Ecaterina Bica

TUNGSTEN TRIOXIDE
UNCONVENTIONAL MATERIALS WITH SPECIAL OPTICAL AND ELECTRICAL PROPERTIES

Summery of PhD thesis

Scientific advisor
Phd Prof. Ionel Cătălin Popescu

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Ecaterina Bica

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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 Brunauer-Emmet-Teller method
- CTAB – Cetyl trimethylammonium bromide
- CV – Cyclic Voltammetry
- DTA - Differential Thermoanalysis
- Eg – Band Gap Energy
- FTIR- Fourier Transform- 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 - Transmission 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 WO3 films present the highest coloring efficiency in visible and infrared spectral domain1, 2. For this reason, optical, electrochemical and structural morphological characterization is a mandatory requirement to establish their quality and efficiency.

The literature data shows that the specific properties of tungsten trioxide based materials (electrochromism and photocatalysis) are in correlation with the composition, morphology and dimension particles, the porosity and optical characteristics of WO3 films and powders. This properties are influenced by the obtaining process3, 4, 5, 6. From this reason, the WO3 powders were obtain by methods that allows the control of properties since the preparation stage. The doping of powders increase the efficiency of this materials in applications7, 8.

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 WO3 films and powders. The specific characteristics and the diversity of domain applications revealed by literature data determined the study of WO3 films and powders.

The second part contains the original research realized in order to obtain new WO3 films with applicative potential in electrochromic devices domain and also to obtain new WO3 undoped and doped powders, using as photocatalysts 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 WO3 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 nanostructured powders were prepared by precipitation and sol-gel methods. By sol-gel method were obtain WO3 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 WO3 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, Brașov (Prof. Dr. Anca Duță).
II. ORIGINAL CONTRIBUTIONS

2. Research on WO₃ thin films

2. 2. Synthesis of the WO₃ thin films

Ion exchange method⁹,¹⁰ is based on passing a solution of sodium tungstate over an ion exchange resin, loaded with H⁺ 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 WO₃ were performed several cycles of deposition, by several dipping-drying cycles. After deposition, WO₃ conversion was performed after the thermal treatment at 250-550⁰C.

Another series of films were deposited in a hydrated WO₃ sol obtained by sol-gel method, from the reaction of tungsten powder and hydrogen peroxide. The method allowed the study of the influence of certain preparative factors on WO₃ thin films properties: dipping-drying cycle’s number, adding the polymer agent (PEG400, PEG600)¹¹, roughing type (ethylene glycol: NaOH for optical glass support and acetone: ethanol for ITO glass support), substrate type and annealing temperature (350-550⁰C).

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 350⁰C, and the organic materials are total eliminated only at 550⁰C.

2. 3. Characterization of WO₃ thin films obtained by ion exchange method

2. 3. 3. Optical properties

The monolayer and multilayer WO₃ films show constant transmittance on the entire visible domain. The monolayer WO₃ 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-structures¹⁰ (Figure 2.4).

The thermal treatment determines the decreases of the transmittance; in parallel with the temperature increase, both structures WO₃/Glass/WO₃ and structures WO₃/ITO/Glass/WO₃. The thermal treatment also produces the color change of transparent films from colorless to yellow pale, thus suggesting some morpho-structural variation¹⁰.
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, ~ 79%, had a film whose support was treated with ammonia solution.

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

The band gap energy of WO₃ films, evaluated from the Tauc plot’s, \( [(\alpha h\nu)^{1/2} \text{ vs } h\nu] \), varies between 2.9 and 3.2eV, in agreement with the literature data \(^{12}\)(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 WO₃ 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°C to 550°C, leads to the formation of larger crakes in the WO₃ film \(^{10}\).
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](image)

Figure 2.8. SEM images of WO3 film surface: one layer: 350°C (a) and 550°C (b)\(^\text{10}\)

![Figure 2.9](image)

Figure 2.9. Cyclic voltamograma of WO3 films, ion exchange method, WO3/ITO/Glass/WO3 in 0.01M H\(_2\)SO\(_4\), CE – Pt, E=-1V ÷ +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\(_3\) 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°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°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](image)

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

![Figure 2.13](image)

**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 WO3 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°) triclinic compound characteristic Na2W4O13 (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$_3$ and seem to adopt a crystalline arrangement of type Na$_x$WO$_3$, strong diffraction bands located at 22.5°, 24.7°, 28.9°, 33.5° are characteristic Na$_{0.10}$WO$_3$ tetragonal (JCPDS 05-0389).

