



A CASE STUDY ON

DEPOSITION OF TIO₂ NANOPARTICLES ON OPTOELECTRONIC MATERIALS FOR ACHIEVING DYE-SENSITIZED SOLAR CELLS

by

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BACKGROUND

The study of nanoparticles comprises many fields. It is well known that having respective sizes, nanoparticles have special properties. One of the areas where nanoparticles entered is production of electricity. This is a very important resource for humans. Many methods of electricity generation have big disadvantages:

- pollutes the air with harmful gases and greenhouse gases (e.g. electric power plants);
- can be a source of radioactive pollution (e.g. nuclear power plants);
- have high costs (e.g. traditional photovoltaic cells based on silicon).

A prospective method of obtaining electrical energy is to use organic dye sensitized solar cells (DSSC) (Fig. 1.).

Dye sensitized solar cells (DSSC) does not pollute the environment and have the much lower cost compared to conventional solar cells.







Fig. 1. Dye-sensitized solar cell structure

How help the nanoparticles to production of electricity?

The main components of a dye-sensitized solar cell, as well as to all other solar cells, are the ptype and n-type. In thereof case, the p-type element is a dye, which interacts with the electromagnetic radiation, and the n-type element is formed from TiO_2 particles. The electron transition occurs at the interface n-p, therefore it is important that between these two elements to be a larger contact area. If the n-type element is made TiO_2 nanoparticles, the area of contact between the element n and p increases.

One of the stages of production of DSSC is deposition of TiO_2 nanoparticles on the optoelectronic material (this has the role of the electrode). Method of submission is very important to achieve good adhesion of the nanoparticles to the electrode.

The theme of this research case study is studied by not only teachers and researchers, but also by PhD students. Through this activity, they should observe what deposition method of TiO₂ nanoparticles is better and what factors influence the nanoparticles deposition on the electrode.

In this experimental work, PhD students will apply the following techniques to deposit TiO_2 nanoparticles:





- Liquid phase deposition (LPD);
- Hydrothermal method.

Through this activity, PhD students will approach in the NANO area the following concepts:

- Methods of obtaining dye-sensitized solar cells;
- Related knowledge to TiO₂ nanoparticles;
- Knowledge about the influence of nanoparticles in improving of the photoelectric effect;
- Additional materials related to nanoparticles;
- Methods of obtaining TiO₂ nanoparticles;
- Knowledge about the used dyes in DSSC and mode of their interaction with TiO_2 nanoparticles.

PURPOSE OF THE STUDY

The main reason for this activity is to attract more PhD students to study NANO area. PhD students must realize several laboratory experiments with nanoparticles. In experiment participate only PhD students in engineering sciences, because for experiments is needed knowledge of physics, chemistry.

1. Obtaining of TiO₂ nanoclusters by liquid phase deposition (LPD)

Liquid phase deposition (LPD) is a very good method for preparing thin films of oxide in aqueous solution under normal conditions. Deposition of ceramic layers on polymers is a technological change due to polymer sensitivity to various factors (thermal, chemical). In recent years, greatly increase interest to this technique, due to working conditions at low temperatures. Most often, this technique was used to deposit SiO₂, but it had deposited and other materials such as TiO₂. Nagayama has investigated liquid phase deposition process, which was discovered in recent years, for the first time in 1988. Herbing has used LPD to brew TiO₂ thin films also for study their work photovoltaic. This technique is better compared to sputtering, because it does not require vacuum





and can work with different surface geometry. These characteristics of LPD make this method ideal for producing thin films.

To deposit the titanium oxide by LPD may be used three methods:

- a. LPD with TiF₄: The procedure consists in immersing a sample (vertical position) in a solution of H_3BO_3 0.3 M and $(NH_4)_2TiF_6$ 0.1 M at room temperature. The sample should be left in solution from 4 to 48 hours, and then washed with water and dried using a drying procedure.
- b. LPD with TiF₄ by addition of HCI: As with the first method, the sample is immersed vertically in a solution of H_3BO_3 0.15 M and $(NH_4)_2TiF_6$ 0.05 M (can be made deposition on any type of polymer). Hydrochloric acid (HCI) is added to adjust the pH to 2.88. The solution should be heated to 50 ° C and hold the sample in the solution 2 to 22 hours after which is taken out and washed with water. After this step, the sample is heated.
- c. LPD with [CH3CH(O)-CO₂NH₄]₂-Ti(OH)₂: The procedure is similar to the other methods, except that the solution is based on [CH₃CH(O)-CO₂NH₄]₂-Ti(OH)₂. pH was maintained at 1.76 and the temperature at 70 ° C.

