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Preparation and characterization of WO₃ nanoparticles, WO₃/TiO₂ core/shell nanocomposites and PEDOT:PSS/WO₃ composite thin films for photocatalytic and electrochromic applications

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Abstract. In this study, monoclinic WO₃ nanoparticles were obtained by thermal decomposition of (NH₄)_xWO₃ in air at 600 °C. On them by atomic layer deposition (ALD) TiO₂ films were deposited, and thus core/shell WO₃/TiO₂ nanocomposites were prepared. We prepared composites of WO₃ nanoparticles with conductive polymer as PEDOT:PSS, and deposited thin films of them on glass and ITO substrates by spin coating. The formation, morphology, composition and structure of the as-prepared pure and composite nanoparticles, as well thin films, were studied by TEM, SEM-EDX and XRD. The photocatalytic activity of both the WO₃ and core/shell WO₃/TiO₂ nanoparticles was studied by decomposing methyl orange in aqueous solution under UV light irradiation. Cyclic voltammetry measurements were performed on the composite PEDOT:PSS/WO₃ thin films, and the coloring and bleaching states were studied.

INTRODUCTION

Tungsten trioxide (WO₃) has been the most widely researched and used electrochromic material. It has wide potential of technological applications in various electrochromic devices as displays, smart windows and optical switching coatings [1-3]. Also, WO₃ is one of the most promising photocatalysts [4-6], and it can be also used in gas sensing [7-10], solar energy conversion [3], water splitting [11], memory devices [12], etc.

In WO₃ the photo-generated holes are oxidizing enough to generate •OH radicals from water, but the photo-excited electrons cannot reduce O₂, which decreases its photocatalytic activity. But since WO₃ absorbs visible light in the most intensive part of the solar spectrum, this makes it a very good material for preparing composite photocatalysts, for example combined with TiO₂, which though has excellent photocatalytic properties, absorbs only UV light [5,13]. In addition, preparing composites of WO₃ and other transition metal oxides, could be beneficial also for many electrochromic applications [2,3,14].

In order to possess higher photoactivity, the catalyst particles should be so small to offer high number of active centres per unit mass or the catalyst to have high specific surface area, such as the nanoparticles [6,15]. To prepare pure monoclinic WO₃ nanoparticles we optimized the annealing conditions of hexagonal ammonium tungsten bronze, (NH₄)_xWO₃. Recently, we also demonstrated the atomic layer deposition (ALD) can be effectively used to deposit TiO₂ shell layer on WO₃ nanostructures [13]. ALD is a vapor phase deposition technique based on sequential, self-limiting reactions, capable to produce highly conformal and uniform thin films with thickness control of sub-nanometer precision [16-18].

For the most applications, it is preferred the powder WO_3 photocatalyst to be immobilized onto a support, which is transparent and preferably conductive or semi-conductive, which does not disturb the photo-electron transitions. Such a transparent conductive composite thin film containing WO_3 nanoparticles is promising also for electrochromic applications.

In the present study, novel WO_3/TiO_2 core/shell composite nanoparticles were prepared by employing controlled annealing of $(\text{NH}_4)_x\text{WO}_3$ to obtain m- WO_3 and subsequent ALD deposition of TiO_2 . Then we obtained composites of WO_3 nanoparticles with conductive polymer as PEDOT:PSS, and deposited thin films of them on glass and ITO substrates by spin coating. PEDOT:PSS itself possesses electrochromic properties, which could be improved by adding nanoparticles of WO_3 , which has stronger electrochromic effect. Electrochromic studies of such composite PEDOT:PSS/ WO_3 films were not previously performed and lack of knowledge exists how these materials can be combined, in order to be used in electrochromic devices.

The as prepared nanoparticles and nanocomposites, as well as the composite thin films, were characterized by various techniques (TEM, SEM-EDX, XRD). Their photocatalytic and electrochromic properties were also studied.

EXPERIMENTAL

Monoclinic WO_3 (m- WO_3) nanoparticles were prepared by annealing hexagonal ammonium tungsten bronze, $(\text{NH}_4)_x\text{WO}_3$ at 600 °C in air. $(\text{NH}_4)_x\text{WO}_3$ was prepared by the partial reduction of ammonium paratungstate tetrahydrate, $(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 4\text{H}_2\text{O}$ (APT), in H_2 environment [19]. The as-prepared m- WO_3 nanoparticles were covered with TiO_2 films by ALD in a Picosun SUNALE R-100 reactor at 300 °C using tetraisopropoxide (TTIP, $\text{Ti}(\text{O}^i\text{Pr})_4$) and H_2O as precursors. The precursor pulse times were 1 s for both TTIP and H_2O , while the purge times were 30 s, and 130 ALD cycles were used. Such ultra-thin ALD TiO_2 films were previously prepared and characterized by our team [13, 20].

