PHOTOANODE OF DYE-SENSITIZED SOLAR CELLS BASED ON TITANIUM DIOXIDE WITH REDUCED GRAPHENE OXIDE

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Resume

Dye-sensitized solar cells are one of the most promising new generation of photovoltaic cells due to their low cost, easy fabrication and high energy conversion. One of the key components of DSSC is photoanode that supports dye molecules and helps in the electron transfer. Titanium dioxide film used as a photoanode should have nanocrystalline structure, mesoporous nature and be semi-transparent. A thin semiconductor layer consist of nanocrystalline grains, therefore, DSSCs are also called nanocrystalline solar cells. Transparency is also an important issue of photovoltaic cells, especially when used in building integrated photovoltaics (BIPV) on glass and metal substrates. Moreover, the transparency allows their use in tandem cells.

The paper presents the results of the structure investigation, optical and electrical properties of a photoanode in dye-sensitized solar cells with reduced graphene oxide in the structure of photoanode. Photoanode with rGO achieve the conversion efficiency of 4.5 % while standard DSSC achieves 4.3 %. A dye-sensitized solar cells with reduced graphene oxide exhibit greater light-harvesting efficiency and absorbance in comparison to photoanode without reduced graphene oxide. Using a reduced graphene oxide in photoanode of dye-sensitized solar cell allows to produce two dimensional structures between nanoparticles of titanium dioxide, that increase rate of electron transport and reduce recombination in DSSCs.

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1. Introduction

The environmental issues such as ozone hole, acid rain, greenhouse effect, etc., affect every human, animal and nation on this planet and are a threat to both health and life. They result from, among other factors, mass burning of fossil fuels such as coal and oil. In the common perception fossil fuels will be replaced by cleaner and cheaper renewable energy sources, the use of which is not associated with long-term deficits, because their supply is renewed in a short time. Humanity consumes enormous amounts of energy resources, and most of this energy come from fossil fuels (Fig. 1). The growing public awareness that oil reserves on Earth can be exhausted as early as in this century also drives the development of renewables [1, 2].

