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Optical Properties and Chemical Stability of WO_3 and TiO_2 Thin Films Photocatalysts

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Abstract. The aim of the paper is to explain the correlations between the optical properties of WO_3 and TiO_2 films and the chemical stability in different environments required for a future utilisation as catalysts in wastewater treatment and in building a photoelectrochemical cell (PECC). The crystallinity was investigated using X-Ray Diffraction and the electrical properties were determined by current – voltage analysis. The optical properties of the films were the subject of UV – VIS analysis.

Keywords: photoactivity, WO_3, TiO_2.

1. Introduction

Many different semiconducting materials have been used as photocatalysts for water decomposition to hydrogen and oxygen. Among them metals oxides have been found to give the best activity and stability in a variety of organic and inorganic photocatalytic reactions and during long-time irradiation. In the systems reported so far, most of the materials that where used are wide band gap semiconductors, which necessitates the use of mainly ultraviolet ($\lambda < 400$ nm) so as to achieve the photoexcitation and charge separation, [1–3].

Tungsten oxide is the most investigated and used material for electrochromic devices in which coloration and bleaching can be reversibly obtained by an electrochemical process, [4]. According to the deposition conditions, it is possible to obtain different polymorphs such as monoclinic ($> 17 - 330°$C), orthorhombic (330–740°C) and tetragonal ($> 740°$C) WO_3 [5–7].

The TiO_2 (anatase) is an n-type semiconductor. Thin films of TiO_2 used as optical coatings, integrate circuits, solar cell and electro-chromic windows capacitor dielectrics, heat reflecting layers and waveguides have also been shown to be resistant to corrosive and mechanical attack and to show stability over long time periods. TiO_2 exists as three polymorphs: anatase, rutile and brokite [8].

Tungsten (VI) oxide and TiO_2 can been combined in a photoelectrochemical cell (PECC) based on a TiO_2 anode and a WO_3 cathode. The PECC is suitable for oxidative removal of toxic organic pollutants and for water photolysis [9].

It is know that the ability of a semiconductor to generate hydrogen and oxygen by water photoelectrolysis is critically dependent upon the interfacial contact characteristics between the semiconductor and the electrolyte solution [9].

This paper present the optical properties of WO_3 and TiO_2 films in different aqueous environments as an essential factor for building an electronic device activated by photoexcitation. The experimental investigation concerns the structural, electrical and optical characteristics. The application of this device concern many important areas like renewable energy production, photodegradation of wastewater pollutants, "smart" windows, hydrogen production, etc.

2. Experimental

2.1. Materials

TCO (transparent conducting glass, F doped SnO_2 coated glass – Libbey Owens Ford TEC 20/2.5 nm) was used as a substrate for TiO_2 deposition and glass was used as a substrate for WO_3 deposition.

The nanoporous TiO_2 (anatase) layer was deposited using: titanium(IV) izopropoxide, ($Ti[OCH(CH_3)_2]_4$, TTiP, 99.999%, Sigma-Aldrich) as precursor, acetyl acetone, (2,4 pentadione, 99%, $CH_3COCH_2COCH_3$, AcAc, Aldrich) as complexation agent and absolute ethanol (C_2H_5OH, EtOH, J.T. Baker) as solvent. The precursor $(NH_4)_2WO_4$ was obtained by mixing WO_3 powder (99.8%, Alfa Aesar) with ammonium solution (25%, J.T. Baker) at the average temperature of 60°C under 30 min continuous stirring.

2.2. Preparation of TiO_2 and WO_3 thin films

The SPD (spray pyrolysis deposition) was used for obtaining thin nano and mezostructured layers.

The deposition temperature was 270°C for WO_3 and 400°C for TiO_2 and air was used as carrier gas. A post – annealing process was performed at 350°C for WO_3 films and 500°C for TiO_2 films in air for improving the structural quality of the films.

2.3. Films characterization

Reflectance and absorbance measurements were recorded in the range of 200–600 nm, using a UV - Visible spectrophotometer (Perkin Elmer Lambda 25 UV/VIS), allowing the calculus of the thickness and band gap of the thin films.

The XRD measurements (Bruker D8 Advance Diffractometer) were used to evaluate the crystal structure of the films.

The I-V (the current-voltage curves in dark) and absorption was performed using a DC Source Meter (Keithley, model 2400) and a Parker 3000k Analyser.

Tests were performed at three pH value (4, 6 and 8) measure by Hanna pH-meter, HI 991300.

