



Ecaterina Bica

# TUNGSTEN TRIOXIDE UNCONVENTIONAL MATERIALS WITH SPECIAL OPTICAL AND ELECTRICAL PROPERTIES

Summery of PhD thesis

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### Summary of PhD thesis

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**Key words:** tungsten trioxide, films, ion exchange, sol-gel, un-doped powders, doped powders, photo catalysts, electrochromism, photo degradation

#### Abbreviations

- > **BET** Specific Surface Area Measurements by <u>**B**</u>runauer-<u>**E**</u>mett-<u>**T**</u>eller method
- > CTAB Cetyl trimethylammonium bromide
- CV Cyclic Voltammetry
- > DTA Differential Thermoanalysis
- ➢ Eg − Band Gap Energy
- FTIR- Fourrier Transformer- Infra Red)
- > ICP-OES- Inductively Coupled Plasma Optic Emission Spectroscopy
- > ITO indium-tin oxide
- ➤ MA- metacrylic acid
- ➢ NLS sodium lauryl sulfate
- > PEG- poliethylene glycol
- SEM Scanning Electronic Microscopy
- **TEM Transmision Electronic Microscopy**
- ➤ TGA- Thermogravimetric Analysis) ⇔ TG Thermogravimetric curves and DTG -Differential Thermogravimetric curves
- > UV-VIS Ultraviolet-Visible spectroscopy
- > XRD X Ray Diffraction

#### **INTRODUCTION**

The practical importance of tungsten trioxide (WO3) is determined that it is a semiconductor with special optical, electrical, structural and morphological properties, properties that can be controlled by the method of preparation used and facilitate the use of tungsten trioxide in a wide range of applications, both as a fine powder and as thin layer (film) deposited on different types of support.

WO3 films present a fundamental and applied interest because they possess electrochromic properties. Comparative with other electrochromic devices, the WO<sub>3</sub> films present the highest coloring efficiencein in visible and infrared spectral domain<sup>1, 2</sup>. For this reason, optical, electrochemical and structural morphological characterization is a mandatory requirement to establish their quality and efficiency.

The literatures data shows that the specific properties of tungste trioxide based materials (electrochromism and photo catalysis) are in corelation with the composition, morphology and dimension particles, the porosity and optical characteristics of WO<sub>3</sub> films and powders. This properties are influenced by the obtaining process<sup>3, 4, 5, 6</sup>. From this reason, the WO<sub>3</sub> powders were obtain by methods that allows the control of propeties since the preparation stage. The doping of powders increase the efficience of this materials in applications<sup>7, 8</sup>.

The PhD thesis contributes to knowledge development in an area of great interest internationally, the materials based on tungsten trioxide with applications in energy and environmental remediation, used to manufacture solar cells (Photo electrochemical, electrochromic devices) and photo catalysts for degradation of pollutants in the environment. The multiple possibilities of using these materials argue the practical importance of investigations.

*In the first part* of the thesis were systematized the bibliographic data on methods of synthesis, characterization and applications of WO<sub>3</sub> films and powders. The specific characteristics and the diversity of domain applications revealed by literature data determinated the study of WO<sub>3</sub> films and powders.

*The second part* contains the original research realized in oreder to obtain new WO<sub>3</sub> films with applicative potential in electrochromic devices domain and also to obtain new WO<sub>3</sub> undoped and doped powders, using as photocataysts in dyes photodegradation.

The films were deposited on optical glass and conductive glass support, using a single deposition technique - dip-coating method. The used substrate was treated by different asperization methods allowing good adhesion of the film and avoid interaction with the support. It made a comparison between the  $WO_3$  films deposited on ITO support from soil obtained by two

different starting materials, either from sodium tungstate (ion exchange method) or from tungsten metal (sol-gel method). It been shown the importance of preparative conditions: the asperization treatment of the substrate, the method for obtaining soil and subsequent thermal treatment. In order to confirm the structure and composition of synthesized materials, these were characterized by: Thermal analysis - TG/DTG/DTA, Infrared Absorption Spectroscopy (FTIR), UV-Vis absorption spectroscopy, X-ray diffraction, Scanning electron microscopy - SEM and cyclic voltammetry (CV). Highlighting the potential applicability of new WO3 films as electrochromic materials, by optical (UV-Vis spectroscopy) and electrochemical measurements (cyclic voltammetry CV) and as photo anodes in electrochemical cells, by cyclic voltammetry measurements.

Meso-porous and nanostructurated powders were prepared by precipitation and sol-gel methods. By sol-gel method were obtain WO<sub>3</sub> powders with various additives to improve their properties. Structural (thermal analysis TG / DTG / DTA, FTIR spectroscopy, specific surface area and porosity - BET, X-ray diffraction XRD, UV-Vis spectroscopy) and morphological (scanning electron microscopy - SEM and transmission electron microscopy - TEM) characterization of prepared materials was performed.

Were prepared new materials based on tungsten trioxide powders doped with transition metal oxides (Cu, Ni, Mn, Ag) and doped with ions of noble metals (Pt and Pd), method used in the latter case was first used for doping powder obtained by sol-gel method. Doping WO<sub>3</sub> powder allowed the successful use as photocatalysis in the degradation of dyes (methylene blue and methyl orange), due to special morpho-structural and optical properties that have these powders. The materials obtained were characterized by powder specific methods: BET - specific surface area and porosity, X-ray diffraction - XRD, UV-Vis spectroscopy, scanning electron microscopy – SEM, transmission electron microscopy - TEM, elemental analysis - ICP-OES. The evaluation of photo catalytic activity was achieved from the reaction of catalysis and evidence was made by UV-Vis spectroscopy measurements.

The researches were made at the Faculty of Chemistry and Chemical Engineering, Chemistry-Physics Department, Cluj-Napoca (Prof. Dr. Ionel Cătălin Popescu); at the "Raluca Ripan" Institute for Research in Chemistry, Solid-state Chemistry Laboratory, Cluj-Napoca (CSI Dr. Elisabeth-Jeanne Popovici) and at Transilvania University, Braşov (Prof. Dr. Anca Duță).

#### **II. ORIGINAL CONTRIBUTIONS**

#### 2. Research on WO<sub>3</sub> thin films

#### 2. 2. Synthesis of the WO<sub>3</sub> thin films

<u>Ion exchange method</u>  $^{9, 10}$  is based on passing a solution of sodium tungstate over an ion exchange resin, loaded with H<sup>+</sup> by treatment with HCl. To prevent gelling, tungsten acid thus prepared was dissolved in hydrogen peroxide, and peroxo-tungstic acid obtained was stabilized with alcohol.

Before deposition, the supports surface was treated with alcoholic solution, in ammonia or hydrogen peroxide, to ensure the stability of the film on the support. To strengthen the structure's WO<sub>3</sub> were performed several cycles of deposition, by several dipping-drying cycles. After deposition, WO<sub>3</sub> conversion was performed after the thermal treatment at  $250-550^{\circ}$ C.

Another series of films were deposited in a hydrated WO3 sol obtained by <u>sol-gel method</u>, from the reaction of tungsten powder and hydrogen peroxide. The method allowed the study of the influence of certain preparative factors on WO<sub>3</sub> thin films properties: dipping-drying cycle's number, adding the polymer agent (PEG400, PEG600)<sup>11</sup>, roughing type (ethylene glycol: NaOH for optical glass support and acetone: ethanol for ITO glass support), substrate type and annealing temperature (350-550<sup>o</sup>C).

TGA / DTG and FT-IR analysis of precursors indicated the formation of peroxo-tungstic acid, in the ion exchange method, and tungsten acid, in the sol-gel method, and showed that their conversion takes place at  $350^{\circ}$ C, and the organic materials are total eliminated only at  $550^{\circ}$ C.

#### 2. 3. Characterization of WO<sub>3</sub> thin films obtained by ion exchange method

#### 2.3.3. Optical properties

The monolayer and multilayer WO<sub>3</sub> films show constant transmittance on the entire visible domain. The monolayer WO<sub>3</sub> film (R4I1) shows the highest transmittance of about 80% on the entire visible domain. As expected, the multilayer films R4I2, R4I3, R4I4 and R4I5 have a lower transmittance (50 -80 %) as compared with the monolayer hetero-structures<sup>10</sup> (**Figure 2.4**).

The thermal treatment determines the decreases of the transmittance; in parallel with the temperature increase, both structures  $WO_3/Glass/WO_3$  and structures  $WO_3/ITO/Glass/WO_3$ . The thermal treatment also produces the color change of transparent films from colorless to yellow pale, thus suggesting some morpho-structural variation<sup>10</sup>.



Figure 2.4. Transmission spectra of WO<sub>3</sub> films, annealed at 350°C<sup>10</sup>

In addition, it highlighted the influence of roughing treatment of the ITO platelets that were treated with ethylene glycol: NaOH, except for samples: R4I6-hydrogen peroxide, R4I7-ammonia and R4I8-ethanol-amine.

In terms of adhesion and film uniformity, best behavior,  $\sim$  79%, had a film whose support was treated with ammonia solution.



**Figura 2.6**. Plot of  $(\alpha h v)^{1/2} v s h v$  for WO<sub>3</sub> films<sup>10</sup>

In terms of reflectance, the reflection maximum is situated in the blue range of the spectral domain.

The band gap energy of WO<sub>3</sub> films, evaluated from the Tauc plot's,  $[(\alpha h\nu)^{1/2} vs h\nu]$ , varies between 2.9 and 3.2eV, in agreement with the literature data<sup>12</sup>(Figure 2.6).

#### 2. 3. 4. Morpho-structural properties

To identify the crystalline structure of the precursors and films based on tungsten oxide, the X -ray diffraction technique was used. It was observed that thermal treatment of precursor (based on tungsten oxide hydrate) leads to its conversion into WO<sub>3</sub> with a high crystallinity.

The SEM images (**Figure 2.8**) illustrate that WO3 film consists on nano-metric particles that creates a homogeneous surface. The increase of the annealing temperature from  $350^{\circ}$ C to  $550^{\circ}$ C, leads to the formation of larger crakes in the WO<sub>3</sub> film<sup>10</sup>.