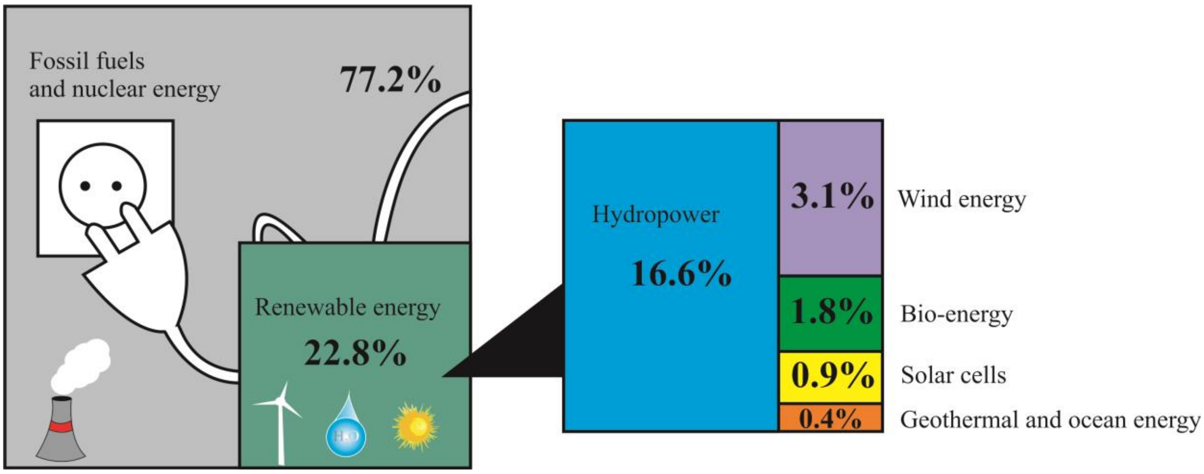

Fig. 1. World production of electricity in 2013 [1, 2].
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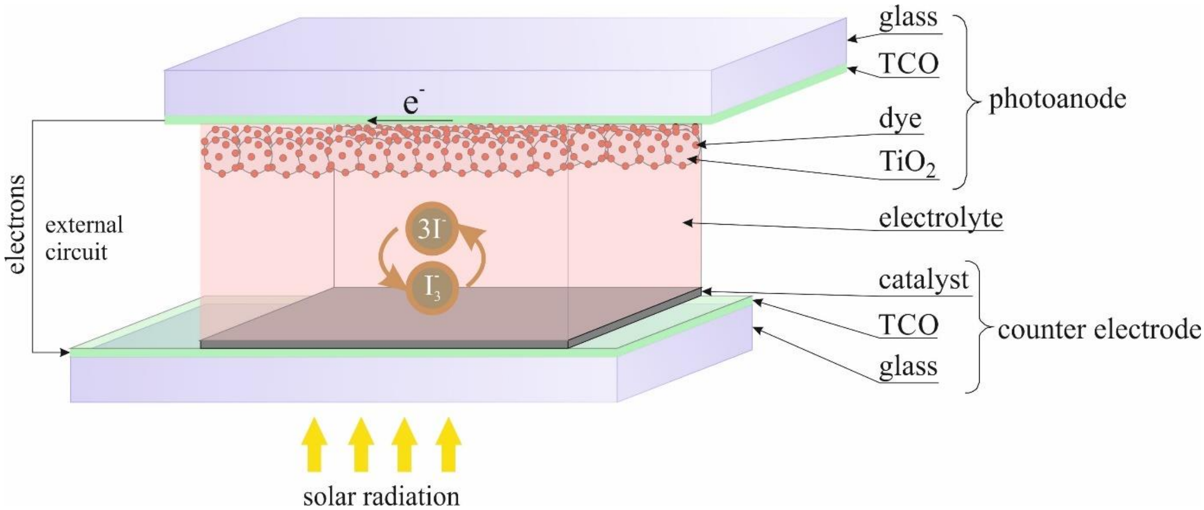

Fig. 2. Schematic of construction and operation principle of dye-sensitized solar cells.
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A lot of interest in renewable energy sources enjoys the solar energy. To convert sunlight into electrical power are used photovoltaic cells [3 - 5].

Today's photovoltaic market is dominated by photovoltaic solar cells with a p-n junction between solid state inorganic materials, usually from a crystalline or amorphous silicon, using the experience of very well-developed electronics industry. Silicon solar cells account for over 80 % of the photovoltaic industry [3 - 5]. In the recent years, this domination was disturbed by the emergence of photovoltaic cells based on nanocrystalline materials and conductive polymer films. This type of photovoltaic cells offers the prospect of low-cost production with a combination of various attractive features like flexibility, transparency and lack of toxicity of mainly used materials [3, 6]. It is possible to complete separation of the semiconductor junction devices by replacing the contact phase of the semiconductor through the electrolyte, resulting in a photoelectrochemical cell. Contrary to expectations, the devices based on interpenetrating networks of mesoscopic semiconductor show a surprisingly high conversion efficiency (14 % in the laboratory) [7] so that they can compete with conventional solar cells. One example of this type of the solar cell is a dye-sensitized solar cell (DSSC) in which the optical absorption and charge separation process is achieved through the use of the dye as the material absorbing light from a nanocrystalline semiconductor with a wide energy band gap [6 - 10]. Usually, a DSSC is composed of transparent conductive oxide (TCO) coated glass, a nanoporous titanium dioxide film with absorbed dye, a counter electrode and a liquid electrolyte containing iodide/triiodide redox couple. In Fig. 2 schematics of the construction and operation principle of DSSC is shown.

One of the key components of DSSC is a photoanode that supports dye molecules and helps in the electron transfer. The titanium dioxide film used as a photoanode should have a nanocrystalline structure, a mesoporous nature and be semi-transparent [10, 11]. A thin semiconductor layer contains nanocrystalline grains. Therefore, DSSCs are also called nanocrystalline solar cells. Compounds such as titanium dioxide, zinc oxide, tin oxide, niobium oxide, zirconium oxide can be used as semiconductors in a photoanode. The titanium dioxide is the most commonly used due to its excellent structural stability in solutions and during solar radiation, as well as light sensitivity and low price [11]; it is a widely available non-toxic material used in everyday products as toothpaste, sun-protection creams or paint. It comes in three natural forms: rutile, anatase and brookite. Dye-sensitized solar cells require the most active form of titanium dioxide – polymorphic anatase due to its relatively high energy band gap and high energy of conduction band edge. Anatase is an n-type semiconductor with energy band gap equal to 3.2 eV, which corresponds to the optical onset of approximately 390 nm to light absorption. Conventional crystalline silicon solar cells require silicon purity of 99.9999 % (less than 1 ppm total impurities). Requirements for anatase in the dye-sensitized cells are less stringent but nevertheless significant. The high-quality batch of titanium oxide as the one used in the commercial production of titanium dioxide paste has a phase purity of at least 99 %. Currently, the most popular paste of titanium dioxide available on the market contains 80 % anatase and 20 % rutile [12, 13].

