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Full Length Article

Fabrication and characterization of photoelectrochemically-active Sb-doped Sn_x-$W_{(100-x)\%}$-oxide anodes: Towards the removal of organic pollutants from wastewater

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ABSTRACT

Sn_x-$W_{(100-x)}$-oxide coatings (x = 0, 20, 40, 60, 80 and 100) doped with Sb (~3 at.%) were formed on a Ti substrate by a thermal deposition method in order to evaluate their potential use as electrodes for the photoelectrochemical oxidation of organic compounds. Surface microstructure/morphology and chemical composition of the coatings, as well as their photoelectrocatalytic activities were investigated using electrochemical and surface-characterization techniques. It was found that the surface roughness of the coatings depends on their composition, yielding an average value of $R_a = 1.1 \pm 0.5\ \mu m$. The band gap energy was found to be independent on the coating composition up to the relative W/Sn at. ratio of 4/6, yielding an average value of 3.53 ± 0.05 eV (which corresponds to the band gap of doped SnO_2), but then it decreased for the three coatings with the highest W content, to an average value of 2.56 ± 0.10 eV (which corresponds to the value of pure WO_3). All the coatings were found to be photoactive under the anodic bias. Further, all the coatings were found to be photoelectrochemically active towards the degradation of phenol red dye solution under UV light irradiation. The intrinsic photoelectrocatalytic activity was found to be highest for the $Sn_{80\%}$-$W_{20\%}$-oxide electrode coating.

1. Introduction

One of the most serious environmental concerns of the 21 st century is the increasing presence of synthetic and naturally occurring chemicals in the aquatic environment [1,2]. These compounds include pharmaceuticals, hormones and phenolic organic contaminants which are prevalent in the wastewater of a number of industries such as oil refining, textiles, pharmaceuticals, pulp and paper, and plastics [3,4], and have the potential to cause adverse ecological and/or human health effects. Conventional treatment methods such as physical, chemical or biological processes are in certain cases ineffective or insufficient in the removal or destruction of organics [5]. In recent decades, more and more efforts have been put in developing new technologies for the treatment of persistent organic contaminants [6,7]. Ozonation and Advanced Oxidation Processes (AOPs) such as UV and visible light irradiation-based oxidation (e.g. photocatalysis) and electrochemical methods are among the most investigated techniques for the elimination of organic contaminants [8–10]. Electrochemical methods have proved to be effective for the treatment of organic-containing wastewaters, especially when it is combined with the photochemical oxidation process [11–14]. These processes involve the generation of strong oxidants such as hydroxyl radicals (•OH), because of the formation of electron-hole pairs in semiconductors upon photo-radiation, and consequent oxidative decomposition of organic molecules. In addition, direct electrochemical oxidation at the electrode surface (anode) is possible. The photo- and electrochemical technology offers many advantages such as low cost, simplicity, versatility, modularity, ease of control, environmental compatibility, and minimum waste production [15,16].

Metal oxide materials are of great importance for environmental applications because of their photoactivity (capability to generate charge carriers when exposed to photo-radiation), electrochemical activity, and good stability [17]. Since the discovery of photoelectrochemical water splitting using TiO_2 electrodes [18], this semiconductor photocatalyst has been of particular interest for wastewater purification as well as production of hydrogen as a renewable energy source [19,20]. Until now, TiO_2 has been the most promising photocatalyst, because of its low cost, non-toxicity and good stability under irradiation [21,22]. However, the lack of visible light activity due to its relatively wide band gap (3.2 eV) and low

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quantum efficiency, in addition to its low electrocatalytic activity for the anodic oxidation of organics, limits its practical applications. Therefore, more photo/electroactive metal oxide anode materials are needed. More closely, it is desirable to decrease the bandgap to facilitate the production of photogenerated charge carriers, while increasing (or at least maintaining) the electrochemical activity. In order to address the above-mentioned drawbacks, doping of TiO_2 and other metal-oxide photoactive electrode materials with a range of metals has been applied: anion-doping with N [23], C [24], S [25] and I [26], and cation-doping with some transition metals such as Pt [27], Au [28], Ag [29], Mg [30], Mn, Ru, Rh and Ir [31] to name but a few.

Sb-doped SnO_2 is considered as one of the most promising electrode materials for electrochemical degradation of organic pollutants [32–34], while undpoed SnO_2 (*n*-type semiconductor; $E_g \approx 3.5$ eV) cannot be used directly as an anode material due to its low conductivity at room temperature [35]. Another approach in the development of more (photo)electroactive anode materials is the use of coupled semiconductors such as SnO_2-TiO_2 [36,37], WO_3-TiO_2 [38,39], CeO_2-TiO_2 and ZrO_2-TiO_2 [37], which allows the desirable matching of their electronic band structure. It is generally accepted that the coupled systems offer higher degradation rate and efficiency in organic wastewater treatment [36]. In recent years, multi-component metal oxide semiconductors have also been extensively investigated for the effect of composition on their band gap and thus, the photocatalytic activity [40–46]. The ternary and quaternary systems have shown enhanced solar-light response in addition to providing the possibility of band gap tuning, due to their various morphologies [47]. Zhang et al. [20] thoroughly reviewed the research and development of photoelectrocatalytic materials for environmental applications in their feature article.