Figure 2.8. SEM images of WO3 film surface: one layer: 350°C (a) and 550°C) (b)<sup>10</sup>

#### 2.3.5. Electrochemical properties

All films of WO3 (WO3/ITO/Glass/WO3 - working electrode) subject to cyclic voltammetry presents the typical shape of tungsten trioxide. Evidence shows two anodic peaks which reverses its intensity depending on the type of treatment applied to the substrate and the number of layers deposited on the support (R4I6-monolayer, support treated with hydrogen peroxide; R4I7-multilayer, support treated with ammonia).



Figure 2.9. Cyclic voltamograma of WO3 films, ion exchange method, WO<sub>3</sub>/ITO/Glass/WO<sub>3</sub> in 0.01M H<sub>2</sub>SO<sub>4</sub>, CE – Pt, E=- $1V \div +1V vs Ag/AgCl/KCl_{sat}$ 

Studies have shown that morpho-structural and optical properties of the films are influenced by: the number of layers, annealing temperature and roughing treatment.

#### 2. 4. Characterization of WO<sub>3</sub> thin films obtained by sol-gel method

#### 2. 4. 1. Additive influences

#### 2. 4. 1. 4. Morpho-structural properties

Evaluation porosity of materials prepared was done by measuring the specific surface of precursors, annealed 30 minutes at  $550^{\circ}$ C in air. It was noted that the materials are porous whatever the presence of polymeric additive which contributes to increasing porosity.

SEM images (**Figure 2.12**) show that surfaces WO3 films without additive, annealed at  $550^{\circ}$ C, are composed by irregular prismatic particles of well-packed with small inclusions of amorphous material, growing by adding PEG's, making it become predominant. For thick films of WO3, estimated from SEM images of films in transverse position, found the following values: FW2S3 ~ 500 nm; FW3S3 ~ 400 nm.



Figure 2.12. SEM images of WO3 films prepared without additive (a) and with PEG400 (b)



Figure 2.13. X-ray diffraction patterns of WO3 precursor and WO3/Glass/WO3 heterostructures obtained from sol without (left) and with PEG400 (right)

All WO<sub>3</sub> precursors prepared from sol with or without organic additives and annealed at 550°C, have monoclinic crystal structure with varying degrees of crystallinity (**Figure 2.13**).

X-ray diffraction patterns of WO3/Glass/WO3 heterostructures present diffraction lines (21.8°, 25.5°, 32.9°) ttriclinic compound characteristic  $Na_2W_4O_{13}$  (JCPDS 27-1425), accompanied by very weak bands of monoclinic WO3's (JCPDS 71-2141). When films are grown on glass with polymer additive, PEG400 and annealed at 550°C (Figure 2.13, right),

compounds have a larger amount of WO<sub>3</sub> and seem to adopt a crystalline arrangement of type NaxWO<sub>3</sub>, strong diffraction bands located at 22.5°, 24.7°, 28.9°, 33.5° are characteristic Na<sub>0.10</sub>WO<sub>3</sub> tetragonal (JCPDS 05-0389).

It can be assumed that at 550°C, the nanoparticles of  $WO_3xH_2O$  precursor interact superficial with the glass substrate resulting in a crystalline product from the system  $Na_2WO_4$ - $WO_3$ . To our knowledge this possibility of interaction of  $WO_3xH_2O$  nanoparticles with the glass substrate not yet been reported in literature.

#### 2.4.1.5. Optical properties

Optical properties of films were shown by UV-Vis spectroscopy, more precisely based on total reflectance spectra (incidence angle  $8^0$ ), diffuse reflectance spectra (incidence angle  $0^0$ ) and specular reflectance spectra.



Figure 2.16. Reflectance spectra for WO<sub>3</sub> film

Multiple bands of WO<sub>3</sub> films without additives (**Figure 2.16a**) suggests that light passes through layers with different refractive indices due to heterogeneity film, phenomenon illustrated by XRD and SEM data.

Total reflectance spectra shows three maximum located in the blue, green and red spectral region. Reflection color film and specular reflectance spectrum appearance is similar to chromatic and metallic luster characteristic of sodium tungstate bronzes.

#### 2. 4. 2. Thermal treatment influence

To stabilize the  $WO_3$  film and avoid interaction with the support on which is deposited film, a study focused on the difference between drying and annealings layers between successive deposits and the final annealing temperature.

X-ray diffraction patterns of WO<sub>3</sub> films thermal treated at  $4x350^{\circ}C$  indicates that they are amorphous, with a tendency to monoclinic organization. WO<sub>3</sub> film obtained at 350°C (with 4 annealing steps) is amorphous, presents cracks and many morphological defects (lumps). In order to control the film quality, the recommended thermal treatment is at  $350^{\circ}C$  with 1-step annealing stage performed at the end of the deposition cycle (**Figure 2.19**)<sup>13</sup>.



Figure 2.19. SEM images of WO3 films annealed at  $4x \ 350^{\circ}C^{13}$ 

#### 2. 4. 3. Support influence

#### 2. 4. 3. 2. Morpho-structural characteristics

WO3 films with WO3/ITO/Glass/WO3 hetero structures  $(350^{0}C/30 \text{ minutes in air})$  WO<sub>3</sub>(PEG400)/ITO/Glass/WO<sub>3</sub>(PEG400) have relatively smooth surface with regular particles.



Figure 2.21. SEM images of hetero structures: a) WO<sub>3</sub>/ITO/Glass/WO<sub>3</sub> (FW10I2) and b) (PEG400)/ITO/Glass/WO<sub>3</sub>(PEG400) (FW11I2)



Figure 2.22. X-ray diffraction patterns of WO3 precursors and films

A 200nm thick film was estimated from SEM measurements, the films are placed in transverse position (Figure 2.22).

WO<sub>3</sub> precursors have the monoclinic structure, while WO<sub>3</sub> films are amorphous with a tendency to organize monoclinic crystalline phase. From X-ray diffraction patterns WO<sub>3</sub>'s band is observed, located at  $2\theta$ =23.12 (**Figure 2.22**), and bands corresponding to ITO, showing that the films were not dissolved and have not interacted with the support.

#### 2.4.3.3. Optical properties

The study of materials by optical absorption provides information about the quality of thin films and band gap characteristics. Transmittance of WO3 films deposited on conductive support remains constant, ~ 60% throughout the visible domain, multiple deposits from sol without additive does not influence the transmittance of films and adding PEG's improves the quality of WO<sub>3</sub> films transmission (**Figure 2.23**).



**Figure 2.23**. Transmission spectra of WO<sub>3</sub>/ITO/Glass/ WO<sub>3</sub> (350<sup>o</sup>C) with different number of layers without additive (a) and with PEG400 additive (b)



**Figure 2.24**. Reflectance spectra of WO<sub>3</sub> films annealed at 350<sup>o</sup>C: (a) without additive (FW10 I2); (b) with PEG400 additive (FW11 I2)

 $WO_3$  films with and without polymer additive have similar reflectance spectra, with high reflection located at 400 nm and 650 nm (Figure 2.24). These similarities indicate that the

supports identical materials were deposited, confirming the XRD data. The band gap energy (Eg) value is located in the 3.1-3.4 eV domain, in agreement with literature data.

#### 2. 4. 3. 4. Electrochemical properties

To choose the optimal working conditions was chosen one of the samples obtained (FW10-I3) and have studied the influence of applied potential, scan rate and electrolyte concentration on the electrochemical properties (Figure 2.26).



**Figure 2.26**. Cyclic voltamograma of WO3/ITO/Glass/WO3 films: a) different applied potential; b) at different scanning speeds c) at different concentrations

WO<sub>3</sub> films applied potential influence on electrochemical properties of these involves the recording of the electrochemical behavior of WO<sub>3</sub> film for 4 different potential areas of: E<sub>1</sub>=-1.2V  $\div$  1.2V; E<sub>2</sub>=-1V $\div$ 1V; E<sub>3</sub>=-0.8V  $\div$  0.8 V; E<sub>4</sub>=-0.6V  $\div$  0.6V vs. Ag/AgCl/KCl<sub>sat</sub> (0.5M H<sub>2</sub>SO<sub>4</sub>, v =50mVs<sup>-1</sup>). It is noted that at the application of different potential areas the bit stream increases proportional to the applied potential, voltamograma form remains unchanged (**Figure 2.26a**). Ranging *the scan speed* from 10 to 800mVs-1 (0.5M H<sub>2</sub>SO<sub>4</sub>, E=-1V $\div$ 1V vs. Ag/AgCl/KCl<sub>sat</sub>) can see a well-defined anodic pick moving towards more positive potential with increasing scan rate (**Figure 2.26b**). As *the concentration of electrolyte solution* (0.5, 0.1 and 0.01M H<sub>2</sub>SO<sub>4</sub>, v =50 mVs<sup>-1</sup>; E=-1V $\div$ 1 V vs. Ag/AgCl/KCl<sub>sat</sub>) it was observed that when it takes the 0.5M H<sub>2</sub>SO<sub>4</sub> value the anodic current has the highest recorded intensity, 0.011 µA (**Figure 2.26b**).

Study of electrochemical properties of  $WO_3$  films was continued by examining the influence of the preparation of films on the electrochemical properties, namely the number of layers and porosity agent (**Figure 2.30**). Anodic peaks were well defined, indicating oxidation of W ions with tungsten trioxide coloring layer, showing electro chromic films.



**Figure 2.30**. Cyclic voltamograma of mono- and multi-layers films without additive (a) and with PEG400 additive in 0.01M H<sub>2</sub>SO<sub>4</sub> solution, CE-Pt, v=50mVs<sup>-1</sup>, E=-1.2V ÷ 0.6 V vs. Ag/AgCl/KCl<sub>sat</sub>

Porous nature of the films is favorable insertion and extraction of ions through the coloring-fading process, discoloration, allowing the electrolyte to penetrate relatively slowly. Decrease in active material increases stability, increased ion storage capacity.

#### 3. Research on meso-porous WO<sub>3</sub> powders

#### 3. 2. Synthesis of the WO<sub>3</sub> powders

WO<sub>3</sub> powders were obtained by <u>precipitation method</u><sup>14</sup> of tungsten acid annealed at  $550^{0}$ C, 60 minutes, in the air, from the reaction between sodium tungstate and hydrochloric acid. To determine the influence of experimental conditions on the properties of WO<sub>3</sub> powders, reactants ratio Na2WO4: HCl = 1:20 ÷ 1:35 was varied.

