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Preparation by dip coating method and characterisation of WO_3 thin films

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Preliminary results referring to the synthesis of tungsten oxide thin films with possible utilization as photoanode for water splitting are presented. WO_3 thin films were deposited on optical glass substrate by dip coating method, using aqueous solutions of peroxotungstic acid (PTA). The dipping solution was prepared from tungsten oxide hydrate ($WO_3 \cdot xH_2O$) and hydrogen peroxide in well controlled conditions. After coating, the sol-gel derived films were heated at 250-550^{0}C to complete the dehydration of the tungsten oxide precursors. Different characterisation techniques were used to evaluate the cristalline structure (X Ray Diffraction-XRD), the morphology and particle size (Scanning Electron Microscopy-SEM), the behavior during the heating procees (Thermal Analysis- TGA-SDTA) and optical and structural properties (UV-Vis and FTIR Spectroscopy) of tungsten oxide precursors and WO_3 films.A correlation between preparation conditions and the characteristics of tungsten oxide precursors and WO_3 films was established.

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1. Introduction

WO_3, TiO_2, V_2O_5 are semiconductor materials with a band gap at around 3eV and good chemical stability in aqueous solutions. They presents specific characteristics in order to be used as photoelectrodes [1,2,3,4]

Tungsten oxide (WO_3) can be used as efficient photoanode for water splitting under visible light illumination [5,6] or in detection of gas [7,8]. Moreover, WO_3 thin films are also interesting electrochromic materials due to their nanocristalline nature which affords an open and porous structure [9].

The influence of the defects on the electrical conduction in WO_3 photoelectrodes used for water spertting was studied in [10].

Deposition methods are various and depend on the applicative domain. In this respect, tungsten oxide films were synthesized by several physical and chemical routes such as: chemical vapor deposition [11], spray pirolisys [12,13], sol-gel processing [14] and chatodic electrodeposition [15].

In this paper WO_3 thin films were prepared by dip coating method from tungstic acid and peroxotungstic acid in order to be used as electrodes for photoelectrolisys by splitting water.

2. Experimental part

Tungsten oxide thin films were obtained by dip coating method following several steps: a) synthesis (precipitation) of the tungstic acid (TA) from sodium tungstate and hydrochloric acid in controlled conditions; b) preparation of peroxotungstic acid (PTA) solution by dissolution of TA in hydrogen peroxide; c) deposition by dip coating of tungsten oxide based thin films on optical glass (40x30x1mm); d) thermal treatment of the samples at 250^{0}C and 550^{0}C respectively. Yellow tungstic acid ($WO_3 \cdot xH_2O$) was first prepared under continuous stirring by adding of 0.5 M sodium tungstate solution ($Na_2WO_4 \cdot 2H_2O$ - Aldrich) in a concentrated HCl - HNO_3 solution. After decantation, the precipitate was three times washed with demineralised water, and finally centrifuged and dried at 110^{0}C. The as obtained tungstic acid powder (TA) is used for preparation of the dip coating solution. As results a certain amount of TA was dissolved in hydrogen peroxide (30%) in order to obtain a yellow translucent solution. Three types of colloidal solutions were prepared using hydrogen peroxide and methylic alcohol at different reaction temperature and molar ratio. Tungsten oxide thin films (mono-layer) were obtained by depositing the colloidal solution on optical glass substrates by one dip coating stage with a withdrawal speed of 3cm/min. Conditions of the thin film preparation and samples code are summarised in table 1. In order to establish if the treatment of the optical glass influence the adherence and characteristics of the thin films, the glass substrate was used either dry or wet by keeping it immersed for 24h in water before deposition.

WO_3 powders were characterised by thermal analysis-TG-DTG-DTA (Mettler Toledo TGA/SDTA851; heating rate 5º C/min; nitrogen atmosphere), infrared absorption spectroscopy -FTIR spectra (JASCO 610 FTIR Spectrometer; KBr pellets technique), X-ray diffraction–

XRD patterns (DRON 3M Diffractometer, CuKα radiation) meanwhile the thin films were characterised by UV-Vis absorbtion/reflectance spectroscopy (UNICAM Spectrometer UV4, with RSA-UC-40 integrating sphere accessory) and scanning electronic microscopy-SEM images (JEOL –JSM 5510LV Microscope; Ag-coated powders).

