DOI: 10.1515/amm-2016-0140

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NANOCRYSTALLINE TiO_2 POWDER PREPARED BY SOL-GEL METHOD FOR DYE-SENSITIZED SOLAR CELLS

In this study titanium dioxide nanopowder has been manufactured and examined. Nanocrystalline TiO_2 powder has been obtained by hydrolysis and peptization of a solution of titanium isopropoxide and isopropanol. Subsequently, produced powder has been subjected to structural analysis by using a transmission electron microscope, X-ray diffractometer, and Raman spectrometer. For comparison purposes, a commercially available titanium dioxide powder (i.e. titanium white) was also used. Thin layers have been made from this powder and further have been examined by using a UV/VIS spectrometer. Completed research shows the nanocrystalline structure of obtained layers and their good properties such as absorbance at the range of wavelength equal 200 – 1000 nm.

Keywords: sol-gel; nanopowder; titanium dioxide; dye-sensitized solar cell

1. Introduction

The titanium oxide is a typical n-type semiconductor. It has three crystalline forms found in nature: brookite, anatase, and rutile. The first of them is quite rare. Rutile is stable at high temperature while anatase does not show this feature. Temperatures transitions between the different phases are as follows [1-3]:

- brookite – rutile; 500-600°C,
- anatase – rutile; 850°C.

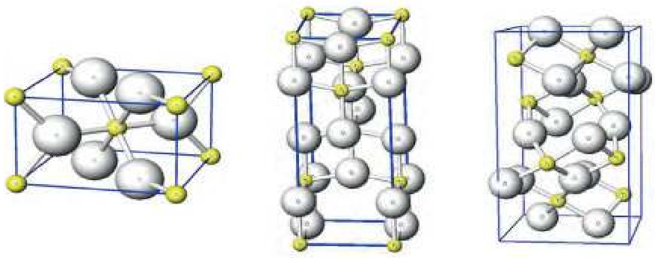

Fig. 1. The structures of the elementary cells of crystalline forms of titanium dioxide

Crystal structure of titanium oxide depends on the arrangement of octahedrons and the way in which individual units TiO6 are connected. For rutile, neighboring octahedra share with each other one corner and arranged along the long axis with mutual twisting equal to 90º. In the case of the form of anatase, the next octahedra shared a common edge and in brookite point of attachment are the both corner and edge [1-3]. The research works most concern anatase and rutile. Rutile is built of parallel chains of octahedrons, a little deformed, but each of them is connected to the ten neighboring the same units. Octahedrons in the anatase have a warpage of the prism, and each octahedron is connected to eight other. In the anatase, Ti-Ti distance is longer, and Ti-O shorter than it is in the rutile form.

Titanium dioxide is a non-toxic semiconductor with a wide band gap, which is commonly used as a white pigment in toothpaste, paints, paper, etc. The material has unique properties because of its excellent chemical stability. It can be used as a photocatalyst in the splitting of water induced by UV radiation. The holes potential in the valence band is low enough to oxidize most of the organic compounds, which is causing a wide range of applications of titanium dioxide on the self-cleaning surfaces. In comparison to other semiconductors with similar energy bandgap energy is not subject to photodegradation under the influence of the excitation [4-8].

The advantages of titanium dioxide thin films is a large value of refractive index (over 2.3) and very good transparency (over 90%) over a wide spectral range (from about 320 to about 6000 nm). In addition to good optical properties of TiO_2 it has also many other desirable properties such as high mechanical resistance, and long term stability. Therefore, the titanium oxide thin films are widely used as anti-reflective coatings in optics and photovoltaics [9-12].

In the dye-sensitized solar cells (DSSC) anatase titanium dioxide form is most often used. To increase the active surface of the light absorption, a semiconductive oxide layer has the nanocrystalline structure. If the surface is smooth and is covered with a monolayer of dye, absorbed of incident monochromatic light is less than 1%. For the use in a DSSC, titanium dioxide must have an n-type conductivity, order to conduction electrons transferred from the sensitizer [5]. This oxide is considered as the best material to cover the DSSC electrode due to the width energy bandgap and the position of the edge of the conduction band sufficiently low in relation to

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the redox potential of organic substances in aqueous solution. Therefore, it is possible to use dyes that absorb light in the visible range. The surface development and the size of the pores present in the layer are two parameters that must be selected so that the guaranteed performance is maximized light absorption and freely filling the pores by the electrolyte [4]. The purpose of titanium oxide in the dye-sensitized solar cell is a transfer electron to the external circuit. The way of transition of an electron in the DSSC is shown in Fig. 2.

