Archives of Materials Science and Engineering

Volume 70
Issue 2
December 2014
Pages 70-76

International Scientific Journal published monthly by the World Academy of Materials and Manufacturing Engineering

Technology of dye-sensitized solar cells with carbon nanotubes

L.A. Dobrzański*, A. Mucha, M. Prokopiuk vel Prokopowicz, A. Drygała, K. Lukaszkowicz

[a] Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland

* Corresponding e-mail address: leszek.dobrzanski@polsl.pl

Received 30.10.2014; published in revised form 01.12.2014

ABSTRACT

Purpose: The aim of the paper is to fabricate the dye-sensitized solar cells DSSC with carbon nanotube.

Design/methodology/approach: The main aim this work was to improve the technological conditions of conventional dye solar cells by the application of nanostructured materials (MWCNTs) as one of the electrodes of the cell and to prove that the use of this type of nanomaterials increases the efficiency of dye solar cell electrodes.

Findings: Carbon materials can be used as a counter electrode in dye-sensitized photovoltaic cells by replacing a costly platinum.

Research limitations/implications: It has been found that due to the technology of developed conventional DSSC and cells with the carbon nanotubes, it is possible to lowering a production costs. It is advisable to take into account in the further experiments application of variables of different kinds of materials in the selected process parameters, and research for the use them in DSSC cells production.

Practical implications: Presented in this paper results showed possibilities of modifying DSSC cells in terms of architecture, which should be correlated with the parameters of current-voltage and optical. DSSC cells are an interesting alternative to silicon solar cells. The stage of scientific research conducted around the world suggests that in the near future DSSC are fully commercially available.

Originality/value: It was shown that the DSSC cells can be used as promising materials used in building-integrated photovoltaic.

Keywords: Dye-sensitized solar cells; Carbon materials; Carbon nanotube

Reference to this paper should be given in the following way:

L.A. Dobrzański, A. Mucha, M. Prokopiuk vel Prokopowicz, A. Drygała, K. Lukaszkowicz, Technology of dye-sensitized solar cells with carbon nanotubes, Archives of Materials Science and Engineering 70/2 (2014) 70-76.

MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Protecting the environment from degradation due to pollution, as well as reducing the resources of fossil fuels tend to look for alternative sources of energy. The key to a solution to these issues is the development of renewable energy. A great interest has a photovoltaics, which are an alternative and environmentally friendly technology of electricity production. Photovoltaic cells (also known solar cells or PV cells) are used to convert solar energy into electricity, and the phenomenon is called the photovoltaic effect. Due to the low cost of ownership and ease the photovoltaic systems are ideal for supplying both the objects that are beyond to the power network and connected to it [1,2].

Today, thanks to advances in the field of materials science and nanotechnology in photovoltaic, solar cells are divided into few generations, depending on the composition and structure [3,4]:

- I generation solar cells – photovoltaic solar cells based on mono and polycrystalline silicon,
- II generation solar cells – like solar cells from I generation based on p-n junction formed from doped semiconductors. These include the cell based on: cadmium telluride (CdTe), copper selenide indium (CIGS) and amorphous silicon (a-Si),
- III generation solar cells – photovoltaic cells based on organic compounds which do not have typical in I and II generation of solar cells a p-n junction. These include dye-sensitized solar cells DSSC, tandem solar cells and volume solar cells.
- IV generation solar cells – quantum dot sensitized solar cells QDSSC.

On the PV market contribution of solar cells made from crystalline silicon exceeds 80%, of which one-third includes monocrystalline silicon and two-thirds – polycrystalline silicon. The remaining part of the market falls on thin-film solar cells, most of which are silicon amorphous structure [5,6].

In science and technology related to photovoltaic dominate the structure using a p-n junction of two semiconductors like for example in silicon photovoltaic cells. On the border of both areas there is a very large concentration gradient of electrons and holes. This gradient causes a diffusion of holes from the p to n area and diffusion of electrons from the n to p. As a result of the diffusion near the junction line are formed the positive and negative space charges region. The p-n junction manages the three tasks, which are necessary for a properly work of photovoltaic devices [3-6]:

- charge generation from light absorption,
- separating the hole from the electron,
- charge transport.

