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**Nanostructured TiO<sub>2</sub>-based oxide layers sensitized with  
organic compounds having photoelectrocatalytic potential**

*- PhD thesis abstract -*

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***PhD thesis support:***

December 9, 2011, 12 a.m., room no. 97

Faculty of Chemistry and Chemical Engineering, Cluj-Napoca,

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## KEYWORDS:

TITANIUM DIOXIDE

PHOTOELECTROCATALYTIC ACTIVITY

DYES

DSSC SOLAR CELLS

## *Introduction*

Nanoscience field exploration led to the development of new materials with unique/special properties which can open opportunities of the most diverse range of application areas: bioscience (biophysics, biochemistry, bionics, computational biology), biomedicine (diagnosis techniques, drugs, prosthesis and implants), materials science (nanomaterials), electric engineering (nanoelectronics, nanodevices), mechanical engineering ((NEMS – *nano-electro-mechanical system*), interface and colloidal chemistry (nanodispersions, nanoemulsions, aerosols), chemical engineering (nanopolimers, nanowires/nanotubes Zn, Si, Ti oxides), environmental science (purification air/water materials) [1].

Nanostructured materials, with particle size less than 100 nm, possesses special characteristic properties, referring to structural (network symmetry, unit cell size), electronic (band gap, quantum size effect) or physical-chemical (crystalline structure, particles size, surface area, chemical reactivity/stability).

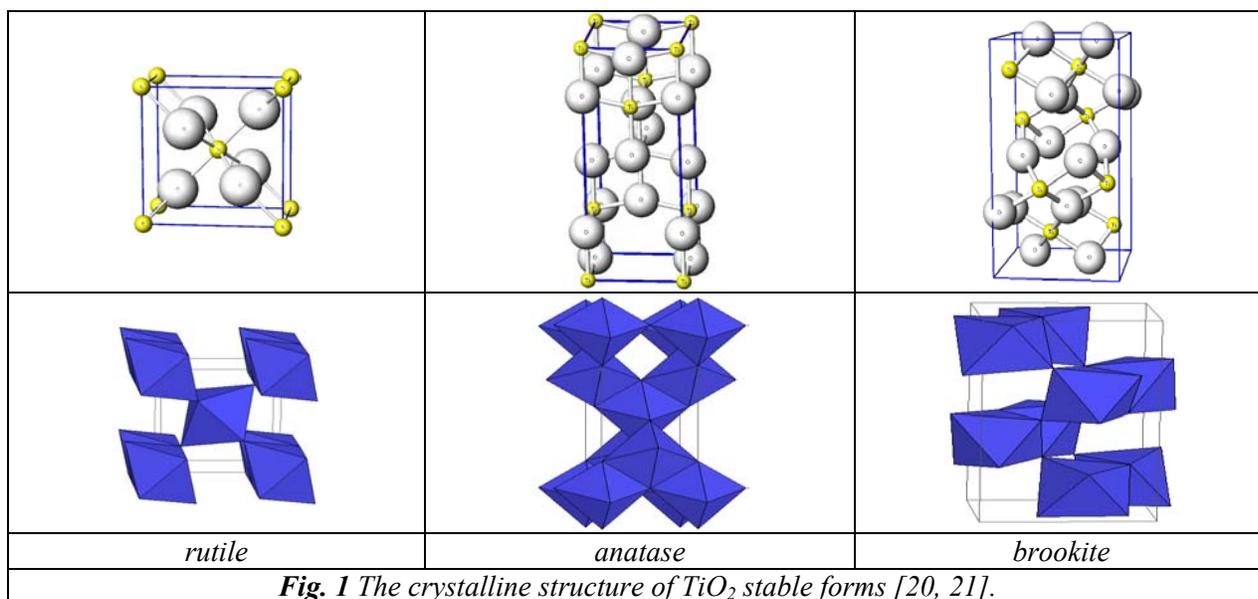
Metal oxides play an important role in many areas of chemistry, physics and materials science being used in the field of microelectronic circuits, sensors, piezoelectric devices, catalysts and others [2].

The bulk state of the oxides usually leads to a robust and stable system with well-defined crystalline structures [2]. In the case of nanostructured materials, with particle size reduction, a number of physical properties (mechanical, electrical, optical, etc.) are very different in comparison with those of macroscopic systems [2-4] thanks to a big ratio between number of the surface and volume atoms (which leads to a larger contact area), the decrease of surface free energy and appearance of so-called *quantum size effect* [2, 5, 6].

The interest on titanium dioxide, in the photoelectrochemical field, is due to its special properties:

- chemical: chemical stability [7, 8], corrosion/photocorrosion resistance, photocatalytic potential [9],
- electrical: high dielectric constant ( $\epsilon_r \approx 60-100$ ) [10-12], increased electrical conductivity [13],
- optical: sensitivity to UV field [1-16], favourable band gap [7, 8, 17], very high refractive index (2,6-2,9) [13, 14, 18];
- biological: non-toxicity, biocompatibility [13, 19];
- economical: availability at low cost, in the form of ilmenite ( $\text{FeTiO}_3$ ) or  $\text{TiO}_2$  rutile deposits in Norway, Finland, Canada, Russia, Australia, USA, India, South Africa [17-19].

$\text{TiO}_2$  is presented in three stable polymorphic states: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) (Figure 1) [20, 21].



TiO<sub>2</sub> is a *n*-type semiconductor due to oxygen vacancies, and its conductivity increases with the degree of oxygen loss in the lattice [18, 22-24].

TiO<sub>2</sub> has a wide band gap (3.2 eV - anatase, 3.00 eV - rutile and 3.13 eV - brookite) [25-27], which limits its absorption in the UV region of solar spectrum (~ 5% of the incoming solar energy on the earth's surface) [17, 28, 29].

In order to extend optical spectral response, quantum efficiency improvement and increasing photoactivity of titanium dioxide a number of methods have developed, such as coupling with narrow band gap semiconductors, doping metals/nonmetals or surface sensitization of TiO<sub>2</sub> nanoparticles with photosensitive organic compounds [9, 17, 18, 30, 31].

The coupling of TiO<sub>2</sub> with a narrow band gap semiconductor, with a level of energy more negative than band conduction (CB) of TiO<sub>2</sub>, so that the photogenerated electrons transition can take place from the CB of narrow band gap semiconductor in valence band (VB) of TiO<sub>2</sub>, induce positive effects (efficient charge separation, a diminution of recombination processes of them), translated by increasing the efficiency of titanium dioxide photoactivity [31, 32].