It can be assumed that at 550°C, the nanoparticles of WO$_3$·H$_2$O precursor interact superficial with the glass substrate resulting in a crystalline product from the system Na$_2$WO$_4$-WO$_3$. To our knowledge this possibility of interaction of WO$_3$·H$_2$O 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°), diffuse reflectance spectra (incidence angle 0°) and specular reflectance spectra.

![Figure 2.16. Reflectance spectra for WO$_3$ film](image)

Multiple bands of WO$_3$ 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$_3$ films thermal treated at 4x350°C indicates that they are amorphous, with a tendency to monoclinic organization. WO$_3$ 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°C with 1-step annealing stage performed at the end of the deposition cycle (Figure 2.19)

13.
2. 4. 3. Support influence

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

WO3 films with WO3/ITO/Glass/WO3 hetero structures (350°C/30 minutes in air) WO3(PEG400)/ITO/Glass/WO3(PEG400) have relatively smooth surface with regular particles.

![Figure 2.19. SEM images of WO3 films annealed at 4x 350°C.](image)

![Figure 2.21. SEM images of hetero structures: a) WO3/ITO/Glass/WO3 (FW10I2) and b) (PEG400)/ITO/Glass/WO3(PEG400) (FW11I2).](image)

![Figure 2.22. X-ray diffraction patterns of WO3 precursors and films.](image)
A 200nm thick film was estimated from SEM measurements, the films are placed in transverse position (Figure 2.22).

WO$_3$ precursors have the monoclinic structure, while WO$_3$ films are amorphous with a tendency to organize monoclinic crystalline phase. From X-ray diffraction patterns WO$_3$'s band is observed, located at 20=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 WO$_3$ 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$_3$ films transmission (Figure 2.23).

![Figure 2.23. Transmission spectra of WO$_3$/ITO/Glass/ WO$_3$ (350°C) with different number of layers without additive (a) and with PEG400 additive (b)](image)

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

![Figure 2.24. Reflectance spectra of WO$_3$ films annealed at 350°C: (a) without additive (FW10 I2); (b) with PEG400 additive (FW11 I2)](image)
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).

![Cyclic voltamogram of WO3/ITO/Glass/WO3 films](image)

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

**WO3 films applied potential influence on electrochemical properties** of these involves the recording of the electrochemical behavior of WO3 film for 4 different potential areas of: E1=-1.2V ÷ 1.2V; E2=-1V÷1V; E3=-0.8V ÷ 0.8 V; E4=-0.6V ÷ 0.6V vs. Ag/AgCl/KCl sat (0.5M H2SO4, $v = 50 \text{mVs}^{-1}$). It is noted that at the application of different potential areas the bit stream increases proportional to the applied potential, voltamogram form remains unchanged (Figure 2.26a). Ranging **the scan speed** from 10 to 800mVs-1 (0.5M H2SO4, E=-1V÷1V vs. Ag/AgCl/KCl sat) 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 H2SO4, $v = 50 \text{mVs}^{-1}$, E=-1V÷1 V vs.Ag/AgCl/KCl sat) it was observed that when it takes the 0.5M H2SO4 value the anodic current has the highest recorded intensity, 0.011 $\mu$A (Figure 2.26b).

Study of electrochemical properties of WO3 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 voltamogram of mono- and multi-layers films without additive (a) and with PEG400 additive in 0.01M H₂SO₄ solution, CE-Pt, v=50mVs⁻¹, E=-1.2V ÷ 0.6 V vs. Ag/AgCl/KCl_sat

3. 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 WO₃ powders

3.2. Synthesis of the WO₃ powders

WO₃ powders were obtained by precipitation method of tungsten acid annealed at 550°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 WO₃ powders, reactants ratio Na₂WO₄: HCl = 1:20 ÷ 1:35 was varied.