However, due to the high cost of raw materials in monocrystalline and polycrystalline silicon solar cells and high energy inputs in the production of photovoltaic modules and systems make the payback time several decades and blocks the use of photovoltaic technology on a large scale. Therefore is extremely important to study new materials such as nanostructured materials and their applications in photovoltaics. Particularly promising is the development of photoelectrochemical solar cells, which include dye-sensitized nanostructured/nanocrystalline solar cells (DSSC) also known as the Grätzel cell was originally co-invented in 1988 by Brian O'Regan and Michael Grätzel at UC Berkeley. The DSSC has a number of attractive features [1-4]:

- easy to make using conventional printing techniques,
- semi-flexibility and semi-transparence,
- much higher esthetical compared to the solar cell I generation,
- most of the materials used are low-cost,
- performance is independent of temperature changes in the range of 25-65°C,
- low toxicity,
- possibility to choose the colour,
- less demands on purity,
- no needing high vacuum equipment.

Opposite to traditional semi-conductive photovoltaic cells, dye-sensitized cells are a photoelectrochemical device consisting of two electrodes deposited on a conductive substrate and combined by means of a redox electrolyte layer [7,8].

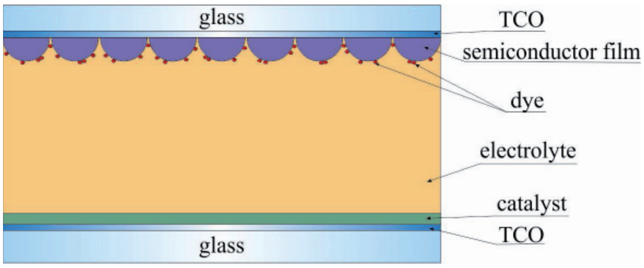

Fig. 1. Schematic of dye-sensitized solar cell [7,8]

Basically, a dye-sensitized photovoltaic cell consists of 5 layers [9,10] (Fig. 1):

- mechanical base covered with a layer of transparent conductive oxides TCO,
- semiconductor film, e.g. TiO_2 deposited on the anode to activate electronic conduction,

- dye absorbed on the semiconductor's surface to enhance light absorption,
- electrolyte including a redox carrier,
- counter electrode suitable to regenerate a redox carrier made of glass coated with a catalyst such as e.g. platinum to facilitate electron collection.

1.1. Operation principle of dye-sensitized solar cells

When light strikes the surface of DSSC solar cell electron transport processes occur in the following steps as it is shown in Fig. 2 [11]:

1. The dye molecules S become excited S^* to a higher electron state as a result of photon absorption,
   $$S + h\nu \rightarrow S^* \quad (1)$$
2. Excited dye molecule gives an electron e^- into the semiconductor layer of TiO2, leaving oxidized dye S+
   $$S^* \rightarrow S^+ + e^- \quad (2)$$
3. Then electrons are wander between nanoparticles of titanium dioxide to the glass with a TCO and the external circuit to the counter electrode,
4. I^- ion leads to reduction of excited state of dye molecules, and this ion is oxidized to the I_3^-,
   $$S^+ + e^- \rightarrow S \quad (3)$$
5. Triiodide anion is reduced with use of electron from counter electrode. Then the system returns to an energy balance state and is ready to receive the next photon, and the process began again.
   $$I_3^- + 2e^- \rightarrow 3I^- \quad (4)$$

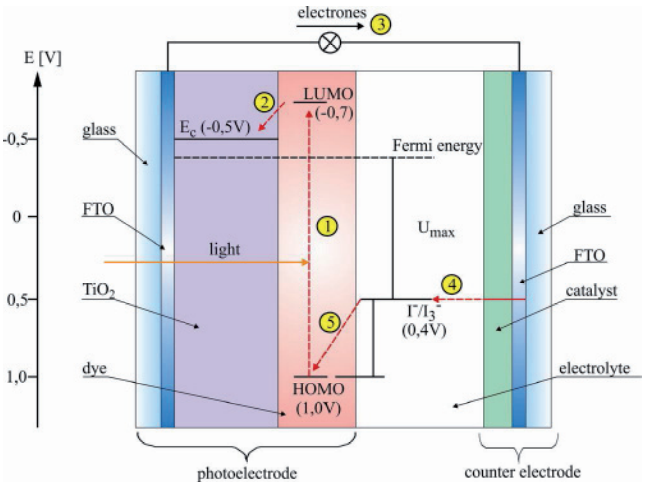

Fig. 2. Operation principle of DSSC, where, E_c – bottom of the conduction band, U_{max} – maximum voltage obtained in DSSC cell, HOMO – valence band, LUMO – conduction band [11]

