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Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

SYNTHESIS OF TUNGSTEN TRIOXIDE MESOPOROUS POWDERS PREPARED BY INORGANIC SOL-GEL ROUTE

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ABSTRACT. Powders of mesoporous tungsten trioxide (WO_3) have been synthesized by an inorganic sol-gel route, in presence of polyethylene glycol PEG as porosity regulating agent. The influences of PEG addition and calcination regime on powder properties were investigated. Samples characterization was performed by thermal analysis, UV-Vis spectroscopy, as well as by surface area and porosity measurements.

Keywords: *Tungsten trioxide powders, sol-gel method, porosity, optical properties.*

INTRODUCTION

Tungsten trioxide (WO_3) is a semiconductor with special optical and electrical properties which explain its use as photoanode in electrochemical hydrogen production or as photocatalyst in pollutants photodegradation [1-4]. The energy band gap of 2.3 - 2.8 eV allows hole generation and quick formation of electron-hole pairs under UV light irradiation, which confer WO_3 a good photocatalytic activity [5, 6]. The morpho-structural properties of the powder, i.e. crystalline structure, porosity, surface morphology, particles size and optical characteristics are strongly influenced by the synthesis route and subsequent treatment conditions [7, 8].

Among the preparation methods, the sol-gel route offers many advantages such as molecular-scale homogeneity, high purity and reactivity, as well as controlled particles size and shape of the obtained product [9-12]. By this synthesis route, mesoporous WO_3 powders could be obtained in special preparation conditions. Their high photocatalytic activity in oxidation

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processes is correlated with a large surface area, with many active sites, which can adsorb water, molecular oxygen or hydroxyl group in order to produce active oxidizing species [13].

The present paper continues our studies concerning the preparation of WO_3 powders and thin films, with well defined properties [14-17]. In this context, tungsten trioxide powders were prepared by sol-gel method, in presence of polyethylene glycol (PEG), as porosity regulating agent. The influences of polymer additive and calcination regime on WO_3 powder properties were also investigated. Because the main goal of our studies is the preparation of WO_3-based materials with good photocatalytic properties, special attention was given to the powder porosity control.

RESULTS AND DISCUSSIONS

Tungsten trioxide powders were obtained from tungstic acid precursors ($WO_3.xH_2O$) prepared by sol-gel method, in the presence of polyethylene glycol with variable polymerization degree (PEG200, PEG400, PEG600). The thermal treatment was performed at 550^0C for 30 - 90 minutes (Table 1).

Table 1. Synthesis conditions of WO_3 samples

Precursor code	Polymer additive	Sample code	Thermal treatment
Pr_SG1	-	**SG1-30**	550^0C / 30 min
		SG1-90	550^0C / 90 min
Pr_SG2	PEG200	**SG2-30**	550^0C / 30 min
		SG2-90	550^0C / 90 min
Pr_SG3	PEG400	**SG3-30**	550^0C / 30 min
		SG3-90	550^0C / 90 min
Pr_SG4	PEG600	**SG4-30**	550^0C / 30 min
		SG4-90	550^0C / 90 min

In order to establish the optimal calcination regime, the tungstic acid precursors were investigated by thermal analysis. Thermogravimetric (TGA), differential thermogravimetric (DTG) and differential thermal analysis (DTA) results illustrate the difference between the thermal behavior of $WO_3.xH_2O$ precursors prepared with or without polymer additive (Fig.1).

The sample with no polymer additive (Pr-SG1) shows a total weight loss of ~12%. The two main decomposition steps are associated with the removal of physically (25-200^0C) and chemically bonded water (200-400^0C). The endothermic effect observed at 305^0C corresponds to the tungstic acid decomposition.

