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# WO<sub>3</sub> nanoparticles and PEDOT:PSS/WO<sub>3</sub> composite thin films studied for photocatalytic and electrochromic applications

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**Abstract.** WO<sub>3</sub> is a widely studied material for electrochromic and photocatalytic applications. In the present study, WO<sub>3</sub> nanoparticles with a controlled structure (monoclinic or hexagonal) were obtained by controlled thermal decomposition of hexagonal ammonium tungsten bronze in air at 500 °C and 600 °C, respectively. The formation, morphology, structure and composition of the as-prepared nanoparticles were studied by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDX). The photocatalytic activity of the monoclinic and hexagonal WO<sub>3</sub> nanoparticles was studied by decomposing methyl orange in aqueous solution under UV light irradiation. In order to study the electrochromic properties of the WO<sub>3</sub> nanoparticles, as well to introduce them for self-cleaning photocatalytic surface applications, thin films were prepared from the WO<sub>3</sub> particles together with a conductive polymer. For this, PEDOT:PSS was used, which gives excellent opportunities for obtaining transparent and conductive thin films, suitable for both electrochromic and photocatalytic applications. By spin-coating, transparent PEDOT:PSS/WO<sub>3</sub> composite thin films were prepared, on which cyclic voltammetry measurements were performed, and the coloring and bleaching states were studied. Our initial results for the PEDOT:PSS/WO<sub>3</sub> composite thin films are promising, suggesting that such composites, after further development, might be successfully used in electrochromic devices and photocatalysis.

## 1. Introduction

Tungsten trioxide (WO<sub>3</sub>) is one of the most studied inorganic materials with a wide potential of technological applications in fields like large scale electrochromic devices as displays, smart windows and optical switching coatings [1, 2]. In addition, WO<sub>3</sub> can be also used for many other applications, such as photocatalysis [3-5], water splitting [6], gas sensors for various toxic and flammable gases [7-14], and catalysis [15].

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WO<sub>3</sub> is one of the most widely researched photocatalysts because of its very good reductive and oxidative properties combined with the excellent abilities to absorb both visible and UV light, having a bandgap of 2.4-2.8 eV. Its photo-generated hole (h<sup>+</sup>) is oxidizing enough to generate •OH radical from water, but the photo-excited electron (e<sup>-</sup>) cannot reduce O<sub>2</sub>, which decreases its photocatalytic activity. However, this is compensated by the fact that WO<sub>3</sub> absorbs visible light in the most intensive part of the solar spectrum.

WO<sub>3</sub> has several crystalline modifications, but those with better photocatalytic properties are the monoclinic (m-) WO<sub>3</sub> (m-WO<sub>3</sub>) and the hexagonal (h-) WO<sub>3</sub> (h-WO<sub>3</sub>). The h-WO<sub>3</sub> has a three- and six-dimensional channel-system along its structure, which is stabilized by cationic impurities, e.g. NH<sub>4</sub><sup>+</sup>, in the hexagonal channels [16, 17]. The m-WO<sub>3</sub>, on the other hand, is completely oxidized, and therefore has a better photocatalytic activity [3]. Both h-WO<sub>3</sub> and m-WO<sub>3</sub> can be prepared by thermal annealing under different conditions. We optimized the annealing conditions of hexagonal ammonium tungsten bronze, (NH<sub>4</sub>)<sub>x</sub>WO<sub>3-y</sub> (HATB), through previous thermal studies (TG/DTA) in order to obtain the WO<sub>3</sub> samples with appropriate crystal structures and compositions [18]. Furthermore, both the monoclinic and hexagonal WO<sub>3</sub> have excellent electrochromic properties.