Table 1 Synthesis conditions for dip coating solution from different types of reagents and their corresponding samples codes.

Precursor synthesis conditions						T_s^* /glass treatment (min)	Sample Code**	Sample code***
Colloidal Solution No.	Reagents	Molar ratio	Reaction Temperature	Time (h)	Residure code			
	H_2WO_4	TA	-	-	-	-	-	-
1	H_2WO_4 + H_2O_2	1:5	100^0C	2	PTA1	0/dry	W1	W1c
						0/dry	W2	W2c
						0/dry	W3	W3c
2	H_2WO_4 + H_2O_2	1:6	50^0C	4	PTA2	2/dry	W8	W8c
						4/dry	W9	W9c
						6/dry	W10	W10c
						10/dry	W11	W11c
3	H_2WO_4 +MeOH	1:12	80^0C	20	ETA	2/wet	W4	W4c
						4/wet	W5	W5c
						2/dry	W6	W6c
						4/dry	W7	W7c

** t_s- stationary time before withdrawing ** thermal treated at 250^0C, *** thermal treated at 550^0C,1h,*

3. Results and discussion

In order to determine the composition of the precursor (TA) and colloid powders (residue obtained by drying the dipping solution used for WO_3 thin film preparation) thermal analysis was performed. The residue was obtained by slow evaporation at ~ 50 ^{0}C of the tungsten oxide based dip coating solution. Fig. 1 presents the thermal analysis TG and DTA of precursor and tungsten oxide based residue. The thermal analysis (TG-DTG) of the tungstic acid (TA) prepared by precipitation of sodium tungstate in hydrochloric acid, suggests that the as mentioned precursor consists of an monohydrate tungsten oxide ($WO_3 \cdot H_2O$). The experimental value for weight water loss (7.32%) is in agreement with the theoretical value (7.204%). The water loss take places in a single decomposition step at 227^0C.

Three types of tungsten oxide based residues are obtained depending on the synthesis conditions. From DTG curves one can see that the weight loss take place in one, two or multiple steps meanwhile from DTA curves, exothermic peaks are observed for samples prepared with hydrogen peroxide. From weight loss data one can say that sample PTA1 is peroxo - tungsten oxide ($WO_3 \cdot H_2O_2$) that decomposes in one step at 206^0C; presence of exothermic peaks situated at 370^0C suggests decomposition of peroxo-compounds due to the presence of H_2O_2.

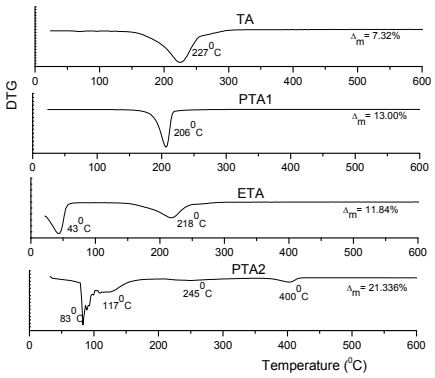


Fig. 1. Thermal analysis DTG (a) and DTA (b) for tungsten oxide precursor (TA) and residue tungsten oxide from dip coating solutions (PTA1, ETA, PTA2).

Sample PTA2 has a more complex composition than sample PTA1 as can see from DTG curve and weight mass value (21.336%). The formula ascribed for PTA2 is $WO_3 \cdot 0.42H_2O_2 \cdot 2.7H_2O$. Sample ETA prepared from TA refluxed for 20 hrs in MeOH and water corresponds to $WO_3 \cdot 1.7H_2O$. The decomposition step situated at 43^0C (in DTG curve figure 1) corresponds to the presence of organic residues. In Figure 2 are presented the FT-IR spectra for PTA1, PTA2, ETA powders.

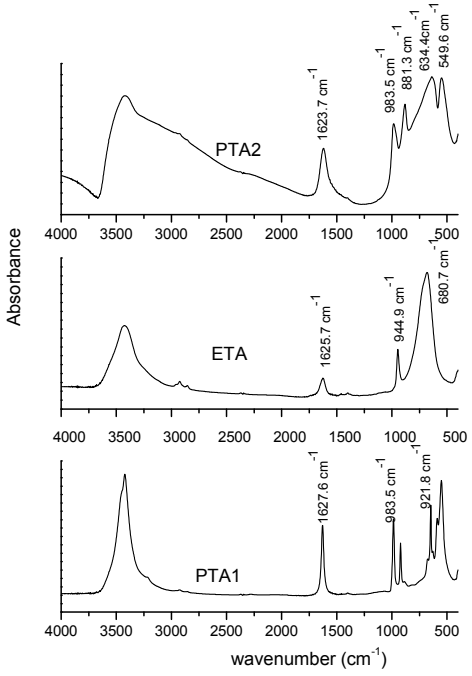


Fig. 2.FT-IR spectra for some tungsten based residue used for dip coating solution.