Transmission electron microscopy (TEM) images were taken by an FEI Morgagni 268D device. A JEOL JSM 5500LV scanning electron microscope (SEM) was used for the SEM-EDX study. XRD patterns were recorded by a XRD applying a PANalytical X'pert Pro MPD X-Ray diffractometer using $\text{Cu K}\alpha$ irradiation.

The photocatalytic activity of the samples was tested by studying the degradation of methyl orange (MO) in aqueous solution (0.133 mg/mL) under UV light. 3 mg of the pure WO_3 and composite WO_3/TiO_2 nanoparticles were placed inside a quartz cuvette together with 3 mL MO solution. After 30 min adsorption time in dark, the UV lamps (2 parallel Osram 18 W blacklights) were switched on and the absorbance of MO was measured by a Jasco V550 UV-Vis spectrophotometer at 463 nm in every 30 min.

Spin-coating method was used to prepare PEDOT:PSS/ WO_3 composite thin films on glass and ITO transparent conductive (TCO) glass substrates. Dispersion of the 200 mg 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, altogether with the studied PEDOT:PSS/ WO_3 films on ITO glass sheets. The electrodes were immersed in a 1 mol/L LiClO_4 electrolyte dissolved in propylene carbonate (PC).

RESULTS AND DISCUSSION

The morphology of the prepared WO_3 and composite WO_3/TiO_2 nanoparticles was studied by TEM and SEM. The WO_3 were built of 60-90 nm of nm particles. After the ALD reaction, a uniform ~4 nm thick TiO_2 film covered the nanoparticles; thus, the successful preparation of WO_3/TiO_2 core/shell nanocomposites was confirmed (Fig. 1a). The as-prepared composite PEDOT:PSS/ WO_3 thin films were observed by SEM. In the backscattered electrons SEM image (Fig. 1b) of these composite films, the WO_3 nanoparticles could be very well distinguished from the polymer. The EDX study confirmed the formation of pure WO_3 particles, detecting only W and O in them. In the WO_3/TiO_2 composite the presence of Ti was also detected.

XRD showed that the $(\text{NH}_4)_x\text{WO}_3$ annealed to 600 °C had the typical patterns of monoclinic WO_3 (ICDD 43-1035). The sample was highly crystalline, which was important, as from our previous studies it was determined that WO_3 with higher degree of crystallinity had better both photocatalytic [6] and electrochromic properties [21]. Since the TiO_2 layer was too thin, it could not be detected by XRD [13].

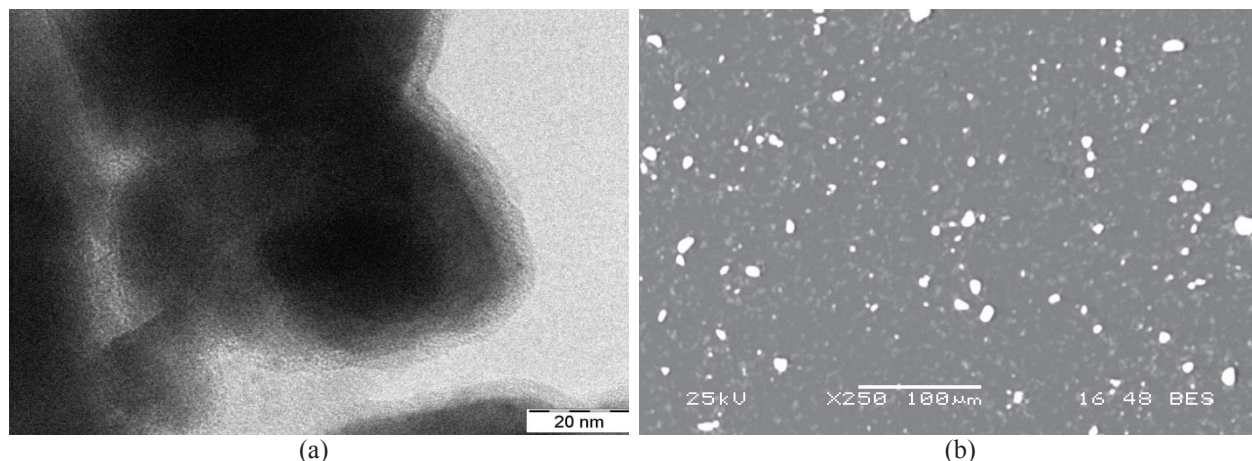


FIGURE 1. (a) TEM image of aggregate of m-WO₃ nanoparticles, covered with ultra-thin TiO₂ ALD film; (b) Backscattered electrons SEM image of composite PEDOT:PSS/m-WO₃ thin film on ITO glass substrate.