The embedment of metal or nonmetal ions in TiO<sub>2</sub> network creates intermediate allowed energy states located in the band gap of titanium dioxide which act as "traps" for electrons/holes leading to the extension of TiO<sub>2</sub> absorption in the visible field [32, 33].

Surface modification of semiconductor materials with dyes by sensitization processes involves: (i) adsorption of dyes molecules onto TiO<sub>2</sub> nanoparticles surface via physical or chemical interactions, (ii) under the influence of visible light the dye molecules go into an excited state thus generating electron-hole pairs and (iii) the photogenerated electrons are injected to the conduction band of the semiconductors causing an enhance photoactivity of semiconductor [34, 35, 36].

## *Aim of the thesis*

The documentation, studies, experiments and materials which are the subject of this thesis, focuses on oxide materials based on TiO<sub>2</sub> nanoparticles arranged in layers, in order to rise their photoactivity by coupling with narrow band gap semiconductors, doping with transition metals and sensitization with different organic compounds having photoelectrocatalytic potential, with the main goal of improving titanium dioxide efficiency in the solar cells devices.

## *Experimental details*

In all experiments, the materials used to prepare the TiO<sub>2</sub>-based layers were: TiO<sub>2</sub> commercial powder P25 Degussa, kindly supplied by Degussa AG (Germany), methylcellulose (Serva, Germany), acetyl acetone (Merck, Germany), polyethylene glycol (Macherey-Nagel, Germany) and Triton X-100 (Fluka, Switzerland).

The pastes obtained by mixing the mentioned additives were spread onto ITO glass substrates (sheet resistance  $\leq 20 \Omega/\text{square}$ , Praezision Glas & Optik, Germany) by spin-coating method. The samples were dried by lyophilization in order to develop porous materials with a higher surface area. In the next step the samples were heat-treated in air to remove the organic additives, to immobilize the semiconductor layer onto substrate, to establish the electrical contact between TiO<sub>2</sub> and conductive ITO glass, to determinate a better adherence on support, to improve the crystallinity of nanocomposite films and to induce higher degree of porosity and greater thickness [37, 38].

It was used different type of dyes for sensitizing TiO<sub>2</sub> layers only in the one concentration ( $2 \times 10^{-4} \text{M}$ ).

The TiO<sub>2</sub>-based layers were evaluated in terms of morphostructural and optoelectronic characteristics of obtained oxidic systems, and finally it has tested their photoactivity efficiency by assembling *DSSC* solar cells and recording their functional parameters.

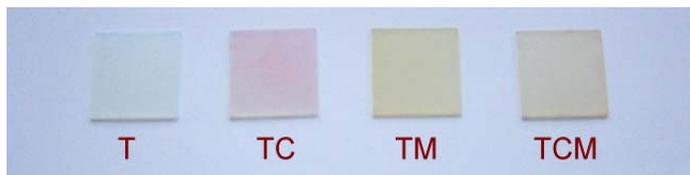
## IMPROVING PHOTOACTIVITY OF TiO<sub>2</sub>-BASED LAYERS SENSITIZED WITH CARMINE AND MORIN DYES

This chapter presents the preparation and characterization of sensitized TiO<sub>2</sub>-based layers with carmine and morin (Figure 2) in order to obtain new systems with photocatalytic potential.



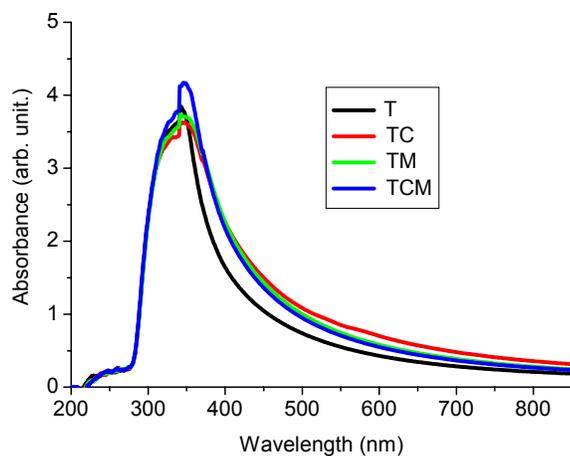
**Fig. 2** Structural formula of dyes: a) carmine [39], and b) morin [40].

The obtained TiO<sub>2</sub> layers (Figure 3) were named according to the dye used for sensitization, namely: TC - TiO<sub>2</sub> layer sensitized with carmine, TM - TiO<sub>2</sub> layer sensitized with morin, and TCM - TiO<sub>2</sub> layer sensitized with carmine/morin solution. The sample called T was used as a standard; in this case the TiO<sub>2</sub> layer was not sensitized.



**Fig. 3** The prepared TiO<sub>2</sub>-based layers.

UV-VIS spectra of sensitized TiO<sub>2</sub> layers (Figure 4) show a shift of absorption to the visible region; this effect is due to adsorption of dye molecules on the surface of oxide nanoparticles.



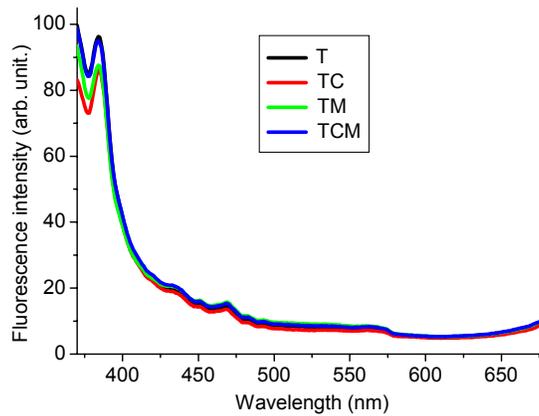
**Fig. 4** UV-VIS absorption spectra of TiO<sub>2</sub>-based layers.

The values of band gap energy are obtained by linear extrapolation from UV-VIS spectra and using the Tauc formula:  $(\alpha h\nu)^2 = A (h\nu - E_g)$ . In the case of sensitized layers,  $E_g$  decrease slightly compared with the known value  $E_{g, TiO_2} = 3.00-3.2$  eV, (Table 1).