The thermal behavior of all PEG containing precursors was similar, the major difference being the total weight loss. Between 25-150°C, there are two steps of weight loss, associated with the removal of physical adsorbed water and alcohol. The weight loss step noticed at 150-250°C was related with PEG decomposition. DTG curves illustrate that the maximum weight loss is at ~215°C (Pr_SG2), ~201°C (Pr_SG3) and ~191°C (Pr_SG4). On DTA curves, the corresponding endo-thermal peaks can be noticed at ~220°C (Pr_SG2), ~207°C (Pr_SG3) and ~201°C (Pr_SG4). For PEG containing powders, one additional small exo-thermal effect can be observed at ~250°C (Pr_SG2), ~246°C (Pr_SG3) and 242°C (Pr_SG4) that could be ascribed to the self-ignition of the residual polyalcohol.

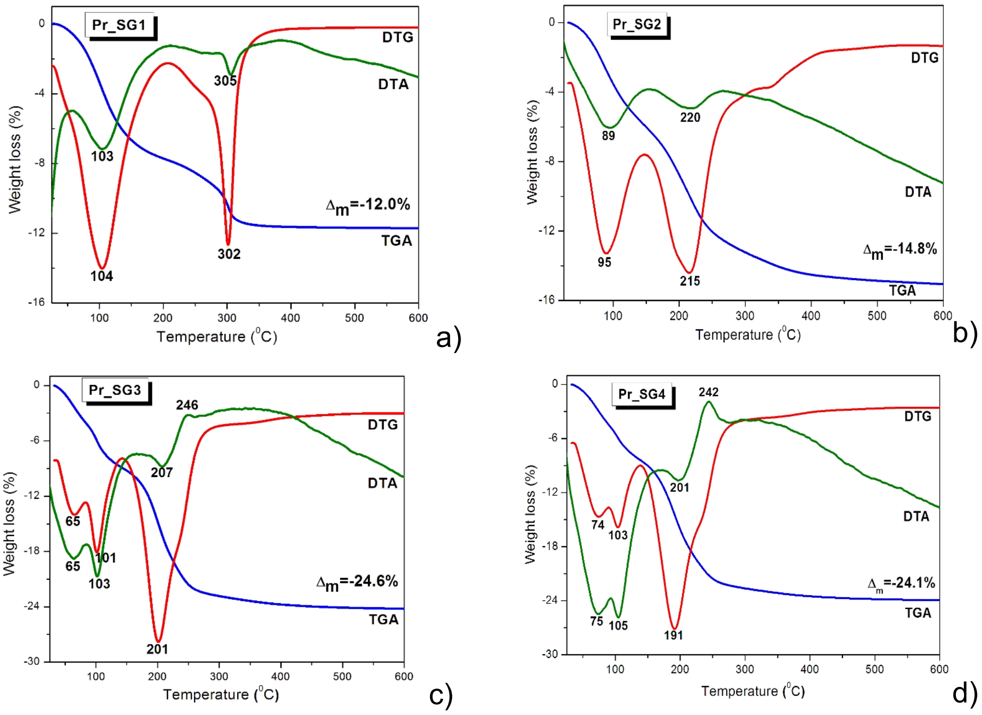

Figure 1. TGA/DTG/DTA curves of precursors with no polymer (a), PEG200 (b), PEG400 (c) and PEG600 (d) additive

According to the thermal analysis results, the conversion of precursors with or without polymer addition into tungstic oxide powders is finalized at 500°C.

In order to obtain WO_3 powders with controlled porosity properties, the thermal treatment regime was investigated. For this reason, precursor samples were thermally treated for 30 min (short thermal treatment) and 90 min (long thermal treatment) at 550^0C. Subsequently, the specific surface area and porosity were determined using the nitrogen adsorption isotherms (Fig. 2).

The BET (Brunauer, Emmett & Teller) specific surface area was calculated by determining the monolayer volume of adsorbed gas (Table 2). The micro-pores (d<2nm) volume and area were calculated from the t-plot (thickness curve) using the Broekhoff-de Boer equation, involving the thickness evaluation of the monolayer of adsorbed gas. The mesopore (d = 2 - 50nm) and macropore (d > 50nm) volume and area distribution were determined using BJH (Barett, Joyner & Halenda) calculation, based on the variation of the thickness of both the adsorbate layer and the condensed liquid, with porosity [18].