In order to enhance the photocatalytic activity, the catalyst particles should be small to have a high specific surface area and to offer a high number of surface active centers by unit mass. Dispersion of WO<sub>3</sub> particles during photocatalytic treatment of wastewater or any polluted liquids shows excellent photoactivity, but requires other troublesome and high-cost post-filtering processes to separate the nano-sized catalyst from the treated liquid. Thus, especially for long-term commercial applications, the powder photocatalyst needs to be immobilized onto a support, which is transparent and preferably conductive or semi-conductive, and which does not disturb the photo-electron transitions. One of the most widely studied and used materials for immobilizing the catalytic particles, i.e. resins, are usually insulators, which is a drawback, though their positive side is their low price. In our study, we proposed that a thin film of conductive polymer, as PEDOT:PSS, with dispersed photocatalytic nanoparticles could be also applied in photocatalysis.

Such a transparent conductive composite thin film containing WO<sub>3</sub> nanoparticles is promising also for electrochromic applications. PEDOT:PSS itself possesses electrochromic properties; these could be improved by adding nanoparticles of WO<sub>3</sub>, which show an even stronger electrochromic effect. Electrochromic studies of such composite PEDOT:PSS/WO<sub>3</sub> films have not been previously performed, and knowledge is needed on how these materials can be combined in order to be used in electrochromic devices.

## 2. Experimental

Hexagonal and monoclinic WO<sub>3</sub> nanoparticles were prepared by annealing hexagonal ammonium tungsten bronze (HATB), (NH<sub>4</sub>)<sub>x</sub>WO<sub>3-y</sub>, in air at 500 and 600 °C, respectively. (NH<sub>4</sub>)<sub>x</sub>WO<sub>3-y</sub> was prepared by the partial reduction of ammonium paratungstate tetrahydrate, (NH<sub>4</sub>)<sub>10</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>42</sub>].4H<sub>2</sub>O (APT), in H<sub>2</sub> for 6 h at 400 °C [19]. At temperatures over 450-500 °C, WO<sub>3</sub> crystallizes in a hexagonal, while over this temperature, predominantly in a monoclinic structure [20].

The crystalline structure of the samples was confirmed by XRD using a P'Analytical X'pert Pro MPD X-ray diffractometer using Cu Kα irradiation. Transmission electron microscopy (TEM) images were taken by an FEI Morgagni 268D device. The SEM-EDX study was performed by a JEOL JSM-5500LV scanning electron microscope (SEM).

The photocatalytic activity of the samples was tested by studying the degradation of methyl orange (MO) in aqueous solution under UV light. The absorbance of the MO solution, proportional to the MO concentration, was measured by UV-Vis spectroscopy. 1 and 3 mg of the WO<sub>3</sub> particles were placed inside a quartz cuvette, after that 3 mL of the MO solution (1 mg/mL) was pipetted into the cuvette. It was then sealed (with Parafilm), and left in the dark for 30 min, so that an adsorption equilibrium of the dye on the surface of the particles can be reached. This was required since the absorbance decays during the first 30 minutes in dark due to the adsorption of MO on the surface of the catalyst, which might lead to a false photocatalytic degradation result, if not taken into account. In order to avoid this

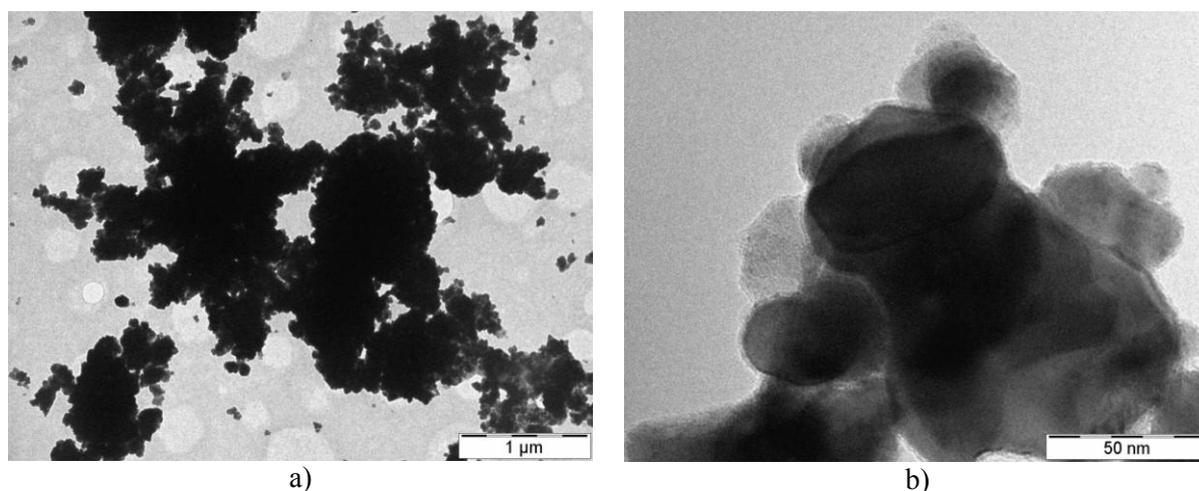
error, the measurement started after this waiting time of 30 min without any illumination. Then the cuvette was placed between two parallel 18 W black lights (Osram) providing UV light irradiation for 240 minutes, and the absorbance was measured every 30 minutes.