The FT-IR spectra for the residue powders consists of some characteristic bands such as: ν(HOH) and ν(OH) ~3500-2800cm^{-1}; δ H_2O ~1600-1650 cm^{-1}; ν(W=O) ~1000-970 cm^{-1}; ν(W-O_{inter}-W) and ν (W-O_{intra}-W) ~ 600-800 cm^{-1}.

XRD patterns illustrate that the precursor as well as the tungsten oxide based powders consist of well-formed crystalline phases. According to the literature, the tungsten oxide precursor contains orthorhombic tungsten oxide hydrate ($WO_3 \cdot H_2O$) in concordance with PDF 430679. On the other hand the structure of the powders corresponds to peroxo-tungstic oxide having the general formula $WO_3 \cdot xH_2O_2 \cdot yH_2O$ (PDF430699). The WO_3 thin film (sample W1) deposited onto glass presents a large band in $2\theta = 20 \div 30$ domain that suggests an amorphous structure (figure 3) with beginning of the crystallisation. The line situated at $2\theta = 15.8$ was found also in the PTA1 residue, which suggests that the film is not entirely converted in tungsten oxide.

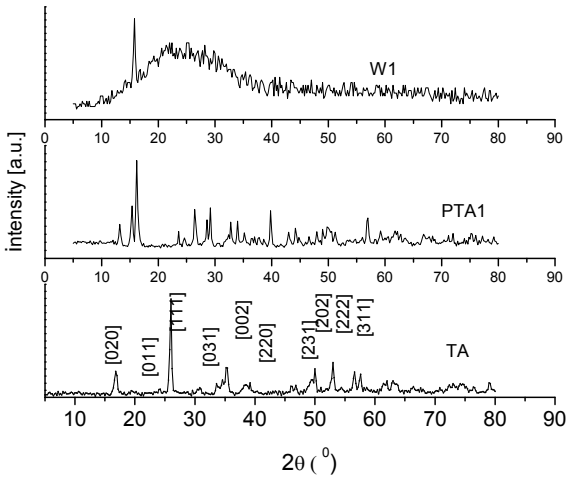
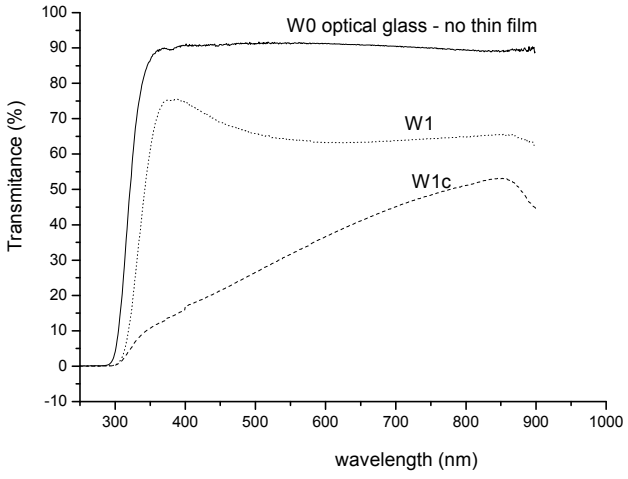
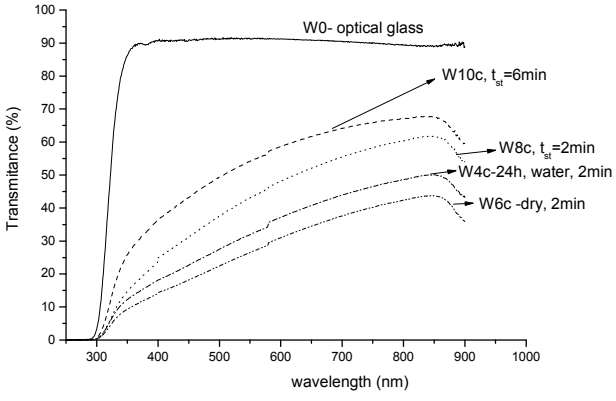


Fig. 3. XRD patterns for TA precursor tungsten oxide precursor; PTA1 powder and W1 thin film deposited on optical glass substrate.