In order to increase the TiO_2 nanoclusters on ITO glass, the easiest LPD-based method is considered by using the precursors H_2TiF_6 and H_3BO_3 (Fig. 17). Reaction steps to obtain TiO_2 nanoclusters are shown below. In reaction 1, H_3BO_3 is responsible for formation of $Ti(OH)_6^{2+}$ that is converted to TiO2 by heat treatment.

$$(TiF_{6})^{2-} + nH_{2}O \leftrightarrow TiF_{6-n}(OH)_{n}^{2-} + nHF$$
(1)

$$H_3BO_3 + 4HF \leftrightarrow BF^{4+} + H_3O + 2H_2O$$
 (2)

Here it is studied the influence of deposition variables including time of filing and post-heat treatment on TiO_2 layer microstructure and layer photovoltaics properties. The LPD system of TiO_2 layer deposition is shown schematically in Fig. 2.



Fig. 2. Immersion of ITO glass plates in solution of $(NH_4)_2 TiF_6 + H_3BO_3$ to obtain TiO₂ deposition

Differences of I-V characteristics of DSSC assembled using TiO₂ films deposited in different period of time, with surface and cross section morphology appropriate films were observed. Regardless of the procedure, on the sample surface are formed TiO₂ nanoclusters. It was also seen that the IV characteristics are sensitive to the time of TiO₂ film deposition, but respond nonlinear to deposition time. Analysis of surface morphology of different samples on which has been performed a LPD deposition with different time duration, has showed that keeping of sample too long in the solution leads to formation of cracks on the film surface. Thus, the sample surface will not have characteristics of nanoclusters, but will have cracks. Due to the occurrence of these defects are affected V_{oc} (open circuit potential) and short circuit current intensity (I_{sc}). Section morphology examination of TiO₂ films according to the time of deposition shows that film thickness does not respond linearly to the deposition time. There is a gradual loss of reactivity of the liquid electrolyte. Therefore, it is not practical to increase the film thickness by extending the time of deposition.

After that TiO_2 deposition occurs on the TCO material by LPD, drying procedure should be performed. It was observed that the drying temperature is very important. With XRD patterns of TiO_2 films passed through heat treatment at different temperatures are observed effects of different





materials. Heat treatment provides heat as a driving force to move the activation energy required for nucleation and crystal growth. The best state (phase) of TiO_2 for DSSC is anatase.

The problem is that the formation of anatase occurs at a temperature of 400 °C (observed from XRD patterns). It would not hurt a heat treatment at 600 °C, however the practice shows that shift to this temperature leads to ITO glass distortion.

Moreover, excessive increase of treatment temperature leads to decrease of IV characteristics of DSSC cells (Fig. 20). On TiO_2 film surface are formed a large number of small nanocracks with increasing of treatment temperature. It is observed that the IV characteristics are sensitive to treatment temperature of TiO_2 films and I_{SC} increase maximally if the heat treatment was performed at 600 °C. Apparently, the increase of I_{SC} may be associated with reformation of TiO2 film morphology and increasing of film crystallinity. By formation of numerous small nanocracks, TiO_2 film has a higher specific surface area after heat treatment and achieves high efficiency in dye adsorption. However, the negative effect of heat treatment is a significant increase in electrical resistance of ITO material, causing a significant decrease in V_{OC} .

In any case, the overall photovoltaic efficiency depending on the temperature of treatment is encouraging result of this study using PLD for obtain TiO_2 films and for anodes preparation for DSSC.

LPD was used to obtain TiO₂ layers on ITO glass at room temperature, followed by post-heat treatment of anode for DSSC. These results are very closely related to the change in microstructure including both specific area and crystalline structure. This demonstrative work confirms that LPD method is capable to producing TiO₂ nanoclusters with crystalline anatase structure by suitable heat treatment. Unfortunately, unacceptable film increase by LPD has led to other problems in obtaining of TiO₂ nanostructured layer.