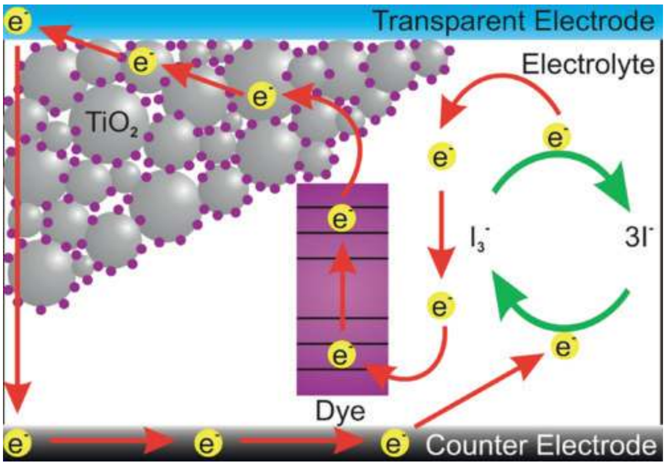


Fig. 2. The transition of an electron in the dye-sensitized solar cell

The large surface development of the TiO_2 allows absorb a greater amount of dye and increased absorption of light, i.e. improved efficiency. To increase the surface absorption of photons, this layer is porous and nanocrystalline. Titanium dioxide is a poor conductor of electricity but combined with organic dye molecules increases its conductivity.

2. Materials and methodology

The purpose of the experiment was the preparation of the nanocrystalline titanium dioxide powder by using a sol-gel method and research confirmation of its morphology and structure. For comparison purposes, a commercially available titanium dioxide powder (i.e. titanium white) was also used. Nanopowder was synthesized by using titanium tetra isopropoxide (TTIP) as a precursor. First has prepared a solution consisting of tetra isopropoxide and isopropanol by mixing using a magnetic stirrer. At the same time, the acidic solution of distilled water was prepared, which is a catalyst for the precipitation of the powder. By varying the amount of nitric acid, the pH of the solution was changed. These solutions were mixed with a magnetic stirrer at temp. 60÷70°C for 20 hours. To evaporate the rest of water, the calcination process was carried out, by heating the chemical compound below its melting point. Then, the titanium dioxide thin films from as prepared nanopowder and commercial powder were deposited on an ITO glass substrate by using a doctor blade technique.

The high-resolution transmission electron microscope S/TEM Titan 80-300 FEI company was used to confirm that the as-prepared powder is nanocrystalline. Observations were carried out with energy 300 kV in the classical model (TEM) and in the beam surface-scanning mode (STEM). For this purpose, prepared powder was deposited on the special copper mesh preparations used in electron microscopy. The structure of titanium oxide was investigated by X-ray crystallography. A variety of crystalline TiO_2 was also confirmed by using the Raman spectrometer. The TiO_2 thin films have been examined by using an Evolution 220 UV-VIS spectrometer Thermo Scientific company. The study of surface morphology of commercial TiO_2 powder was performed by using a scanning electron microscope Zeiss Supra 35. The accelerating voltage was 1 kV. To obtain images of the surface topography, the detection of secondary electrons (by the detector In Lens) was used.

3. Results and discussion

Studies of the surface morphology of as-prepared titanium oxide nanopowder were performed by using S/TEM. The HRTEM image documents the polycrystalline structure of TiO_2 (Fig. 3). The diameter of the nanoparticles of own prepared powder does not exceed a few nanometers. In the study, the STEM imaging mode also was used. Titan 80-300 microscope is equipped with a three coaxial detectors dedicated to STEM mode: bright field – BF, annular dark-field – ADF and High-angle annular dark-field – HAADF. Images, complementary with the HRTEM mode are shown in Figures 4a and 4b.