The transmittance spectra between 300 ÷ 900nm wavelength range for some of the WO_3 thin films annealed at 250 and 550^0C respectively are illustrated in figure 4a and Fig. 4b.



a



b

Fig. 4. UV –vis spectra for some WO_3 thin films prepared in different synthesis conditions.

A relatively good transmittance of ~75 % is observed for samples dried at 250^0C(W1 sample figure 4 a). As the annealing temperature increase to 550^0C the transmittance decrease dramatically due to the thin film structure changes (sample W1c). This behaviour can be explained also by the appearance of the films, after drying at 250^0C the film is transparent with blue reflection and after thermal treatment the film lose the transparency and become light yellow due to the structure modifications. Figure 4b present the transmittance for samples prepared in different conditions. It seems that the stationation time before withdrawing of the glass from dip solution (t_s) can be an important parameter that influences the optical properties of the films (sample W10c). Another parameter that should not be neglected is the glass treatment before the deposition, even if the influence on the transmittance is not very spectaculars (samples W8c, W4c). The specular reflectance is evaluated as difference between total reflectance and diffuse reflectance (Fig. 5).

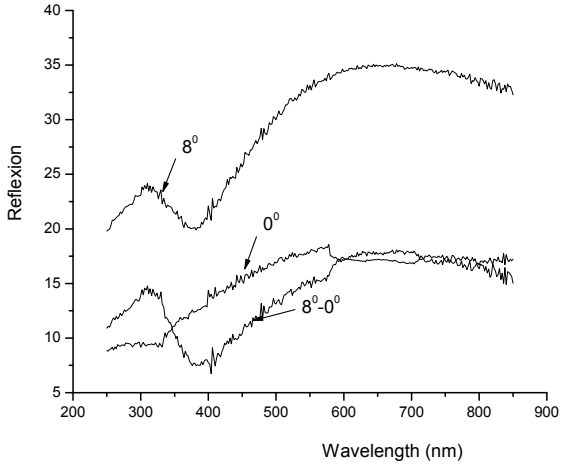


Fig. 5.Reflectance spectra for WO_3 thin films at 250^0C.

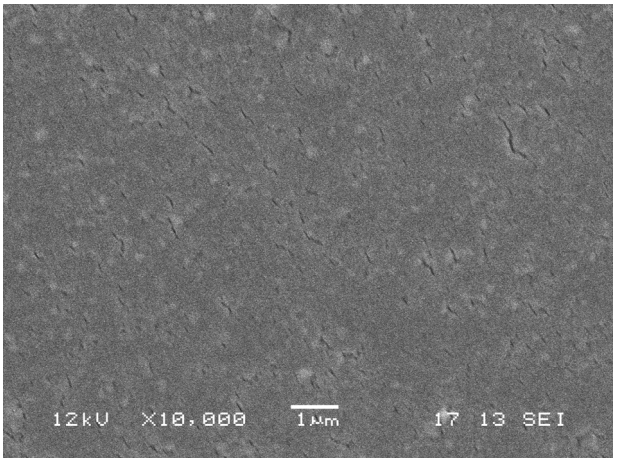


Fig. 6.SEM images for WO_3 thin films at 250^0C.

The surface morphology of the WO_3 film is put in evidence from SEM images in Fig. 6. The film is adherent relatively homogeneous and nano-structurated having small cracks and larger particles in some places

4. Conclusions

WO_3 thin films were prepared by dip coating technique on optical glass substrates (40x30x1mm) from aqueous solution of peroxotungstic acid. TG-DTA, FT-IR and XRD investigations, suggest that the dip coating solution corresponds to a tungsten oxide hydrate or peroxotungstic acids. The optical transmittance is influenced by the synthesis conditions such as thermal treatment, conditioning of the substrate, conditions of dip coating technique. In this respect the WO_3/Glass/WO_3 monolayer has a good transmittance between 350-450 nm if dried at 250^0C and decrease dramatically as films are fired at 550^0C. Further experiments are to be performed in order to improve the characteristics of the WO_3 thin films and to study there use as photoanodes .

Acknowledgements

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