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The influence of natural and synthetic dyes on the absorbance of nanocrystalline TiO_2 used in dye sensitized solar cells

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ABSTRACT

Purpose: The purpose of the paper is to examine the impact of selected dyes, organic and synthetic, on the absorbance of nanocrystalline titanium oxide. It is a major component of the working electrode of dye sensitized solar cells. Those devices belonging to the third generation of solar cells are an attractive alternative to inorganic solar cells. Therefore it intensive research on increasing their efficiency were carried out.

Design/methodology/approach: Nanocrystalline titanium dioxide powder was manufactured with the use of sol gel method. Then, the titanium dioxide layers were deposited on a glass substrate using a doctor blade technique. On the prepared layers commercial synthetic dye N_3 and natural dye obtained from blueberry were deposited. The structure of manufactured TiO_2 nanopowder was investigated using the high resolution transmission electron microscope. Optical properties of TiO_2 layer with and without dye have been examined using an UV–VIS spectrometer.

Findings: Results and their analysis show that it is possible to obtain nanocrystalline titanium dioxide using sol-gel method and then deposition of the various types of dyes effectively extending the range of the absorbance of light radiation.

Practical implications: Nanocrystalline layers of titanium oxide are an essential element of the working electrode of dye sensitized solar cells. It is extremely important to search for new materials for sensitizing titanium dioxide to enhance the efficiency of the type of solar cell.

Originality/value: The paper presents results of investigations of the influence of natural and synthetic dyes on the absorbance of noncommercial nanocrystalline TiO_2 used in dye sensitized solar cells.

Keywords: Dye sensitized solar cells; Titanium dioxide; Dye

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PROPERTIES

1. Introduction

Dye sensitized solar cells belong to the third generation of solar cells. Those devices are photoelectrochemical where it is not dealt with a typical p-n junction. Dye sensized solar cells (DSSC) have been developed by Michael Grätzel and Brian O`Regan in 1991 and since then has been intensively studied. However, their disadvantage is the low efficiency. Efficiency of such cells is almost half that of an inorganic cell. The working principle of DSSC is different that the common solar cells. Typical dye sensitized solar cell is made of two glass plates with a conductive layer (TCO), constituting the electrode (Fig. 1) [1-5].

On the surface of working electrode there is a layer of n-type semiconductor, whose function is to transfer electrons to an external circuit. The wide energy band gap of the 3.2eV, allows for the absorption only of ultraviolet radiation. To increase the area of photon absorption the semiconductor layer is porous. On the semiconductor layer a dye should be adsorbed, otherwise it is known as a sensitizer which absorbs electromagnetic radiation with a photon of energy 1.6-3.0eV, the length of 400-800nm. Dye molecule absorbing a photon, temporarily increases its energy (is excited) and passes it semiconductor in the form of a free electron, which carries an electrical charge to the rear electrode. The dye is reduced by the reaction with the electrolyte, which in turn returns to the initial state by taking an electron from the counter electrode (TCO glass plate with a layer of platinum) [6-8].

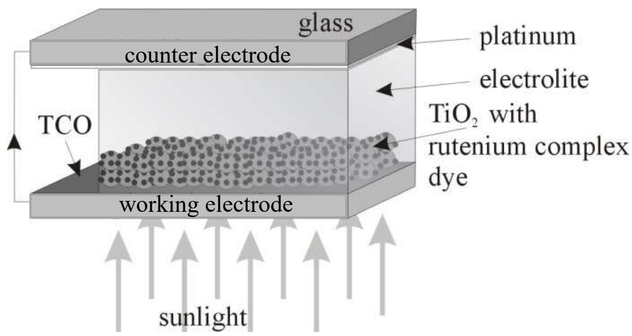

Fig. 1. Schematic structure of typical dye sensitized solar cell [9]

Each element of DSSC affect its efficiency. In particular, an important element is an inorganic semiconductor of n-type. Titanium oxide is the most commonly used. It is possible to use also other oxides such as: ZnO, SnO_2, Al_2O_3 and Nb_2O_2 [10]. To increase the surface absorption of photons TiO_2 layer is porous and nanocrystalline. Titanium oxide is a poor conductor of electricity but combined with organic dye molecules increases its conductivity. The dye is called also a sensitizer, which absorbs photons of solar radiation in the range between 400 and 700 nm. The particle sensitizer should contain functional groups which enable their adsorption on the surface of the semiconductor [11-13]. An important requirement is also that the energy level of the excited state of the dye has been higher than the conduction threshold of semiconductor that there was a transfer of an electron and the value of the redox potential was large, and the basic state low, so that there may be a regeneration of the sensitizer. Such an effective dye used in the DSSC should be characterized by [14]:

- intense absorption in the visible region (from 400 to700nm),
- strong adsorption on the surface of the semiconductor,
- a high extinction coefficient,
- stable in its oxidized form allowing it to be reduced by an electrolyte,
- be stable enough to carry out $\sim 10^8$ turnovers, which typically correspond to 20 years of solar cell work.

