polyethylene naphtalate).

ACKNOWLEDGMENTS

This work was financially supported by Ministry of Education and Science of Russian Federation, the government contract No. 16.513.11.3133 and by the LG Chem. Company, Korea

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