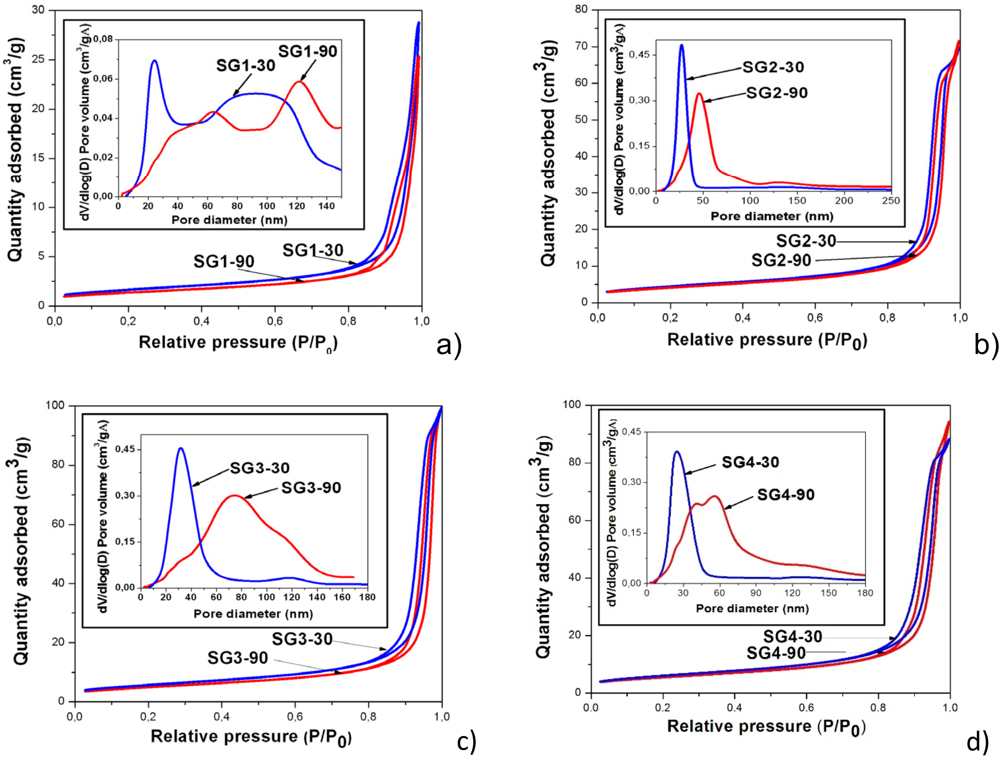

Figure 2. Adsorption-desorption isotherms of WO_3 samples and the volume pores distribution curve in function of pore diameter (inset): a) SG1 (WO_3); b) SG2 (WO_3/PEG200); c) SG3 (WO_3/PEG400); d) SG4(WO_3/PEG600)

Table 2. The surface area and porosity characteristics of WO_3 samples

Sample code	**Specific surface area BET (m^2/g)**	**Micro-pores (t-plot)**		**Meso and Macro-pores (BJH-desorption)**		
		Total volume (cm^3/g)	**Total area (m^2/g)**	**Total volume (cm^3/g)**	**Total area (m^2/g)**	**Average diameter (nm)**
SG1-30	5.9	0.0003	2.1	0.0453	5.7	103.7
SG1-90	4.9	0.0004	2.0	0.0400	4.8	33.7
SG2-30	16.2	0.0007	5.6	0.1121	18.5	123.1
SG2-90	15.0	0.0013	6.6	0.1132	16.5	27.5
SG3-30	20.3	0.0013	7.8	0.1577	22.7	108.8
SG3-90	17.6	0.0014	7.2	0.1545	18.6	33.2
SG4-30	21.7	0.0009	7.4	0.1409	24.9	116.5
SG4-90	19.6	0.0018	8.4	0.1498	22.4	26.7

The distribution curve of the no polymer containing WO_3 is multimodal which accounts for the heterogeneous porosity of the powder (Fig. 2a).

