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# Influence of Screen Printed Nanowires/Nanoparticles $TiO_2$ Nanocomposite Layer on Properties of Dye-Sensitized Solar Cells

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Semiconducting nanowires indicates several characteristics making them interesting for solar cells applications. One promising solution in DSSCs is to increase the electron diffusion length in the photoanode by using the nanowires/nanoparticle $TiO_2$ composite layer. In this work two pastes for screen printing were prepared. In one active component were $TiO_2$ nanowires in the second $TiO_2$ nanoparticle. In both cases, the binder and carrier were terpineol and ethyl cellulose. The pastes were screen printed onto the TCO glass alternately in varied order and with different number of prints. The best efficiency of as prepared dye-sensitized solar cells was $\sim 4.5\%$. The research has shown the possibility of using screen printed nanowires/nanoparticles $TiO_2$ nanocomposite layer as element of photoanode of dye-sensitized solar cells. These results show that employing $TiO_2$ nanowires represents a promising approach for further improving the efficiency of dye-sensitized solar cells.

topics: dye-sensitized solar cells DSSC, nanocomposites, nanoparticles, nanowires

## 1. Introduction

The possibility of increasing the efficiency of photovoltaic devices while reducing the costs of their production is particularly attractive. In this regard, dye photovoltaic cells (DSSC) are promising devices for large-scale solar energy conversion. Moreover, this device is an alternative option for silicon solar cell, because of their flexibility, transparency and low cost [1]. Additionally it was proven and DSSCs are enable to operation with diffuse sunlight (e.g., in case cloudy environment) what is unavailable in case of thin-film solar devices [2]. However the widespread use of DSSC technology into the photovoltaic market requires devices refinement especially in terms of improving cell efficiency. Improving the operation of cells requires in particular optimization of the electrical properties of the optical elements of the cell through the days of materials, modification of their structure and surface morphology as well as geometric form. In particular, a lot of effort is currently being put into work on electrodes (photoanode and counter-electrode). Photoanode is responsible for light absorption and electrons transferring to the substrate in DSSC systems [3]. These parameters are extremely important for the operation of the cell and for achieving high efficiency.

Nowadays one of the most efficient methods of increasing carrier mobility and dye loading is combining nanostructures like nanoparticles (NPs), nanowires (NWs), nanorods (NRs), nanotubes, nanoflowers (NFs), and hollow hemispheres [4, 5]. The idea is based on combining zero and one-dimensional (0D, 1D) $TiO_2$ with 3D structures, ensuring large specific area and hence effective dye adsorption in comparison with high and direct electron pathways [6]. Same 0D and 1D nanostructures nanowires, nanorods, nanotubes present higher light scattering capability but they don't have enough specific surface areas for dye loading [7]. 3D structures and microstructures and especially hierarchical microstructures built by small entities such as nanofibers, nanoparticles, nanotubes, or nanosheets [8] with morphologies distribution reaching micrometers. Such combine structures ensures high light scattering and dye adsorption with faster electron transport. That morphologies repeatedly ensures greater cell efficiency. It has been proven that 7.1% of efficiency ensures $TiO_2$ NRs / NPs bilayer structures [9]. In addition high efficiences of 7.39% has been obtain by use a bilayered structure of photoanode consisting of $TiO_2$ NRs and NPs [7].

Considering the above studies, the Authors focus on promising solution in DSSCs is to increase the electron diffusion length in the photoanode by using the nanowires/nanoparticle $TiO_2$ composite layer. The aim of such a solution has been to use the effective transport and collection of excited electrons generate by 1D material with the high value of dye-loading capacity by utilizing the $TiO_2$ nanoparticles layers. An article present innovative production method of a DSSC of high efficiency using modern methods ensures high dimensional, as well as structural repeatability, and modern materials combination of nanoparticles/nanorods photoelectrode.

## 2. Figures, tables and footnotes

The tests included the production Dye Sensitized Solar Cell (DSSC) with the combine structure:

- substrates/fluorine doped tin oxide (FTO)/ $TiO_2$ nanoparticles layer (NP)/nanowires $TiO_2$ layer (NW)/di-tetrabutylammonium cis-bis(isothiocyanato) bis(2,2-bipyridyl-4,4'-dicarboxylato) ruthenium(II)-N-719 dye/ EL-HSE high stability electrolyte/platinium counter kathode.
- substrates/fluorine doped tin oxide (FTO)/$TiO_2$ nanowires layer (NW)/$TiO_2$ nanoparticles $TiO_2$ layer (NP)/ di-tetrabutylammonium cis-bis(isothiocyanato) bis(2,2-bipyridyl-4,4'-dicarboxylato) ruthenium(II)-N-719 dye/EL-HSE high stability electrolyte/platinium counter kathode.