By <u>sol-gel method</u> were obtained WO3 powders, after the tungsten acid obtained from the reaction between tungsten powder and hydrogen peroxide was calcined (drying at  $70^{\circ}$ C and calcined in air at  $550^{\circ}$ C/30 minutes). This method allowed the study of the influence of surfactants on the properties of WO<sub>3</sub> powder by adding, during the preparation, of porifer (PEG200, PEG400, PEG600) and control agents of particle morphology (MA, CTAB, NLS)<sup>15</sup>. To elucidate the influence of thermal treatment, samples were thermally treated at  $550^{\circ}$ C, in air, for short (30 minutes) and longer (90 minutes)<sup>16</sup>.

#### 3. 3. Characterization of WO<sub>3</sub> powders obtained by precipitation method

#### 3. 3. 1. Evaluating the conversion of precursors

From thermo gravimetric analysis is noted that the samples show a mass loss of ~ 9.0% to ~  $300^{\circ}$ C, exclusively associated with dehydration precursor. The maximum effect occurs between 188-212°C and occurs in several steps corresponding water loss physical related and tungsten acid decomposition (**Figure 3.1a**).

If uncalcined WO<sub>3</sub> precursors, in FT-IR spectrum (**Figure 3.1b**) in addition to bands associated with vibrations of the water links, between 900-600 cm<sup>-1</sup> may occur bands assigned to stretching vibrations of W-O and W-O-W. It is noted that tungsten trioxide hydrate precursors, water loss by annealings with the formation of tungsten trioxide.



Figure 3.1. TGA and DTG curves of uncalcined WO3 precursor (a) and FT-IR spectra of calcined and uncalcined sample (b)

#### 3. 3. 3. Optical properties

Using UV-Vis spectroscopy has studied the optical properties of WO<sub>3</sub> powders obtained by precipitation method (**Figure 3.4**). All obtained WO<sub>3</sub> powders reflects green, reflection remains strong throughout the area visible, varying between 72% and 68% due to the ratio of reactants. The highest value of the reflectance was obtained for the powder with the report  $[WO_4]^{2-}:[H^+] = 1:20.$ 

Derivatives reflectance curves (Figure 3.4b) has one maximum for all samples (~ 442.3 nm), spectra is of sigmoid type, highlighting the relatively pure nature of WO<sub>3</sub>.



Figure 3.4. Diffuse reflectance spectra (a) and derivative diffuse reflectance spectra (b) of WO3 powders

Energy band gap of WO3 powders was estimated by the lambda "cut-off" and "absorption onset" methods, the results vary very little (2.58-2.63 eV).

#### 3. 3. 4. Morpho-structural characteristics

WO<sub>3</sub> powder obtained by precipitation method is porous,  $\sim 17.2 \text{m}^2/\text{g}$ , V<sub>pores</sub> =0.072m<sup>2</sup>/g, composed of meso-and macro pores, of nanometric particles  $\sim 49$  nm and triclinic structure.

Figure 3.7 shows that the surface powder is rough and porous, with spherical and elongated particles. Sizes range from 20 to 200nm. It is noted that although samples were prepared with different ratio of reactants, does not influence the shape or size of  $WO_3$  powder particles.



Figura 3.7. Imagini SEM (a) și TEM (b)a pulberii WO<sub>3</sub> (proba PP1)

#### 3. 4. Characterization of WO<sub>3</sub> powders obtained by sol-gel method

Thermograms obtained by TGA / DTG / DTA thermo gravimetric analysis and FT-IR spectra of precursors are typical tungsten trioxide hydrate, in the FT-IR spectra the formation of tungsten trioxide is indicated by its specific bands<sup>Error! Bookmark not defined.</sup>

#### 3. 4. 1. Additive inflence

Determination of **specific surface** allowed evaluation of tungsten trioxide powders porosity annealed at  $550^{\circ}$ C, in air for 30 minutes.

1	able 3.4. Specific sur	face and porosity of w	$O_3$ powders obtained in	the presence of porfier ag	ents
Sample	Composition	Specific surface	Average diameter	Average diameter	Particle
		BET method	meso-pores	macro-pores	size
		(m <sup>2</sup> /g)	BJH method (nm)	BJH method (nm)	(nm)
<b>SG1</b>	$WO_3$	5.9	22.5	81.2	141.3
SG2	WO <sub>3</sub> (PEG200)	16.2	22.8	101.3	51.9
SG3	WO <sub>3</sub> (PEG400)	20.3	25.7	83.2	41.2
SG4	WO <sub>3</sub> (PEG600)	21.7	21.5	96.0	38.6
SG6	WO <sub>3</sub> (MA)	17.7	14.1	110.1	47.3
<b>SG7</b>	WO <sub>3</sub> (CTAB)	31.4	10.2	92.0	26.7
<b>SG8</b>	WO <sub>3</sub> (NLS)	7.8	15.3	80.5	107.0

Table 3.4. Specific surface and porosity of WO<sub>3</sub> powders obtained in the presence of porifer agent

Higher specific surface of samples with PEG prove increasing porosity with the addition of porosity agent, the highest values for pore volume and surface area resulting in the mesopores. Particle size decreases with the addition of PEG and with increasing molecular weight, from 141 nm (SG1-WO<sub>3</sub>) at 38 nm (SG4-PEG600). The presence of regulators size particles increases the specific surface of WO3 powders and changes their porosity, become from the macro to the meso-porous powders. Particle size decreases with the addition of additives, values ranging between 141 nm (WO<sub>3</sub>-SG1) and 26.7 nm (CTAB-SG7).

#### 3.4.1.3. Optical properties

From recorded diffuse reflectance spectra, it appears that all powders reflects green colour (**Figure 3.15**). Reflectance not remains constant throughout the visible, the highest values being on the 482.5-530 nm domains. Maximum reflectance ranges from 67%, for the SG1 sample without additives and to 31% for the SG7 sample with CTAB.

Derivatives reflectance curves (**Figure 3.15b**) shows a single maximum at  $\sim 453$  nm. The corresponding derived reflectance curves of samples SG7- CTAB and SG8-NSL 2 maximum is observed, indicating that these powders also contain traces of additives, while other particles are relatively homogeneous, phenomenon revealed by sigmoid type of reflection spectra.



**Figure 3.15**. Diffuse reflectance spectra (a) and derived of diffuse reflectance spectra curves (b) of WO<sub>3</sub> powders prepared by sol-gel method

Powders behaviour in the ultraviolet was evaluated from absorption spectra (**Figure 3.16**). Depending on the additive used absorption threshold moves slightly to the left for all the samples, absorption peaks are located between 325 nm - 359 nm.



Figure 3.16. Absorption spectra obtained from diffuse reflectance spectra of powders of WO<sub>3</sub>

The band gap energy was estimated between 2.53-2.64 eV, by "on-set absorption" and "lambda "cut-of" methods, values obtained are in agreement with data from the literature for WO<sub>3</sub> powders.

#### 3. 4. 1. 4. Morpho-structural properties

From *structural point of view* (Table 3.9), the composition of WO3 powder is a mixture of phases, monoclinic (JCPDS 43-1035 sheet) and hexagonal (JCPDS 33-1387 sheet). WO3 powders prepared with organic modifiers contain crystallites of nanometric dimensions, significantly reducing particle size from 24.8 nm (SG1) to 11.4 nm (SG6, modifier MA) and 14.8 nm (SG7, modifier CTAB).

Although SG8 sample with modifier NSL probably contains crystallites of nanometric dimensions, however the addition of NSL does not decrease but increase particle size. Average crystallite size, D<sub>eff</sub>, determined by Warren-Averbach method, has values between 12 to 25 nm. Hence it can be concluded that nanostructured materials are obtained.

able 3.9. Microstructural parameters and parameters of the elementary cell of wO3 powders								
Sample	D <sub>eff</sub> [Å]	$< \varepsilon^{2} > \frac{hkl}{x10^{2}}$	a [Å]	b [Å]	с [Å]	V [Å] <sup>3</sup>	Beta [degrees]	Phase composition
801	249	0.200	7.311	7.542	7.698	424.55	90.32	89 vol. % mcl <sup>*</sup> -WO <sub>3</sub> (JCPDS 43-1035)
SGI	248	0.288	7.268	7.268	3.876	177.38	-	11 vol. % hxl**-WO <sub>3</sub> (JCPDS 33-1387)
			7.308	7.517	7.681	421.98	90.49	93 vol. % mcl-WO <sub>3</sub> (JCPDS 43-1035)
SG2	172	0.439	7.198	7.198	3.925	176.13	-	7 vol. % hxl-WO <sub>3</sub> (JCPDS 33-1387)
SC4	121	0.312	7.307	7.512	7.673	421.23	90.58	98 vol. % mcl-WO <sub>3</sub> (JCPDS 43-1035)
SG4	121	0.512	7.295	7.295	3.886	179.15	-	2 vol. % hxl-WO <sub>3</sub> (JCPDS 33-1387)
806	114	0 221	7.314	7.502	7.664	420.63	90.43	96 vol. % mcl-WO <sub>3</sub> (JCPDS 43-1035)
560	114	0.321	7.281	7.281	3.907	179.46	-	4 vol. % hxl-WO <sub>3</sub> (JCPDS 33-1387)
807	144	0.511	7.304	7.489	7.653	418.69	90.53	94 vol. % mcl-WO <sub>3</sub> (JCPDS 43-1035)
SG7	144	0.311	7.198	7.198	3.960	177.71	-	6 vol. % hexagonal-WO <sub>3</sub> (JCPDS 33-1387)
SG8	101	0.142	7.357	7.508	7.723	4.266	90.37	91 vol. % mcl-WO <sub>3</sub> (JCPDS 43-1035)
	484	0.142	7.284	7.284	3.916	179.97	-	9 vol. % hxl-WO <sub>3</sub> (JCPDS 33-1387)

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\*mcl - monoclinic

\*\*hxl - hexagonal



Figure 3.19. SEM images of WO3 powders (SG1), WO3-MA (SG6) and WO3-CTAB (SG7)

Of *morphologically WO<sub>3</sub> powders* obtained by sol-gel method consist of particles spherical, submicron, adherent (SEM images, **Figure 3.19**). As organic modifier is added there is a densification of the particles. TEM images in **Figures 3.20** of SG1 and SG6 powders indicate that WO<sub>3</sub> is uneven size. WO3 particle size is of 80 nm, and the powder with CTAB ranges from 23-60 nm.