A semiconductor mesoporous film is the main part of a dye-sensitized solar cell. Because of low costs, availability and nontoxicity titanium dioxide is used as a semiconductor [12].

Titanium dioxide may have a tetragonal crystalline structure and occurs as anatase or rutile, and orthorhombic structure occurs as brookite. Nanoparticles of TiO_2 has a crystalline structure of anatase. On this account, dye-sensitized photovoltaic cells are also called nanostructured photovoltaic cells. Titanium dioxide is sintered together to allow for electronic conduction to take place. Titanium dioxide has band gap equal 3.2 eV and in large extent absorb ultraviolet radiation but in just a few percent absorb visible light. That is why organic dyes absorbed on the TiO_2 surface are used. Dyes absorb light in range 400-700nm, that is 1.6-3.0eV. Among many of dyes the most widely used are two complex of ruthenium red dye and black dye [12,13]. They are characterized by wide range of light absorption, long lifetime in excited state and chemical stability [14].

Substrate is covered with a layer of transparent conductive oxides TCO like ITO (indium tin oxide) or cheaper and more stable FTO (fluorine tin oxide) [15].

Triiodide/iodine is used as the main redox pair. Conductive layers in the form of an electrode and counter electrode are an important component of dye-sensitized photovoltaic cells. The task of the counter electrode is to gather electrons flowing from the outer current and to catalyse the reduction of triiodide ions. Platinum is the most common material used as a counter electrode. Despite the fact that platinum shows a high catalytic activity, its shortage in resources, high costs and corrosion possibility through a triiodide solution inhibit its application on a large scale in the future. Because of that reason, there is a search for alternative materials which are characterized by an electrochemical activity and chemical stability. So far platinum, carbon, conductive plastics, CoS, WO_2, Mo_2C and WC, TiN, have been used as a counter electrode [14-17].

Inexpensive and available carbon materials such a carbon black, graphite, carbon nanotubes, fullerenes and porous coal are alternative materials for platinum because of their high corrosive resistance, high reactivity for triiodide reduction and low costs. Although disadvantages in a catalytic activity in comparison to platinum may be compensated by increasing an active surface of a catalytic layer using the porous structure, conversion efficiency is still lower than in the case of counter electrodes based on platinum. Forming high-quality carbon band on a substrate gives prospects for using carbon as a counter electrode. Because of that several methods have been developed such as: overprint of coal paint including graphite and/or black coal or depositing by means of a special strike using colloidal configuration of TiO_2 as a binding material [18-22].

The main objective of present work is to produce dye-sensitized solar cells with carbon materials as a counter electrodes in order to decrease cost of DSSC.

2. Materials

As a mechanical base for anode and cathode a glass plates with dimensions 30 mm x 30 mm (10 Ω/□) covered with a layer of fluorine doped tin oxide FTO was used.

Titanium dioxide paste was prepared by mixing 2 ml of nitric acid with ethanol and titanium oxide nanopowder and stirring until obtaining uniform paste.

As the counter electrode to facilitate electron collection carbon nanotubes were used prepared on silicon substrate in thermal catalytic chemical vapor deposition CVD process and then characterized by Scanning Electron Microscope SEM. Carbon nanotubes were mixed with highly conductive PEDOT:PSS.

Organic dye was used as a sensitizer to enhance light absorption. A triiodide solution including a redox carrier was used as a electrolyte.

Transmittance of particular layer of dye-sensitized solar cell was measured.

3. Experimental procedure

The production steps of dye-sensitized solar cells were shown in Fig. 3.