**Table 1.** Band gap energy values for the investigated samples.

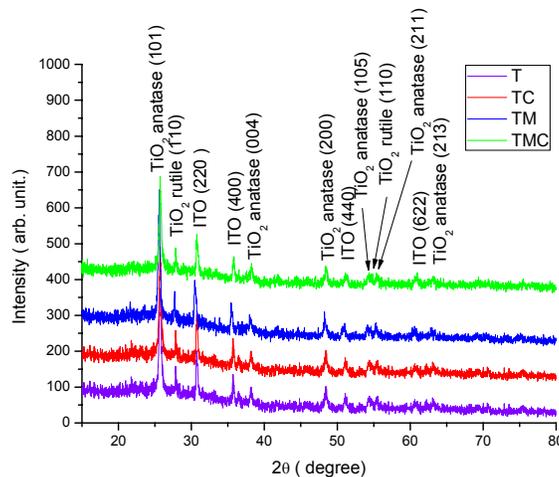
Sample's name	Sample's description	$E_g$ (eV)
<b>T</b>	TiO <sub>2</sub> layer nonsensitized (standard sample)	3.13
<b>TC</b>	TiO <sub>2</sub> layer sensitized with carmine	2.95
<b>TM</b>	TiO <sub>2</sub> layer sensitized with morin	2.98
<b>TCM</b>	TiO <sub>2</sub> layer sensitized with carmine/morin	3.05

The fluorescence emission spectra of TiO<sub>2</sub>-based layers do not show notable changes between the fluorescence emissions of the investigated layers (Figure 5).



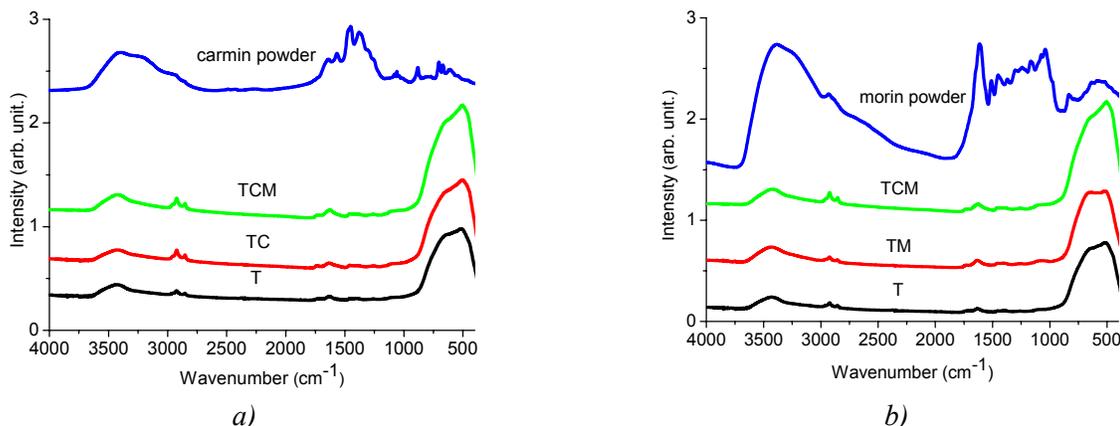
**Fig. 5** Fluorescence spectra of T, TC, TM and TCM samples.

The XRD patterns of TiO<sub>2</sub>-based samples show the presence of crystalline anatase and rutile phases in optimal proportion (84% anatase and 16% rutile) for a high photocatalytic activity (Figure 6).



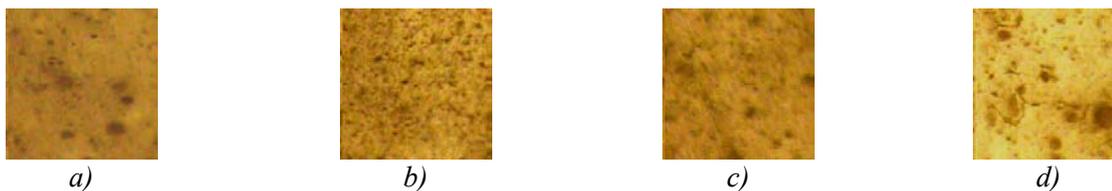
**Fig. 6** X-ray diffraction patterns of T, TC, TM and TCM samples.

IR absorption spectra of the sensitized layers, compared with the corresponding absorption spectra of dyes are shown in Figure 7, and prove the presence of dye molecules on TiO<sub>2</sub> obtained layers.



**Fig. 7** IR spectra of TiO<sub>2</sub> layers compared with: a) carmine, b) morin.

IR microscopy images obtained in transmission mode (Figure 8) show a relatively homogeneous surface (300x300 μm), uniform for all investigated samples; titanium dioxide appears opaque due to observation mode chosen for investigation.



**Fig. 8** Images obtained by IR microscopy in transmission mode of TiO<sub>2</sub> samples: a) T, b) TC, c) TM, and d) TCM.

The nitrogen adsorption–desorption isotherms recording led to the determination of physical-chemical properties of TiO<sub>2</sub>-based material prepared, freeze-dried and heat-treated which proved superior than TiO<sub>2</sub> commercial P25 Degussa (Table 2)

**Table 2.** Physical-chemical properties of TiO<sub>2</sub> prepared materials versus TiO<sub>2</sub> P25 Degussa.

Sample's name	Surface area (m <sup>2</sup> /g)	Specific pore volume (cm <sup>3</sup> /g)	Radius pore size (Å)
<b>TiO<sub>2</sub> P25 Degussa</b>	42.3	0.050	50-260
<b>TiO<sub>2</sub> powder prepared</b>	50.0	0.088	15-220

Modification of titanium dioxide by sensitization with natural dyes: carmine and morin, led to increased response capacity under light irradiation, and obtain a blue shift to its photoactivity.

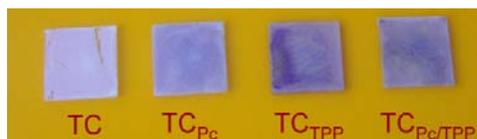
## PHOTOCATALYTIC PROPERTIES EVALUATION OF TiO<sub>2</sub>/CdS NANOCOMPOSITES SENSITIZED WITH PHTHALOCYANINE AND MESO-TETRAPHENYLPORPHINE

In order to extend the absorption spectra of TiO<sub>2</sub> to the visible region and to improve its photocatalytic efficiency, titanium dioxide has been associated with a narrow band gap semiconductor, cadmium sulphide (CdS). Also, with intention to obtain more efficient photoelectrodes to use in photoelectrochemical processes, the modification of TiO<sub>2</sub>/CdS nanocomposites aimed to sensitize them with *meso*-tetraphenylporphine (TPP) and phthalocyanine (Pc) dyes (Figure 9).