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

3.3. Characterization of WO₃ 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°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$_3$ precursors, in FT-IR spectrum (Figure 3.1b) in addition to bands associated with vibrations of the water links, between 900-600 cm$^{-1}$ 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)](image)

3.3.3. Optical properties

Using UV-Vis spectroscopy has studied the optical properties of WO$_3$ powders obtained by precipitation method (Figure 3.4). All obtained WO$_3$ 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$_4$]$_2^2$:[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$_3$.

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

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

WO₃ powder obtained by precipitation method is porous, \( \sim 17.2 \text{m}^2/\text{g} \), \( V_{\text{pores}} = 0.072 \text{m}^2/\text{g} \), composed of meso- and macro pores, of nanometric particles \( \sim 49 \text{ nm} \) 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 200 nm. It is noted that although samples were prepared with different ratio of reactants, does not influence the shape or size of WO₃ powder particles.

![SEM and TEM images of WO₃ powder](image)

**Figure 3.7.** Imagini SEM (a) și TEM (b) a pulberii WO₃ (proba PP1)

3.4. Characterization of WO₃ 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.

3.4.1. Additive influence

Determination of specific surface allowed evaluation of tungsten trioxide powders porosity annealed at 550°C, in air for 30 minutes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Specific surface BET method (m²/g)</th>
<th>Average diameter meso-pores BJH method (nm)</th>
<th>Average diameter macro-pores BJH method (nm)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG1</td>
<td>WO₃</td>
<td>5.9</td>
<td>22.5</td>
<td>81.2</td>
<td>141.3</td>
</tr>
<tr>
<td>SG2</td>
<td>WO₃(PEG200)</td>
<td>16.2</td>
<td>22.8</td>
<td>101.3</td>
<td>51.9</td>
</tr>
<tr>
<td>SG3</td>
<td>WO₃(PEG400)</td>
<td>20.3</td>
<td>25.7</td>
<td>83.2</td>
<td>41.2</td>
</tr>
<tr>
<td>SG4</td>
<td>WO₃(PEG600)</td>
<td>21.7</td>
<td>21.5</td>
<td>96.0</td>
<td>38.6</td>
</tr>
<tr>
<td>SG6</td>
<td>WO₃(MA)</td>
<td>17.7</td>
<td>14.1</td>
<td>110.1</td>
<td>47.3</td>
</tr>
<tr>
<td>SG7</td>
<td>WO₃(CTAB)</td>
<td>31.4</td>
<td>10.2</td>
<td>92.0</td>
<td>26.7</td>
</tr>
<tr>
<td>SG8</td>
<td>WO₃(NLS)</td>
<td>7.8</td>
<td>15.3</td>
<td>80.5</td>
<td>107.0</td>
</tr>
</tbody>
</table>

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 meso-pores. Particle size decreases with the addition of PEG and with increasing molecular weight,
from 141 nm (SG1-WO3) 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 (WO3-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 ~ 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 WO3 powders prepared by sol-gel method](image)

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 WO3](image)
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 WO₃ 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_{eff}, determined by Warren-Averbach method, has values between 12 to 25 nm. Hence it can be concluded that nanostructured materials are obtained.

Table 3.9. Microstructural parameters and parameters of the elementary cell of WO₃ powders

