Structure, morphology and electrocatalytic properties of WO$_x$ thin films prepared by reactive pulsed laser deposition

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Abstract. Nanostructured WO$_x$ films were prepared by pulsed laser deposition in air from W target. The pressure of air was varied in a range of 10 – 100 Pa and the temperature of a glassy carbon substrate during the film deposition was 22 or 500°C. For the films deposited at 22°C, thermal post-treatment in air of laboratory humidity at 500°C was applied. The increase of air pressure during PLD at 22°C caused both a decrease in packing density of ball-like amorphous nanoclusters of WO$_x$ and decline of their size. Post-treatment in air at 500 °C has initiated crystallization of the nanoclusters but characteristic morphology of the films was preserved in a whole. The PLD of WO$_x$ on a heated substrate resulted in the formation of nano-needles and nanosheets. Fairly good catalytic properties in hydrogen evolution reaction (HER) and in electrolytic Pt deposition were revealed for the WO$_x$ films that consisted of loosely packed ball-like nanocrystals possessing a size of ~20 nm. The catalytic activity of the films consisted of nanoneedles and nanosheets was not good enough. Adjustable electrolytic deposition of Pt on the nanostructured WO$_x$ support film allowed to prepare effective hybrid HER catalyst containing only ~7 µg/cm$^2$ of Pt.

1. Introduction

Nanostructured materials possessing different complex morphology have stimulated great interest due to their importance in basic scientific research and technological applications. Tungsten oxide (WO$_x$), an important n-type semiconductor, has received much attention for its potential application in fabricating the electrochromic and photochromic devices, gas sensors, and solar/hydrogen energy devices. The WO$_x$-containing materials could be successfully used for preparing electrocathodes for hydrogen evolution reaction (HER) in acid solutions as well as for obtaining photoanode for hydrogen generation by photocatalytic splitting of water.

For an area of HER application, the importance demands control over the dimension, size, and crystal structure of WO$_x$ nanoparticles for higher technology applications. Zhuikov et al. [1] have shown that orthorhombic β-WO$_3$ nanoflakes with thickness of about 7 to 9 nm is a superior material as a hydrogen production electrode of HER compared to hexagonal WO$_3$ nanowires and commercial WO$_3$. Ham et al. [2] prepared monoclinic WO$_3$ (m-WO$_3$) nanoplates and nanorods that showed much
higher electrocatalytic activity for HER from water than that of the commercial bulk m-WO₃. Rajeswari et al. [3] revealed that WO₃ nanorods with monoclinic structure, constitute a better electrocatalytic system for HER in acid medium compared to their bulk counterpart.

Chhina et al. [4], Lori et al. [5] and some other investigators considered WOₓ as a candidate material as an alternative to a traditional (e.g., carbon) catalyst support. The interaction between the WOₓ support material and the metal catalysts such as Pt could result in an increased HER activity of a hybrid Pt/WOₓ film.

Filipescu et al. [6], Bailini et al. [7] and other investigators have shown that pulsed laser deposition (PLD) allowed to prepare thin-film WOₓ coatings possessing various structures and morphology. The laser deposited WOₓ films are successfully used for preparing the gas sensors (e.g., Zuev et al. [8]). However, catalytic activity of pulsed laser deposited WOₓ films for HER hardly investigated. In this work, to obtain the WOₓ films with different structures and morphology, pulsed laser deposition was performed under various pressure of reactive gas (air) at low and higher temperatures of glassy carbon (GC) substrates. Electrocatalytic activity of the as-prepared WOₓ films and the hybrid Pt/WOₓ film for HER was studied. The hybrid Pt/WOₓ film were prepared by cathodic deposition of Pt on the WOₓ films.

2. Experimental details

“Solar” laser with wavelength of 266 nm was used for ablation of W target. A pulse duration was 15 ns, a repetition rate was 25 Hz, and a pulse energy did not exceed 40 mJ. The fluence in the laser spot was ~8 J/cm². Laser pulses of ~18000 were used to obtain the films. The chamber with targets and substrates was evacuated to residual pressures of 10, 40 and 100 Pa. The laser-initiated plume was directed along the normal toward the surface of the substrate that was located at 4 cm from the target. The substrates were made of polished glassy carbon and cleaned in ultrasonic bath with acetone. The temperature of the substrate during deposition of the films was 22 or 500°C. Some samples prepared at 22°C were annealed at 500°C in 60 min in air.