2. TiO₂ nanowires grown by hydrothermal method

Hydrothermal method is a very good technology for achieving semiconductor nanowires at low temperatures. An important feature of this method is that by exposing the material to the particular requirements can be formed nanoscopic morphology that cannot be formed by





conventional reactions. Nanoscopic morphology can be controlled by varying different parameters of the reaction (pH, temperature, surfactant, organometallic or coordinative compounds).

Hydrothermal under pressure method can produce 1D nanomaterials without using catalysts. Because 1D nanomaterials (such as nanowires) have a relatively high rate of transfer of electric charge and a specific surface area comparable with spherical particles of TiO₂ and TiO₂ nanoclusters, simple operation, rapid formation and low cost make this method very interesting process to be used to produce TiO₂ nanowires. The idea is that by increasing TiO₂ nanowires by hydrothermal method (HR) on TiO₂ layer deposited by arc ion coating - AIP (as matrix during hydrothermal method and a barrier layer while working as predeposition on ITO glass), the film obtained should be able to provide the desired properties of anode. AIP is able to produce with a very high growth rate high-density films with high adhesion to the substrate without additional heating. The test results have shown that TiO₂ randomly oriented nanowires have been formed on the AIP-TiO₂ matrix. By TiO₂ powder content in hydrothermal bath (g/l) and the temperature of post-treatment were evaluated microstructure and photovoltaic efficiency of assembled DSSC devices. Hydrothermal system and method of preparation of TiO₂ nanowires are shown in Fig. 3.



NaOH 10 M solution at 110 °C

Fig. 3. Hydrothermal system and method of TiO₂ nanowires preparation on ITO





It was observed that the IV characteristics of DSSC assembled using the hydrothermal technique on deposited anode with different content of TiO_2 powder with their corresponding surface morphology and film section as shown in the figure. Dense lower layer of columnar AIP-TiO₂ can partly be seen through to the section of each specimen. Hydrothermal method is a good method for TiO_2 nanowires deposition on ITO surface. TiO_2 concentration is very important in the chemical bath. With increasing of TiO_2 content in the bath (eg, 75 g/l) obtained nanowires are very long and form powdered clumps. This reduces the surface area and dye will adsorb lesser on the surface of TiO_2 , this will decrease the photovoltaic efficiency (also observed a decrease of I_{SC}). The best efficiency (3.63%) was observed in the case of using a solution of TiO_2 50 g/l.

Because obtained by hydrothermal method TiO_2 nanowires are amorphous, ISC of DSSC were lower. Arc ion coating provides a level of TiO_2 crystallinity on lower layer facilitating diffraction peaks shown in the XRD patterns, although TiO_2 nanowires obtained by hydrothermal method covers everything. By knowing this, samples of TiO_2 nanowires obtained by hydrothermal method on matrix shown in the XRD patterns show a gradual increase in peak intensity with increasing temperature treatment. Apparently, this is due to the crystallinity of TiO_2 nanowires obtained by hydrothermal method by heat treatment. This helps to increase the I_{SC} of DSSC.

Crystallized after heat treatment, TiO_2 nanowires, obtained by hydrothermal method provide a larger area for dye adsorption and thus increase the I_{SC} of DSSC. The side effect of the TiO2 nanowires heat treatment is low V_{OC} of DSSC. This can be attributed to the change in the amount of TiO_2 obtained by hydrothermal method which produces open channels for I_2 + Lil liquid electrolyte to create direct contact with the layer of TiO_2 produced by arc ion plating. In this study was obtained photovoltaic efficiency of 3.63%. By using this method, curing temperature should be chosen very carefully in order not to affect the I_{SC} and V_{OC} of DSSC.

In this study, hydrothermal method has shown the possibility of obtaining randomly oriented TiO_2 nanowires on TiO_2 matrix obtained by arc ion plating.