<table>
<thead>
<tr>
<th>Sample</th>
<th>D_{eff} [Å]</th>
<th>(\langle\varepsilon^2\rangle^{1/2})</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>V [Å³]</th>
<th>Beta [degrees]</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG1</td>
<td>248</td>
<td>0.288</td>
<td>7.311</td>
<td>7.542</td>
<td>7.698</td>
<td>424.55</td>
<td>90.32</td>
<td>89 vol. % mcl-WO₃ (JCPDS 43-1035)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.268</td>
<td>7.268</td>
<td>3.876</td>
<td>177.38</td>
<td>-</td>
<td>11 vol. % hxl-WO₃ (JCPDS 33-1387)</td>
</tr>
<tr>
<td>SG2</td>
<td>172</td>
<td>0.439</td>
<td>7.308</td>
<td>7.517</td>
<td>7.681</td>
<td>421.98</td>
<td>90.49</td>
<td>93 vol. % mcl-WO₃ (JCPDS 43-1035)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.198</td>
<td>7.198</td>
<td>3.925</td>
<td>176.13</td>
<td>-</td>
<td>7 vol. % hxl-WO₃ (JCPDS 33-1387)</td>
</tr>
<tr>
<td>SG4</td>
<td>121</td>
<td>0.312</td>
<td>7.307</td>
<td>7.512</td>
<td>7.673</td>
<td>421.23</td>
<td>90.58</td>
<td>98 vol. % mcl-WO₃ (JCPDS 43-1035)</td>
</tr>
<tr>
<td>SG6</td>
<td>114</td>
<td>0.321</td>
<td>7.314</td>
<td>7.502</td>
<td>7.664</td>
<td>420.63</td>
<td>90.43</td>
<td>96 vol. % mcl-WO₃ (JCPDS 43-1035)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.281</td>
<td>7.281</td>
<td>3.907</td>
<td>179.46</td>
<td>-</td>
<td>4 vol. % hxl-WO₃ (JCPDS 33-1387)</td>
</tr>
<tr>
<td>SG7</td>
<td>144</td>
<td>0.511</td>
<td>7.304</td>
<td>7.489</td>
<td>7.653</td>
<td>418.69</td>
<td>90.53</td>
<td>94 vol. % mcl-WO₃ (JCPDS 43-1035)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.198</td>
<td>7.198</td>
<td>3.960</td>
<td>177.71</td>
<td>-</td>
<td>6 vol. % hexagonal-WO₃ (JCPDS 33-1387)</td>
</tr>
<tr>
<td>SG8</td>
<td>484</td>
<td>0.142</td>
<td>7.357</td>
<td>7.508</td>
<td>7.723</td>
<td>4.266</td>
<td>90.37</td>
<td>91 vol. % mcl-WO₃ (JCPDS 43-1035)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.284</td>
<td>7.284</td>
<td>3.916</td>
<td>179.97</td>
<td>-</td>
<td>9 vol. % hxl-WO₃ (JCPDS 33-1387)</td>
</tr>
</tbody>
</table>

*mcl - monoclinic
**hxl - hexagonal
Of morphologically WO₃ 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 WO₃ is uneven size. WO₃ particle size is of 80 nm, and the powder with CTAB ranges from 23-60 nm.

Results obtained by transmission electron microscopy are consistent with the values obtained from profile analysis of diffraction bands which confirms the nanometric WO₃ powders prepared.

3. 4. 2. Thermal treatment influence

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

Thermal treatment of 550°C for 30 minutes or 90 minutes, 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).
Table 3.11. Specific surface and porosity characteristics of WO3 powders

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area BET (m²/g)</th>
<th>Micro pore (t-plot)</th>
<th>Meso- and macro pore (BJH-desorption)</th>
<th>Particle size * (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total volume cm³/g</td>
<td>Total Area m²/g</td>
<td>Total volume cm³/g</td>
<td>Average diameter nm</td>
</tr>
<tr>
<td>SG1-30</td>
<td>5.93</td>
<td>0.000331</td>
<td>2.14</td>
<td>103.73</td>
</tr>
<tr>
<td>SG1-90</td>
<td>4.87</td>
<td>0.000398</td>
<td>1.9641</td>
<td>33.65</td>
</tr>
<tr>
<td>SG2-30</td>
<td>16.15</td>
<td>0.000725</td>
<td>5.6</td>
<td>123.10</td>
</tr>
<tr>
<td>SG2-90</td>
<td>14.99</td>
<td>0.001333</td>
<td>6.5793</td>
<td>27.49</td>
</tr>
<tr>
<td>SG3-30</td>
<td>20.34</td>
<td>0.001327</td>
<td>7.73</td>
<td>108.81</td>
</tr>
<tr>
<td>SG3-90</td>
<td>17.56</td>
<td>0.001420</td>
<td>7.2189</td>
<td>33.16</td>
</tr>
<tr>
<td>SG4-30</td>
<td>21.69</td>
<td>0.000931</td>
<td>7.37</td>
<td>116.51</td>
</tr>
<tr>
<td>SG4-90</td>
<td>19.57</td>
<td>0.001774</td>
<td>8.3792</td>
<td>26.73</td>
</tr>
<tr>
<td>SG6-30</td>
<td>17.72</td>
<td>0.000736</td>
<td>5.96</td>
<td>124.22</td>
</tr>
<tr>
<td>SG6-90</td>
<td>14.73</td>
<td>0.001207</td>
<td>6.0838</td>
<td>15.77</td>
</tr>
<tr>
<td>SG7-30</td>
<td>31.35</td>
<td>0.00224</td>
<td>11.92</td>
<td>101.23</td>
</tr>
<tr>
<td>SG7-90</td>
<td>14.92</td>
<td>0.001374</td>
<td>6.6572</td>
<td>25.70</td>
</tr>
<tr>
<td>SG8-30</td>
<td>7.83</td>
<td>0.000926</td>
<td>6.64</td>
<td>95.07</td>
</tr>
<tr>
<td>SG8-90</td>
<td>3.79</td>
<td>0.000513</td>
<td>1.9247</td>
<td>25.31</td>
</tr>
</tbody>
</table>