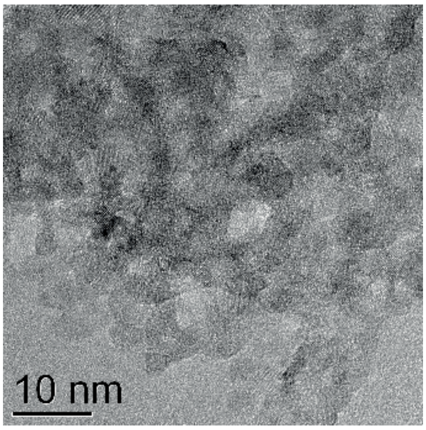


Fig. 3. HRTEM image of the produced titanium dioxide nanopowder

a) b)

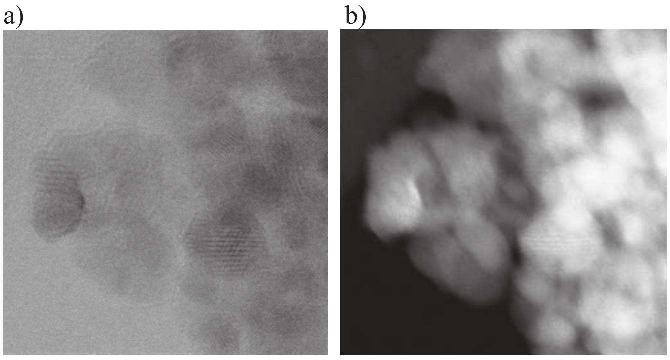


Fig. 4. Image of the produced titanium dioxide nanopowder: a) BF_DF; b) HAADF

Using an energy dispersion spectrometer (EDS), the reflection characteristic for the copper and carbon (from the substrate), and the titanium and oxygen (from the sample) was documented (Fig. 5).

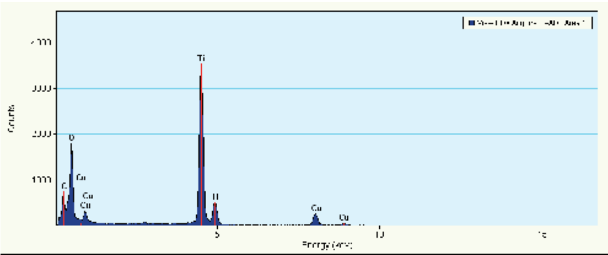
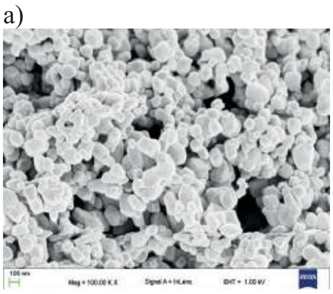


Fig. 5. EDS spectrum of TiO_2 nanopowder

Studies of the surface morphology of titanium oxide commercially micro powder was performed by using scanning electron micrographs and shown in Figures 6a and 6b. It can be observed visible layer composed of the microparticles. Only at a magnification, more than 250 kx the diameter of the microparticles can be analyzed. Using the Image J program was determined that the diameter of the purchased a commercial TiO_2 powder particles is in the range from 90 to 400 nm comparison with the own prepared powder nanoparticles does not exceed a few nanometers.

a)



b)

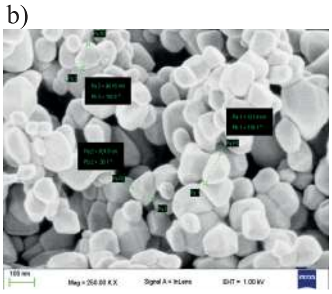


Fig. 6. SEM image of TiO_2 micro powder registered at a magnification: a) 100 kx, b) 250 kx

To confirm that the tested micro powder is a titanium oxide also was made a qualitative study of the chemical composition by using energy dispersive spectrometer and was shown as graphs in Figure 7. The spectra were registered the reflections characteristic for the titanium and oxygen from the sample.

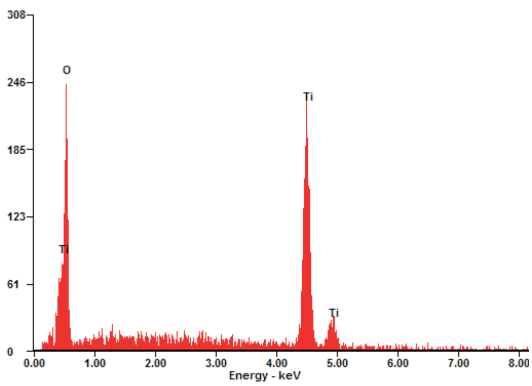
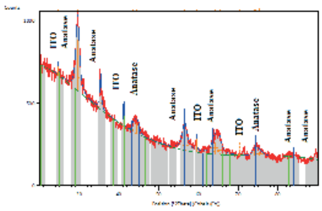