Organometallic compounds, including the ones of ruthenium, osmium, copper are the most commonly used. Examples are shown in Figure 2. The most commonly used dyes are red or black compounds of ruthenium. From the first group they absorb light in the range between 400 and 800 nm and from second group they absorb wavelengths up to 900 nm [15, 16].

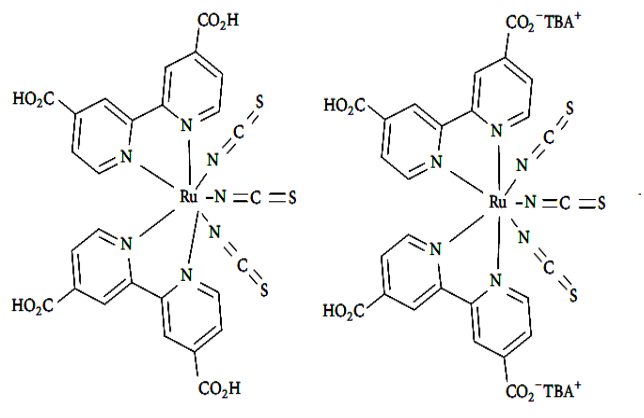

Fig. 2. Example of organometallic compounds used as dyes

Expensive ruthenium compounds have tried to be replaced by synthetic dyes which do not contain metal particles in their structure. However, along with the low costs of the materials walked their low efficiency. The general mechanism of working electrode structure containing an organic dye, without metal particles is shown in Figure 3. The substituents which act as a donor and an acceptor are separated by a conjugated system [17].

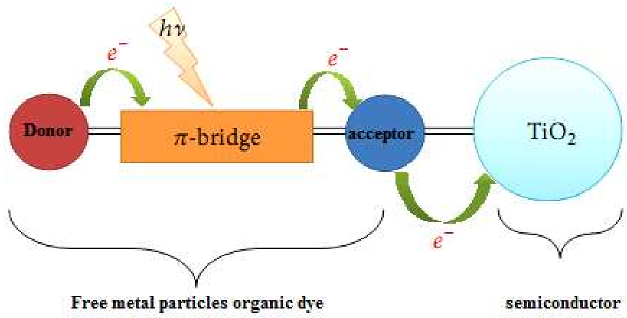

Fig. 3. Mechanism of a working electrode structure containing an organic dye, without metal particles [17]

An alternative to synthetic dyes are natural dyes that are in flowers, leaves or fruits. Dye extraction method can be used on flowers such as rhododendron, petunia, begonia, rose, violet and marigold. The acquisition of dyes is also possible with different fruits: raspberries, blueberries and mangosteen.

2. Materials and methodology

Nanocrystalline titanium dioxide powder was prepared by a sol gel method. The TiO_2 powder has been obtained by hydrolysis and peptization solution of titanium isopropoxide (TIPO) and isopropanol. Subsequently, produced powder has been subjected to structural analysis using a transmission electron microscope (TEM). TEM investigations have been performed with a field-emission transmission electron microscope (FEI Titan 80-300 TEM/STEM) with a supertwin lens operated at 300kV and equipped with an annular dark-field detector. Observations were carried out with energy 300kV in the classical model (TEM) and in the beam surface-scanning mode (STEM). For this purpose, prepared powder have been deposited on the special copper mesh preparations used in an electron microscopy.

The TiO_2 layers have been made from powder by the doctor blade technique (Fig. 4). After that the TiO_2 thin film have been examined using an Evolution 220 UV-VIS Spectrometer, Thermo Scientific (Fig. 5).

The aim of the research has been to comparise the optical properties of two different kinds of dyes. The commercial ruthenium complex named N3 is the first one and the second one is dye obtained from fruits. N3 dye is a commonly used in the construction DSSC to extend the absorption spectrum of light radiation, and it has been supplied by Sigma-Aldrich in powder form. The natural dye has been obtained from American blueberries (Fig. 6).

The fruits have been cleaned under water and then dried in a laboratory dryer. When the fruits have been quite dry then they have been crushed in a ceramic mortar for about half an hour. In order to compare the properties of both dyes it has been necessary to dissolve the dye in ethyl alcohol. Two homogeneous solutions with intense dark red color have been obtained (Fig. 7).