Figure 3.20. TEM image of WO<sub>3</sub> powder without (SG1) and porosity agent (SG4)

Results obtained by transmission electron microscopy are consistent with the values obtained from profile analysis of diffraction bands which confirms the nanometric WO<sub>3</sub> powders prepared.

#### 3. 4. 2. Thermal treatment influence

#### 3. 4. 2. 1. Surface area and porosity

Thermal treatment of 550<sup>o</sup>C for 30 minutes or 90 minutes<sup>16</sup>, influence the specific surface and porosity of these samples (**Table 3.11**). It is noted that extension of the thermal treatment lowers the specific surface area.

Isotherms of adsorption-desorption of the WO3 sample can say that the pores sample are of the split regardless of the time of annealing (**Figure 3.22**). SG1-30 powder porosity is in the range meso-pores, and once with increasing annealing time (SG1-90) that undergoes a shift to the macro-pores (**Figure 3.22** top left).

	Surface	Surface Micro pore (t-plot)		Mes (B	Particle		
Sample	area BET (m²/g)	Total volume cm <sup>3</sup> /g	Total Area m²/g	Total volume cm <sup>3</sup> /g	Total Area m²/g	Average diameter nm	size * (nm)
SG1-30	5.93	0.000331	2.14	0.0453	5.72	103.73	141.30
SG1-90	4.87	0.000398	1.9641	0.0400	4.76	33.65	171.98
SG2-30	16.15	0.000725	5.6	0.1121	18.50	123.10	51.90
SG2-90	14.99	0.001333	6.5793	0.1132	16.46	27.49	55.87
SG3-30	20.34	0.001327	7.73	0.1577	22.67	108.81	41.20
SG3-90	17.56	0.001420	7.2189	0.1545	18.64	33.16	47.71
SG4-30	21.69	0.000931	7.37	0.1409	24.90	116.51	38.63
SG4-90	19.57	0.001774	8.3792	0.1498	22.42	26.73	42.82
SG6-30	17.72	0.000736	5.96	0.0829	21.87	124.22	47.29
SG6-90	14.73	0.001207	6.0838	0.0762	16.39	18.58	56.9
SG7-30	31.35	0.00224	11.92	0.1097	36.64	101.23	26.73
SG7-90	14.92	0.001374	6.6572	0.1013	15.77	25.70	56.16
SG8-30	7.83	0.000926	6.64	0.0529	7.96	95.07	107.04
SG8-90	3.79	0.000513	1. 9247	0.0206	3.25	25.31	220.57

Table 3.11. Specific surface and porosity characteristics of WO3 powders

Particle size was calculated with the formula:  $d = 6/Sx\rho_{WO3}$ , where  $\rho_{WO3} = 7.16g/cm^3$ , WO<sub>3</sub> theoretical density



**Figure 3.22**. Adsorption-desorption isotherms of WO<sub>3</sub> samples calcined for different durations (SG1-30 and SG1-90) and volume distribution of pores according to pore diameter (inset)<sup>16</sup>

Adding PEG site (**Figure 3.23**) determines the adjustment pores in the meso-pores domain, regardless of duration of thermal treatment. Comparing SG2-30 and SG2-90 see that the maximum of pore volume distribution curve moves to larger, sample containing a mixture of meso-and macro-pores.



**Figure 3.23**. Adsorption-desorption isotherms of WO<sub>3</sub> - PEG200 samples calcined for different durations (SG2-30 and SG2-90) and volume distribution of pores according to pore diameter (inset)<sup>16</sup>



**Figure 3.26**. Adsorption-desorption isotherms of  $WO_3$  - MA samples calcined for different durations (SG6-30 and SG6-90) and volume distribution of pores according to pore diameter (inset)

Adding methacrylic acid to  $WO_3$  powder and extended thermal treatment causes the regulation in the meso-pores, the distribution peaks at ~ 18 nm for the sample SG6-30, and sample SG6-90 ~ 32.6 nm, 44.7 nm and 67.5 nm. SG6-30 powder specific surface and porosity is greater than SG6-90 powder, powder porosity decreasing extension of thermal treatment (**Figure 3.26**).

Annealing time prolonged from 30 to 90 minutes leads to modification of porosity powder from meso- in macro-porous, so of sample prepared with porifer agents and those prepared with the particle size adjustment.

#### 3. 4. 2. 2. Optical properties

Some of the optical characteristics of WO<sub>3</sub> powders, based on diffuse reflection spectra are listed in **Table 3.12**. All WO<sub>3</sub> samples, with and without additives, have higher reflectance of 50% when subjected to thermal treatment for 90 minutes (**Figure 3.29**).

The best reflectance presents WO<sub>3</sub> powder, irrespective of thermal treatment applied. The extension of annealing time probably improved reflectance of the sample from 67% to 81%. Reflectance of the PEG200 sample not vary depending on thermal treatment time applied, as short polymer chain allowed the his removal of the sample after annealing at 550<sup>o</sup>C for 30 minutes<sup>Error! Bookmark not defined.</sup>



Figure 3.29. Diffuse reflectance spectra of WO<sub>3</sub> powders, without additives and with additives, thermal treated for 30 or 90 minutes

PEG's presence lowers the reflectance (between 56-53%) regardless of the molecular weight of polymer. The extension of annealing time to 90 minutes provides better removal of the additive, as evidenced by significantly increasing the reflectance with ~ 30% for PEG400, respectively PEG600 samples<sup>16</sup>.

A prolonged thermal treatment increases the reflectance with 30-40% for samples with MA (SG6) and CTAB (SG7), values close to those obtained for pure WO<sub>3</sub> sample. The result shows that these organic compounds are removed completely from the sample after treatment for 90 minutes at 550<sup>o</sup>C. Sodium lauryl sulfate (SG8) was not completely removed even when the sample was subjected to thermal treatment at 550<sup>o</sup>C for 90 minutes (at 30 minutes 41%, and 90 minutes 51%).

The samples treated for 30 minutes and 90 minutes, derived reflectance curve presents a single maximum (**Figure 3.30**). Maximum of the samples treated at  $550^{\circ}$ C/30 minutes is located at ~ 453nm and moving slightly to the red zone when adding PEG's and methacrylic acid. WO3 powders thermal treated for 90 minutes are cleaner; additives are removed completely or almost completely.



Figure 3.30. Derived diffuse reflectance spectra curves of WO<sub>3</sub> powders thermal treated for 30 or 90 minutes

In the extended thermal treatment from 30 to 90 minutes the optical properties of WO3 powders are improved considerably in the ultraviolet, absorption maximum being at higher values for all samples (**Figure 3.31**, **Table 3.12**).



Figure 3.31. Absorption spectra of WO<sub>3</sub> powders without additives and with additives, thermal treated for 30 or 90 minutes

Samula	Maximum	reflectance	Maximum :	absorbance	Wavelength	Fa
Sample	Wavelength	Reflectance	Wavelength	Absorbance	"cut-off"	Eg (eV)
cou	λ (nm)	R (%)	λ (nm)	A (u. a.)	$\lambda_{\text{cut-off}}$ (nm)	(ev)
SG1-30	519	67	352	0.54	481.5	2.58
SG1-90	563	81	360	0.61	488.9	2.54
SG2-30	495	52	327	0.44	484.6	2.56
SG2-90	496	53	328.5	0.43	485	2.55
SG3-30	512	56	330	0.46	490.8	2.53
SG3-90	548	78	334	0.60	496.1	2.50
SG4-30	510	55	325	0.47	482.9	2.57
SG4-90	545	80	332	0.60	494.1	2.51
SG6-30	509	49	359	0.40	487.8	2.54
SG6-90	545	80	355	0.60	495.7	2.50
SG7-30	482.5	31	335	0.19	469	2.64
SG7-90	549	71	334	0.54	495.4	2.50
SG8-30	496.5	41	350	0.32	481.3	2.58
SG8-90	496.5	51	354	0.40	482.5	2.57

Table 3.12. Optical characteristics of WO3 powders thermal treated for 30 or 90 minutes

Energy band gap (Eg) was evaluated in the absorption spectra obtained from the conversion of diffuse reflectance spectra (2.50-2.58 eV), values decrease as the addition of additives, and increase the duration of annealing.

Using a relatively long thermal treatment to obtain WO<sub>3</sub> powders improves their optical properties but lowers the porosity.

#### 4. Research on doped WO<sub>3</sub> powders

#### 4. 2. WO<sub>3</sub> powders doped with transitional metals

#### 4. 2. 1. Synthesis of the powders

WO<sub>3</sub> powders doping with transition metals (Cu, Ni, Mn and Ag) was achieved by impregnation of tungsten acid (sol-gel method), followed by thermal dissociation at 550°C for 30 minutes, in the air.

#### 4.2.2. Characterization of powders

#### 4. 2. 2. 1. Elemental analysis

Elemental analysis (ICP-OES method) of the doped powder showed the actual amount of dopant oxide (MOX), the results are close to those theoretically expected (Table 4.2).

Sample	Theoretical estimate	ICP-OES determination	The degree of ions
	$1 g MO_x / 100 g WO_3$	1gMO <sub>x</sub> $/100$ gWO <sub>3</sub>	conversion (%)
SG18-Cu	1	0.988	98.8
SG18-Mn	1	1.025	102.5
SG18-Ni	1	0.702	70.20
SG18-Ag	1	0.794	79.40
SG16-Cu 0.5	0.5	0.464	92.8
SG16-Cu 1	1	0.988	98.8
SG16-Cu 2	2	2.166	108.30
SG18-Ag 0.5	0.5	0.423	84.6
SG18-Ag 1	1	0.794	79.40
SG18-Ag 2	2	0.846	42.30

1 1 1 1 1 1 1 1

It can be concluded that the impregnation method by the thermal dissociation used to obtain MOx/WO3 powder, allowed obtaining WO3 powders doped with the desired oxide amount.

#### 4. 2. 2. 2. Surface area and porosity

Specific surface area and porosity measurements allowed the determination of specific surface, volume and total area of micro-, meso-and macro-pores of WO<sub>3</sub> powders doped with metal oxides. Surface area decreases when adding oxides in WO<sub>3</sub> powder, while under the influence of the type of oxide used the powder porosity increases. WO<sub>3</sub> powder doping with transition metals determines the movement of the maximum volume/area meso-pore distribution curve from the meso- to the macro-pores region (Figure 4.1). Average volume of meso- and

macro-pores increases with the addition of different oxides due to diversification every shape and size of pores.