The increase of the calcination time decreases the surface area (from 5.9 to 4.9 m^2/g), at same time with the decrease of the meso- and macropore volume and area. Additionally, the average pore diameter decreases from ~103.7 nm to ~33.7 nm.

The addition of polyethylene glycol determines the regularization of pore dimensions, for both types of thermally treated samples. All distribution curves become unimodal (Fig. 2b-d). At the same time, the surface area of WO_3 powders increases in direct relation with the enlargement of the pore volume and area. The effect is stronger for polyalcohol with high polymerization degree. It can be concluded that PEG additive acts as porosity regulator.

The prolongation of the thermal treatment shifts the maximum of the distribution curve from mesopore to macropore domain. This suggests that the small size pores coalesced under the thermal treatment.

Tungsten trioxide powders prepared with PEG additive are mesoporous and show a relative homogeneous porosity as compared with no polymer containing WO_3 powder. The effect was stronger for sample prepared with PEG200.

The use of PEG with higher molecular weight increases the pore volume and area and consequently enlarges the BET specific surface area. The prolongation of the thermal treatment determines a slow displacement of pores size toward macropore domain, due to the complete removal of the organic material.

All tungsten trioxide powders absorb light in the visible domain and have a lime-fruit color. The influence of the polymer addition and thermal synthesis regime on the WO_3 powder color was put in evidence by the diffuse reflectance spectra depicted in Fig. 3. The no polymer containing WO_3 powder (SG1-30) presents a good reflection in the yellow-green spectral domain with a maximum at 519 nm. Moreover, the powder reflection is improved with about 15% by the thermal treatment (SG1-90).

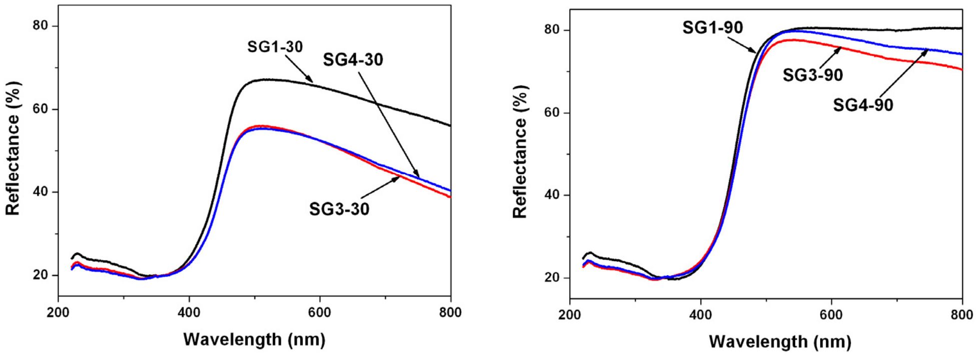

Figure 3. Diffuse reflectance spectra of WO_3 powders with no polymer containing (SG1), PEG400 (SG2) and PEG600(SG3) addition

The PEG addition seems to a blue-shift of the maximum reflectance and to decrease the reflectivity of WO_3 powders. The prolongation of the thermal treatment improves the powder reflectivity with about 20%.

Some of the optical characteristics of WO_3 powders, determined on the basis of the diffuse reflectance spectra, are summarized in Table 3. The optical band gap (Eg) was evaluated from the absorption spectra obtained by conversion of the diffuse reflectance spectra.

Table 3. Optical characteristics of WO_3 powders

Code probe	Maximum reflectance (R_{max}) Wavelength λ (nm)	Maximum reflectance (R_{max}) Reflectance R (%)	Wavelength cut-off $\lambda_{cut-off}$ (nm)	Eg (eV)
SG1-30	519	67	481.5	2.58
SG1-90	563	81	488.9	2.54
SG3-30	512	56	490.8	2.53
SG3-90	543	78	496.1	2.50
SG4-30	510	55	482.9	2.57
SG4-90	545	80	494.1	2.51

According to the literature data, the band gap energy of semiconductors can be estimated from the wavelength cut-off ($\lambda_{cut-off}$) representing the intersection point between the tangent at the absorption curve and the x axe [19, 20]. The band gap energy is calculated using the relation Eg (eV) = 1240 / $\lambda_{cut-off}$ (nm).