Prepared dyes have been deposited on a glass substrate by spin coating technique at different spin speed. Using the disposable pipette 0.2ml of the dye deposited on glass substrates using a spin coater have been collected. The substrate has been set in rapid rotation, and the excess of the applied substance is removed outside the edges of the sample by centrifugal force. The result is that the entire surface of the substrate is coated with an almost uniform layer of dye. The time and the spin speed have been determined experimentally (2000rpm by 50s) so as to obtain layers of the same thickness. Then, after drying the samples, the optical properties of thin films have been measured with using a UV-VIS spectrometer. The prepared dyes have been adsorbed also on the surface of the nanocrystalline titanium dioxide and also have been measured using a UV-VIS spectrometer.

Fig. 4. Titanium dioxide layer prepared by a doctor blade technique

Fig. 5. UV-VIS Spectrometer, Evolution 220, Thermo Scientific

Fig. 6. American blueberries used to obtain the natural dye

Fig. 7. Vials with two different dyes: A-prepared from American blueberry; N3-ruthenium complex

3. Results and discussion

The TiO_2 powder has been characterized using a high resolution transmission electron microscope S/TEM. HRTEM image shows that the powder particle size have few nanometers, but not exceeding 10nm (Fig. 8). By selecting the direct electrons (BF) and the scattered electrons (DF) was shown that the most of the particles have a regular structure (Fig. 9).

The optical properties of two different kinds of dyes deposited on a glass substrate by spin coating technique were compared using a UV-VIS spectrometer. Fig. 10. shows the absorbance dependence from the wavelength for two different kinds of a dye. A continuous line has been marked by the commercial N3 dye, a dotted line-dye obtained from fruits. The absorbance dependence from the wavelength shows that the both dyes have similar absorbance, which reaches a maximum at a wavelength in the range of ultraviolet. In the whole range of visible spectra they are characterized by the same high absorbance (at the 1.5), with the indication that the absorbance of the dye N3 is slightly higher than the natural dye.

Absorbance of TiO_2 layer with and without dye have been examined using an UV–VIS spectrometer. The titanium dioxide has a high absorbance of light in the UV range, but weakly absorbs visible light in the range of 400 to 800nm (Fig. 11).

The adsorption of N3 dye onto a titanium dioxide has increased the absorption in the visible range (Fig. 12). The highest absorbance value is 1.25 in wavelength of 550nm.

After adsorbed the natural dye on the nanocrystalline TiO_2 layer the absorption increases in the wavelength range from 400nm to higher values (Fig. 13). In this case the highest absorbance value is 0.7 in wavelength of 550nm.

Both used dyes expand the range of absorption of the visible spectrum.

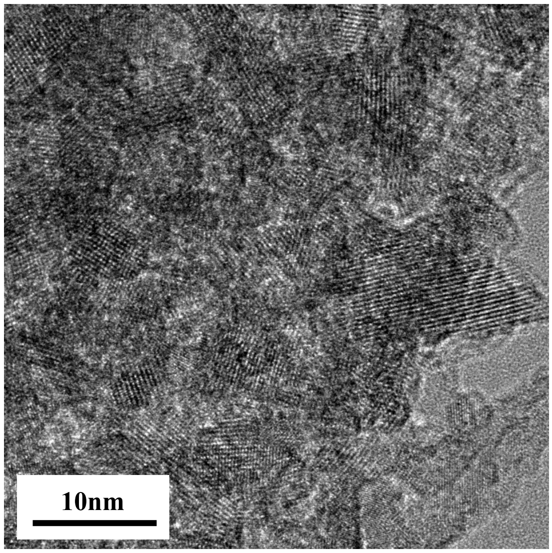

Fig. 8. HRTEM image of nanocrystalline particle of TiO_2 obtained by hydrolysis and peptization of TIPO solution