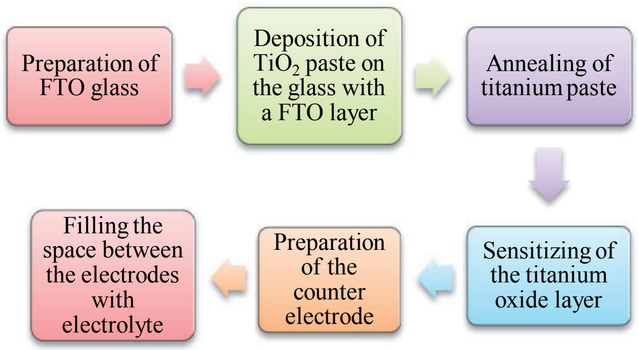

Fig. 3. The production steps of dye-sensitized solar cells

FTO glasses were cleaned from surface contamination by ultrasonic cleaning in deionized water, acetone, ethanol and isopropanol and holding in each liquids for 15 minutes. FTO glass was covered with a layer of tape (Fig. 4) in order to match the active surface of DSSC.

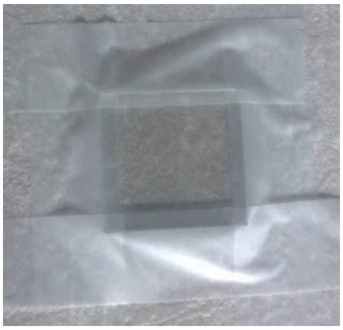

Fig. 4. FTO glass covered with a layer of tape

Doctor blade technique was used to uniformly spreading the TiO_2 paste over FTO glass (Fig. 5). Then FTO glass covered with titanium dioxide paste was annealed in a furnace at 450°C and then air-cooled. Photoanode prepared in that way was then immersed in organic dye for 24 h at room temperature (Fig. 6) and then washed from excess dye. The cathode was formed by deposition on FTO glass a thin layer of carbon materials with PEDOT:PSS (Fig. 7). The anode and the cathode were combined with the sealing strip, which simultaneously serves as a separator. The last step was placement the electrolyte, between the photoanode and the counter electrode.