Spin-coating was used to prepare PEDOT:PSS/ $\text{WO}_3$  composite thin films on glass and ITO transparent conductive (TCO) glass substrates. Dispersion of the 200 mg  $\text{WO}_3$  nanoparticles into 1 mL commercial PEDOT:PSS and 3 mL water for spin-coating (Sigma-Aldrich) was prepared and mixed in an ultrasonic bath. A homemade spin-coating apparatus was used for the deposition, and the process parameters were tuned and controlled for obtaining homogenous films with thickness around a few hundred nm.

Cyclic voltammetry experiments were performed in a standard three-electrode set-up. The cell used Pt as a counter electrode and a saturated calomel electrode as a reference electrode, together with the studied PEDOT:PSS/ $\text{WO}_3$  films on ITO glass sheets. The electrodes were immersed in a 1 mol/L  $\text{LiClO}_4$  electrolyte dissolved in propylene carbonate (PC).

### 3. Results and discussion

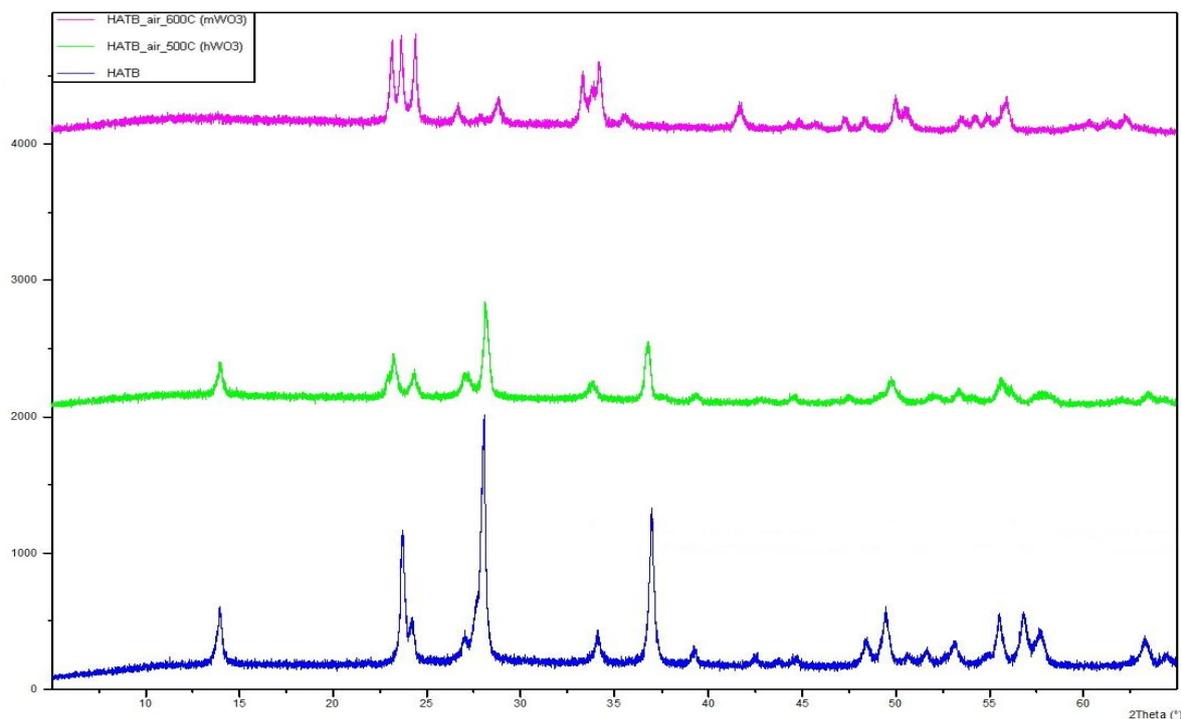
The morphology of the prepared  $\text{WO}_3$  samples was studied by TEM and SEM. Both the as-prepared hexagonal and monoclinic  $\text{WO}_3$  powders consisted of smaller particles and aggregates of these particles with different size (figure 1a)). The performed TEM imaging revealed that the  $\text{WO}_3$  particles were built of grains with a size of about 50-80 nanometers (figure 1b)). Such structures are both beneficial for photocatalysis and electrochromism, as the open structure of the particle aggregates means a higher specific surface area, and for electrochromic applications it is generally better to apply particles with a smaller size, in order to increase the transparency in bleached mode.



