PHOTOELECTROCHEMICAL ACTIVITY OF SOL-GEL DERIVED WO_3 FILMS IN ARTIFICIAL PHOTOSYNTHESIS

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Artificial photosynthesis is a process, which converts solar energy to chemical energy stored in small molecules or compounds, for instance, H_2, H_2O_2, HCOOH, CH_3OH, etc. by using a manmade device that mimics the structure that can run the natural photosynthesis [1]. Tungsten (VI) oxide is a promising n-type transition metal oxide semiconductor with a band gap of about 2.5 – 2.8 eV which can absorb approximately 12% of solar light with maximum ~ 6.3% energy conversion efficiency and therefore has received a lot of attention. Photoelectrocatalytic properties of WO_3 are of particular interest because the energy of photoinduced holes in the valence band of WO_3 is sufficient to oxidize H_2O, Cl^- SO_4^{2-}, etc., and that is why the outcome of the photoanodic reaction depends greatly on the electrolyte composition [2].

In this work, WO_3 thin films on conducting glass (fluorine doped tin oxide - FTO) substrate were prepared by sol-gel method in aqueous solution by dip-coating technique. Firstly, peroxytungsten acid (PTA) was synthesized as precursor using sodium tungstate dehydrate (Na_2WO_4 x $2H_2O$), nitric acid and hydrogen peroxide. Next PTA was dissolved in ethanol obtaining PTA sol-gel, which was deposited on FTO substrate by dip-coating technique. After coating procedure samples were annealed at 500 °C for 2 h with heating rate of 5 °C/min. The coatings were characterized using X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and photoelectrochemical measurements in sulphate and chloride solutions.

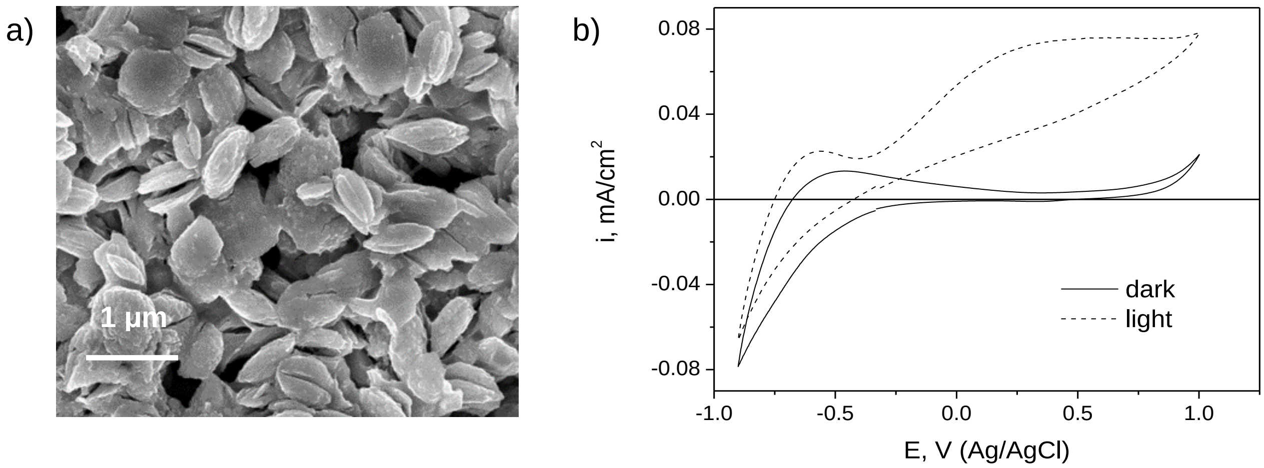

Fig. 1. a) SEM image of sol-gel derived WO_3 film, b) cyclic voltammograms of FTO/WO_3 photoelectrode in 0.5 M NaCl + 1.0 M KOH solution in dark and under illumination (100 mW cm^{-2}) run at 50 mV/s

SEM images revealed that sol-gel derived WO_3 films are composed of tiny plates with dimensions of several hundreds nanometers (Fig. 1a). Structure of the coatings was analyzed using XRD technique. The results showed crystalline structure of the films annealed at 500°C. Obviously patterns at 2θ= 23.13°, 23.56°, 24.33°, 41.67°, 44.38°, 45.74°,47.24°, 48.35°, 49.89°, 50.62°, 51.83°, 53.63°, 54.25°, 54.88°, 55.86° corresponded to monoclinic WO_3 structure in accordance with ICDD 01-083-0950. Also $Na_2W_4O_{13}$ and FTO crystalline phases were observed. According to literature [3], the structure of bulk tungsten oxide annealed at 500°C should be orthorhombic (β -WO_3, 330 °C to 740 °C), whereas annealed at lower temperatures should be monoclinic (γ-WO_3, 170 °C to 330 °C). In this study structure of tungsten oxide was found to be monoclinic, implying that substrate also influences phase structure of the coating.

Cyclic voltammograms of FTO/WO_3 photoanodes recorded in alkaline chloride solution in dark and under illumination revealed remarkable photoelectrochemical activity with almost 8-fold increase in anodic photocurrent at E = 0.5 V (Ag/AgCl) (Fig. 2b). The dependence of photoelectrochemical performance of sol-gel derived WO_3 films on the anionic composition and pH of the electrolytes along with stability of the photoactive material were investigated and the results will be presented at the conference.

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[3] H. Zheng, J.Z. Ou, M.S. Strano, R.B. Kaner, A. Mitchell, K. Kalantar-Zadeh, Nanostructured tungsten oxide - Properties, synthesis, and applications, Adv. Funct. Mater. 21 (2011) 2175–2196. doi:10.1002/adfm.201002477.