ACTIVITY OBJECTIVES

Following this activity, the PhD students will get several important capabilities:

- To work in groups;
- To interpret the obtained data;
- To improve their working mode;
- To implement new methods of working;
- Study the impact of various factors on the working method;
- To achieve good and real results;
- To learn new working methods;
- To learn to work with various tools of analysis;
- To make analysis of the surface of the materials;
- To interpret the SEM analysis, XRD (X-ray diffraction).

In the NANO area, PhD students will learn more about:

- Importance of nanoparticles in DSSC;
- How to obtain TiO₂ nanoparticles;
- Electronic transitions at the interface of TiO₂ nanoparticles and dye;
- The advantages of using TiO₂ nanoparticles compared with the use of particles of different sizes;
- The dyes with best photoelectric properties;
- Electrolytes used for obtaining DSSC;
- The electrodes used for deposition of TiO₂ nanoparticles;
- Using of other nanoparticles types in DSSC.

This activity was performed for PhD students in Engineering Sciences (Year I and II) to integrate their research topics with the NANO area or to improve research activities to get closer to the NANO.





LEARNING RESULTS

After retrieving the information and after the practical activities, PhD students are able:

- to make a report with the obtained results;
- to put into practice the knowledge about nanoparticles;
- to identify how nanoparticle size influences the efficiency of DSSC;
- to examine the advantages and disadvantages of this technology based on nanoparticles;
- to develop individual knowledge about NANO;
- to produce and publish scientific papers in ISI journals and present at national and international conferences;
- to improve deposition techniques TiO2 nanoparticles on optoelectronic materials.

Group management & sequence of events

 TiO_2 nanoparticles are of high importance regarding their use as n-type element in dye sensitized solar cells (DSSC). Now, it is manifested an increased interest for technologies related to this type of photovoltaic cells. Therefore, the study of the properties and their deposition techniques require improvements.

Before starting the practical work, PhD students have studied the theoretical aspects related to methods of TiO_2 nanoparticles deposition. Also, they have received materials (scientific articles and books related to the deposition techniques).

To expand the horizon of knowledge in NANO, PhD students have started to consult materials of *NTSE Virtual Lab Project* (<u>http://vlab.ntse-nanotech.eu/NanoVirtualLab/</u>) - especially dedicated to nanoparticles (see the video-clip "*Iron Nanoparticles*" from *Experiments Room*), and *NTSE Repository* (<u>http://ntse.ssai.valahia.ro/</u>), starting with the consultation of the article: "*The current state of public understanding of nanotechnology*", authors: Anna M. Waldron, Douglas Spencer and Carl A. Batt uploaded in the NTSE Repository, at URI: <u>http://ntse.ssai.valahia.ro/id/eprint/20</u>, and of book specific paragraphs: Kenneth Kuno - "*Introduction to Nanoscience and Nanotechnology: A Workbook*", uploaded in the NTSE Repository, at URI: <u>http://ntse.ssai.valahia.ro/id/eprint/35</u>.





After the documentation stage, with the view to facilitate the assimilation of the *Nano* knowledge related to the studied *Nano* theme (*Deposition of TiO*₂ *nanoparticles on optoelectronic materials*), the work has been divided into several sections:

Section	Location	Activity
Section 1	Chemistry Lab	The instructor does an introduction in the field of dye-sensitized
	(60 – 90 min)	solar cells (DSSC) and explains the importance of ${\rm TiO_2}$
		nanoparticles in them. PhD students are divided into groups (2
		groups of 4 people) and receive work instructions for realization
		of experiments.
Section 2	Outside Lab	Consultation of materials and study of nanoparticle ${\rm TiO_2}$
		deposition methods
Section 3	Chemistry Lab	The first group of PhD students begins the TiO_2 nanoparticles
	(60 – 120 min)	deposition by liquid phase deposition (LPD) (48 h).
		In parallel, the second group begins experiment of $\mathrm{TiO}_{\mathrm{2}}$
		nanowires deposition by hydrothermal method (24 h).
Section 4	Outside Lab	Individual study related to deposit methods.
Section 5	Chemistry Lab	Meeting with the second group after 24 h and finalization of ${\rm TiO_2}$
	(45 – 60 min)	nanowires deposition experiment by hydrothermal method and
		removing of FTO plates from chemical bath.
Section 6	Chemistry Lab	Meeting with the first group after 48 h and finalization of TiO_{2}
	(45 – 60 min)	nanoparticles submission experiment by liquid phase deposition (LPD).
Section 7	Outside Lab	PhD students study observed phenomena in experimental work
		and seek additional material.
Section 8	Chemistry Lab	The first group of PhD students begins the experiment of $\mathrm{TiO}_{\mathrm{2}}$
	(60 – 120 min)	nanowires deposition by hydrothermal method (24 h).
		In parallel, the second group starts the deposition of TiO_{2}
		nanoparticles by liquid phase deposition (LPD) (48 h).