Fig. 7. EDS spectrum of TiO_2 micropowder

The entire structural studies were complemented by using X-ray researches (Fig. 8a and 8b). Registered diffraction pattern of titanium oxide nanopowder (Figure 7a) shows the reflection characteristic for the indium tin oxide ITO (coming from the conductive layer located on the glass substrate) and the reflection characteristic for the titanium oxide - a variety of anatase (coming from the sample). Registered reflections derived from anatase have characteristic wide shape that indicates fine crystalline structure. On the other hand, the diffraction pattern registered for the titanium oxide micro powder (Figure 8b) shows the reflections from the only anatase. Reflections are sharp and with a slim shape characteristic for the microcrystalline structure.

a)



b)

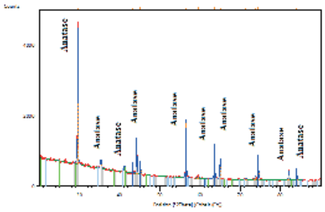


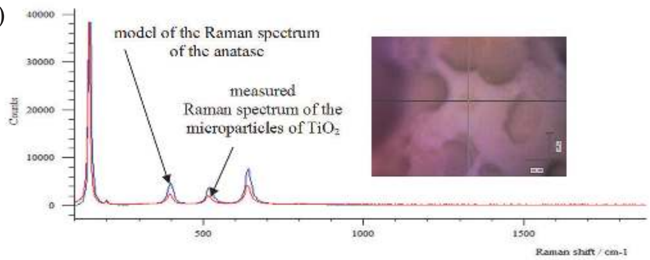
Fig. 8. The diffraction pattern produced titanium oxide nanopowder (a) and micro powder (b)

Further testing of structural of deposited layers is made by using an inVia Reflex Raman spectrometer equipped with an Ar ion laser with a 514,5 nm length. Spectral range is 150 – 3200 cm-1. Raman spectra of samples for nano and micro powder were registered (Fig. 9a and 9b). Using confocal microscope images, the data point on the sample was presented. The results were processed by using the WiRE 3.1 program determining the structure of the deposited layers as anatase, a variant of titanium oxide that confirms earlier research done by using the X-ray crystallography.

Prepared by doctor blade layers were tested for absorbance. Samples were determined as follows:

- A – Layer obtained from a powder prepared using neutralized distilled water;
- B – Layer obtained from a powder prepared using distilled water with a pH equal to 3;
- C – Layer obtained from a powder prepared using distilled water with a pH equal to 2;
- D – Layer obtained from commercial TiO_2 micro powder.

a)



b)

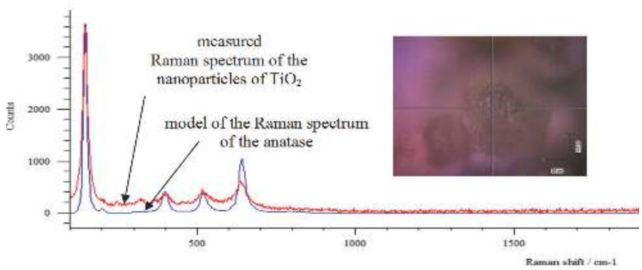


Fig. 9. Raman spectrum of titanium oxide micro powder (a) and nanopowder (b)

From the graph in Fig. 10 it can be concluded that the highest absorbance characterized the A sample. An absorption of 1.541 for a wavelength of 228 nm was achieved. Samples B and C has almost the same absorption capacity equal to about 1.401 for a wavelength of 226 nm. The lowest absorption has a sample D equal to 1.223 at a wavelength of the incident wave equal to 310 nm. It can, therefore, be concluded that the grain size affects in a significant way the absorption capacity. The value of absorbance of titanium dioxide was increased by reducing the grain size. This will have a significant impact on the ability to a generation of electric charge during electrochemical processes taking place in the dye-sensitized solar cells.