Materials for cell manufacturing were purchased from Sigma-Aldrich, The basic task in the research was to deposited photoanode with architecture: Glass/(FTO conducted layer)/nanostructural $TiO_2$ hybrid layer/N-719, using screen printing method provided to uniformity structure of the layer and repeatability of the production process. Photoanodes has been deposited on glass substrates with FTO coating (resistivity 10 $\Omega$/sq). On the FTO conductive surface paste containing $TiO_2$ nanoparticles and paste containing nanowires was applied by screen printing method. Then the order of application was inverted. The hybrid $TiO_2$ semiconducting layers were annealing at temperature of 400 °C for 1 h to remove the organic components. In the next step on the prepared medium N719 dye was deposited which sensitization of $TiO_2$ in the visible spectrum up to a wavelength of $\sim$ 750 nm. For the preparation of 25 ml of the N719 dye solution, 8 mg of N719 powder was dissolved in 15 ml of ethanol. The blend was mixed and sonicated to improve dissolution. The photoelectrodes was immersed in the N719 dye for 12 h at room temperature, without light access. The platinum counter electrode has been deposited with use screen printing method. In the last step electrolyte has been supplied between the manufactured photoanode and the counter electrode.

### 2.3. Research methodology

In order to determine the structure and morphology of the surface of deposition layers, the following tests were carried out:

- structural investigation using the Zeiss Supra 35 scanning electron microscope. Observations of topography and surface morphology of the screen printed layer were carried out in a scanning electron microscope Supra-35 from Zeiss. Magnification ranged from 20.00 k×–200.00 k×, accelerating voltage 2–3 kV, work distance 3–3.5 and InLens mode selected for flat and nanometric samples were used. Qualitative studies of chemical composition were also performed using the Energy Dispersive Spectrometer (EDS).
- investigations of optical properties of photoanodes were conducted using the Thermo Scientific Evolution 220 spectrophotometer with a xenon lamp with a wavelength range from 200 to 1200 nm. Absorbance was measured before and after dye deposition on the FTO/$TiO_2$, layers.
- I–V characteristics of created DSSC have been invstigated using PV Test Solutions Tadeusz Zdanowicz Solar Cell I–V Tracer System and Keithley 2410 source meter under Standard Test Conditions (AM 1.5, 100 W/$m^2$).

## 3. Results

### 3.1. Structure and surface morphology

Based on the observation of the surface topography of the photoanode produced on the basis of titanium dioxide nanoparticles, it was found that the applied $TiO_2$ layer has a granular structure with a significant number of pores (Fig. 1a). $TiO_2$ particles form evenly distributed clusters of size in the range of 10–30 nm of irregular shape. Figure 1b shows a layer of titanium dioxide nanowires deposited on glass plates with a one-sided deposited FTO layer by screen printing. Microscopic studies show a fairly uniform distribution of $TiO_2$ nanowires on the surface of the substrate. Their length is in the range from 100 nm to over 1 $\mu$ m. In both cases, 50.00 kx magnification and InLens mode were used. In the first case, a continuous layer was recorded with components of titanium oxide nanoparticles with a characteristic oval shape. In the second case, a layer of nanowires arranged in horizontal orientation in different directions was recorded. Surface morphology studies showed additionally continuous nanocomposite layer with characteristic components in the form of nanowires and nanoparticles (Fig. 1a). The energy scattered X-ray spectroscopy reveals the reflections characteristic for titanium and oxygen were recorded for deposited layers and for sodium derived probably from the glass substrate (Fig. 1b).

### 3.2. Optical properties

The results of testing optical properties of the $TiO_2$ layer are shown in Figure 2. Based on the absorbance studies of the produced photovoltaic cells, it was found that after applying titanium dioxide, the wavelength range for which solar absorption is increased from 300 nm (for the substrate) to about: 390 nm for $TiO_2$ NP/NW and 389 nm for $TiO_2$ NW/NP.