Because of the wide band gap (~ 3.2 eV), titanium dioxide only absorbs UV light, including a small fraction (~ 5 %) of the solar spectrum. The organic compounds which absorb visible radiation are used as dyes in the dye-sensitized solar cells due to their stability in the presence of light and have groups which allow the permanent bonding of the semiconductor surface. Natural dyes, such as chlorophyll, carotene and anthocyanins are widely available in plants, flowers and fruit. In the laboratory, dye-sensitized solar cells based on natural dyes reached an efficiency of 7.1 % [14]. Because of their high absorption of visible light, a long lifetime after excitation and the effectiveness of charge transfer metal - ligand most often used are ruthenium-based N3, N719 and Z-907 dyes [13 - 15].

Transparency is also an important issue of photovoltaic cells, especially when used in building integrated photovoltaics (BIPV) on glass and metal substrates. Moreover, the transparency allows their use in tandem cells [16].

One of the promising methods for increasing the collection efficiency of the charge in dye-sensitized solar cells is changing the morphology of the titanium dioxide by using a mixture of titanium dioxide with highly conductive carbon materials. Among various carbon materials, to enhance the electron transport and thereby increase the efficiency of the dye-sensitised solar cell, reduced graphene oxide have been used. Using a reduced graphene oxide rGO in photoanode of dye-sensitized solar cell allows to produce two dimensional structures between nanoparticles of titanium dioxide, that increase rate of electron transport and reduce recombination in DSSCs.

The primary objective of this work is to present the results of the structure investigation of a photoanode in dye-sensitized solar cells using the titanium dioxide with reduced graphene oxide and N3 dye by using scanning electron microscope and X-ray diffraction. The effect of N3 dyes and titanium dioxide layers on absorbance, transmittance and light harvesting efficiency, was investigated. The electrical properties of dye-sensitized solar cells were measured.

2. Experimental

2.1 Materials

The FTO (fluorine-doped tin oxide) glass substrates (10 $\Omega \cdot sq^{-1}$, 3D Nano) were cut into pieces with a size of 2.5 × 2.5 cm^2 and ultrasonically cleaned in distilled water, acetone and ethanol for 15 min, respectively.

Ruthenium dye N3 - Cis-diisothiocyanato-bis(2.2'-bipyridyl-4.4'-dicarboxylic acid) ruthenium(II), Iodolyte electrolyte and highly dispersed titania nanoparticle paste for the photoanode were purchased from Solaronix (Switzerland). The platinum paste was purchased from 3D Nano (Poland). The graphene oxide was obtained from CheapTubes. Reduced graphene oxide was prepared according to the procedure in previous work [18].

2.2 Photoanode preparations

The productions steps of photoanode preparations are shown in Fig. 3. In order to prepare photoanode with reduced graphene oxide to the titanium dioxide paste was added 5% wt. of reduced graphene. Three layers of titanium dioxide with or without reduced graphene oxide were screen printed on previously cleaned FTO glass or glass without FTO (Fig. 3a), and each one was dried at 105°C. Then the films were annealed in an air stream at 500°C for 30 min (Fig. 3b), cooled down to 80°C, and then placed in the anhydrous ethanol solution of 0.5 mM. N3 dye for 24 h and without access to light (Fig. 3c). Once removed, the electrode was washed with ethanol to remove excess dye and allowed to dry.

2.3 Dye-sensitized solar cells preparation

Dye-sensitized solar cells were made by combining the platinum counter electrode (screen printed on FTO glass and annealed in 500°C for 30 min) and the photoanode. The space between electrode was filled with high-performance electrolyte with high-concentration of triodide (from Solaronix).

2.4 Measurements

Scanning Electron Microscopic (SEM) images were taken with a Zeiss Supra 35. The X-ray Diffraction (XRD) analysis was recorded on a Panalytical X'Pert Pro diffractometer using filtered radiation from the lamp with copper anode. X-ray phase analysis was performed in the Bragg-Brentano geometry by using X'celerator strip detector.