**Figure 1.** TEM images of h- and m- $\text{WO}_3$  nanoparticles: a) aggregate of h- $\text{WO}_3$  particles; b) m- $\text{WO}_3$  nanoparticles.

The hexagonal and monoclinic crystalline systems were confirmed by the XRD study (figure 2). The HATB samples (ICDD 42-0452) annealed to 600 °C showed the typical patterns of monoclinic  $\text{WO}_3$  (ICDD 43-1035), while those annealed to 500 °C exhibited the hexagonal  $\text{WO}_3$  pattern (ICDD 85-2460). These results indicated that the samples were made up by pure m- $\text{WO}_3$  and h- $\text{WO}_3$  phases. Also, from the XRD study it can be concluded that both the h- and m- $\text{WO}_3$  particles were highly crystalline, which was important, since from our previous studies it was determined that  $\text{WO}_3$  with a higher degree of crystallinity showed better both photocatalytic [3] and electrochromic [21] properties.

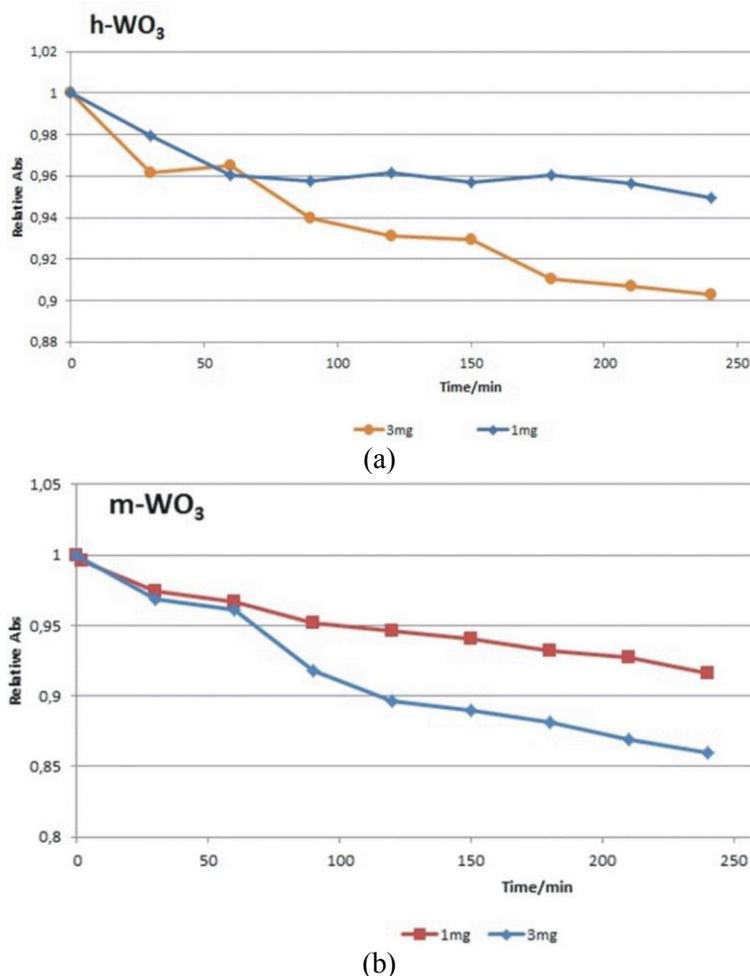
The performed EDX study confirmed the formation of pure m- $\text{WO}_3$ . The signal of nitrogen originating from residual  $\text{NH}_4^+$  was not observed, thus proving the full decomposition of HATB. The hexagonal  $\text{WO}_3$  powders contained traces of  $\text{NH}_4^+$ , the N signal in this case was difficult to be clearly distinguished from the noise. Still, their presence is expected, as they are important to stabilize the channel structure.