*Particle size was calculated with the formula: \( d = \frac{6}{S \rho_{WO3}} \), where \( \rho_{WO3} = 7.16 \text{g/cm}^3 \), WO3 theoretical density.

Figure 3.22. Adsorption-desorption isotherms of WO3 samples calcined for different durations (SG1-30 and SG1-90) and volume distribution of pores according to pore diameter (inset)\(^{16}\)

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.
Adding methacrylic acid to WO$_3$ powder and extended thermal treatment causes the regulation in the meso-pores, the distribution peaks at $\sim$ 18 nm for the sample SG6-30, and sample SG6-90 $\sim$ 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 WO3 powders, based on diffuse reflection spectra are listed in Table 3.12. All WO3 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 WO3 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°C for 30 minutes.

![Figure 3.29](image_url) Diffuse reflectance spectra of WO3 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.

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 WO3 sample. The result shows that these organic compounds are removed completely from the sample after treatment for 90 minutes at 550°C. Sodium lauryl sulfate (SG8) was not completely removed even when the sample was subjected to thermal treatment at 550°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°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.
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).

<table>
<thead>
<tr>
<th>Sample cod</th>
<th>Maximum reflectance</th>
<th>Maximum absorbance</th>
<th>Wavelength ( \lambda_{\text{cut-off}} ) (nm)</th>
<th>Eg (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \lambda ) (nm)</td>
<td>Reflectance R (%)</td>
<td>Absorbance A (u. a.)</td>
<td>( \lambda_{\text{cut-off}} ) (nm)</td>
</tr>
<tr>
<td>SG1-30</td>
<td>519</td>
<td>67</td>
<td>352</td>
<td>0.54</td>
</tr>
<tr>
<td>SG1-90</td>
<td>563</td>
<td>81</td>
<td>360</td>
<td>0.61</td>
</tr>
<tr>
<td>SG2-30</td>
<td>495</td>
<td>52</td>
<td>327</td>
<td>0.44</td>
</tr>
<tr>
<td>SG2-90</td>
<td>496</td>
<td>53</td>
<td>328.5</td>
<td>0.43</td>
</tr>
<tr>
<td>SG3-30</td>
<td>512</td>
<td>56</td>
<td>330</td>
<td>0.46</td>
</tr>
<tr>
<td>SG3-90</td>
<td>548</td>
<td>78</td>
<td>334</td>
<td>0.60</td>
</tr>
<tr>
<td>SG4-30</td>
<td>510</td>
<td>55</td>
<td>325</td>
<td>0.47</td>
</tr>
<tr>
<td>SG4-90</td>
<td>545</td>
<td>80</td>
<td>332</td>
<td>0.60</td>
</tr>
<tr>
<td>SG6-30</td>
<td>509</td>
<td>49</td>
<td>359</td>
<td>0.40</td>
</tr>
<tr>
<td>SG6-90</td>
<td>545</td>
<td>80</td>
<td>355</td>
<td>0.60</td>
</tr>
<tr>
<td>SG7-30</td>
<td>482.5</td>
<td>31</td>
<td>335</td>
<td>0.19</td>
</tr>
<tr>
<td>SG7-90</td>
<td>549</td>
<td>71</td>
<td>334</td>
<td>0.54</td>
</tr>
<tr>
<td>SG8-30</td>
<td>496.5</td>
<td>41</td>
<td>350</td>
<td>0.32</td>
</tr>
<tr>
<td>SG8-90</td>
<td>496.5</td>
<td>51</td>
<td>354</td>
<td>0.40</td>
</tr>
</tbody>
</table>
Energy band gap (E_g) 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_3 powders improves their optical properties but lowers the porosity.