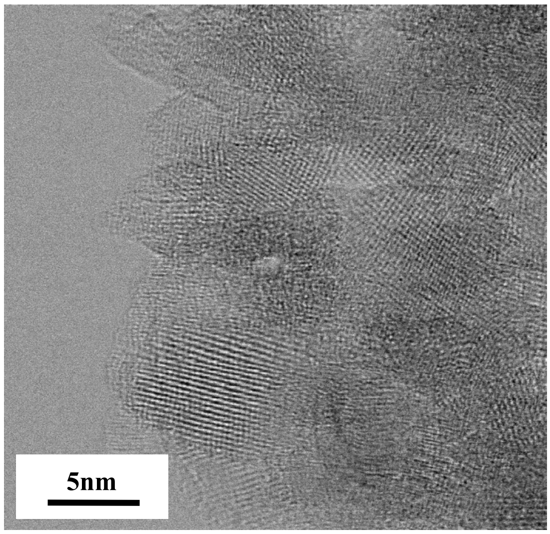

Fig. 9. BF DF TEM image of nanocrystalline particle of titanium dioxide

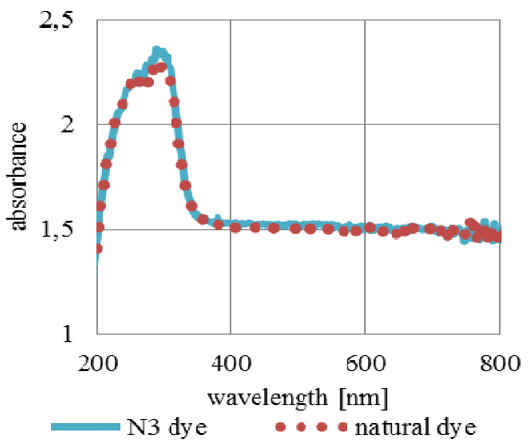

Fig. 10. The absorbance spectrum as a function of wavelength for two different kinds of a dye deposited on glass substrate by spin-coating technique

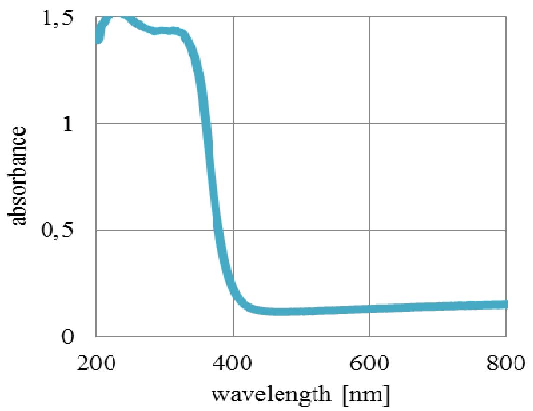

Fig. 11. The absorbance spectrum as a function of wavelength for TiO_2 nanoparticles

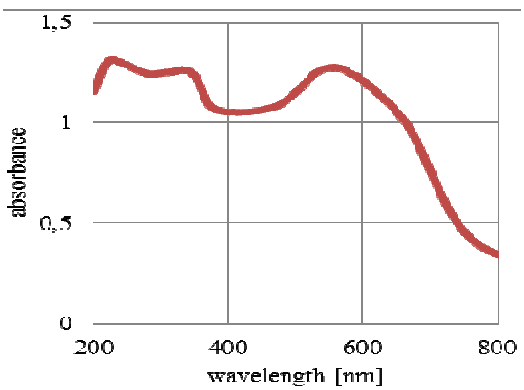

Fig. 12. The absorbance spectrum as a function of wavelength for TiO_2 with N3 dye adsorbed

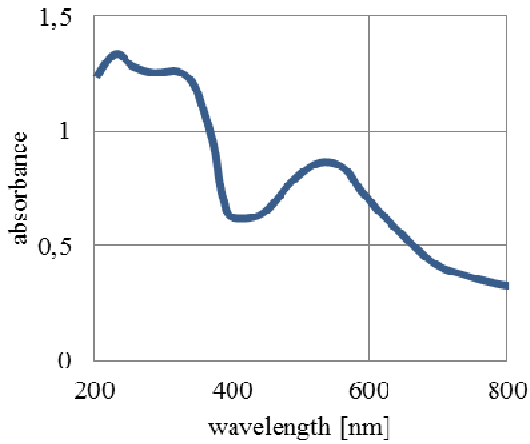

Fig. 13. The absorbance spectrum as a function of wavelength for TiO_2 with natural dye adsorbed

4. Conclusions

Results and their analysis allowed to conclude that the TiO_2 powder obtained by hydrolysis and peptization of solution of TIPO and isopropanol is nanocrystalline. The titanium dioxide has high absorbance of light in the ultraviolet range, but weakly absorbs visible light in the range of 400 to 800nm. The adsorption of the dye on titanium dioxide expands the range of absorption of the visible spectrum. Absorbance of N3 dye on TiO_2 is higher than natural dye. Its reason is could be that more molecules of N3 dye has been adsorbed in titanium dioxide. Nanocrystalline layers of titanium dioxide are an essential element of the working electrode of dye sensitized solar cells. It is extremely important to search for new materials for sensitizing titanium dioxide to enhance the efficiency of that type of solar cell.

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Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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