The obtained films were examined by the methods of scanning electron microscopy (SEM) using secondary electrons (SE) and back scattered electrons (BSE), energy dispersive X-ray spectroscopy (EDS), and micro-Raman spectroscopy (MRS).

The HER activity of the WOₓ films was investigated at room temperature using a traditional three-electrode electrochemical cell. An electrochemical cell E-1C has a separated reference electrode container with two electrolytic keys. A Pt wire counter electrode was located in a special chamber that is connected with main working volume through a glass tube, inside which a porous glass plate is installed. It is necessary to divide electrolytic volumes of the working and counter electrodes, while ensuring the electrical contact between them. The aqueous 0.5 M H₂SO₄ solution was used for the HER studies. The cathodic polarization curves were measured at a slow change in the voltage (1.0 mV/s). The potential was measured relative to the standard hydrogen electrode.

For electrolytic Pt deposition on the WOₓ films, a Pt sheet (counter electrode) was located in front of the working electrode at a distance of 4 mm. A low content of KCl was added in 0.5 M H₂SO₄ solution to accelerate dissolution of Pt counter electrode under anodic polarization. The HER activity of the prepared WOₓ and Pt/WOₓ films was compared with that of the Pt film prepared on GC substrate by PLD.

3. Results and discussions

All the obtained WOₓ films had blue color that indicates an effective interaction of the laser-deposited W plume with oxygen from the residual gas and, consequently, the formation of substoichiometric film composition (x<3). The morphology of the prepared WOₓ films is found to be dependent on both the gas pressure and the temperature of substrate at the PLD (Figures 1 and 2). For air pressures of 10 and 40 Pa, the GC substrate was relatively uniformly covered with the WOₓ film. Homogeneity and continuity of the films were visibly disturbed when the air pressure was increased up to 100 Pa.
The deposition at 22°C caused the formation of ball-like nanoparticles of WO₅. The size of the particles and their packing density decrease if the air pressure is increased. The morphology of the film changes from dense/spheroidal to highly porous/fractal. Post-treatment in air at 500 °C resulted in discontinuity of the coating layer (Figure 3). Ball-like particles in the bulk of the film have grown to some extent, however the morphology of the films was not changed significantly (Figure 4).

**Figure 1.** BSE SEM images of WO₅ films prepared on GC at 22°C by PLD at 10 (a), 40 (b), and 100 Pa (c).

**Figure 2.** SE SEM images of a bare GC (a) and WO₅ films prepared on GC 22°C by PLD at 10 (b), 40 (c), and 100 Pa (d).

**Figure 3.** BSE SEM images of WO₅ films prepared at 22°C on GC at 10 (a), 40 (b), and 100 Pa (c) by PLD with thermal post-treatment.

**Figure 4.** SE SEM images of the WO₅ films prepared at 22°C on GC at 10 (a), 40 (b), and 100 Pa (c) by PLD with thermal post-treatment.
Figure 5 shows the results of SEM study for the WO$_x$ films prepared by PLD on the hot substrate. Independently on air pressure the growth of nanoneedles and nanosheets was revealed. These nanoelements were predominantly perpendicularly to the substrate surface.

![Figure 5](image)

**Figure 5.** SE SEM images of the WO$_x$ films prepared on GC at 500°C by PLD at 10 (a), 40 (b), and 100 Pa (c).

Figure 6 allows to reveal the dependence of WO$_x$ crystallinity on the preparation conditions. Annealing in air caused the crystallization of the WO$_x$ films that were obtained at 22°C. Relatively sharp lines at 270, 327, 700, and 800 cm$^{-1}$ appeared in the spectra of annealed films (Figure 6b) instead of broad lines in a range 600 – 900 cm$^{-1}$ that are characteristic of disordered structure of the WO$_x$ (Figure 6a). Two lines in a range 1200 – 1700 cm$^{-1}$ are due to GC substrate. The PLD on the hot substrates caused the formation of crystalline structure at relatively high pressure of air (40 and 100 Pa). However, for low pressure of 10 Pa, the structure of the nanoneedles was strongly disordered (Figure 6c).