Figure 4.1. Volume size distribution (a) and area (b) pore for MO<sub>x</sub>/WO<sub>3</sub> series

The decrease of specific surface powders with increasing meso-and macro-porosity is because these MO<sub>x</sub>/WO<sub>3</sub> powders were prepared by thermal dissociation, while WO<sub>3</sub> powder was obtained by sol-gel method.

#### 4. 2. 2. 3. Optical properties

Initial WO<sub>3</sub> powders (SG18) shows a strong reflection throughout the visible spectrum, peaks are situated in the green-yellow spectral range (**Figure 4.4**). WO<sub>3</sub> powder doping with oxides determines the maximum to higher wavelengths and reduce reflection. Change spectra is evidenced by the corresponding differential curves, the appearance of additional peak associated with the presence of  $MO_X$ , indicating multi-sigmoidal reflection spectra due to the effect of inclusion of oxides.



Figure 4.4. Diffuse reflectance spectra of (a) and derived diffuse reflectance spectra (b) of MO<sub>x</sub>/WO<sub>3</sub> systems

To estimate the energy band gap, according to the literature, we used the "lambda cutoff" value, with values between 2.55-2.43eV, band gap narrowing is because the metal was incorporated into the WO<sub>3</sub> powder after thermal cleavage (**Table 4.5**).

<b>Table 4.5.</b> The main absorbance characteristics of the $MO_x/WO_3$ s						
Samula	Lambda	a cut-off	Maximum absorbance			
Sample	$\lambda_{c}$ (nm)	E <sub>c</sub> (eV)	λ (nm)	A (a.u.)		
SG18	485.5	2.55	363.5	0.77		
SG18-Cu	509.6	2.43	358	0.68		
SG18-Mn	497.5	2.50	362	0.77		
SG18-Ni	507.9	2.44	360	0.82		
SG18-Ag	505.1	2.45	384	0.82		

If the variable amount of CuO doping is a reflection of the maximum displacement to higher wavelengths and a decrease in reflectivity, which at its peak position seems to not depend on the amount of oxide (Figure 4.6a). All derivative curves contain the same peak / band, in different reports, depending on the amount of CuO. Since the peaks on the derived curve correspond to the corresponding sigmoid inflection points, the maximum indicates the existence of several multi-sigmoidal reflection spectrums - an effect of CuO inclusions (Figure 4.6b).



Figure 4.6. Diffuse reflectance spectra (a) and derived diffuse reflectance spectra of CuO/WO<sub>3</sub> systems with different concentrations of dopant

CuO doping decreases monotonous of the band gap energy (band gap) with the workload, leading to 2.31 eV.

#### 4. 2. 2. 4. Morpho-structural properties

In the **Figure 4.8** the SEM images are presented of the WO<sub>3</sub> powders loaded with oxides of transition metals, compared with unchanged WO<sub>3</sub> powder.

Initial WO3 powder (sample SG18), unchanged, and is composed of submicron-sized spherical particles that form aggregates of varying sizes (**Figure 4.8a**).

MOx/WO3 samples prepared by impregnation of the WO<sub>3</sub>xH<sub>2</sub>O precursor with metal nitrates, followed by annealing at  $550^{\circ}$ C, kept broadly unchanged appearance WO<sub>3</sub> powder. The addition of salts of transition metals seems to promote the growth of primary particles, which indicates a slight action mineralization (**Figure 4.8b-e**).



Figure 4.8. SEM images of WO3 powders doped with transition metal oxides
a) SG18 (WO<sub>3</sub>); b) SG18-Ag (Ag<sub>2</sub>O/WO<sub>3</sub>); c) SG18-Cu (CuO/WO<sub>3</sub>);
d) SG18-Mn (MnO<sub>2</sub>/WO<sub>3</sub>); e)SG18-Ni (NiO/WO<sub>3</sub>)



Figure 4.11. TEM images of WO3 and MnO<sub>2</sub>-WO<sub>3</sub> powders (at different size)

SG18 sample is WO<sub>3</sub> powder containing particles of irregular shape with sizes ranging from 50-100nm (**Figure 4.11**). Manganese oxide is included in the WO<sub>3</sub> powder after impregnation, the particles are irregularly shaped, spherical and elongated, forming aggregates square (TEM image of 500nm). The presence of MnO<sub>2</sub> determines the particles increases to  $\sim$  200-300 nm.

#### 4. 2. 2. 5. Structural properties

X-ray diffraction patterns (**Figure 4.12**) shows that all samples obtained in our synthesis conditions have WO<sub>3</sub> monoclinic crystalline structure (according to ICSD 80 056 sheet), but the presence of oxides or mixed oxide is not found in any of the doped samples. Micro structural parameters and the average size of crystallites and the rate of deformation illustrates the inclusion of CuO,  $MnO_2$ , NiO and  $Ag_2O$  atoms in the monoclinic structure of WO<sub>3</sub> (**Table 4.8**).



Diffraction angle  $2\theta$  (degrees)

Figure 4.12. X-ray diffraction patterns of MO<sub>x</sub>/WO<sub>3</sub> samples

Sample	a [Å]	b [Å]	c [Å]	Angle γ [degrees ]	Elementary cell volume [Å <sup>3</sup> ]	The average size of crystallites D <sub>eff</sub> [nm]	<b>Deformation</b> <b>coefficient</b> $<\varepsilon^2 >^{1/2}_m \ge 10^3$
SG18	7.3255	7.5386	7.7095	90.241	425.746	94.7	1.908
SG18-Cu	7.3377	7.5452	7.7111	90.547	426.901	64.2	2.205
SG18-Mn	7.3514	7.5375	7.7104	90.601	427.219	84.2	1.479
SG18-Ni	7.3538	7.5379	7.7075	90.834	426.097	46.6	3.679
SG18-Ag	7.3260	7.5582	7.7150	90.339	427.172	63.3	1.141
SG16	7.3307	7.5466	7.7088	90.503	426.449	85.1	2.376
SG1-Cu2	7.3319	7.5479	7.7107	90.506	426.697	87.1	2.426

Table 4.8. Micro structural parameters of the MO<sub>x</sub>/WO<sub>3</sub> systems

Mean square coefficient of lattice deformation changes depending on how the inclusion of particle oxide Cu, Mn, Ni or Ag in WO<sub>3</sub> powder.

#### 4. 3. WO3 powders doped with noble metals

#### 4.3.1. Synthesis of the powders

WO<sub>3</sub> powders obtained by sol-gel method (SG16, SG18) were doped with noble metals, Pt and Pd by photolytic reduction.

#### 4.3.2. Characterization of powders

#### 4. 3. 2. 1. Elemental analysis

The quantities of ions of platinum and palladium introduced in the reaction were different from those determined by elemental analysis of samples, the highest conversion of ions  $Pt^{4+}$  in  $Pt^{0}$ , 3.44%, was achieved for SG16-Pt1 powder with 0.93g  $Pt^{4+}/100g$  WO<sub>3</sub>.

Since the amount of noble metal ions introduced in reaction different than that determined by elemental analysis, it can be said that photolytic reduction derives not controlled.

#### 4. 3. 2. 2. Surface area and porosity

WO<sub>3</sub> powder coating platinum increases the BET surface area from  $\sim 8.3\text{m}2 / \text{g} \sim 9.0\text{m}2 / \text{g}$  (SG16-Pt2), and porosity. The results can be explained by the high state of dispersion of platinum powder made by photolysis on the surface of WO<sub>3</sub> grains.

WO<sub>3</sub> powder doped with ions of palladium is meso-porous. These samples behave similar to those coated with platinum, because the loading of palladium ions increases the specific surface from ~  $8.3m^2/g$  to ~  $9.1m^2/g$  (SG18-Pd0.5) and porosity from ~ 0.0449 to ~  $0.0496cm^3/g$  compared to the starting powder.



Figure 4.14. Volume size distribution (a) and area (b) pore, Pt/WO<sub>3</sub> series

Submission platinum particles does not change much allure pore distribution curves and determine maxima only a slight shift of distribution to their higher values. The shape and position of peaks curves of distribution area and of the pore volume of Pt/WO<sub>3</sub> powder is similar to WO<sub>3</sub> powder. One can say that the surface of WO<sub>3</sub> particles is covered with nano particles of platinum.

#### 4.3.2.3. Optical properties

Initial WO<sub>3</sub> powders (SG16-Pt0) shows a strong reflection throughout the visible spectrum, with peaks situated in the green-yellow spectral range (**Figure 4.13a**).



Figure 4.13. Diffuse reflectance spectra and their derivatives for Pt/WO<sub>3</sub> systems

If doping platinum, reflection tends to move towards smaller wavelengths and decrease progressively with load factor, but reflection decrease is not directly proportional to the amount of platinum, suggesting that photolytic reducion not within control (**Figure 4.13**). WO3 particles that are coated with noble metal ions, platinum or palladium is shown by derived diffuse sigmoidal reflectance spectra with one maximum due to the mono-component and homogeneous powder (**Figure 4.13b**).

Coverage with noble metal monotonous increases the energy band gap with load factor (2.58-2.62eV), which could be correlated with nano-size metal particles. However small differences between the band gap energy values of clean and noble metal powder suggests once again that metal is deposited on the  $WO_3$  surface.

#### 4. 3. 2. 4. Morphological properties

WO<sub>3</sub> powders surface morphology was visualized by scanning electronic microscopy (SEM), **Figure 4.16**. It is noted that initial WO<sub>3</sub> powder (SG16 sample) is composed of submicron-sized spherical particles that form aggregates of varying sizes, which compacts the dispersion in an aqueous medium (SG16-Pt0). SEM images do not allow evidence certainly noble metal particles. On the surface of macro-particles can be observed other nano-particles "clusters"(noble metal).

TEM images indicate that WO<sub>3</sub> powder dispersed in water acidulated, SG18-Pd0, not change shape and size of particles initial WO<sub>3</sub> powder (spherical, <100nm).  $M^0/WO_3$  powder (SG16-Pt2, SG18-Pd2) contains with WO<sub>3</sub> particles, metal nanoparticles which are distributed unevenly throughout their surface (**Figure 4.18**).