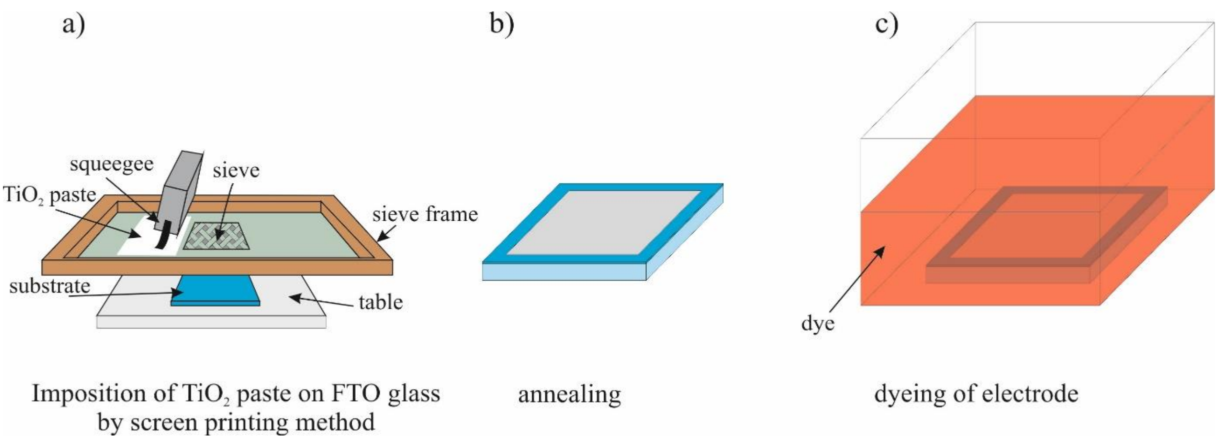

Fig. 3. Schematic of photoanode production steps in dye-sensitized solar cells.
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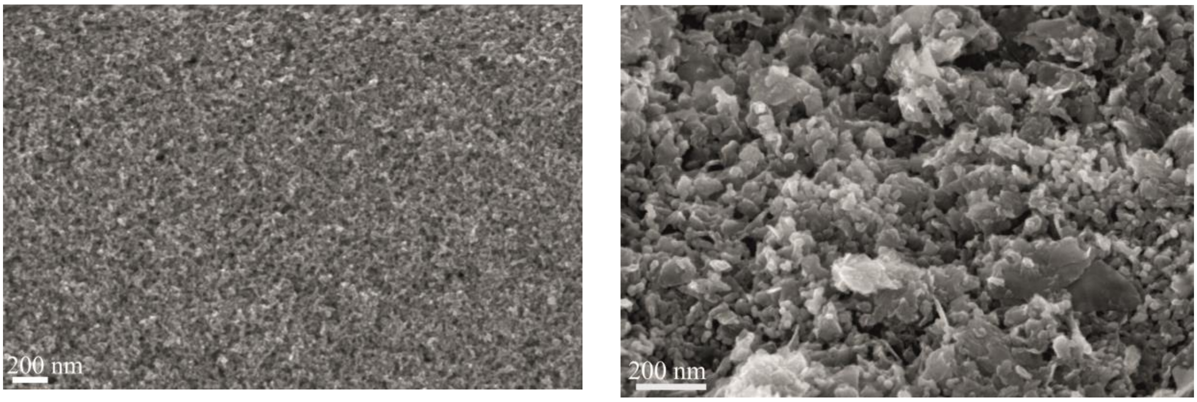
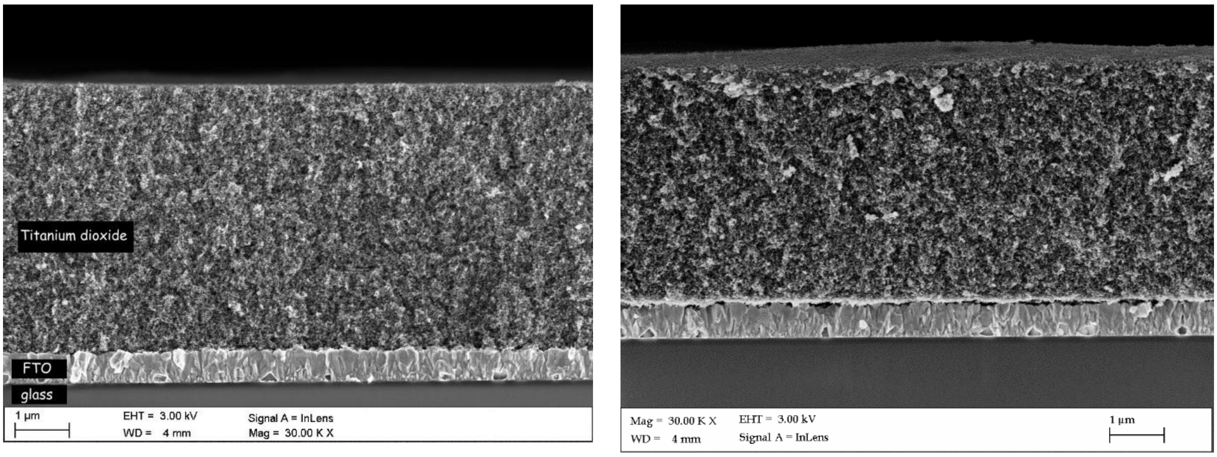


a) titanium dioxide *b) titanium dioxide with reduced graphene oxide glass*

Fig. 4. The morphology of a) titanium dioxide b) titanium dioxide with reduced graphene oxide on glass after sintering, SEM.



a) before dyeing *b) after dyeing*

Fig. 5. Cross-section of FTO glass coated with titanium dioxide before a) and after b) dyeing, SEM.