4. Research on doped WO_3 powders

4.2. WO_3 powders doped with transitional metals

4.2.1. Synthesis of the powders

WO_3 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).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical estimate 1g MOX / 100g WO_3</th>
<th>ICP-OES determination 1g MOX /100g WO_3</th>
<th>The degree of ions conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG18-Cu</td>
<td>1</td>
<td>0.988</td>
<td>98.8</td>
</tr>
<tr>
<td>SG18-Mn</td>
<td>1</td>
<td>1.025</td>
<td>102.5</td>
</tr>
<tr>
<td>SG18-Ni</td>
<td>1</td>
<td>0.702</td>
<td>70.2</td>
</tr>
<tr>
<td>SG18-Ag</td>
<td>1</td>
<td>0.794</td>
<td>79.4</td>
</tr>
<tr>
<td>SG16-Cu 0.5</td>
<td>0.5</td>
<td>0.464</td>
<td>92.8</td>
</tr>
<tr>
<td>SG16-Cu 1</td>
<td>1</td>
<td>0.988</td>
<td>98.8</td>
</tr>
<tr>
<td>SG16-Cu 2</td>
<td>2</td>
<td>2.166</td>
<td>108.30</td>
</tr>
<tr>
<td>SG18-Ag 0.5</td>
<td>0.5</td>
<td>0.423</td>
<td>84.6</td>
</tr>
<tr>
<td>SG18-Ag 1</td>
<td>1</td>
<td>0.794</td>
<td>79.4</td>
</tr>
<tr>
<td>SG18-Ag 2</td>
<td>2</td>
<td>0.846</td>
<td>42.30</td>
</tr>
</tbody>
</table>

It can be concluded that the impregnation method by the thermal dissociation used to obtain MOX/WO_3 powder, allowed obtaining WO_3 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_3 powders doped with metal oxides. Surface area decreases when adding oxides in WO_3 powder, while under the influence of the type of oxide used the powder porosity increases. WO_3 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.

The decrease of specific surface powders with increasing meso-and macro-porosity is because these MO₅/WO₃ powders were prepared by thermal dissociation, while WO₃ powder was obtained by sol-gel method.

4.2.2.3 Optical properties

Initial WO₃ powders (SG18) shows a strong reflection throughout the visible spectrum, peaks are situated in the green-yellow spectral range (Figure 4.4). WO₃ 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 MOX, indicating multi-sigmoidal reflection spectra due to the effect of inclusion of oxides.

To estimate the energy band gap, according to the literature, we used the „lambda cut-off” value, with values between 2.55-2.43eV, band gap narrowing is because the metal was incorporated into the WO₃ powder after thermal cleavage (Table 4.5).
Table 4.5. The main absorbance characteristics of the MOₓ/WO₃ system

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lambda cut-off (nm)</th>
<th>Eₜ (eV)</th>
<th>Maximum absorbance (λ (nm), A (a.u.))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG18</td>
<td>485.5</td>
<td>2.55</td>
<td>363.5, 0.77</td>
</tr>
<tr>
<td>SG18-Cu</td>
<td>509.6</td>
<td>2.43</td>
<td>358, 0.68</td>
</tr>
<tr>
<td>SG18-Mn</td>
<td>497.5</td>
<td>2.50</td>
<td>362, 0.77</td>
</tr>
<tr>
<td>SG18-Ni</td>
<td>507.9</td>
<td>2.44</td>
<td>360, 0.82</td>
</tr>
<tr>
<td>SG18-Ag</td>
<td>505.1</td>
<td>2.45</td>
<td>384, 0.82</td>
</tr>
</tbody>
</table>

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/WO₃ 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 WO₃ powders loaded with oxides of transition metals, compared with unchanged WO₃ 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 WO₃xH₂O precursor with metal nitrates, followed by annealing at 550°C, kept broadly unchanged appearance WO₃ 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 (WO3); b) SG18-Ag (Ag2O/WO3); c) SG18-Cu (CuO/WO3);
d) SG18-Mn (MnO2/WO3); e) SG18-Ni (NiO/WO3)

Figure 4.11. TEM images of WO3 and MnO2-WO3 powders (at different size)
SG18 sample is WO₃ powder containing particles of irregular shape with sizes ranging from 50-100nm (Figure 4.11). Manganese oxide is included in the WO₃ powder after impregnation, the particles are irregularly shaped, spherical and elongated, forming aggregates square (TEM image of 500nm). The presence of MnO₂ determines the particles increases to ~ 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 WO₃ 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, MnO₂, NiO and Ag₂O atoms in the monoclinic structure of WO₃ (Table 4.8).