Figure 4.16. SEM images of WO<sub>3</sub> (SG16); WO<sub>3</sub> ultrasonic (SG16-Pt0); Pt/WO<sub>3</sub> (SG16-Pt2) and Pd/WO<sub>3</sub> (SG18-Pd2) powders



Figure 4.18. TEM images of Pt/WO3 and Pd/WO3 powders with Pt and Pd nanoparticles view

It can be said that the noble metal particles are distributed on the surface of WO<sub>3</sub> powder due to thermal treatment, WO<sub>3</sub> obtained at  $550^{\circ}$ C and at M<sup>0</sup>/WO3 at  $120^{\circ}$ C, and because the preparation method of powders.

#### 4.3.2.5. Structural properties

X-ray diffraction patterns of samples prepared were used to calculate the elementary cell parameters and the average crystallite size (**Table 4.14**).

	Table	4.14. Micr	ostructural	parameters t	for Pd/WO3 and	Pt/WO3 systems	
Sample	a [Å]	b [Å]	с [Å]	Angle γ [degrees ]	Elementary cell volume [Å <sup>3</sup> ]	The average size of crystallites D <sub>eff</sub> [nm]	Deformation coefficient <ε <sup>2</sup> > <sup>1/2</sup> <sub>m</sub> x 10 <sup>3</sup>
SG16	7.3302	7.5449	7.7067	90.501	426.208	85.1	2.426
SG16-Pt 0	7.3296	7.5531	7.7141	90.514	427.048	100.4	1.739
SG16-Pt 2	7.3235	7.5458	7.7063	90.561	425.843	103.4	2.201
SG18	7.3255	7.5386	7.7095	90.241	425.746	94.7	1.908
SG18-Pd 0	7.3296	7.5531	7.7141	90.514	427.048	100.4	1.739
SG18-Pd 2	7.3305	7.5601	7.7190	90.368	427.773	85.8	1.205

 $WO_3$  powders contain crystallites with sizes between 85-95nm which the ultrasonic tend to exceed 100nm. The presence of metal ions does not influence the crystallite size or deformation coefficient.

X-ray diffraction patterns X (**Figure 4.19**) illustrates that all samples obtained in our synthesis conditions have the monoclinic crystalline structure of WO<sub>3</sub>, according to the ICSD80056 sheet<sup>17</sup>.



Figure 4.19. X-ray diffraction patterns of Pt/WO3 and Pd/WO3 systems

Powder loaded with platinum ions, palladium, respectively, does not change the monoclinic structure of WO<sub>3</sub>. From X-ray diffraction patterns it not observed the presence of Pt in the sample SG16-Pt2 or Pd in the sample SG18-Pd2. This confirms that the noble metal nanoparticles are dispersed uniformly on the surface of WO<sub>3</sub> particles.

#### 5. Research on applicative potential of WO<sub>3</sub> films and powders

#### 5. 2. WO<sub>3</sub> thin films

#### 5. 2. 2. Electrochromism evaluation

Highlighting electrochromic properties of the films was done by investigating the optical properties after application of electric current and evaluating the coloring efficiency. For a better comparison of results, optical measurements were made for each sample after 20 cycling; working conditions are those of the cyclic voltametry are those of the electrochemical study.

#### 5. 2. 2. 1. Influence of electric current on the optical properties

 $WO_3$  films transmittance throughout the visible is good. After applying electric current films change color in bright blue, the maximum transmission moving to lower wavelengths, in 491-504 nm domain (**Figure 5.4**). The transmittance of films decreases by 10-30%, depending on the number of layers deposited on the support, regardless of sol composition, the thickness and type of treatment applied to the substrate.



Figure 5.4. Transmission spectra of WO<sub>3</sub>/ITO/Glass/WO<sub>3</sub> multilayer film, sol-gel method (a) and ion exchange method(b), before and after application of electric current



Figure 5.7. Tauc representations,  $(\alpha h v)^{1/2} vs. hv$ , of WO<sub>3</sub>/ITO/Glass/WO<sub>3</sub> samples, sol-gel method (a) and ion exchange method (b), before and after application of electric current

*Band gap energy of the films* is an important optical parameter in the use of films as electrochromic devices. For sol-gel films additive does not affect the value of gap energy, but applying electric current causes a slight increase from 3.3 to 3.4eV (**Figure 5.7**). WO<sub>3</sub> films obtained by ion exchange method have thicknesses ranging from 35-92 nm. For these films band

gap energy value is between 3.1-3.5eV, film thickness influence this value. After current application, Eg increases for all films,  $Eg_c = 3.4 - 3.6eV$  (Figure 5.7).

#### 5. 2. 2. 2. Coloring efficiency

Coloring efficiency and stability of WO<sub>3</sub> films are important characteristics of electrochromic devices, with their help assessing the performance of electrochromic materials obtained. Coloring efficiency ( $\eta$  (EC)) requires the correlation of cyclic voltammetry measurements (interleaved charge Q) with optical transmission measurements of the films (optical density OD) (**Table 5.3**) and was due to electrochemical and optical films analyzed.

Table 5.3. Coloring efficiency of WO3 films										
Sample	T <sub>c max</sub> (%)	λ <sub>c</sub> max (nm)	Charge q (C)	Optical density (ΔΟD)	Coloring efficiency η(CE) (cm²/C)					
R4 I1	85	475	0.007	-0.0325	-41.8					
R4 I2	61	544	0.039	0.0179	4.1					
R4 I6	89	478	0.185	-0.0629	-3.1					
R4 I7	51	464	0.092	0.0932	9.1					
R4 I8	81	478	0.025	-0.0444	-15.8					
FW10 I2	55	507	0.101	0.0514	9.1					
FW10 I3	42	489	0.158	0.0521	5.9					
FW10 I4	36	491	0.165	0.0775	8.4					
FW11 I2	63	648	0.050	0.0190	6.8					
FW11 I3	64	624	0.132	0.0067	0.9					
FW11 I4	60	569	0.160	0.0141	1.6					

All WO<sub>3</sub> films obtained by sol-gel method, without and with polymer additive, have a positive coloring efficiency, located between 0.9-9.1 cm<sup>2</sup>/C, because the absorption increases the ion insertion. WO<sub>3</sub> films prepared by ion exchange method have coloring efficiency of both positive and negative staining. Negative values are determined by the decreased of absorption the ion insertion due to low thickness, film in- homogeneity films and surface loss due to existing water molecules were not completely removed from the thermal treatment.

Given that the films obtained by sol-gel method are amorphous and those obtained by ion exchange method has monoclinic structure, one can say that the crystalline structure does not affect the coloring efficiency of the films.

#### 5. 2. 2. 3. Stability

For this study we have chosen the following WO<sub>3</sub> films: **R4 I7** ( $\eta$ (CE)=9.1 cm<sup>2</sup>/C); **FW10 I3** ( $\eta$ (CE)=5.9 cm<sup>2</sup>/C); **FW11 I2** ( $\eta$ (CE)=6.8 cm<sup>2</sup>/C).

 $WO_3$  films were cycled for a long time in 0.01M H<sub>2</sub>SO<sub>4</sub> electrolyte to analyze their degradation over time (**Figure 5.9**). R4 I7 film (ion exchange method, support treated with ammonia) is the most stable. Film on the substrate resistance is very high, along insertion, extraction protons respectively during the 100 cycling, has one anodic peak, suggesting that the

film has a tendency to detach from the substrate, or with naked eye there was no damage to the film.

The FW10 I3 film lasted 72 cycling, WO<sub>3</sub> deposited layers do not form a single layer support, but three consecutive layers between which water molecules can easily infiltrate and destabilize layers deposited on the ITO support.

FW11 film with porosity agent FW11 I2 (WO<sub>3</sub>(PEG400)) behave FW10 I3 analog film, the difference is that the porous nature of its water molecules penetrate more easily and contributes to the deterioration of electrochemical. Damage electrochemical behavior after a certain number of the cycling is due to surface loss.



**Figure 5.9**. Cyclic votamograma of multi-layer films: R4 I7, FW10 I3, FW11 I2, testing electrolyte stability 0.01M H<sub>2</sub>SO<sub>4</sub>, v=50mVs<sup>-1</sup>, E=-1V ÷ +1 V vs. Ag/AgCl/KCl<sub>sat</sub>

Increased stability of these films, and good coloring efficiency that has, allows these films to be successfully used in the manufacture electrochromic and photo electrochemical cells.

#### 5. 3. Meso-porous WO3 powders

#### 5. 3. 1. General presentation of photo catalytic tasted powders

Photocatalytic activity of prepared powders was highlighted by the study of photodegradation of two dyes, methylene blue and methyl orange, where WO<sub>3</sub> powder was used as photocatalyst. Photodegradation efficiency of methylene blue on WO3 powder was: 20% WO<sub>3</sub>- precipitation; 82% WO<sub>3</sub>-sol-gel and 32% WO<sub>3</sub>(PEG400)-sol-gel. This can be explained by the fact that the sol-gel method were obtained meso-porous WO3 powders, which favors photocatalytic activity.

Of the three WO<sub>3</sub> powder, was chosen sample prepared by sol-gel method without additive, whose properties have been improved by doping with different metals or metal oxides, and then used as photocatalysis for degradation of dyes, methylene blue and methyl orange.

#### 5. 3. 3. Photo catalytic activity evaluation

#### 5. 3. 3. 1. Methylene blue degradation

Photocatalysis tests were conducted by immersing the  $TiO_2$  and  $WO_3$  powder in solution of methylene blue, 0.0125 mM concentration. These tests were repeated in the presence of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%) that brings a surplus of electrons necessary to reduce the influence of recombination process of charge carriers.

In **Figure 5.10** we can see that all samples have the photodegradation efficiency of 50%. The best results were obtained for WO<sub>3</sub> samples doped with platinum, whose yields are up to  $\sim$  80%.



Figure 5.11. . Methylene blue photodegradation efficiency in  $H_2O_2$  presence

With the addition of hydrogen peroxide solution (**Figure 5.11**) reveals photodegradation efficiency by the value of ~ 90% (SG16-Pt2 sample). Except for the sample of titanium dioxide, all the other samples have efficiencies of between 80 and 90%. If WO3 is used as a catalyst, the low photoactivity of catalyst is due to rapid recombination of electrons and holes photo generated.