3. Results and discussions

3.1. XRD Analysis

In photocatalysis process the optical properties are very important and required high crystalline structure. The X-ray diffraction measurements confirm the formation of TiO_2 anatase film, Fig. 1, according to JCPDS 73-1764 and WO_3 monoclinic structure, Fig. 2, according to JCPDS 72-0677. Tetragonal crystalline anatase TiO2 structure was identified (JCPDS 73-1764) and is more attractive than rutil for photo catalytic processes [10].

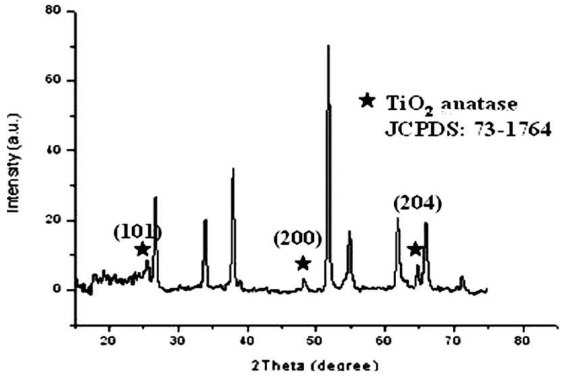

Fig. 1. XRD spectrum of TiO_2 film.

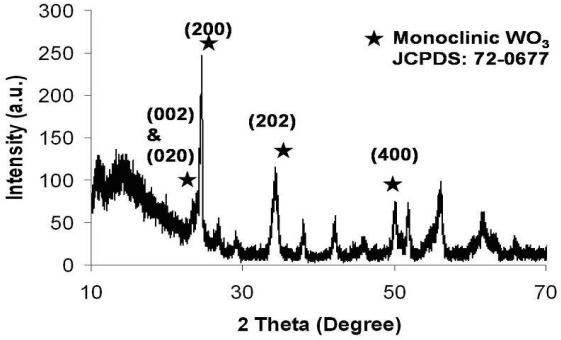

Fig. 2. XRD spectrum of WO_3 film.

The WO_3 films exhibit monoclinic structure (JCPDS 72-0677) and it is possible to have some strain of the dislocation centered on the edge of the shear plane in the body of the crystal that could enhance the chemical reactivity.

3.2. Physical Properties

The films photoexcitation can be expected only if they have good conductivity (suitable energy bands, and lack of traps). When mobile electrons or holes are present even in small concentrations, their relatively high mobility, several orders of magnitude grater than to the overall conductivity.

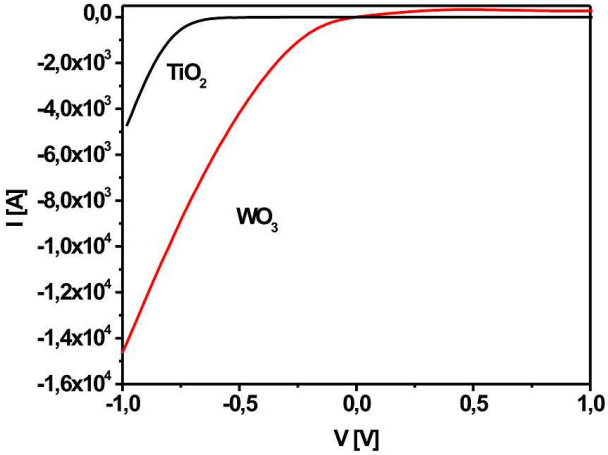

Fig. 3. I-V characteristics of TiO_2 and WO_3.

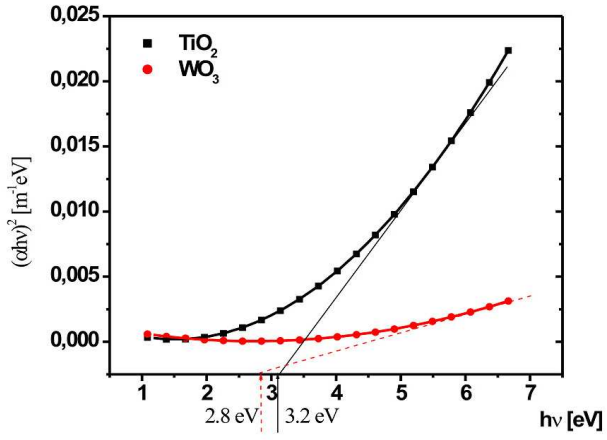

Fig. 4. TiO_2 and WO_3 band gap.

The environment of a periodic lattice and its periodic potential may be accounted for conductivity values. Using the optical absorbance spectra, the absorption coefficient and the band gap of TiO_2 and WO_3 films (before immersion) were evaluated and

estimate 3.2 eV respectively 2.8 eV, Fig. 4. The electrical measurements (current–voltage curves), Fig. 3, show a high conductivity for the both films (diode behavior). WO_3 has a better conductivity comparing with TiO_2. The results are a consequence of the band gap value and the fact that the conductivity depends not only on the electrons and holes but also on the moving ions.