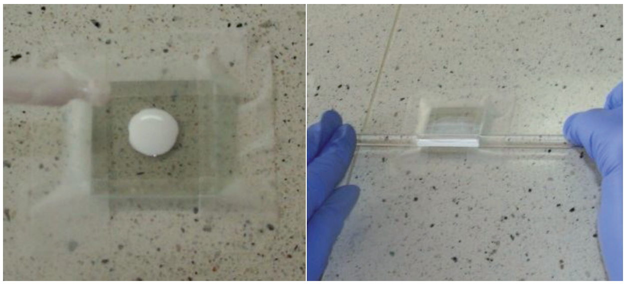

Fig. 5. Imposition of TiO_2 paste on the FTO glass

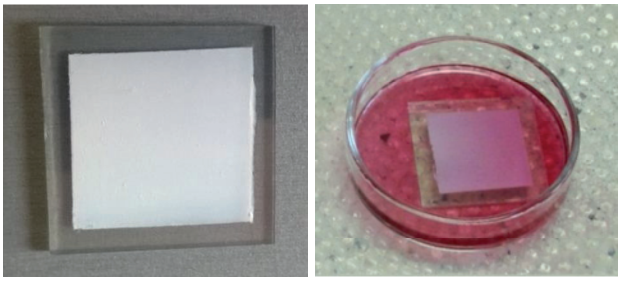

Fig. 6. TiO_2 layer before and during sensitization

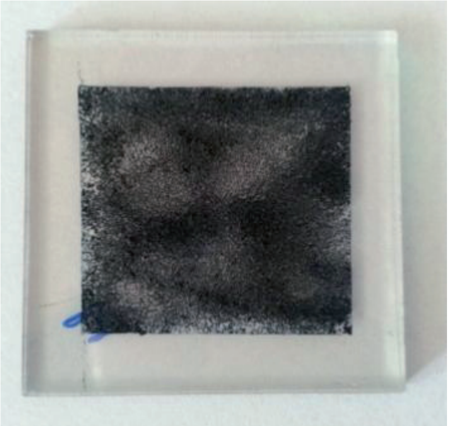

Fig. 7. Counter electrode with the layer of PEDOT:PSS with carbon nanotube

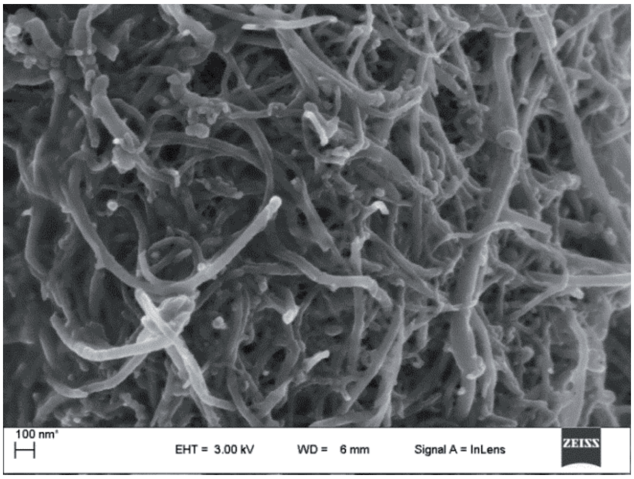

Fig. 8. SEM image of carbon nanotube on glass substrate

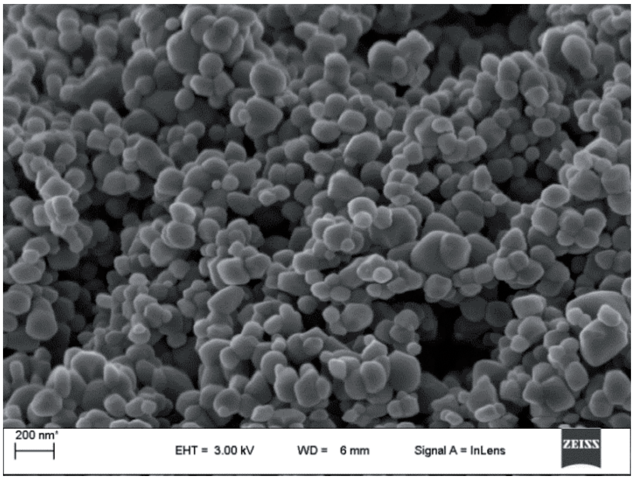

Fig. 9. SEM image of TiO_2 layer coated on FTO electrode

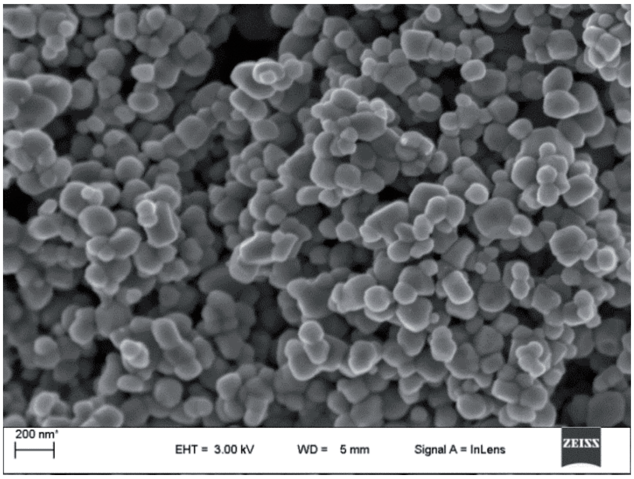

Fig. 10. SEM image of TiO_2 layer with a dye

The voltage of prepared dye-sensitized solar cells was measured by Meter Link Extech EX845 as a source measure unit, which was connected between FTO glass on counter electrode and FTO glass on photoanode.

Because the used carbon elements and titanium oxide consist of nano-metric structural units or single carbon layers, there was used Scanning Electron Microscope.

Transmittance of particular layer was measured by UV-vis spectrophotometer.

4. Result

Multi-walled carbon nanotubes with the diameter of 10-20 nm and length of 10-30 μm fabricated with the Chemical Vapour Deposition (CVD) method was used for production of counter electrode of DSSC. In Fig. 8 is shown the microstructure of MWCNTs counter electrodes. MWCNs are in the form of bundles, they are curled and tangled on the surface of FTO glass. The tangled MWCNTs form is proof that nanotubes have not been modified.