WO<sub>3</sub> doping with transition metal ions slows down the electron-hole recombination, leading to increased photocatalytic activity either by removing electrons or by modifying the surface properties of the material.

#### 5. 3. 3. 2. Methyl orange degradation

The study involved immersion  $WO_3$  powders in methyl orange solution, concentration 0.0125mM, with or without the addition of hydrogen peroxide, degradation process was monitored by UV-Vis spectroscopy, compared with TiO<sub>2</sub> Degussa P25 powder used as a control sample.



**Figure 5.13**. Efficiency of catalysts used in photodegradation of methyl orange solution: a. Methyl orange -H<sub>2</sub>O; b. Methyl orange -H<sub>2</sub>O<sub>2</sub>

In Figure 5.13 we can see that for Methyl orange- $H_2O$  system, all samples were photodegradation efficiency of 15%, doped samples showing greater efficiency than non-modified WO<sub>3</sub> powder. The highest efficiency, ~30.9%, SG18-Pd1 sample has (ICP-OES estimates, 0.068g Pd/100g WO<sub>3</sub>). Note, however, is that all of WO<sub>3</sub> powders have

photodegradation efficiency of methyl orange less than titanium dioxide. The addition of hydrogen peroxide in the investigated system dye causes a dramatic increase in the efficiency of catalysts, over 95% for all samples (**Figure 5.13b**).

The presence of co-catalysts, especially noble metals (they cover the surface of  $WO_3$ ), regardless of the aqueous system used, improves the efficiency of tungsten trioxide in the photodegradation of dyes.

## Establishing optimal working conditions for determining the maximum efficiency of degradation of dyes on the substrate based on $WO_3$ powder

For these studies samples were chosen for the photodegradation efficiency is maximum, namely, **SG18-Pd2**, 35% and **SG16-Pt1**, 31%, and starting materials **SG18**, 24% and **SG18-Pd0**, 22%.

*a)* Influence of irradiation time on the efficiency of photodegradation of methyl orange on WO3, WO3 ultrasonic Pt/WO<sub>3</sub> and Pd/WO<sub>3</sub> substrate

In **Figure 5.18** are showed the photodegradation efficiencies based on the time of irradiation. In a period of 360 minutes was observed that the efficiency changes depending on the sample not only used but also on the time of irradiation. After tests was determined the optimum time of irradiation as follows: - 240 minutes – for the clean WO<sub>3</sub>(SG18) powder

- 180 minutes for ultrasonic WO<sub>3</sub> (SG18-Pt0) powder
- 360 minutes for M<sup>0</sup>/WO<sub>3</sub> (SG18-Pt1 and SG18-Pd2) powder
- *b)* Influence of initial concentration in the photodegradation of the methyl orange on WO<sub>3</sub>, WO<sub>3</sub> ultrasonic Pt/WO<sub>3</sub> and Pd/WO<sub>3</sub> substrate



Figure 5.19. Methyl orange optimal concentration using WO<sub>3</sub> substrate doped with Pd, for optimal irradiation time corresponding

Of the five different concentrations of methyl orange chosen, methyl orange photodegradation efficiency is maximum at the 0.0125 mM concentration of dye.

## c) Influence the amount of photocatalytic powder on the photodegradation efficiency of methyl orange

After determining the optimum time of irradiation and the optimum working concentration, we determined the optimal amount of sample used with maximum efficiency in methyl orange photodegradation (Figure 5.20).



Figure 5.20. Optimum amount of powder for methyl orange photodegradation , SG16-Pt1, 25mL MO, 0.0125 mM, irradiation time 6 hours

Increasing the amount of powder, from 0.025g to 0.2g greatly reduces the efficiency of methyl orange photodegradation, due to powder clogging and reduces the number of active centers. Therefore the optimal amount of WO3 powder is 0.025g in 0.0125mM methyl orange.

Studies were conducted to determine the optimal working conditions recommended:

1. Using  $WO_3$  powder coated with finely divided noble metals:

Pt/WO<sub>3</sub> (SG16-Pt1), Pd/WO<sub>3</sub> (SG18-Pd2);

- 2. Optimum weight is 0.1 g powder / 100 mL methyl orange;
- 3. Optimum concentration is 0.0125 mM;
- 4. Optimum time of irradiation is 360 minutes;
- 5. Using hydrogen peroxide,  $10^{-5}$ mL H<sub>2</sub>O<sub>2</sub> 10% / 1 g powder, improves the photodegradation efficiency.

#### 5. 3. 3. 3. Kinetic aspects of photocatalytic activity

The kinetic aspects study was to examine the kinetic models describing the photodegradation reaction of methyl orange on the substrate of undoped and doped WO<sub>3</sub> powder with noble metals, palladium and platinum.

Photodegradation process takes place in two stages: adsorption of the methyl orange on WO3 substrate, described by Freundlich adsorption isotherm and photodegradation reaction.

Kinetic models that were tested to describe the methyl orange photodegradation on WO<sub>3</sub> powder are: (i) one corresponding to a pseudo-first order reaction, (ii) the corresponding to a

pseudo-second order reactions, (iii) intra-particle diffusion. In addition to these kinetic models, it is important to examine the nature of reaction products resulting from the photocatalysis process.

To determine the kinetic model that better describes the photodegradation of the methyl orange on the WO3 powder doped and doped substrate to compare the rates of reaction constants and regression factors determined for the three kinetic models studied (**Table 5.9**).

Table 5.9. Comparison between rate constants and regression factors determined for kinetic models studied								
	Sample	Langmuir-		Pseudo-second order		Intra-particle diffusion model		
		Hinshelwood model		kinetics model				
		k <sub>L-H</sub>	$\mathbb{R}^2$	k <sub>2</sub> (g/mg*min)	$\mathbb{R}^2$	$k_{dif}$ (mg*min <sup>1/2</sup> /g)	$\mathbb{R}^2$	
	SG18	5.33*10 <sup>-4</sup>	0.57	8.58	0.86	$1.27*10^{-4}$	0.68	
	SG16-Pt0	$4.62*10^{-4}$	0.47	10.02	0.86	$1.13*10^{-4}$	0.59	
	SG16-Pt1	$6.41*10^{-4}$	0.61	5.81	0.80	$1.41*10^{-4}$	0.66	
	SG18-Pd2	$8.98*10^{-4}$	0.79	3.62	0.86	$1.99*10^{-4}$	0.87	

Of these, the pseudo-second order kinetics model has the biggest factor regression, between 0.80-0.86 for all samples with and without platinum or palladium content.

Methyl orange photodegradation process on the substrate of undoped and doped WO3 powder is described by the pseudo-second order kinetics model. With UV-Vis spectroscopy was observed that the reaction takes place without soluble secondary products. The only possible as the gas produced.

#### **GENERAL CONCLUSIONS**

The achieved studies have contributed to the broadening of the domain of scientific knowledge of the oxide semiconductor materials field based on tungsten trioxide with electrochromic and photocatalytic properties and demonstrated the possibilities of application of the materials obtained.

> The WO<sub>3</sub> thin films were obtain by dip-coating technique (*ion exchange and sol-gel methods*), the optimal thermal treatment was  $350^{\circ}$ C/30 minutes at the end of deposition cycles.

➢ In *ion exchange* method, the most efficient asperization treatment is that with ammonia, because gave to the film the best electrochemical stability.

Amorphous structure, small particle size and porous nature are favorable to the growth of the electrochemical response.

 $\succ$  The films obtained by on exchange method presents a good electrochemical stability; an important role have the film thickness, soil deposition and especially the treatment of the substrate before deposition.

> It shown that the WO<sub>3</sub> films deposited on ITO support are electrochromic. The long stability and the high coloring efficiency unsure the success of their use in the manufacture of electrochromic devices and of the electrochemical cells.

 $\succ$  The optical, morphological and structural properties of WO<sub>3</sub> powders, obtain by precipitation method, are not influenced by the ratio of reactants.

> WO<sub>3</sub> powders prepared by *sol-gel method* contain a mixture of meso- and macro-pores. The addition of polimeric agents determines the obtaining of meso-porous powders, 550<sup>o</sup>C/30 minute thermal treatment, and macro-porous powders.

Sol-gel method, unlike the precipitation method, ensures the formation of a WO3 mesoporous powders with a higher degree of dispersion, with better morpho-structural and optical properties.

 $\succ$  WO<sub>3</sub> powders doped with transition metal oxides (CuO, NiO, MnO<sub>2</sub>, and Ag<sub>2</sub>O) and WO<sub>3</sub> powders loaded with platinum and palladium were obtain by impregnation (thermal dissociation) and photolytic reduction method.

> The oprtical and morphological properties of doped powders showed the inclusion of the oxides in WO<sub>3</sub> powder and the cover with the precious metals of WO<sub>3</sub> powder. The synthesis methods used allowed a good degree of doping control with metal oxides, but not of the platinum or palladium.

 $\succ$  The undoped and doped WO<sub>3</sub> powders were used as photocatalysts in degradation of methyl orange and methylene bule dyes.

> Meso-porous WO<sub>3</sub> powder (sol-gel method) showed the best photocatalytic activity, compared with the powder prepared with polymer additive (sol-gel method) and macro-porous WO<sub>3</sub> powder (precipitation method).

 $\succ$  Meso-porous and submicron WO<sub>3</sub> powders doped with CuO, Ag<sub>2</sub>O, MnO<sub>2</sub>, NiO and finely divided Pd and Pt shows efficiency in the photochemical degradation of dyes, especially in aqueous systems with added hydrogen peroxide.

> The photo degradation process takes place without soluble secondary products (evaluated by UV-Vis spectroscopy), the only likely be gaseous products. The studies on the photodegradation process of methyl orange on WO<sub>3</sub> powder lea to the establishment of optimal working conditions.

Some of the obtained results were have made the subject-matter of eight scientific papers, already published or in press and of eight participations in international and national conferences.