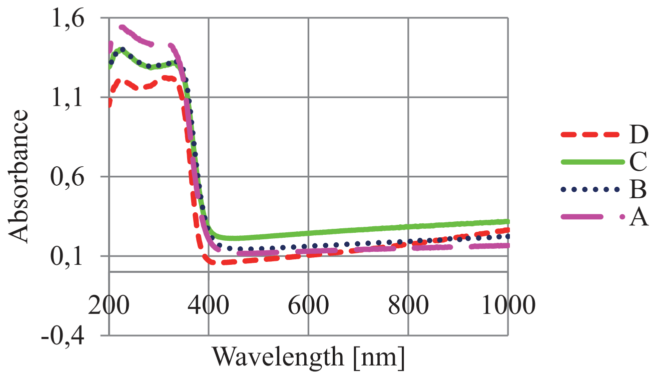


Fig. 10. A graph of absorbance of the titanium oxide depending on the length of the incident wave

In Figure 11 is a graph of the absorption of nano-structured titanium oxide layer that is coated with an N3dye. It can be seen that the dye extends the absorption of titanium oxide with a wavelength of 400-700 nm.

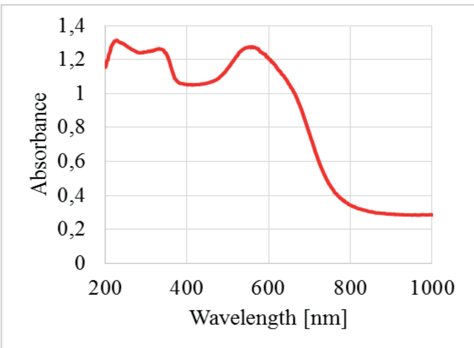


Fig. 11. A graph of absorbance of the titanium oxide covered with N3 dye depending on the length of the incident wave

4. Conclusions

By the sol-gel method, the nanocrystalline powder of titanium oxide was prepared that was confirmed by the research on the transmission electron microscope. Produced nanopowder has anatase structure that was confirmed by X-ray and Raman research. Anatase is the most desirable form of a crystalline structure of titanium oxide from the point of view of its use in dye-sensitized solar cells. The particle diameter of the prepared powder does not exceed a few nanometers and purchased a commercial TiO2 powder particles is in the range from 90 to 400 nm. By this study, it can be concluded that the grain size substantially affects on the ability of absorption. By reducing the grain size, increasing the value of absorbance of titanium dioxide. This will have a significant impact on the ability to a generation of electric charge during electrochemical processes taking place in the dye-sensitized solar cells.

Acknowledgment

The works have been implemented within the framework of the project entitled "Interaction between the nanostructural coatings with carbon nanoelements and substrate of the integrated dye-sensitized photovoltaic cells", funded by the Polish National Science Centre in the framework of the "OPUS" competitions. The project was financed by the National Science Centre granted by the decision number DEC-2013/09/B/ST8/02943. This publication was financed by the Ministry of Science and Higher Education of Poland as the statutory financial grant of the Faculty of Mechanical Engineering SUT.

REFERENCES

[1] J. Domaradzki, A. Borkowska, D. Kaczmarek, E.L. Prociow, Opt. Appl. **35** (3), 425-430 (2005).
[2] A. Borkowska, J. Domaradzki, D. Kaczmarek, Opt. Appl. **37** (1-2), 117-122 (2007).
[3] M. Mazur, D. Wojcieszak, J. Domaradzki, D. Kaczmarek, S. Song, F. Placido, Opto-Electron. Rev. **21** (2), 233-238 (2013).
[4] E. Krysiak, A. Wypych-Puszkarz, K. Krysiak, G. Nowaczyk, M. Makrocka-Rydzyk, S. Jurga, J. Ulanski, Synth. Met. **209**, 150-157 (2015).
[5] A. McEvoy, T. Markvart, L. Castaner, Practical Handbook of Photovoltaics. Fundamentals and Applications, 2012 Academic Press, Waltham.
[6] D.B. Warheit, E.M. Donner, Food and Chemical Toxicology **85**, 138-147 (2015).
[7] Y. Ma, X. Wang, Y. Jia, X. Chen, H. Han, C. Li, Chem. Rev. **114**, (19), 9987-10043 (2014).
[8] Z. Li, B. Hou, Y. Xu, D. Wu, Y. Sun, J. Colloid Interf. Sci. **288**, 149-154 (2005).
[9] S. Mahshid, M. Asakari, M.S. Ghamsari, J. Mater. Process. Tech. **189**, 296-300 (2007).
[10] H.D. Jang., S.-K. Kim, Mater. Res. Bull. **36**, 627-637 (2001).
[11] K.D. Kim, H.T. Kim, Powder Technol. **119**, 164-172 (2001).
[12] M. Stoller, L. Miranda, A. Chianese, Chem. Eng. Trans. **17**, 993-998 (2009).