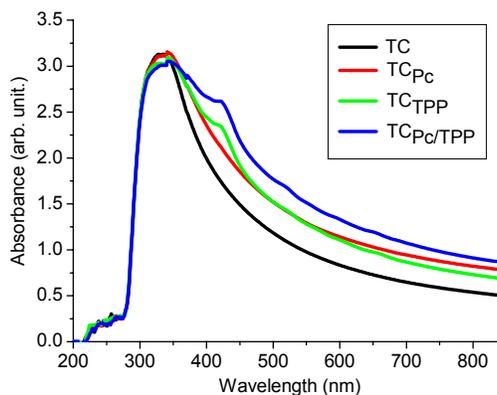
**Fig. 9** Structural formula of: a) phthalocyanine [41]; b) *meso*-tetraphenylporphine [41].

Thus, three sensitized layers were obtained, noted according to the colour used, namely: TC<sub>Pc</sub>, TC<sub>TPP</sub> and TC<sub>Pc/TPP</sub>; all samples were obtained by immersion in 2x10<sup>-4</sup>M dye solutions. Pc/TPP solution was obtained by mixing the two initial solutions in 1:1 volume ratio. TC sample was intentionally left non-sensitized, as standard sample (Figure 10).



**Fig. 10** TiO<sub>2</sub>/CdS nanocomposites samples.

The UV-VIS absorption spectra (Figure 11) exhibit the edges of the TiO<sub>2</sub>/CdS nanocomposites absorption peaks that shift to visible region, which is reflected by lower values of the energy band gap.



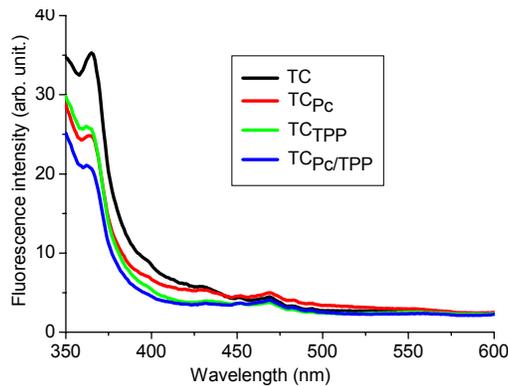
**Fig. 11** UV-VIS spectra of: TC, TC<sub>Pc</sub>, TC<sub>TPP</sub> and TC<sub>Pc/TPP</sub> samples.

The values of band gap energy in direct transition (determined from UV-VIS spectra by linear extrapolation) were higher than TiO<sub>2</sub> band gap energy (3.0-3.2 eV) and lower than the CdS (2.4 eV) one, also through the contribution of dye molecules adsorbed on the surface nanocomposites (Table 3).

**Table 3.** The values of band gap energy in direct transition for all samples.

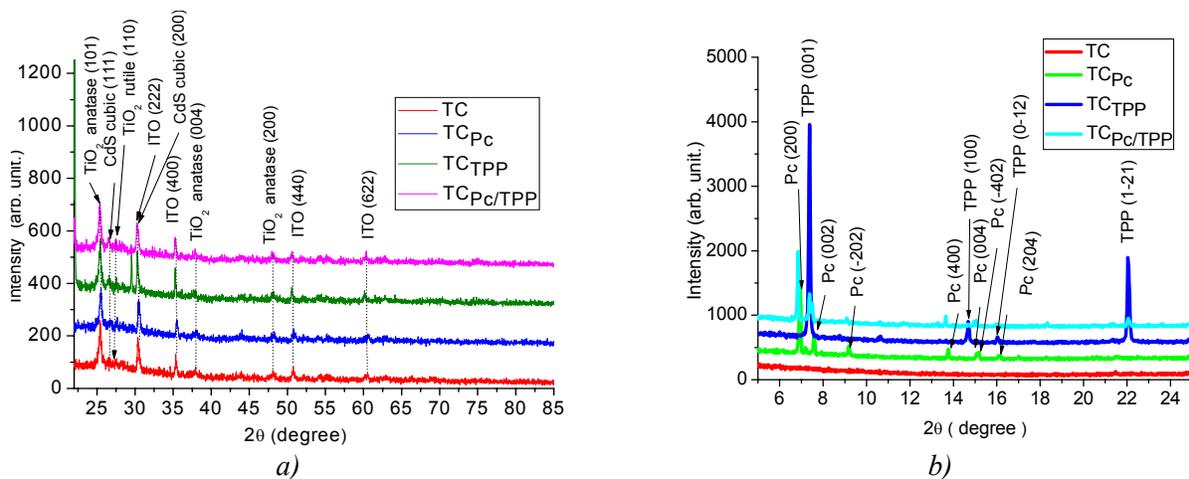
Sample's name	Band gap energy value (eV)
TC	2.96
TC <sub>Pc</sub>	2.82
TC <sub>TPP</sub>	2.73
TC <sub>Pc/TPP</sub>	2.54

Figure 12 shows the effect of Pc and TPP on the emission spectra of TiO<sub>2</sub>/CdS nanocomposites. No significant changes in fluorescence spectra of TiO<sub>2</sub>/CdS-based samples as a result of dyes molecules adsorbed on surface of semiconductor composites were observed.



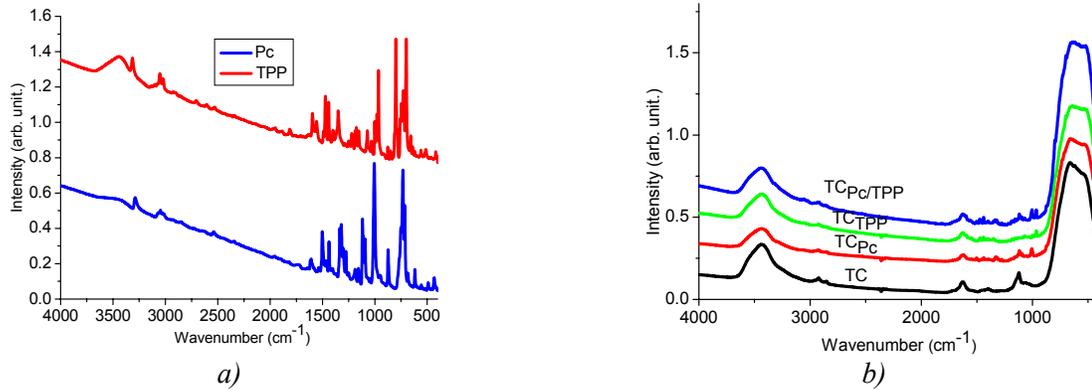
**Fig. 12** Fluorescence spectra of: TC<sub>Pc/TPP</sub>, TC, TC<sub>Pc</sub>, TC<sub>TPP</sub> and TC<sub>Pc/TPP</sub> samples.

The XRD patterns show that TiO<sub>2</sub> (anatase and rutile) and cubic CdS phases coexist in the all samples. Also the crystalline phase of dyes appears, probably due to their crystallization after solvent evaporation (Figure 13).