3.3. Stability in electrolytes

The chemical stability in electrolytes with different pH represents a decisive factor choosing the material for photocatalysation process.

The absorption analysis in electrolyte at different pH is important considering the future utilization of tungsten trioxide and titanium oxide in devices who work using optical properties of these films. Both films were immersed in electrolyte at pH = 4, 6 and 8 for 4 h and 24 h in order to evaluate the chemical stability and optical properties on TiO_2 and WO_3, compared with the films before immersion. The films before immersion show higher amplitude of absorption for tungsten trioxide comparing with titanium oxide.

Titanium oxide presents the absorption spectrum between 340–370 nm and the tungsten oxide has the absorption spectrum between 300–360 nm (Fig. 5). Both films have the significant peaks in the UV domain and it's possible to extend these values close to the VIS domain by tailoring the material.

At pH = 6 the films absorbance is unchanged even after 24 h of immersion proving a high chemical stability of TiO_2 and WO_3. While, titanium oxide is involved in reversible processes in all electrolytes, regardless the pH value, irreversible changes can be identified for tungsten trioxide films:

$$\mathrm{Ti-OH} + \mathrm{H^+} \leftrightarrow \mathrm{Ti-OH_2^+} \tag{1}$$

$$\mathrm{Ti-OH} + \mathrm{OH^-} \leftrightarrow \mathrm{Ti-O^-} + \mathrm{H_2O} \tag{2}$$

$$\mathrm{WO_3} + xe^- + x\mathrm{M^+} \overset{\mathrm{M=H}}{\longrightarrow} \mathrm{M}_x\mathrm{WO_3} \tag{3}$$

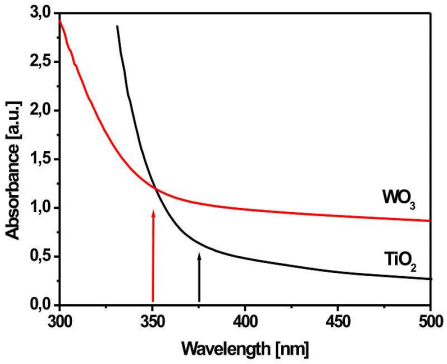

Fig. 5. Absorption spectrum for WO_3 and TiO_2 films before immersion.

The WO_3 amplitude of absorption is reduced after 4 hours of immersion in acid electrolyte (Figs. 6, 7 and 8) and the same behavior can be observed for WO_3 film immersed in alkaline electrolyte.

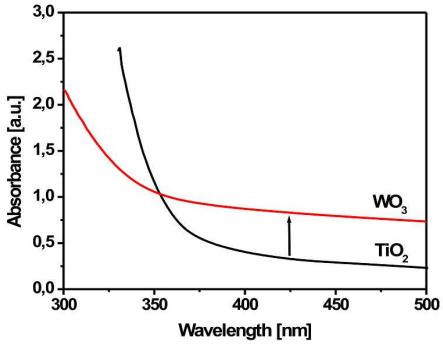

Fig. 6. Absorption spectrum for WO_3 and TiO_2 films after 4 h of immersion in electrolyte at pH 4.

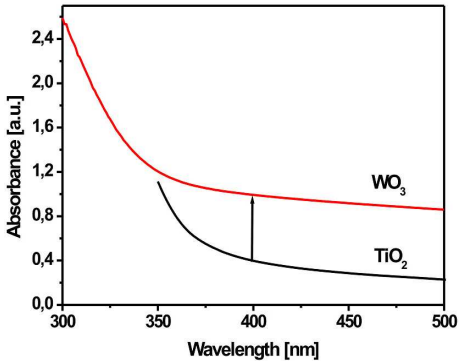

Fig. 7. Absorption spectrum for WO_3 and TiO_2 films after 4 h of immersion in electrolyte at pH 6.

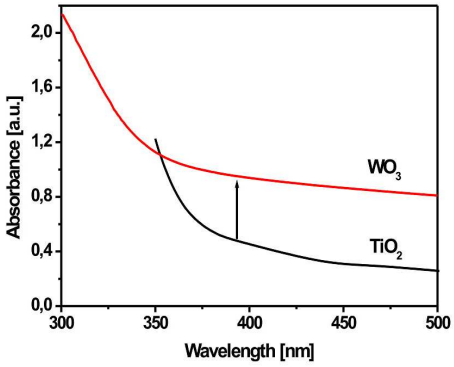

Fig. 8. Absorption spectrum for WO_3 and TiO_2 films after 4 h of immersion in electrolyte at pH 8.