**Figure 2.** Powder XRD patterns of h- and m-WO<sub>3</sub> nanoparticles, compared with the initial HATB before annealing.

The photocatalytic self-oxidation of methyl orange (photolysis) was tested by filling a cuvette with MO solution without any catalyst and irradiating it by UV light for 240 minutes, measuring the absorbance every half an hour. After 4 hours, the MO concentration decreased by almost 4 %. These values were taken as a reference and compared with the values obtained when the h-WO<sub>3</sub> and m-WO<sub>3</sub> samples were used as photocatalysts. Methyl orange was selected as a probe molecule, as its absorption maximum (465 nm) is exactly where WO<sub>3</sub> has a minimum in its UV-Vis spectrum. MO is one of the most widely spread dyes for testing the photocatalytic activity of WO<sub>3</sub> [22]. Figure 3 shows the results from the photocatalytic measurements for 1 mg and 3 mg of h- and m-WO<sub>3</sub> samples in MO. The better photocatalytic activity was found for the m-WO<sub>3</sub> sample showing that MO degradation is accelerated by ~15 % in the presence of 3 mg m-WO<sub>3</sub> photocatalyst. The results were expected, as it was previously revealed that the m-WO<sub>3</sub> is a better photocatalyst [3]. The h-WO<sub>3</sub> is more reduced than the m-WO<sub>3</sub> because it has cationic impurities responsible for the channel-system structure, thus it possesses a lower photocatalytic activity. It was also shown that the amount of photocatalyst clearly influences the degradation of MO, since when 3 mg catalysts were used, the photocatalytic activity was higher.

For immobilizing these photocatalysts onto glass substrates, several issues had to be taken into account. The most important is that the specific surface area decrease (which is unavoidable) should be reduced as much as possible. This means that the nanoparticles should not be stuck into the polymer film, which at the same time has to possess high enough adhesion to both the substrate and the particles and should be stable in the environment of the application. Also, it is preferable that the film be a semiconductor with bandgap energies similar to the photocatalyst, and also to be highly transparent in order not to disturb the photoprocesses. All these requirements are hard to be accomplished simultaneously, so many compromises have to be done. In the present study, we decided to test the applicability of one of the most used conductive polymers, i.e. PEDOT:PSS, for immobilizing photocatalytic nanoparticles. The results showed that when appropriate deposition conditions were applied and the nanoparticles were well dispersed, it was possible to deposit high-quality homogenous composite thin films.