**Fig. 13** X-ray diffraction patterns of TiO<sub>2</sub>/CdS-based samples: a) 25-85 2θ and b) 5-25 2θ domain.

The absorption bands appeared in the IR spectra of all sensitized samples proves the adsorption of Pc and TPP molecules on nanocomposite surface by the appearance of absorption bands characteristic vibrations of dye bonds (NH, C = C, C = N, C<sub>6</sub>H<sub>6</sub>) in the absorption spectra of nanocomposites TiO<sub>2</sub>/CdS sensitized (Figure 14).



**Fig. 14** FT/IR spectra of: a) dyes, b) all TiO<sub>2</sub>/CdS samples.

The FT/IR microscopy images (40x40 μm<sup>2</sup>) revealed that the morphological features of samples are different and caused by the adsorption and crystallization of dye molecules on their surface (Figure 15).



**Fig. 15** FT/IR microscopy images: a) TC, b) TC<sub>Pc</sub>, c) TC<sub>TPP</sub> and d) TC<sub>Pc/TPP</sub>.

In the Table 4 can be observed that the surface area and the specific pore volume of composite were found to be between those of TiO<sub>2</sub> and CdS values. The appearance of small pore radius fraction in nanocomposite caused a narrow range of radius pore size.

**Table 4.** Physical-chemical properties of TiO<sub>2</sub>, CdS and TiO<sub>2</sub>/CdS samples.

Sample's name	Surface area (m <sup>2</sup> /g)	Specific pore volume (cm <sup>3</sup> /g)	Radius pore size (Å)
<b>TiO<sub>2</sub></b>	42.3	0.05	20-250
<b>CdS</b>	55.4	0.13	75-225
<b>TC (TiO<sub>2</sub>/CdS)</b>	48.7	0.07	100-225

The results of experiments show that TiO<sub>2</sub>/CdS nanocomposites could improve its photocatalytic efficiency by formation of highly dispersed composite of TiO<sub>2</sub> and CdS using nanosized materials. The quality of these nanocomposite materials could be also increased by an efficient charge separation, a recombination probability of the electron-hole pairs diminished and an enhancement of photostability, sensitization the nanocomposites with dyes that have an intense photon absorption in the visible light domain.

## ALIZARIN AND FLUORESCHEIN INFLUENCE ON PHOTOACTIVITY OF Ni, Pt, Ru-DOPED TiO<sub>2</sub> LAYERS

The modification of TiO<sub>2</sub>-based oxide materials by embedding metal ions Ni, Pt and Ru in its network, as well as alizarin and fluorescein molecules adsorption on the surface of oxide nanoparticles, lead to improve the photoactive properties of the titanium dioxide under the solar light action.

As starting materials for the preparation of doping TiO<sub>2</sub>-based layers with Ni, Pt and Ru were used: nickel (II) chloride hexahydrate, NiCl<sub>2</sub>·6H<sub>2</sub>O (Reactivul București, Romania); hexachloroplatinic acid, 8%, H<sub>2</sub>PtCl<sub>6</sub> (Sigma-Aldrich, Germany) and ruthenium (III) chloride, RuCl<sub>3</sub> (Merck, Germany).

The structural formula of sensitizers, alizarin and fluorescein, used to sensitize the Ni, Pt, Ru-doped TiO<sub>2</sub> layers are presented in Figure 16.



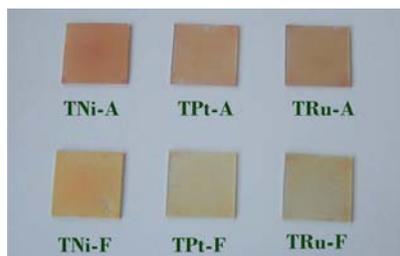
**Fig. 16** Structural systems numbered of: a) alizarin [42] and b) fluorescein [43].

The TiO<sub>2</sub>-based samples obtained are presented in Figure 17, each doping metal ion causing a specific colour of TiO<sub>2</sub> samples, namely: Ni<sup>2+</sup> - green colour, Pt<sup>2+</sup> - brown colour, and Ru<sup>3+</sup> - dark brown colour; TiO<sub>2</sub> layers have a white colour.



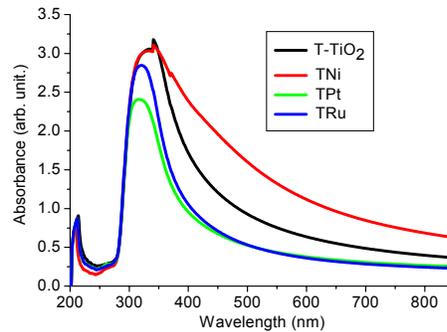
**Fig. 17** Ni, Pt, Ru-doped TiO<sub>2</sub> non-sensitized samples.

Finally, three TiO<sub>2</sub>-based layers (doped with Ni, Pt and Ru) and sensitized with alizarin (A) were obtained and other three layers doped with the same metal ions, and sensitized with fluorescein (F) were prepared (Figure 18). A sample consisting of TiO<sub>2</sub> undoped and non-sensitized layer was used as standard.