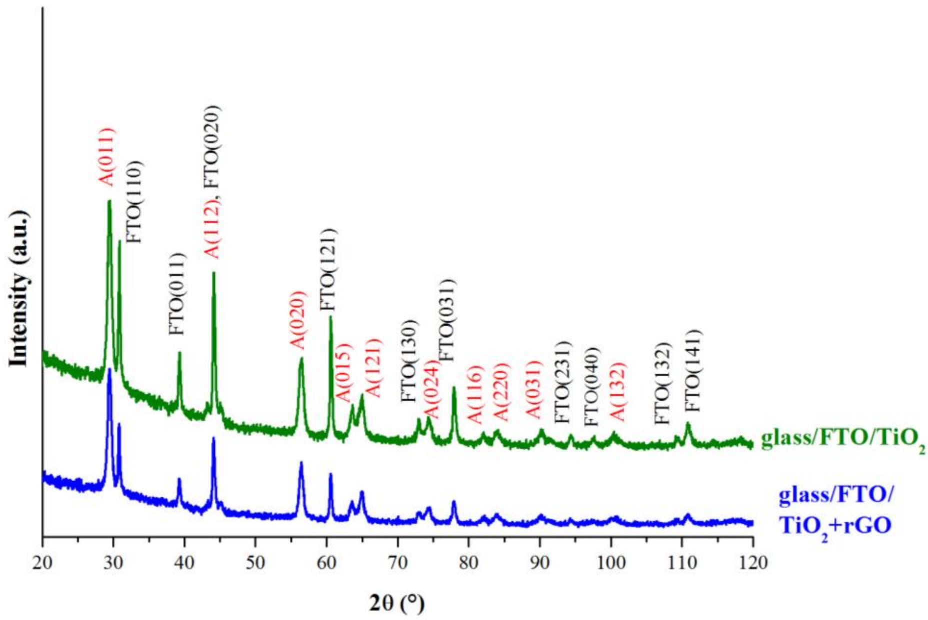


Fig. 6. X-ray diffraction pattern of titanium dioxide layer with and without reduced graphene oxide, where: A - nanocrystalline anatase, glass/FTO - glass substrate coated with FTO, rGO - reduced graphene oxide.
(full colour version available online)

The transmittance and absorbance of titanium dioxide layers with and without dye and reduced graphene oxide were measured by Thermo Scientific Evolution 220 spectrophotometer equipped with a xenon lamp in the wavelength range from 190 nm to 1100 nm. Light harvesting efficiency *LHE* was calculated using the following formula [18]:

$$LHE(\lambda) = \left(1 - 10^{-A(\lambda)}\right) \cdot 100 \quad (1)$$

where *A(λ)* is the absorbance at a specific wavelength.

The studies of electrical properties of experimentally prepared dye-sensitized solar cells containing in its photoanode reduced graphene oxide were performed on a computerized station SS IV CT-02 for measurement of current-voltage (IV) characteristics equipped with AAA sunlight simulator and with low current meter - Keithley 2401 for dye-sensitized photovoltaic cells measurement.

3. Description of achieved results

Fig. 4 shows the SEM images of FTO glass coated with titanium dioxide with and without reduced graphene oxide after sintering at 500°C. Fig. 5a and Fig. 5b show SEM images of cross section of FTO glass coated with titanium dioxide before and after dyeing. The thickness of titanium dioxide layer was measured by SEM to be ~14.92 μm. It can be seen that uniform structure of titanium dioxide film was obtained by screen printing method. Between the reduced graphene oxide and titanium oxide exists good contact. Moreover reduced graphene oxide is consistently distributed in the photoanode.

Fig. 6 shows the X-ray diffraction pattern of titanium dioxide on the FTO glass. The presence of only anatase form of titanium dioxide indicates a high quality of paste. Due to the transparency of titanium dioxide layer on X-ray diffraction pattern, some peaks from FTO can be seen. Reduced graphene oxide due to its small share in photoanode does not change the phase composition of the material.