![X-ray diffraction patterns of MOₓ/WO₃ samples](image)

**Figure 4.12.** X-ray diffraction patterns of MOₓ/WO₃ samples

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SG18</td>
<td>7.3255</td>
<td>7.5386</td>
<td>7.7095</td>
<td>90.241</td>
<td>425.746</td>
<td>94.7</td>
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</tr>
</tbody>
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Mean square coefficient of lattice deformation changes depending on how the inclusion of particle oxide Cu, Mn, Ni or Ag in WO₃ powder.
4. 3. WO3 powders doped with noble metals
4. 3. 1. Synthesis of the powders

WO3 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 Pt4+ in Pt0, 3.44%, was achieved for SG16-Pt1 powder with 0.93g Pt4+/100g WO3.

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

WO3 powder coating platinum increases the BET surface area from ~ 8.3m2 / g ~ 9.0m2 / 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 WO3 grains.

WO3 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 ~ 8.3m2/g to ~ 9.1m2/g (SG18-Pd0.5) and porosity from ~ 0.0449 to ~ 0.0496cm³/g compared to the starting powder.

![Figure 4.14](chart.png)

**Figure 4.14.** Volume size distribution (a) and area (b) pore, Pt/WO3 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/WO3 powder is similar to WO3 powder. One can say that the surface of WO3 particles is covered with nano particles of platinum.
4. 3. 2. 3. Optical properties

Initial WO$_3$ powders (SG16-Pt0) shows a strong reflection throughout the visible spectrum, with peaks situated in the green-yellow spectral range (Figure 4.13a).

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 reduction not within control (Figure 4.13). WO$_3$ 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$_3$ powders surface morphology was visualized by scanning electronic microscopy (SEM), Figure 4.16. It is noted that initial WO$_3$ 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$_3$ powder dispersed in water acidulated, SG18-Pd0, not change shape and size of particles initial WO$_3$ powder (spherical, <100nm). M$^0$/WO$_3$ powder (SG16-Pt2, SG18-Pd2) contains with WO$_3$ particles, metal nanoparticles which are distributed unevenly throughout their surface (Figure 4.18).
Figure 4.16. SEM images of WO₃ (SG16); WO₃ ultrasonic (SG16-Pt0); Pt/WO₃ (SG16-Pt2) and Pd/WO₃ (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 WO₃ powder due to thermal treatment, WO₃ obtained at 550°C and at M/WO₃ at 120°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).

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WO₃ 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 WO₃, according to the ICSD80056 sheet\(^{17}\).

![Figure 4.19. X-ray diffraction patterns of Pt/WO₃ and Pd/NO₃ systems](image)

Powder loaded with platinum ions, palladium, respectively, does not change the monoclinic structure of WO₃. 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 WO₃ particles.
5. Research on applicative potential of WO₃ films and powders

5. 2. WO₃ 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

**WO₃ 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](image)

**Figure 5.4.** Transmission spectra of WO₃/ITO/Glass/WO₃ multilayer film, sol-gel method (a) and ion exchange method (b), before and after application of electric current

![Figure 5.7](image)

**Figure 5.7.** Tauc representations, \((ah\nu)^{1/2} \text{ vs. } h\nu\), of WO₃/ITO/Glass/WO₃ 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 3.4 eV (Figure 5.7). WO₃ 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 = 3.4 - 3.6eV (Figure 5.7).

5. 2. 2. Coloring efficiency

Coloring efficiency and stability of WO₃ films are important characteristics of electrochromic devices, with their help assessing the performance of electrochromic materials obtained. Coloring efficiency (η (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.