**Fig. 18** Ni, Pt, Ru-doped TiO<sub>2</sub> and sensitized with alizarin and fluorescein samples.

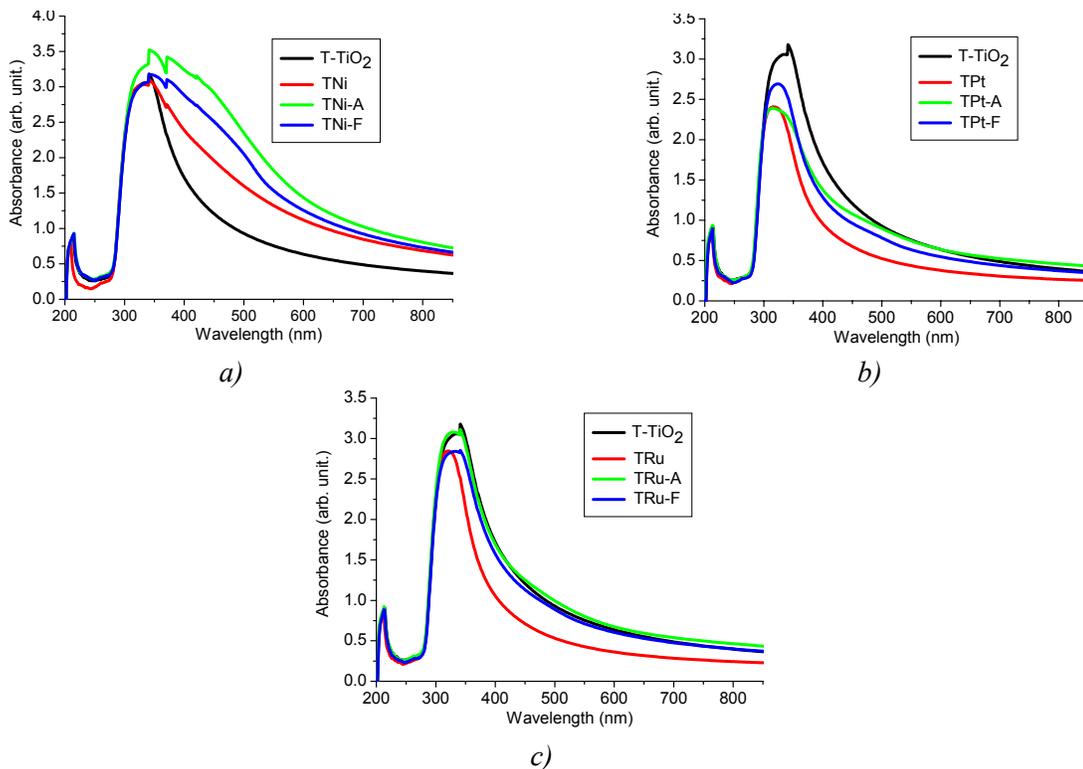
Investigation of optoelectronic properties by UV-VIS spectroscopy shows that Ni-doped TiO<sub>2</sub> layer presents a shift towards the visible absorption and TiO<sub>2</sub> layers doped with Pt and Ru determined a red shift in the absorption spectrum, probably due to an excessive concentration of dopant ions in the structure of TiO<sub>2</sub>.



**Fig. 19** UV-VIS spectra of T-TiO<sub>2</sub>, TNi, TPt, and TRu samples.

In the UV-VIS region, the effect of alizarin and fluorescein on doped TiO<sub>2</sub> layers is translated by the shifted absorption to higher wavelengths.

From two dyes, alizarin causes a more intense optical response shifted to visible, probably due to more efficient coupling process between its molecules and TiO<sub>2</sub>.



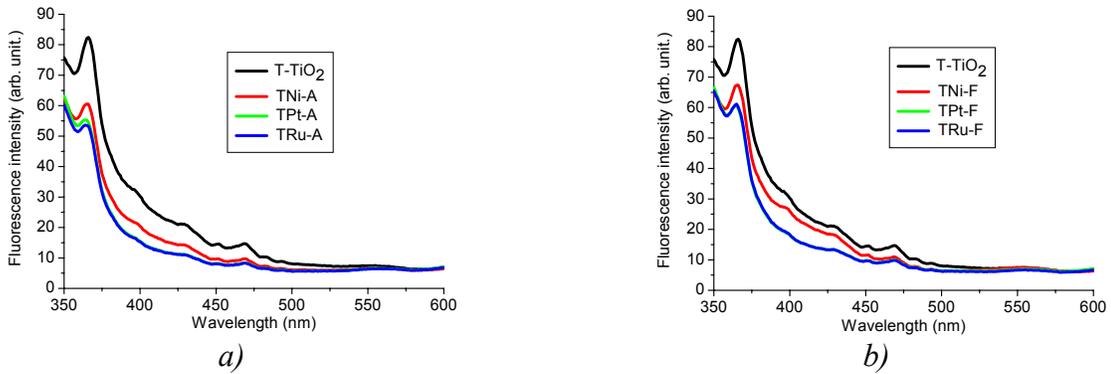
**Fig. 20** UV-VIS spectra of: a) TNi, b) TPt, and c) TRu, as well as additional layers sensitised with alizarin and fluorescein compared to T-TiO<sub>2</sub>.

Calculated values of E<sub>g</sub> samples from UV-VIS spectra and using the relation of Tauc are presented in Table 5.

**Table 5.** Band gap energy values of investigated TiO<sub>2</sub> layers.

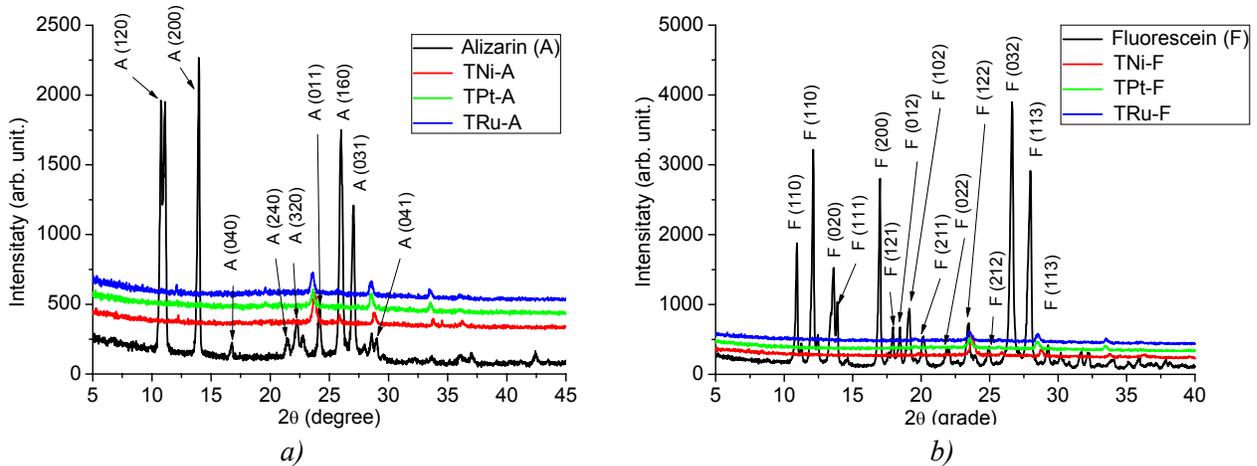
Sample's name	E <sub>g</sub> (eV)	Sample's name	E <sub>g</sub> (eV)	Sample's name	E <sub>g</sub> (eV)	Sample's name	E <sub>g</sub> (eV)
T-TiO <sub>2</sub>	3.07	TNi	2.70	TPt	3.14	TRu	3.15
		TNi-A	2.20	TPt-A	3.07	TRu-A	3.08
		TNi-F	2.35	TPt-F	3.10	TRu-F	3.11

The fluorescence emission spectra of doped and undoped TiO<sub>2</sub> layers have similar forms. Photoluminescence spectra emission of doped and sensitized TiO<sub>2</sub> layers show a decrease in the emission intensities compared to standard sample. The phenomenon of fluorescence quenching is caused by the transition of electrons from the dye excited state in the conduction band of nanoparticles and reflects a high degree of association between dye molecules and TiO<sub>2</sub> [44, 45].