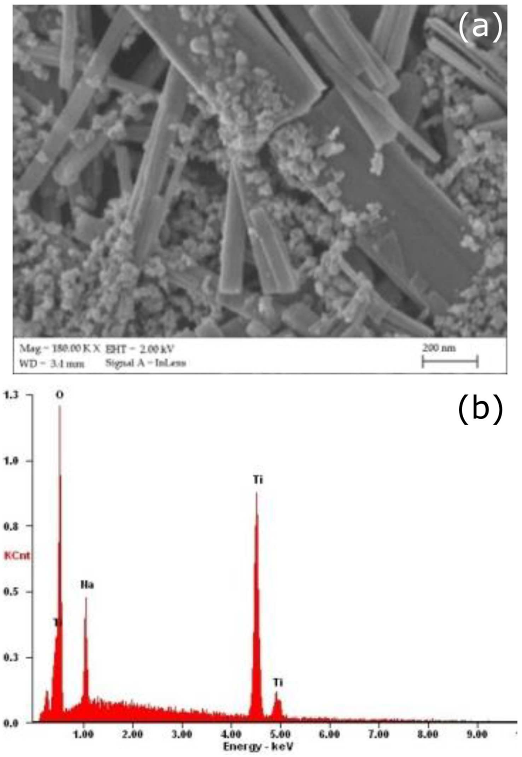


Fig. 1. SEM image (a) and EDS spectrum (b) of nanowires/nanoparticles $TiO_2$ nanocomposite layer deposited by the screen printing method.

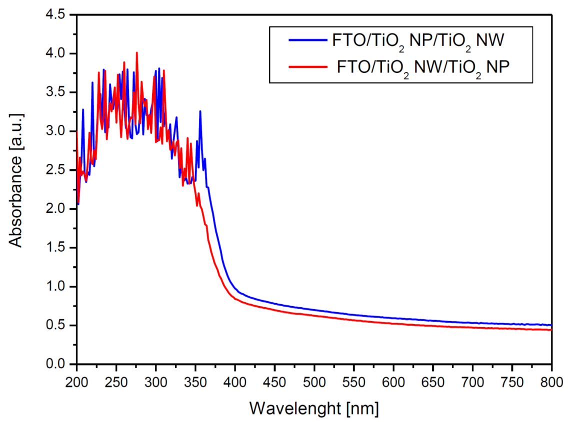


Fig. 2. Absorbance spectra of manufactured photoanodes.

The dye application in case of $TiO_2$ NP/NW layer visible shifts the edge of absorption towards the higher values of wavelengths in the range of 400–800 nm corresponding to the length of visible light. In the absorption spectra of dye loaded $TiO_2$ the additional absorption bands are observed which proves the optical transitions of the charge from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (Fig. 3). However the absorbance in case of $TiO_2$ NW/NP the increase in absorption in visible light is negligible.

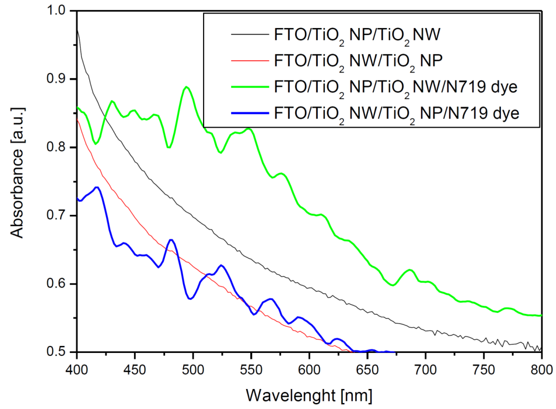


Fig. 3. Absorbance of manufactured photoanodes after dye loading.

TABLE I

Electrical properties of dye photovoltaic cells with a photoanode made of $TiO_2$ nanoparticles and nanowires

| Electrical properties | Photoanodes | |
|---|---|---|
| | $TiO_2$ NP/NW | $TiO_2$ NW/NP |
| $I_{sc}$ [mA] | 4.484 | 0.662 |
| $U_{oc}$ [mV] | 731.020 | 699.961 |
| $I_M$ [mA] | 3.815 | 0.449 |
| $U_M$ [mV] | 486.188 | 535.642 |
| $P_M$ [mW] | 1.855 | 0.240 |
| FF | 0.57 | 0.52 |
| Eff [%] | 4.46 | 0.58 |

### 3.3. Photovoltaic properties research

The current-voltage characteristics of the obtain dye photovoltaic cells produced, were examined and based on them the following electrical properties were determined: short-circuit current — $I_{sc}$, open circuit voltage — $U_{oc}$, current at the maximum power point — $I_M$, voltage at the point of maximum power — $U_M$, maximum solar cell power — $P_M$, fill factor — FF, efficiency — Eff. The obtained electrical properties of DSSCs are summarized in Table I.