The calculated values of the band gap energy are in 2.50 - 2.58 eV range, in good agreement with the literature data [21]. The band gap tends to decrease with both the polymer addition and the annealing duration.

The use of a relative longer thermal treatment is favorable for the obtaining of WO_3 powders with improved optical properties. The effect is stronger for samples prepared with PEG additive, probable in association with a more complete removal of organics.

Some of the tungsten trioxide powders were tested for photocatalytic activity in the dye degradation. For these preliminary tests, SG1-30 (WO_3) and SG3-30 (WO_3/PEG400) samples were used for the methylene blue photo-degradation. The efficiency values were 90% for SG1-30 and 40% for SG3-30, illustrating that WO_3 samples show significant photocatalytic activity. The incomplete removal of the organic material dramatically damages the photocatalytic activity for dye oxidative degradation.

CONCLUSIONS

Tungsten trioxide powders were prepared following an inorganic sol-gel route, in presence of polyethylene glycol i.e. PEG200, PEG400 and PEG600. The surface area and porosity as well as the optical properties of WO_3 powders are influenced by thermal treatment regime and PEG addition.

Tungsten trioxide powders prepared with PEG additive are mesoporous and show a relative homogeneous porosity as compared with the no polymer containing WO_3 powder. The effect is stronger for sample prepared with PEG200. The use of PEG with higher molecular weight increases the pore volume and area and consequently, enlarges the BET specific surface area. The increase of the thermal treatment time determines a slow displacement of pores dimensions toward the macropore domain, due to a better removal of the organic material.

As evidenced by the diffuse reflectance spectroscopy, the polymer addition and the thermal synthesis regime influence the color of WO_3 powder. The PEG addition exerts a blue-shift of the maximum reflectance and decreases the reflectivity of WO_3 powders. The use of a relative longer time for thermal treatment favors obtaining of WO_3 powders with improved optical properties. The calculated band gap energies are in good agreement with the literature data and decrease with both polymer addition and the annealing duration.

Some of the mesoporous tungsten trioxide powders were used as photocatalysts for a reference dye photodegradation. Thus, the tested WO_3 samples show a significant photocatalytic activity for the oxidative degradation of methylene blue. The incomplete removal of the organic material, associated with a short thermal treatment, damages the photocatalytic activity.

EXPERIMENTAL SECTION

Sample preparation

Tungsten trioxide (WO_3) powders were prepared from tungstic acid solution obtained by dissolving 8 g tungsten powder (Merck) into 60 ml 30% hydrogen peroxide (Merck). The dissolution process was conducted under magnetic stirring, at 0 -10^0C (exothermic reaction) and the H_2O_2 excess was removed by catalytic decomposition on Pt black [22]. In order to obtain powders with controlled porosity, polyethylene glycol (Carlo Erba) with variable molecular weight i.e. PEG200, PEG400 or PEG600 was used as additive. The yellow-translucent sol was dried at 70^0C, in air. The as obtained tungstic acid precursors were annealed at 550^0C, in air, for 30 or 90 minutes.

Sample characterization

The tungstic acid precursors were investigated by thermal analysis (Mettler Toledo TGA/SDTA851; heating rate 5^0C/min; N_2 atmosphere).

WO_3 powders were characterized by surface area measurements (Micromeritics Tristar II 3020 instrument, N_2 adsorption; BET method for surface area; the BJH method/desorption branch for pores size distribution) and UV-Vis spectroscopy/diffuse reflectance spectra (Jasco Spectrometer V650, with ILV 724 integrating sphere accessory, light source D2/WI). The photocatalytic activity was evaluated for methylene blue degradation (1g WO_3 powder was used for 100 ml aqueous 0.125 mM solution of methylene blue).

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