Fig. 7 shows the transmittance of particular layers of photoanode in dye-sensitized solar cells. The best transmittance has the pure glass covered with FTO. At a range of 300 – 400 nm within the ultraviolet region, the dye as well as the TiO_2 coated FTO glass exhibited a low value of transmittance but increased gradually through the visible region and obtained maximum values in the infrared region. It can be observed that the transmittance of all samples without reduced graphene oxide was over 70 % of the wavelength between 700 and 1000 nm. In the case of photoanode with reduced graphene oxide, the maximum transmittance was 60 % which indicates on increased absorption of solar radiation.

The absorbance of particular layers in photoanode is presented in Fig. 8. The best absorbance has titanium dioxide with reduced graphene oxide coated FTO glass with absorbed dye. It confirms the importance of dye in DSSC cells and its high absorption of visible light. Besides the optical absorbance and transmittance spectra, LHEs were also calculated for the 200 - 1100 nm wavelength. Fig. 9 shows a light harvesting efficiency of each layer in photoanode. The dye increases the light harvesting efficiency of the wavelength 400 - 600 nm. It can be seen that FTO also affects the light harvesting efficiency when moved towards the visible light. Furthermore, photoanode with a reduced graphene oxide is able to absorb more solar radiation than photoanode without reduced graphene oxide, increasing energy conversion efficiency of solar radiation into electrical energy. This is due to the fact that between the particles of titanium dioxide, by using of the reduced graphene oxide, two-dimensional structures are formed, which provide faster electrons transport to the FTO layer, and thereby they are reducing the degree of recombination of the excited electron with the triiodide anion from the electrolyte.

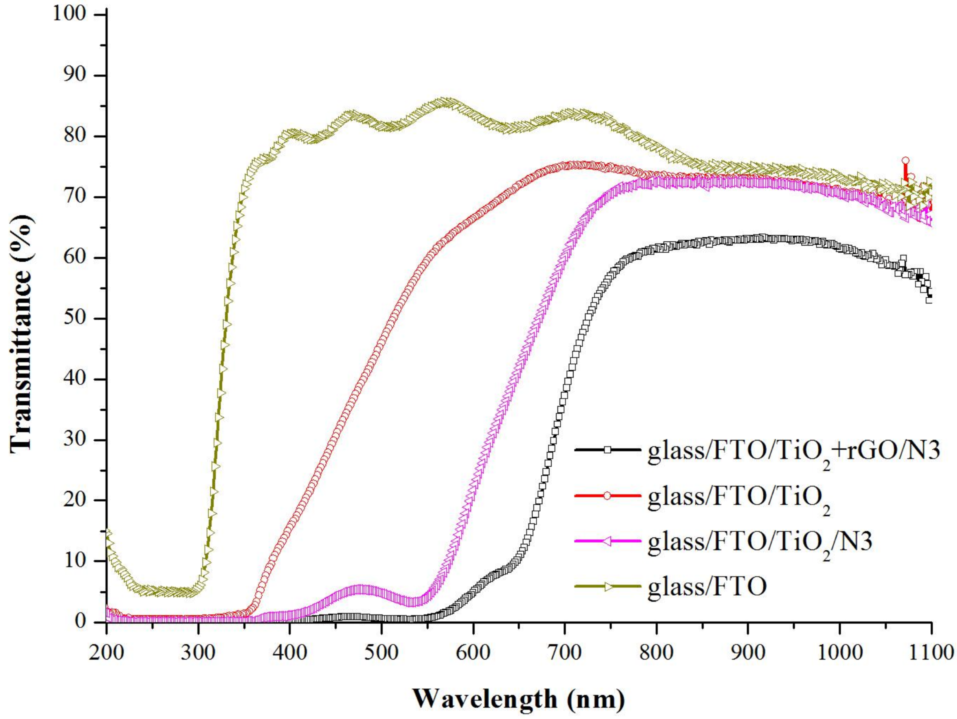


Fig. 7. Transmittance of particular layer of photoanode, where: glass/FTO - glass substrate coated with FTO, TiO_2+rGO - titanium dioxide with reduced graphene oxide, N3 - dye.
(full colour version available online)