Figure 2 shows the results from the photocatalytic measurements for m-WO₃ and m-WO₃/TiO₂ samples. The better photocatalytic activity was found for the m-WO₃ nanoparticles sample, with 14 % of MO decomposed in 240 min. At the same time, the m-WO₃/TiO₂ sample showed only half of photocatalytic degradation of MO. The reason for this is that WO₃ particles formed aggregates and the ALD TiO₂ layer filled the voids between the single particles to some extent, and this decreased the specific surface of the composite, and thus the photocatalytic activity.

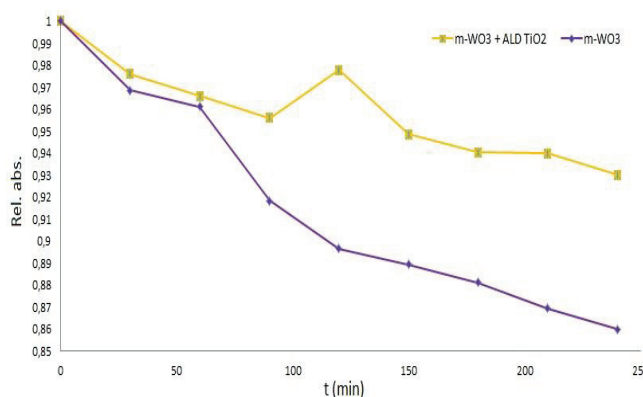


FIGURE 2. Photocatalytic study of m-WO₃ nanoparticles and m-WO₃/TiO₂ core/shell nanocomposite: decomposing aqueous methyl orange by UV light.

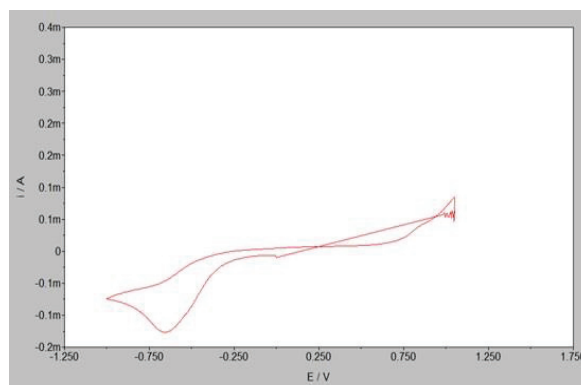


FIGURE 3. Cyclic voltammetry curve of composite PEDOT:PSS/m-WO₃ thin film.

On the composite PEDOT:PSS/WO₃ thin films cyclic voltammetry measurements were performed and the electrochromic effect was observed. The films showed good coloration and fast and full bleaching. It seems that the effect is reversible for many cycles, if low voltages, below ± 0.5 - 0.6 V, are applied. Measured cyclic voltammetry curve in the range ± 1 V is presented in Fig. 3. The coloration process started at -0.25 to -0.3 V, the bleaching started very close to 0 V in the positive voltage region. The left part of the graph is typical but with a high current peak, which shows the “burning up” of the sample. For this reason, smaller voltages should be applied. Also, PEDOT:PSS films cannot be used long in aqueous or polar liquids environment, as they are not stable in such. This limits the application of the PEDOT:PSS/WO₃ films to only photocatalysis in gaseous, aerosol or non-polar liquids environments. For electrochromic applications, the films showed to be stable during the performed tests in the LiClO₄/PC electrolyte, but still for preparing electrochromic devices using dry electrolyte is preferred.

CONCLUSIONS

Monoclinic WO₃ nanoparticles were obtained by annealing (NH₄)_xWO₃ at 600 °C in air. By ALD ~4 nm thick TiO₂ film was deposited on them, thus forming m-WO₃/TiO₂ core/shell nanocomposite. By spin-coating suspensions of the WO₃ nanoparticles in aqueous PEDOT:PSS, composite thin films were deposited onto glass and ITO conductive glass substrates, and their photocatalytic and electrochromic applications were checked. The as-prepared WO₃ and WO₃/TiO₂ nanoparticles and PEDOT:PSS/WO₃ thin films were studied by TEM, SEM-EDX, and XRD.

It was found that the deposition of shell ALD layer on the m-WO₃ nanoparticles decreased the photocatalytic activity, due to filling the voids between the particles and hence reducing the specific surface. Cyclic voltammetry measurements showed good coloration and fast and full bleaching, but it was also shown that higher currents and voltages could cause destruction of the electrochromic film, so they must be avoided. Though there is still much space for further optimization and development, the results are promising for future application of these novel nanocomposites in photocatalysis and electrochromic devices.

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