## 4. Discussion

Images obtained using SEM show a homogeneous surface of $TiO_2$ nanoparticle layers with visible agglomerates of nanoparticles. Images showing $TiO_2$ nanowires suggest structures with varying lengths and diameters. The mixture of nanostructures shows a varied distribution of nanowires. However, the contact of structures is visible, which results in good electron transfer. The mixture of nanostructures and the use of their natural tendency for agglomeration can lead to pores of considerable size, i.e., the so-called mesoporous structure constituting the key element of the dye cell deciding on the transport of charge, loading and radiation absorption. The chosen method of application, in particular in the process of applying many layers, can be assumed to result in such a structure, however, the occurrence of nanostructures of various shapes additionally affects the effect. However, in the case of layers composed only of nanoparticles, layers interface defects may appear, leading to charge recombination and electron transport disorders through interfaces couses by preparing steps. Minimizing this problem is implemented through application on mesoporous layer diluted aqueous solution of $TiCl_4$ to create compact layer [10]. However, in case of presenting results the eradication of chaotically arranged nanowires leads to better contact in the layer and thus to easier electron transfer. Additionally the energy dispersive spectroscopy (EDS) confirms presence Ti, O elements in the deposited film.

The results of the layer absorbance measurements confirm the enlargement absorption range to 400–800 nm characteristic for the dye applied to the $TiO_2$ surface in case of $TiO_2$ NP/NW structure. Given that $TiO_2$ absorbs radiation in close ultraviolet photoelectrochemical performance of photoanodes is beneficial. The results prove that the created structure characterized by an extended surface result in dye loading and hence high light absorption. In addition, the position of the absorption edge was shifted in relation to the layers of waved nanoparticles which corresponds to the particles size. The structure of NW/NP showed a slight increase in absorption in the visible light range, which indicates a low loading density. Such a significant difference may be a consequence of layer surface morphology. Much larger dye loading in the first case may be caused by a different arrangement of nanowires, e.g., oblique and surface expansion. In the second case, the layer containing the nanowires applied first leads to the horizontal arrangement of nanostructures and, to a lesser extent, to the surface expansion.

The I–V results indicate a large discrepancy between the results of electrical properties obtained for DSSC produced using 2 types of photoanodes. In case of $TiO_2$ NP/NW structure all measured electrical properties are much higher than for DSSC with $TiO_2$ NW/NP photoanode. DSSC efficiency in the first case is 4.5% in the second only 0.58%. Such a significant difference is a consequence of the diverse structure of the layers. In the first case, the layer has a more developed surface but also a heterogeneous arrangement of nanowires will ensure more efficient transport of the electrons. In the second case, the horizontal arrangement of the nanowires reduces the degree of surface development, as well as does not ensure proper electrons transport.

Achievements efficiency $\sim$ 4.5% for these types of structures is a result comparable to the achievements of other researchers. NRs $\sim$ 1.56 $\mu$m long of $TiO_2$ combined with nanoparticles with high reached 2.45% of efficiences. A similar efficiency value to that obtained in the article was presented for nanospherical mesoporous $TiO_2$ and it was 4.65% ($I_{sc} = 9.51$ mA/cm$^2$, $V_{oc} = 0.72$ V, FF $= 0.67$) and for C based film on $TiO_2$ aggregates with diameter 90 nm (Eff = 4.3%), and $TiO_2$ nanotubes made on Ti foil couted on FTO glass (Eff = 4.7%). Researchers obtained efficiencies of 6.26% and 4.91% from devices manufacturing with use anatase $TiO_2$ synthesized with sol-gel, acid-base co-catalyst and room temperature colloidal synthesis method. For the photoanode consisting nanowires and nanoparticles was achieved the efficiency of 3.8%. The lower efficiency value for nanowires is associated with a low active surface area that is five times smaller than the active area of nanoparticles [11–13].

Higher efficiency values 6.5–8.43% were also obtained by post-treatment of photoanodes. This suggests the possibility of increasing the results obtained by additional processing of the layers.

## 5. Conclusion

Research results suggest that the order of applying layers in layered photoanode systems has a huge impact on the electrical properties obtained. $TiO_2$ NP/NW layers ensure good electrical properties and relatively high efficiency of the entire cell. While the $TiO_2$ NW/NP value affects the weak electrical properties of DSSC. This condition is probably related to the morphology of the surface of the layer responsible for dye loading and hence the absorption of radiation and the internal structure of the layers responsible for transporting of the charge. At the same time, as the earlier work of the authors of the article [13] indicates, hybrid 1D/3D layers in the case of $TiO_2$ can cause very interesting effects and affect the increase of cell efficiency. However, the results suggest that mixing nanostructures is more effective than producing photo anodes using one layers containing different nanostructures.

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