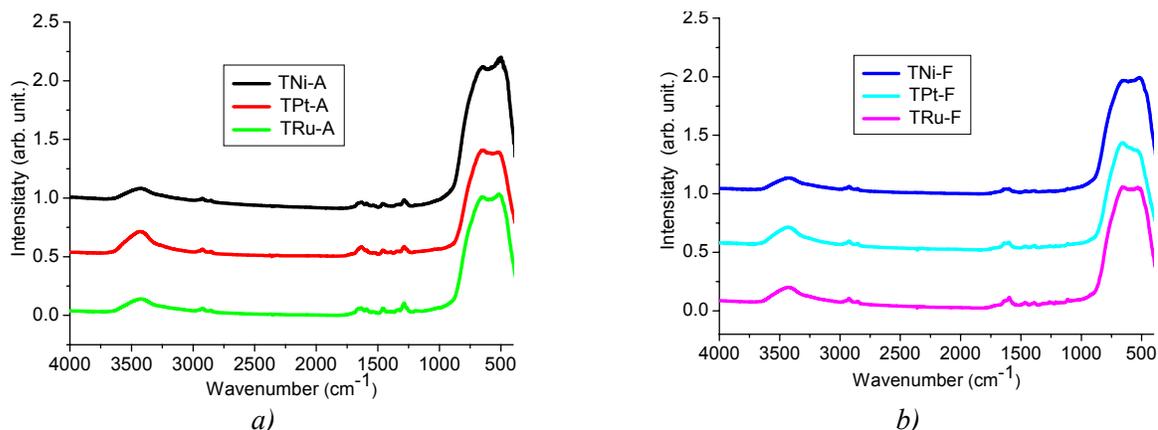
**Fig. 21** Fluorescence spectra of Ni, Pt, Ru-doped and sensitized TiO<sub>2</sub> layers with: a) alizarin, and b) fluorescein.

The XRD patterns of investigated samples (Figure 22) not show the presence of diffraction peaks that confirms the presence of crystalline forms of nickel, platinum or ruthenium oxides, or pure metal phases that suggesting penetration doping ions into the lattice of TiO<sub>2</sub>.



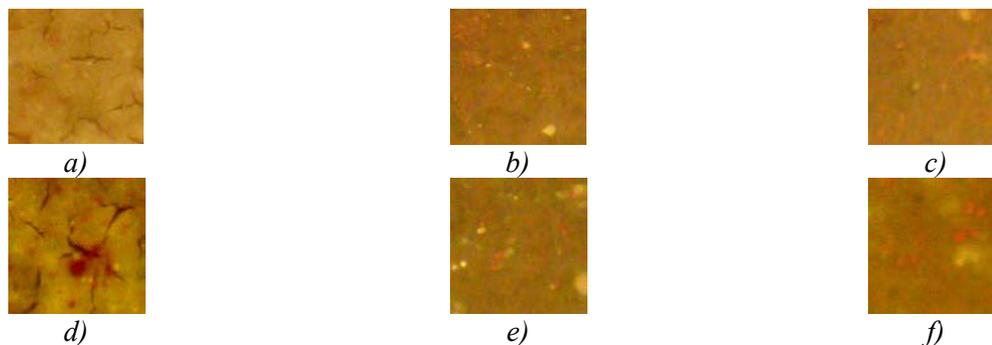
**Fig. 22** X-ray diffraction patterns of Ni, Pt, Ru-doped TiO<sub>2</sub> layers and sensitized with: a) alizarin (A), and b) fluorescein (F).

IR absorption spectra reveal the presence of dye molecules adsorbed on the surface of TiO<sub>2</sub>-based layers (Figure 23).



**Fig. 23** FT/IR spectra of Ni, Pt, Ru-doped TiO<sub>2</sub> layers and sensitized: a) alizarin, and b) fluorescein.

The images obtained by IR microscopy in reflexion mode show a relatively homogeneous surface of the investigated TiO<sub>2</sub> layers, except for those doped with Ni (on their surface microcracks are observed).



**Fig. 24** FT/IR microscopy images: a) TNi-A, b) TPt-A, c) TRu-A, d) TNi-F, e) TPt-F and f) TRu-F.

Surface area and pore volume determined by N<sub>2</sub> adsorption-desorption isotherms of the investigated samples do not differ significantly (Table 6) so that dopants apparently have no appreciable influence on the active surface area and porosity of the prepared materials.

**Table 6.** Physical-chemical properties of TiO<sub>2</sub>-based materials.

Sample's name	Surface area (m <sup>2</sup> /g)	Specific pore volume (cm <sup>3</sup> /g)	Radius pore size (Å)
Ni-doped TiO <sub>2</sub>	45.94	0.102	140-220
Pt-doped TiO <sub>2</sub>	46.15	0.097	140-200
Ru-doped TiO <sub>2</sub>	45.39	0.092	120-220

The investigation results show that TiO<sub>2</sub>-based materials doped with transition metal ions (Ni, Pt, Ru) and sensitized with alizarin and fluorescein possess optoelectronic properties for the optimal development of oxide systems in different photoelectrocatalytic processes.

## TESTING THE EFFICIENCY TITANIUM DIOXIDE-BASED OXIDICE SYSTEMS

A conventional *DSSC* solar cell contains a  $\text{TiO}_2$ -based photoelectrod sensitized with dye molecules, a counter electrode (usually, platinum) and an electrolyte introduced into the space between the two electrodes (containing a redox mediator, such as iodide-triiodide redox couple). In order to test the  $\text{TiO}_2$ -based layers obtained have assembled these cell types (Figure 25).



**Fig. 25** Sample of solar cell assembled.

Recording of current voltage characteristics (I-V) allow the evaluation of solar cells efficiency by determining the functional parameters: fill factor (*FF*) and conversion efficiency ( $\eta$ ) of the dye-sensitized solar cell. The results of experiments are presented in the Table 7.