![Figure 6](image)

**Figure 6.** MRS spectra of the WO$_x$ films prepared by PLD at various air pressures on GC at 22°C before (a) and after thermal post-treatment (b), and obtained at 500°C (c).

Figure 7a shows polarization curves of different WO$_x$ films deposited on GC substrate. Activation of HER was observed only for the WO$_x$ films that were deposited at 22°C in air at pressures of 10 and 40 Pa. The annealing procedure increases the activity of these films. In the case of bare GC, the reduction current density reached -0.03 mA/cm$^2$ at an overpotential around -200 mV. For this overpotential, after the preparation of the WO$_x$(40 Pa/22°C/500°C) film the current density has increased in ~15 times. The deposition of the WO$_x$ film which consisted of nanoneedles and nanosheets adversely affects the HER activity of the samples.

The increased HER catalytic activity of the WO$_x$(40 Pa/22°C/500°C) film facilitates to Pt deposition on the WO$_x$ in Cl-containing 0.5M H$_2$SO$_4$ solution. Reactive molecules of this solution could cause the decomposition of Pt counter electrode. The Pt-containing ions could migrate in the solution to the WO$_x$ surface and initiate Pt nanoparticles growth due to redox processes.
shows SEM images of the WOₓ(40 Pa/22°C/500°C)/GC sample which was polarized in Cl-containing 0.5M H₂SO₄ solution in 6 cycles. The polarization curve of this sample is shown in Figure 7b. The density of cathodic current for the Pt/WOₓ(40 Pa/22°C/500°C)/GC catalyst exceeds that for the Pt/GC catalyst in all range of applied potentials. This effect could be caused by a porous structure of the WOₓ supported layer possessing a specific distribution of Pt on the surface of the metal-oxide layer.

**Figure 7.** (a) polarization curves of the different WOₓ/GC, bare GC and Pt/GC samples in 0.5M H₂SO₄ solution; (b) evolution of the polarization curves for the WOₓ(40 Pa/22°C/500°C)/GC sample in 0.5M H₂SO₄/KCl solution after 1, 4 and 6 cycles of cathodic polarization. The result for Pt/GC sample is presented for comparison.

**Figure 8.** (a,b) SEM images of the WOₓ(40 Pa/22°C/500°C)/GC sample after the electrolytic deposition of Pt; (c) berry-like clusters of WOₓ nanoballs (whiter fragments) loaded with Pt.

Figure 8 shows that some ball-like WOₓ nanoparticles with a size of ~20 nm could break away the GC surface and migrate on the surface of WOₓ film. Berry-like clusters that consisted of weakly bonded nanoballs covered the surface of this catalyst (Figure 8b). Platinum was effectively deposited on these clusters that results in a large area of catalytically active sites for HER (Figure 9). Estimated value of the Pt loading was about 7 µg/cm².

4. Conclusions
Pulsed laser deposition allows to prepare thin-film WOₓ coatings possessing various structures and morphology. Only particular modifications of the nanostructured WOₓ could be used for activation of HER in an acidic solution. These WOₓ films consist of weakly bonded ball-like nanoparticles with a
defective crystalline structure. Catalytically active WO\textsubscript{x} film could be used for preparation of a hybrid Pt/WO\textsubscript{x}/GC catalyst using the method of electrolytic Pt deposition. The hybrid Pt/WO\textsubscript{x}/GC catalyst is superior the Pt/GC catalyst in the efficiency of HER activation.

![EDS distribution of C, O, W, and Pt](image)

**Figure 9.** EDS distributions of C, O, W, and Pt on the surface of the WO\textsubscript{x}(40 Pa/22°C/500°C)/GC sample after electrolytic deposition of Pt in 6 cycles of cathodic polarization.

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