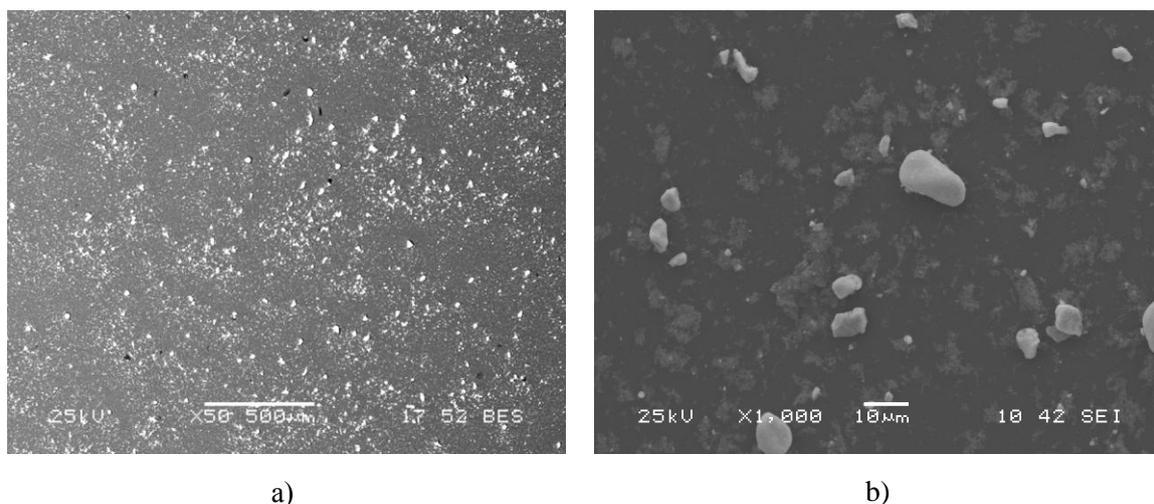


**Figure 3.** Photocatalytic study of h- and m-WO<sub>3</sub> nanoparticles:  
a) photocatalytic activity of h-WO<sub>3</sub> nanoparticles;  
b) photocatalytic activity of m-WO<sub>3</sub> nanoparticles.

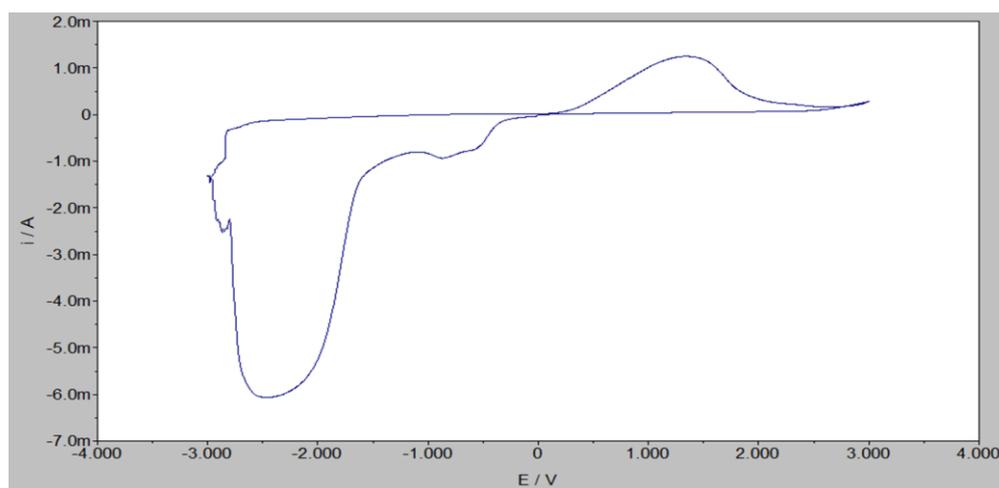
In figure 4a), a backscattered electron SEM image of a composite film is presented, where the m-WO<sub>3</sub> nanoparticles are very well distinguishable from the polymer. In such composite thin films, the size of the particles has to be larger, preferably at least twice as the film thickness, so that a big part of the surface stays out of the film. Note that the m-WO<sub>3</sub> nanoparticles were aggregated into micrometer scale blocks. The thicker films were more homogenous, but in them a big part of the nanoparticles remained in the polymer (figure 4b). Thus, we tried to achieve the smaller possible film thicknesses with the applied spin-coating method. A too thin constant and homogenous film is hard to be deposited, since if the spin-coating speed is too high or the viscosity of the dispersion is too low, the result is islands of the composite or a highly inhomogeneous film. Otherwise, with decreasing the spinning speed or increasing the density, the as-deposited films are thicker and the active surface of the particles is decreased.