In Fig. 9 TiO_2 layer is shown. We can observe that TCO glass with a TiO_2 layer presents a typical porous structure and the TiO_2 particles are uniform and without cracks in the surface. As we know the dye is the photoactive material in DSSC. Therefore, it is possible to produce electricity once it is sensitized by light. The next figure (Fig. 10) show a layer of TiO_2 with a dye. Comparing Figs. 9 and 10 together may be observed a slight change in the structure the TiO_2 layer. The layer of dye characterized by having greater grain size of TiO_2 and smoother edges, bright border suggests that this is a dye.

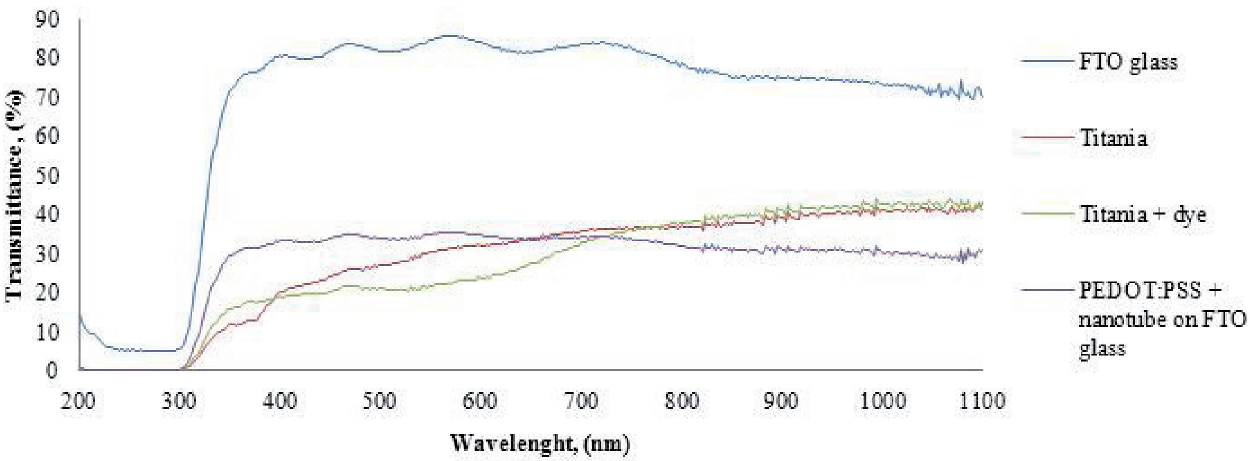

Fig. 11. Transmittance of particular layer of DSSC cell

In Fig. 11 transmittance of particular layer is shown. As it was expected the largest transmittance has FTO glass without TiO_2 and dye. Because of non-transparency of TiO_2 layer on FTO glass, counter electrode has larger transmittance than photoanode. Although it has been found that the values obtained for the cell transmission DSSC confirms relatively low transmission losses of the light compared to pure glass TCO.

The voltage of DSSC with carbon nanotubes counter electrode measured by Meter Link Extech EX845 was 40 mV. Measurements prove that the dye-sensitized solar cells, which as distinct from silicon solar cells don`t have p-n junction in their structure, can also generate electricity.

5. Conclusions

The dye-sensitized nanocrystalline photovoltaic cell has become a validated and credible competitor to p-n junction crystalline silicon solar cells for the conversion of solar energy into electricity. Titanium dioxide is widely used in photoanode of DSSC because of low costs, availability and nontoxicity.

Compared to silicon solar cells, DSSC don`t have the high cost of raw materials and high energy inputs. It is found performance of DSSC is independent of temperature changes in the range of 25-65°C.

In this study, for the purpose of decreasing cost of dye-sensitized solar cells was prepared carbon nanotubes electrode. Because of shortage in resources, high costs and corrosion possibility through a triiodide solution of platinum there is a search for alternative materials such as carbon materials [22].

Acknowledgements

The project was funded by the National Science Centre on the basis of the contract No. DEC-2013/09/B/ST8/02943.

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