All WO₃ films obtained by sol-gel method, without and with polymer additive, have a positive coloring efficiency, located between 0.9-9.1 cm²/C, because the absorption increases the ion insertion. WO₃ 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 inhomogeneity 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 WO₃ films: R₄ I₇ (η(CE)=9.1 cm²/C); FW₁₀ I₃ (η(CE)=5.9 cm²/C); FW₁₁ I₂ (η(CE)=6.8 cm²/C).

WO₃ films were cycled for a long time in 0.01M H₂SO₄ 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, WO3 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 (WO3(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.

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 WO3 powder was used as photocatalyst. Photodegradation efficiency of methylene blue on WO3 powder was: 20% WO3- precipitation; 82% WO3-sol-gel and 32% WO3(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 WO3 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 photocatalyst 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$_2$O$_2$, 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$_3$ samples doped with platinum, whose yields are up to ~80%.

![Figure 5.10. Methylene blue photodegradation efficiency](image)

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 WO$_3$ is used as a catalyst, the low photoactivity of catalyst is due to rapid recombination of electrons and holes photo generated.

![Figure 5.11. Methylene blue photodegradation efficiency in H$_2$O$_2$ presence](image)
WO₃ 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 WO₃ 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 TiO₂ Degussa P25 powder used as a control sample.

![Graph](image)

**Figure 5.13.** Efficiency of catalysts used in photodegradation of methyl orange solution:

a. Methyl orange -H₂O; b. Methyl orange -H₂O₂

In **Figure 5.13** we can see that for Methyl orange-H₂O system, all samples were photodegradation efficiency of 15%, doped samples showing greater efficiency than non-modified WO₃ powder. The highest efficiency, ~30.9%, SG18-Pd1 sample has (ICP-OES estimates, 0.068g Pd/100g WO₃). Note, however, is that all of WO₃ 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 WO₃), 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 WO₃ 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/WO₃ and Pd/WO₃ 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 WO₃(SG18) powder
- 180 minutes – for ultrasonic WO₃ (SG18-Pt₀) powder
- 360 minutes – for M⁰/WO₃ (SG18-Pt₁ and SG18-Pd₂) powder

b) Influence of initial concentration in the photodegradation of the methyl orange on WO₃, WO₃ ultrasonic Pt/WO₃ and Pd/WO₃ substrate

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](image)

**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 WO3 powder coated with finely divided noble metals:
   - Pt/WO3 (SG16-Pt1), Pd/WO3 (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, 10⁻³mL H₂O₂ 10% / 1 g powder, improves the photodegradation efficiency.

5. 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 WO3 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 WO3 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).

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<td>$k_2$ (g/mg*min)</td>
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<td>SG18-Pd2</td>
<td>8.98*10^{-4}</td>
<td>0.79</td>
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</table>

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 WO3 thin films were obtain by dip-coating technique (*ion exchange and sol-gel methods*), the optimal thermal treatment was 350°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.
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_3 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.

The optical, morphological and structural properties of WO_3 powders, obtain by precipitation method, are not influenced by the ratio of reactants.

WO_3 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°C/30 minute thermal treatment, and macro-porous powders.

Sol-gel method, unlike the precipitation method, ensures the formation of a WO_3 meso-porous powders with a higher degree of dispersion, with better morpho-structural and optical properties.

WO_3 powders doped with transition metal oxides (CuO, NiO, MnO_2, and Ag_2O) and WO_3 powders loaded with platinum and palladium were obtain by impregnation (thermal dissociation) and photolytic reduction method.

The optical and morphological properties of doped powders showed the inclusion of the oxides in WO_3 powder and the cover with the precious metals of WO_3 powder. The synthesis methods used allowed a good degree of doping control with metal oxides, but not of the platinum or palladium.

The undoped and doped WO_3 powders were used as photocatalysts in degradation of methyl orange and methylene blue dyes.

Meso-porous WO_3 powder (sol-gel method) showed the best photocatalytic activity, compared with the powder prepared with polymer additive (sol-gel method) and macro-porous WO_3 powder (precipitation method).

Meso-porous and submicron WO_3 powders doped with CuO, Ag_2O, MnO_2, 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_3 powder lead 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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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 Brașov, Faculty Materials Science and Engineering, Department of Chemistry, Prof. Dr. A. Dătă – 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 Brașov, Faculty Materials Science and Engineering, Department of Chemistry, Prof. Dr. A. Dătă – 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.