On the as-prepared composite PEDOT:PSS/WO<sub>3</sub> thin films, cyclic voltammetry tests were performed and the electrochromic effect was observed. Both the pure and composite films showed good coloration (while visually it is stronger for the composite ones) and fast and full bleaching. It seems that the effect is reversible for many cycles, if low voltages, i.e. below  $\pm 0.8$  V, are applied. The measured cyclic voltammetry curve in the range  $\pm 3$  V is presented in figure 5.

The intercalation of ions into the film happens in the first measured period when the voltage goes from 0 V to negative values. Then the positive Li<sup>+</sup> ions are attracted to the electrode and go into the



**Figure 4.** SEM images of a composite PEDOT:PSS/m-WO<sub>3</sub> thin film on a TCO glass substrate: a) backscattered electron image; b) secondary electron image.



**Figure 5.** Cyclic voltammetry curve of a composite PEDOT:PSS/m-WO<sub>3</sub> thin film.

free places of the lattice, which consequently leads to the coloration of the film. When the voltage is reversed, the process starts to go backwards and when the applied voltage turns to positive, a large part of the ions de-intercalate, and the film bleaches. The coloration process starts between  $-0.25$  and  $0.3$  V, while the bleaching starts shortly after  $0$  V in the positive voltage regime. For PEDOT:PSS the voltage required for coloration and bleaching was lower than for WO<sub>3</sub>. Too high currents can cause destruction of the electrochromic films, so they must be avoided. The left part of the graph is typical but with too a high current peak, which shows the “burning up” of the sample. For this reason, smaller voltages should be applied. We determined that the best interval for measuring is  $\pm 0.8$  V, where we could perform successful tests with both the pure PEDOT:PSS films and those with WO<sub>3</sub> particles.

There is an existing problem of usage of PEDOT:PSS films for long terms in aqueous or polar liquids environment, as the films are not stable in such. This limits the application of the PEDOT:PSS/WO<sub>3</sub> films to only photocatalysis in gaseous, aerosol or non-polar liquids environments. Regarding the electrochromic applications, the films showed to be stable during the performed tests in the LiClO<sub>4</sub>/PC electrolyte, but for preparing electrochromic devices the usage of dry electrolyte is recommended.

#### 4. Conclusions

WO<sub>3</sub> nanoparticles with a controlled structure (monoclinic or hexagonal) were obtained by controlled thermal decomposition of (NH<sub>4</sub>)<sub>x</sub>WO<sub>3-y</sub> in air at 500 or 600 °C, respectively. By spin-coating of suspensions of the WO<sub>3</sub> nanoparticles in aqueous PEDOT:PSS, composite thin films were deposited onto glass and ITO conductive glass substrates, and their applicability for photocatalytic and electrochromic applications was checked.

The formation, morphology, composition and structure of the as-prepared nanoparticles and nanocomposite films were studied by TEM, SEM-EDX, and XRD. It was also investigated how the structure and composition of the WO<sub>3</sub> particles influenced the photocatalytic properties of the films and how the technology of preparing organic/non-organic composite layers could be optimized for using them in electrochromic devices and photocatalysis.

Our initial experiments on preparing composite PEDOT:PSS/WO<sub>3</sub> and testing its possible application for electrochromism and photocatalysis were successful and although there is much space for further optimization and development, the results are promising for future application of PEDOT:PSS/WO<sub>3</sub> thin films in electrochromic devices and photocatalysis.

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