Section 9	Chemistry Lab	Meeting with the first group after 24 h and finalization of
	(45 – 60 min)	experiment of TiO ₂ nanowires deposition by hydrothermal
		method and removing of FTO plates from chemical bath.
Section 10	Chemistry Lab	Meeting with the second group after 48 h and finalization of TiO_2
	(45 – 60 min)	nanoparticles deposition experiment by liquid phase deposition
		(LPD).
Section 11	Chemistry Lab	Evaluation and comparison of results. Presentation of research
	(45 – 60 min)	reports.

Additional references are recommended to PhD students (obs.: the full articles can be downloaded from scientific databases, if the university / research institution has been granted with access / permission):

1. Stathatos, E., Lianos, P., Del Monte, F., Levy, D., & Tsiourvas, D. (1997). Formation of TiO2 nanoparticles in reverse micelles and their deposition as thin films on glass substrates. Langmuir, 13(16), 4295-4300.

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3. Jiang, G., Lin, Z., Chen, C., Zhu, L., Chang, Q., Wang, N., ... & Tang, H. (2011). TiO< sub> 2</sub> nanoparticles assembled on graphene oxide nanosheets with high photocatalytic activity for removal of pollutants. Carbon, 49(8), 2693-2701.

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5. Chae, S. Y., Park, M. K., Lee, S. K., Kim, T. Y., Kim, S. K., & Lee, W. I. (2003). Preparation of sizecontrolled TiO2 nanoparticles and derivation of optically transparent photocatalytic films. Chemistry of materials, 15(17), 3326-3331.





6. Reyes-Coronado, D., Rodriguez-Gattorno, G., Espinosa-Pesqueira, M. E., Cab, C., De Coss, R., & Oskam, G. (2008). Phase-pure TiO2 nanoparticles: anatase, brookite and rutile. Nanotechnology, 19(14).

7. Wu, M., Long, J., Huang, A., Luo, Y., Feng, S., & Xu, R. (1999). Microemulsion-mediated hydrothermal synthesis and characterization of nanosize rutile and anatase particles. Langmuir, 15(26), 8822-8825.

8. Koumoto, K., Seo, S., Sugiyama, T., Seo, W. S., & Dressick, W. J. (1999). Micropatterning of titanium dioxide on self-assembled monolayers using a liquid-phase deposition process. Chemistry of materials, 11(9), 2305-2309.

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10. Tsukuma, K., Akiyama, T., & Imai, H. (1997). Liquid phase deposition film of tin oxide. Journal of non-crystalline solids, 210(1), 48-54.

RESOURCES

Procedural resources:

Methods and processes: research-based methods - experimenting, observing, data processing, analyzing, discussing, reporting;

Form of organization: teams/groups, individual.

Material resources / spaces: Electrochemistry Laboratory (instruments, reagents, utilities), PC, Internet access, video-projector, flipchart.

PROCESS FINALIZATION

For finalization of study activity, PhD students must express their personal opinions related to this experimental work, answering to the following questions:





Quality of teaching:

- 1. Has the instructor presented clearly the study materials? (Yes / No)
- 2. Have you had enough study materials? (Yes / No)
- 3. Were there any doubts during the experimental study of the materials related to the activity? (Yes / No)
- 4. If you were in doubt, have you been looking for the help from the instructor or have you been provided with explanations? (Yes / No)

NANO activity:

- 5. Is the performed experimental work useful for the chosen research topic? (Yes / No)
- What is the degree of novelty for you of this experimental work? (Very high / High / Medium / Low / Very Low)
- 7. Hardness of tasks for completion of work (Very high / High / Medium / Low / Very Low)
- 8. Would you also like to participate in such activities? (Yes / No)
- 9. Is related your PhD research theme to the field of NANO? (Yes / No)
- 10. Have you changed your opinion about the importance of the NANO, after carrying out this activity? (Yes / No)
- 11. Will you also study in the near future, the area of NANO? (Yes / No)

Deposition method:

- 12. Do you consider useful the TiO₂ nanoparticles deposition methods in dye sensitized solar cells improvement? (Yes / No)
- 13. Which of the two methods of the TiO_2 nanoparticles deposition worked for you better? (Method of deposition of TiO_2 nanoparticles by liquid phase deposition (LPD) / TiO_2 nanowires deposition by hydrothermal method)
- 14. From the time point of view, which method is better? (Method of deposition of TiO_2 nanoparticles by liquid phase deposition (LPD) / TiO_2 nanowires deposition by hydrothermal method)





- 15. Which method is easier to be implemented? (Method of deposition of TiO_2 nanoparticles by liquid phase deposition (LPD) / TiO_2 nanowires deposition by hydrothermal method)
- 16. In your opinion, which method is more expensive?
- 17. Do you know other methods used for TiO_2 nanoparticles deposition? (Yes / No)

Method of deposition of TiO_2 nanoparticles by liquid phase deposition (LPD):

18. What factors do you think that are important in achieving a qualitative deposition of TiO₂ nanoparticles by this method? (Solution temperature / reagents purity / Time of deposition / concentration of H₃BO₃ / Atmospheric pressure / Concentration of (NH₄)₂TiF₆ / chemical bath material / temperature during heat treatment)

Method of submission of TiO₂ nanoparticles by hydrothermal method:

- 19. What factors do you think are more important in achieving a qualitative deposition of TiO₂ nanoparticles by this method? (Solution temperature during deposition / purity of reagents/ deposition time / Atmospheric pressure / Chemical bath material/ concentration of NaOH / TiO₂ concentration / temperature during heat treatment)
- Evaluation of the experimental activity:
 - 20. How useful is for your this experimental work? (Very useful / Useful / Not very useful / Not Useful)

IMPACT ON STUDENTS / RESEARCHERS

- Improvement of techniques for experimental work;
- Using theoretical concepts in solving practical problems;
- Better understanding and interpretation of the observed phenomena;
- Identification of the nanoparticles role in different areas.





STUDENTS' / RESEARCHERS' FEEDBACK

Expressed feedback:

- Advantages of teamwork;
- Possibility of implementation / improvement of experimental techniques;
- Methods of deposition (advantages / disadvantages) have been discussed;
- Opportunity to consult scientific articles related to nanotechnologies and nanomaterials;
- Possibility of learning of something new.

Processed feedback (graphical results):

PhD students have answered to few questions to evaluate the activity. Below are the graphical outputs of their feed-back:



1. Has the instructor presented clearly the study materials?





2. Have you had enough materials for study?



3. Were there any doubts during the experimental study of materials, in the related activity?







4. If there are doubts, have you been looking for help from the instructor or have you been provided with additional explanations?



5. Is the performed experimental work useful for the chosen research topic?









6. What is the degree of novelty for you of this experimental work?

7. Hardness of tasks for completion of work









8. Would you also like to participate in such activities?

9. Is your PhD research theme related to the field of NANO?







10. Have you changed your consideration about the importance of the NANO after carrying

out this activity?



11. Will you study in the near future NANO-topics?







12. Do you consider useful the TiO_2 nanoparticles deposition methods in dye sensitized solar cells improvement?



13. Which of the two methods of TiO₂ nanoparticles deposition worked for you better?







14. From the time point of view, which method do you consider that is better?



15. Which method is easier to be implemented?









16. In your opinion, which method is more expensive?









18. What factors do you think are more important in achieving a qualitative deposition of



TiO₂ nanoparticles by LPD?

19. What factors do you think are more important in achieving a qualitative deposition of TiO_2 nanoparticles by the hydrothermal method?









20. How useful is for your this experimental work?





PICTURE GALLERY











