**Table 7.** *FF* and  $\eta$  values of tested  $\text{TiO}_2$ -based layers.

Sample's name	Sample's description	$\eta$ (%)	<i>FF</i> (-)
<b>TC</b>	$\text{TiO}_2$ sensitized with carmine (C)	1.99	0.43
<b>TM</b>	$\text{TiO}_2$ sensitized with morin (M)	1.70	0.40
<b>TMC</b>	$\text{TiO}_2$ sensitized with carmine/morin (C/M)	1.87	0.41
<b>TC<sub>Pc</sub></b>	$\text{TiO}_2/\text{CdS}$ sensitized with phtalocyanine (Pc)	1.92	0.40
<b>TC<sub>TPP</sub></b>	$\text{TiO}_2/\text{CdS}$ sensitized with <i>meso</i> -tetraphenylporphine(TPP)	2.44	0.41
<b>TC<sub>Pc/TPP</sub></b>	$\text{TiO}_2/\text{CdS}$ sensitized with Pc/TPP	2.12	0,38
<b>TNi-A</b>	Ni-doped $\text{TiO}_2$ and sensitized with alizarin	2.76	0.51
<b>TPt-A</b>	Pt-doped $\text{TiO}_2$ and sensitized with alizarin	2.41	0,48
<b>TRu-A</b>	Ru-doped $\text{TiO}_2$ and sensitized with alizarin	2.14	0.45
<b>TNi-F</b>	Ni-doped $\text{TiO}_2$ and sensitized with fluorescein	2.52	0.53
<b>TPt-F</b>	Pt-doped $\text{TiO}_2$ and sensitized with fluorescein	2.16	0.50
<b>TRu-F</b>	Ru-doped $\text{TiO}_2$ and sensitized with fluorescein	2.20	0.42

According to the measurements, one can observe that the systems have a photovoltaic effect, but conversion yields are lower compared with those reported in the literature (over 10%). This is normal taking into account that these dyes used in experiments are not entirely adapted to the purpose.

## FINAL CONCLUSIONS

The structural defects of TiO<sub>2</sub> lattice determine the appearance of fast recombination sites between photogenerated charges under light action which leads to electrons and holes concentration decrease, and consequently photoactive properties are reduced.

The aim of these experiments was to remove this effect by doping, association and sensitization of titan dioxide with transition metal ions, narrow band gap semiconductors and/or with different photosensitive organic compounds, such as dyes.

Association, doping and sensitization effects on TiO<sub>2</sub>-based materials, depends on different parameters, such as type and concentration of doping ions or coupled semiconductors, structure and concentration of organic dyes, physical-chemical properties of components, proposed oxide materials preparation methods.

All these contribute to the final aim of experiments, namely to increase the efficiency of converting sunlight into energy in photovoltaic cells using materials TiO<sub>2</sub>-based associated with other semiconductors, doped with metal/nonmetal ions and/or sensitized with various dyes.

Information regarding the opto-electronic, morpho-structural and mechanical properties of TiO<sub>2</sub>-based layers, which makes the object of this thesis, suggests the obtaining of some materials with photoelectrocatalytic potential, efficient candidates in water decomposition processes, water pollutants degradation, solar cell and electrochromic devices.

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## ISI Publications

1. **The Influence of TiO<sub>2</sub> Content in Preparation of ITO/TiO<sub>2</sub> Nanostructured Films** - Marcela-Corina Rosu, Ramona-Crina Suciu, Simina Dreve, T.D. Silipas, I. Bratu, E. Indrea, *Revue Roumaine de Chimie*, 2011, 56(6), 601-605
2. **Phtalocyanine and meso-tetraphenylporphine effects on TiO<sub>2</sub>/CdS nanocomposites photoactivity** M.C. Rosu, R.C. Suciu, M.D. Lazar, I. Bratu, *Journal of Optoelectronics and Advanced Materials*, 2011, 13(12-13), 1345-1351
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## BDI/B+ Publications

1. **A Spectroscopic Study of Dyes Decomposition by Irradiated Nanocrystalline TiO<sub>2</sub>** – Marcela-Corina Rosu, Ramona-Crina Suciu, Irina Kasco, Simina-Virginia Dreve, E. Indrea, T.D. Silipas, *Journal of Physics: Conference Series* 182 (2009) 012078
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1. **TiO<sub>2</sub>/methylcellulose nanocomposite films for photocatalytic applications** – M.C. Rosu, R.C. Suci, S.V. Dreve, T.D. Silipas, I.Bratu, E. Indrea, *sent for publication AIP Conference Proceedings*
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#### List of national/international projects as participant

1. CEEEX - MENER 710/24.07.06 – **”Photo-Electrolytic Production of Hydrogen”- HIDROSOL**, Project Supervisor: senior scientist *dr. Emil Indrea (INCDTIM, Cluj-Napoca)*
2. CEEEX - VIASAN 102/01.08.06 with title: **“ Porphyrin Biocomposites used in Photodynamic Therapy of Cutaneous Malign Tumors” – PORFIDERM**, Project Supervisor: research scientist *dr. Simina Dreve(INCDTIM, Cluj-Napoca)*
3. Program PN II 71-122/2007 - **“Oxidic Micro- and Nano-structured Materials with Controlled Luminiscent Cromatics” – MAMINAL**, Project Manager: Dr. Laura Muresan (*UBB-ICCRR, Cluj-Napoca*), Project Supervisor: Senior Scientist *dr. Emil Indrea (INCDTIM, Cluj-Napoca)*
4. Program PN II 3322/2008 – **“Photocatalytic Production of Hydrogen under Solar Irradiation from Industrial Sulphurous Residues (H<sub>2</sub>S si SO<sub>2</sub>)” – H<sub>2</sub>SOLAR**, Project Manager: *Dr. Terezia Nyari (INCEMC, Timișoara)*, Project Supervisor: Senior Scientist *dr. Emil Indrea (INCDTIM, Cluj-Napoca)*
5. Project PN II 79-190/2008 – **“Biocompozites with Hidroxilapatite for Endodontic Therapy” – ENDODENT**, Project Manager: *Dr. Marioara Moldovan (UBB-ICCRR, Cluj-Napoca)*, Project Supervisor *Dr. Simina Dreve (INCDTIM, Cluj-Napoca)*
6. Project PN II 92-095/2008 – **„ Modern methods of investigation, authentication, preservation and showcasing of the icons from the patrimony of the Transilvania” – CONSICON**, Project Supervisor: *Dr. Zaharie Moldovan (INCDTIM, Cluj-Napoca)*
7. National Core Project 44N /2009, PN 09-44 02 01 – **„Supramolecular systems for trapping and controlled release of bioactive agents”** - Project supervisor: Research Professor *Dr. Ioan Bratu*, Project Technical Assistant: *Dr. Simina Dreve (INCDTIM, Cluj-Napoca)*
8. National Core Project 44N/2009, PN 09-44 02-06 - **“Local structure determination of highly disordered oxides systems with applications in photocatalysis”**, Project Supervisor: Senior Scientist *Dr. Emil Indrea (INCDTIM, Cluj-Napoca)*