Drastically changes of optical properties of tungsten oxide is observed after 24 h of immersion in electrolyte (Figs. 9, 10 and 11) at pH = 4 and pH = 8 when the amplitude of the titanium oxide absorption dominate the WO_3 absorption and in this case chemical changes are expected.

If at high pH, the absorption is reduced due to the formation of tetrahedral oxoanions $[WO_4]^{2-}$ which diffuse into the electrolyte forming Na_2WO_4, at acid pH, hexagons centers are formed characterized by H_xWO_y species and the oxygen vacancy diffuses into the interior of the WO_3 column where some of the H_2O molecules leave the films. The diffusion of the oxygen vacancy may be favourable along the grain boundaries in the interior of the columns. The electron in the conduction band is removed by reaction with the oxygen dissolved in water, and the hole in the valence band can react with predominantly OH^- species, which are adsorbed on the surface. The electron–hole recombination process is in direct competition with space–charge separation of the electron and the hole. The photocatalytic activity of WO_3 will be increased by retarding the electron–hole recombination process, [8].

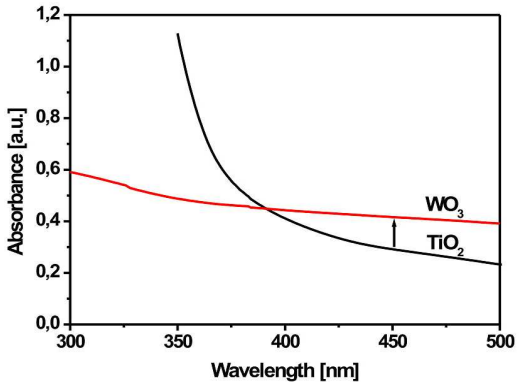

Fig. 9. Absorption spectrum for WO_3 and TiO_2 films after 24 h of immersion in electrolyte at pH 4.

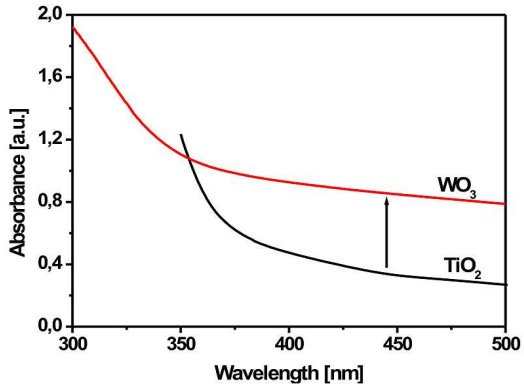

Fig. 10. Absorption spectrum for WO_3 and TiO_2 films after 24 h of immersion in electrolyte at pH 6.

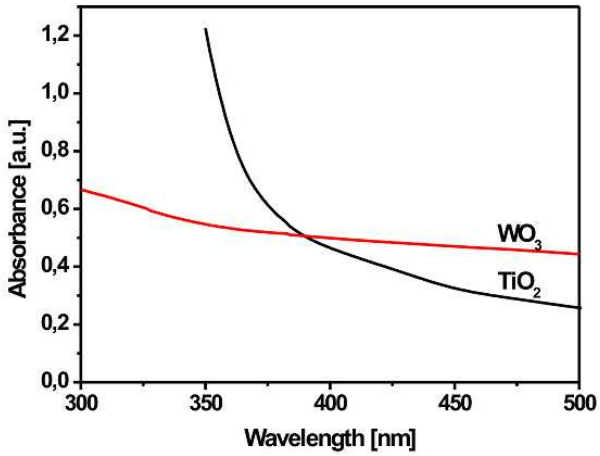

Fig. 11. Absorption spectrum for WO_3 and TiO_2 films after 24 h of immersion in electrolyte at pH 8.

4. Conclusions

The SPD technique allows to obtain thin WO_3 and TiO_2 films with crystalline structure and high conductivity. The optical analysis proves the presence of reversible chemical changes for titanium oxide and irreversible chemical changes concerning tungsten trioxide.

The absorption analysis show o high chemical stability at pH = 6 for the booth films comparing with absorption in acid or alkaline electrolyte.

The absorption range for TiO_2 is 340–370 nm and for WO_3 is 300–360 nm proving the possibility to use a combination of TiO_2/WO_3 in order to build a photoelectrochemical cell as device for pollutants photodegradation and/or hydrogen production, working in aqueous media at pH = 6.

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