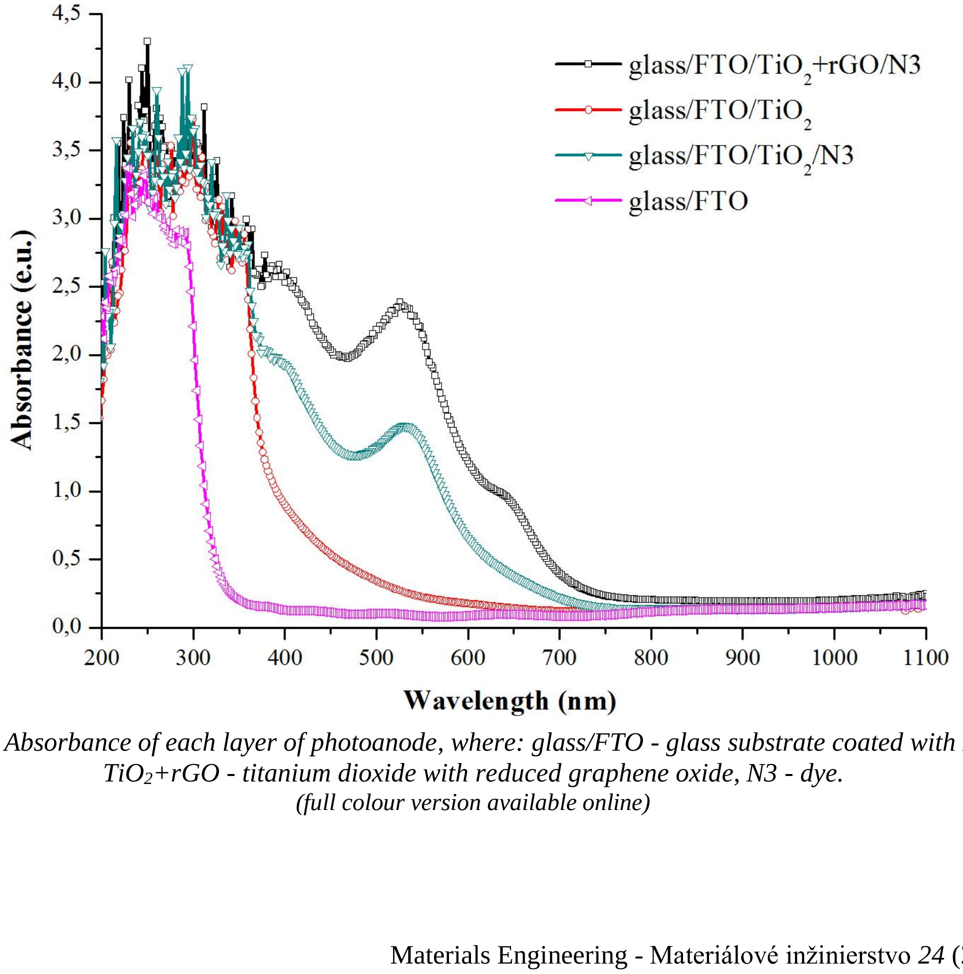


Fig. 8. Absorbance of each layer of photoanode, where: glass/FTO - glass substrate coated with FTO, TiO_2+rGO - titanium dioxide with reduced graphene oxide, N3 - dye.
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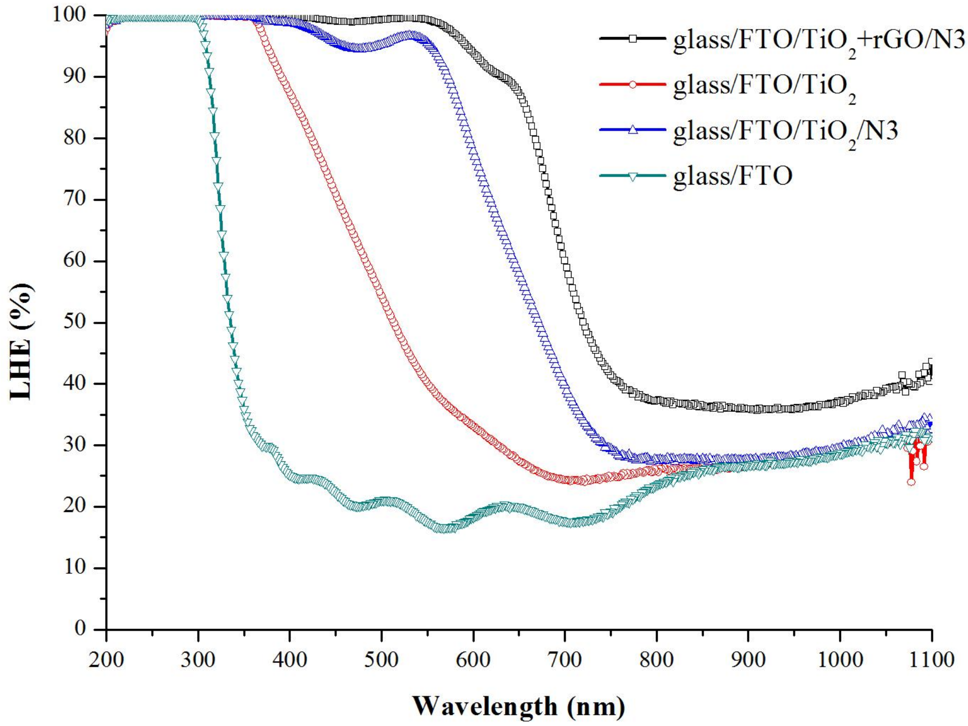