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#### List of scientific works of thesis topic

- M. Stefan, <u>E. Bica</u>, L. E. Muresan, E. Indrea, E. J. Popovici, *Studies on some tungsten trioxide powders*, Journal of Optoelectronics and Advanced Materials Symposia, 2009, 1(6), 1004-1007.
- 2. <u>E. Bica</u>, M. Stefan, L. E. Muresan, E. Indrea, I. C. Popescu, E. J. Popovici, *Characterization of some tungsten trioxide thin films obtained by dip-coating*, Journal of Optoelectronics and Advanced Materials Symposia, **2009**, *1*(6), 1011-1014.
- 3. <u>E. Bica</u>, L. E. Muresan, L. Barbu-Tudoran, E. Indrea, I. C. Popescu, E. J. Popovici, *Studies on WO3 thin films prepared by dip-coating method*, Studia Universitatis Babes-Bolyai, Chemia, LIV, **2009**, *3*, 15-22. (*ISI*)
- 4. M. Stefan, <u>E. Bica</u>, L. Muresan, R. Grecu, E. Indrea, M. Trif, E. J. Popovici, *Synthesis and characterization of tungsten trioxide powders prepared by sol-gel route*, Journal of Optoelectronics and Advanced Materials –Symposia, **2010**, *2(1)*, 115-118.
- <u>E. Bica</u>, M. Stefan, I. C. Popescu, L. E. Muresan, M. Trif, E. Indrea, E.J.Popovici, *Nanostructured tungsten trioxide thin films*, Journal of Optoelectronics and Advanced Materials – Symposia, 2010, 2(1), 107-110.
- 6. <u>E. Bica</u>, E. J. Popovici, M. Stefan, I. Perhaiţa, I. C. Popescu, *Synthesis of tungsten trioxide mesoporous powders prepared by inorganic sol-gel route*, Studia Universitatis Babes-Bolyai, Chemia, XLV, **2010**, 2 (I), 169-177.
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- 8. <u>E. Bica</u>, E.-J. Popovici, M. Ștefan, I. Perhaița, L. Barbu-Tudoran, E. Indrea, I. C. Popescu, *Morphological, structural and optical characterization of tungsten trioxide films prepared by sol-gel route,* trimis la tipar Digest-Journal of Nanomaterials and Biostructures.

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- 1. E. J. Popovici, F. Imre-Lucaci, L. Muresan, M. Stefan, <u>E. Bica</u>, R. Grecu, E. Indrea, *Spectral investigations on niobium and rare earth activated yttrium tantalate powders*, Journal of Optoelectronics and Advanced Materials, **2008**, *10*(9), 2334 2337.
- E. J. Popovici, M. Nazarov, L. Muresan, D. Y. Noh, <u>E. Bica</u>, M. Morar, I. Arellano, E. Indrea, Studies concerning the properties of some europium activated phosphors based on yttrium tantalite, Physics Procedia, 2009, 2, 185–190.
- 3. E. J. Popovici, M. Stefan, F. Imre-Lucaci, L. Muresan, <u>E. Bica</u>, E. Indrea, L. Barbu-Tudoran, *Studies on the synthesis of cerium activated yttrium aluminate phosphor by wet-chemical route*, Physics Procedia, **2009**, *2*, 603–616. (*BDI*)
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- 5. A. I. Cadis, A. R. Tomsa, <u>E. Bica</u>, L. Barbu-Tudoran, L. Silaghi-Dumitrescu, E. J. Popovici, *Preparation and characterization of manganese doped zinc sulphide nanocrystalline powders with luminescent properties*, Studia Universitatis Babes-Bolyai, Chemia, LIV, **2009**, *3*, 23-29.
- 6. L. Muresan, M. Stefan, <u>E. Bica</u>, M. Morar, E. Indrea, E. J. Popovici, *Spectral investigations of cerium activated yttrium silicate blue emitting phosphor*, Journal of Optoelectronics and Advanced Materials-Symposia, **2010**, *2*(*1*), 131 135.
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- M. Stefan, E. J. Popovici, <u>E. Bica</u>, L. E. Muresan, A. Cadis, E. Indrea, *Studies on the synthesis of some oxidic powders with controlled particles size*, 2<sup>nd</sup> European Chemistry Congress, EuChems, Torino, Italia, 2008, no 12765.
- <u>E. Bica</u>, M. Stefan, I. C. Popescu, L. E. Muresan, M. Trif, E. Indrea, E. J. Popovici, *Nanostructured tungsten trioxide thin films*, 4<sup>nd</sup> International Conference Advanced Spectroscopies on Biomedical and Nanostructured Systems, NANOSPEC, Cluj-Napoca, Romania, 2008, p. 103.
- M. Stefan, <u>E. Bica</u>, L. E. Muresan, E. Indrea, E. J. Popovici, *Synthesis and caractherization of tungsten trioxide powders prepared by sol-gel route*, 4<sup>nd</sup> International Conference Advanced Spectroscopies on Biomedical and Nanostructured Systems, NANOSPEC, Cluj-Napoca, Romania, **2008**, p. 138.
- 5. M. Stefan, <u>E. Bica</u>, L. E. Muresan, E. Indrea, E. J. Popovici, *Sol-gel synthesis of nanostructured tungsten trioxide powders*, International Conference on Materials Science and Engineering, BraMat, Brasov, Romania, **2009**, P.6.04.
- <u>E. Bica</u>, M. Stefan, L. E. Muresan, E. Indrea, I. C. Popescu, E. J. Popovici, *Characterization of some tungsten trioxide thin films obtained by dip-coating*, International Conference on Materials Science and Engineering, BraMat, Brasov, Romania, 2009, P.6.05.
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- 8. <u>E. Bica</u>, E. J. Popovici, E. Indrea, R. C. Suciu, M. C. Rosu, *Rietveld refinement of powder X-ray diffraction of nanocrystalline transition metals tungsten trioxide*, 9<sup>th</sup> International Symposium of the Romanian Catalysis Society, RomCat, Iași, România, **2010**, pag. 95-96.

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- S. Astilean, M. Baia, D. Maniu, L. Baia, F. Toderas, <u>E. Bica</u>, M. Iosin, O. Popescu, C. Craciun, L. Barbu-Tudoran, C. Socaciu, J. Popp, P. L. Baldeck, *Bio-plasmonics: Sensing biomolecular interactions with gold nanoparticles*, 2<sup>nd</sup> International Conference Advanced Spectroscopies on Biomedical and Nanostructured Systems, NANOSPEC, Cluj-Napoca, Romania, 2006, p. 61.
- A. Saponar, E. J. Popovici, N. Popovici, <u>E. Bica</u>, G. Nemes, I. Silaghi-Dumitrescu, *Narrow rim alkenyl calix[n]arenes*. *Synthesis and spectral characterization*, 5<sup>th</sup> Conference of Isotopic and Molecular Processes, PIM, Cluj-Napoca, Romania, 2007, p. 206.
- E. J. Popovici, F. Imre-Lucaci, L. E. Muresan, M. Stefan, <u>E. Bica</u>, E. Indrea, Spectral investigations on niobium and rare earth activated yttrium tantalate powders, 5<sup>th</sup> Conference of Isotopic and Molecular Processes, PIM, Cluj-Napoca, Romania, 2007, p. 204.
- L. E. Muresan, E. J. Popovici, M. Stefan, <u>E. Bica</u>, E. Indrea, *Studies on the synthesis of yttrium silicate phosphors from rare earth precursors obtained by wet-chemical route*, The 15<sup>th</sup> International Conference on Luminescence and Optical Spectroscopy of Condensed Matter, ICL'08, Lyon, Franta, **2008**, We-P-111, pag 540.
- E. J. Popovici, M. Stefan, F. Imre-Lucaci, L. Muresan, <u>E. Bica</u>, E. Indrea, L. Barbu-Tudoran, *Studies on the synthesis of cerium activated yttrium aluminate phosphors by wet-chemical route*, The 15<sup>th</sup> International Conference on Luminescence and Optical Spectroscopy of Condensed Matter, ICL'08, Lyon, Franta, 2008.
- 6. L. E. Muresan, E. J. Popovici, M. Stefan, <u>E. Bica</u>, M. Morar, E. Indrea, Spectral investigations

of cerium activated ytium silicate blue emitting phosphor, 4<sup>nd</sup> International Conference Advanced Spectroscopies on Biomedical and Nanostructured Systems, NANOSPEC, Cluj-Napoca, Romania, **2008**, p. 121.

- 7. E. J. Popovici, M. Nazarov, L. Muresan, D. Y. Noh, M. Morar, <u>E. Bica</u>, E. Indrea, *Studies on terbium activated yttrium based tantalate phosphors*, 7th European Conference on Luminescent Detectors and Transformers of Ionizing Radiation, iul 12-17, **2009**, Cracovia, Polonia
- 8. E. J. Popovici, M. Morar, L. Muresan, <u>E. Bica</u>, L.Barbu-Tudoran, E. Indrea, Studii privind sinteza si caracterizarea unui luminofor pe baza de aluminat de ytriu dopat cu ceriu, cu proprietati controlate, a 9-a ediție a Seminarului Național de Nanoștiință și Nanotehnologie, **2010**, București, Romania.
  - 9. A. I. Cadis, E. J. Popovici, <u>E. Bica</u>, I. Perhaița, L. Barbu-Tudoran, E. Indrea, *Studies on the synthesis of manganese doped zinc sulphide nanocrystalline powders using methacrylic acid as additive*, **2010**, International Semiconductor Conference, CAS, Sinaia, Romania, 513-516.

#### List of research projects of thesis topic

- 1. Hydrogen Production by photoelectrolytic way -HIDROSOL (MENER-CEEX-710/2006), research team member, 2006-2009.
- 2. Complex photocatalytic systems for advanced treatment of wastewater from textile industry -FOTOCOMPLEX (**PN2-PARTENERIATE 71-047/2007**), research team member, 2007-2010.

#### **Research internship**

- noiembrie 2008 Institute of Physical Chemistry of the Romanian Academy, Bucharest, CS I Marilena Vasilescu – Spectral methods of characterization of materials with special properties
- noiembrie 2009 Transylvania University Braşov, Faculty Materials Science and Engineering, Department of Chemistry, Prof. Dr. A. Duță Testing the photocatalytic activity of materials based on tungsten trioxide powder in the degradation of dyes; Optical spectroscopy measurements in the ultraviolet visible.
- ianuarie 2010 Transylvania University Braşov, Faculty Materials Science and Engineering, Department of Chemistry, Prof. Dr. A. Duță Testing the photocatalytic activity of materials based on tungsten trioxide powder in the degradation of dyes; Optical spectroscopy measurements in the ultraviolet visible, spectrophotometer *Perkin Elmer Lambda 25*.