Fig. 9. Light harvesting efficiency LHE of particular layer of photoanode, where: glass/FTO - glass substrate coated with FTO, TiO_2+rGO - titanium dioxide with reduced graphene oxide, N3 - dye.
(full colour version available online)

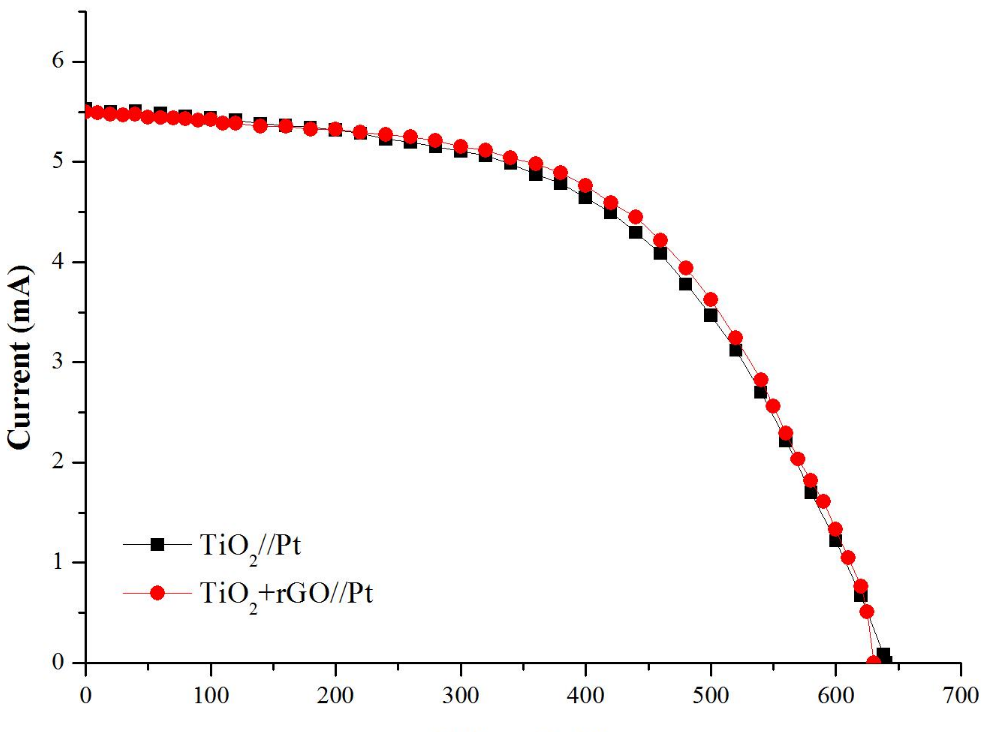

Fig. 10. Current-voltage characteristics of dye-sensitized solar cells.
(full colour version available online)

The current-voltage characteristics of prepared dye-sensitized solar cells with and without reduced graphene oxide in photoanode are shown in Fig. 10. DSSC with standard photoanode shows an open circuit voltage (U_{OC}) of 0.64 V and the short circuit current (I_{SC}) of 5.4 mA with conversion efficiency (η) of 4.3 %. Upon loading the reduced graphene oxide to photoanode, DSSC yielded an I_{SC} of 5.5 mA, U_{OC} of 0.64V and η of 4.5 %. The achieved results can be compared to the data reported by Menghua Zhu in [18] where conversion efficiency of 4.28 % was achieved. Compared to that, the applied screen printing method in the production of photoanode shows simplicity and dye-sensitized solar cells with higher efficiency can be obtained.

4. Conclusions

In conclusion, we demonstrated the titanium dioxide with reduced graphene oxide layers preparing by screen printing method on FTO glass, followed by being sensitized in the N3 dye. It was shown that uniform structure of titanium dioxide photoanode was obtained. In the case of titanium dioxide with reduced graphene oxide it was shown that reduced graphene oxide is consistently distributed in the photoanode. Because of its high transmittance, it is possible to use dye-sensitized solar cells in building integrated photovoltaic. Absorbance, as well as light harvesting efficiency is higher for photoanode with reduced graphene oxide. It indicates stronger absorption in visible light for titanium dioxide with reduced graphene oxide coated FTO glass with dye. The higher conversion efficiency for DSSC with rGO indicates on the higher transfer of electrons between the titanium dioxide and FTO.

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