Because of the interesting properties of doped SnO_2 as an electroactive material [48,49] and WO_3 as a photoactive material [50,51], these two materials were chosen as base electrode materials for their possible use as anodes for the wastewater treatment and disinfection. In this manuscript, we report results on the synthesis of antimony-doped tin-tungsten-oxide electrodes *via* a thermal deposition method and their characterization by electrochemical, optical, surface/structure techniques. Also, the effect of electrode composition on their photo- and electrochemical activity for degradation of phenol red dye was investigated. Their performance as anode materials for the oxidation of a pharmaceutical compound and for the water disinfection will be presented in separate manuscripts.

2. Materials and methods

2.1. Electrode preparation

Sb-doped Sn_x-$W_{(100-x)\%}$-oxide coatings (x = 0, 20, 40, 60, 80 and 100) were prepared on flat titanium substrates employing a thermal method. First, stock solutions of tin, tungsten and antimony salts were prepared by dissolving $SnCl_2{\cdot}2H_2O$ (ACS reagent, ≥98.0%, Sigma Aldrich), $Na_2WO_4{\cdot}2H_2O$ (Certified ACS, 100.0%, Fisher), and $SbCl_3$ (ACS reagent, ≥99.0%, Sigma Aldrich) salts in HCl (37 wt.%, Fisher) and water. All solutions were prepared using ultra-pure deionized water (resistivity: 18.2 MΩ cm). For each coating composition, a precursor solution with a total metal content concentration of 0.3 M was prepared by mixing proper amounts of metal salt stock solutions and adding deionized water to yield a final volume of 15 mL. The proper amount of each solution was calculated based on the desired composition of Sn and W in the coating material (Sb content of 3 mol% was kept constant in all coating compositions).

Titanium substrates, which were used as the support for metal-oxide films, were 15.9 mm diameter discs machined to a thickness of 2 mm for characterization experiments and 50 mm × 100 mm × 2 mm flat sheets for degradation experiments. Ti substrates were pretreated before the deposition of coatings: they were first mechanically polished using 600-grit SiC sandpaper, then washed ultrasonically in deionized water for 15 min, and then etched in a boiling solution of HCl (37 wt.%) and water (1:1, v/v) for 30 min. Lastly, the substrates were rinsed sequentially with acetone, ethanol and deionized water and then dried with argon.

To form metal-oxide coatings, the precursor solution was applied onto the pretreated side of Ti substrate by brushing. The substrate was then dried in an oven at 110 °C for 5 min to evaporate the solvent, and then placed into a preheated air furnace at atmospheric pressure and at 500 °C for 15 min, followed by cooling in air at room temperature for 15 min. This process was repeated ten times (10 coats were formed). After the last application, the electrodes were annealed at 500 °C for 2 h in order to complete the formation of metal oxides in the coatings [52].

2.2. Coating characterization

The active surface area of the as-prepared electrode coatings was determined by electrochemical measurements employing a ferricyanide/ferrocyanide redox reaction, in a three-electrode cell using a computer-controlled Potentiostat (Metrohm/Eco Chemie Autolab PGSTAT30). Graphite, separated from the working electrode compartment by a glass frit, served as counter electrode. All the potentials were measured versus a Saturated Calomel Electrode (SCE) as reference. Electrochemical surface-area-determination experiments were carried out in 80 mL of 1 mM potassium hexacyanoferrate (III) ($K_3Fe(CN)_6$, also known as potassium ferricynide; ~99%, Sigma Aldrich) in 0.1 M KCl (≥99.0%, Fluka) at room temperature. The solution was deoxygenated by purging argon for 1 h before the experiments, but the solution was not purged/stirred during the actual electrochemical experiment to ensure that the redox species were transported towards/form the electrode surface by pure diffusion.

The surface roughness of the coatings was measured by a confocal microscope (Leica DCM8 3D) using *epi*-150X objective lens. To obtain information on the surface microstructure and elemental composition of the coatings, scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) was performed on the samples at different parts of the surface using a Hitachi SU3500 scanning electron microscope. Transmission electron microscopy (TEM) images were obtained using FEI Tecnai G^2 F20 (200 kV) Cryo-STEM. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo Scientific K-Alpha spectrometer equipped with an argon ion gun. The X-ray polychromatic source was AlKα (1486.6 eV). XPS survey scans of all samples were initially recorded to identify the elements present in the coating materials and their high-resolution spectra were acquired subsequently. The spectra were analysed using Avantage software (version 5.932) for data processing. Moreover, to examine the crystalline structure and lattice parameters of the electrode coatings, X-ray diffraction (XRD) analysis was performed employing a Bruker Discover D8-2D diffractometer with 0.5 mm dia. collimated Cu Kα (1.54 A) radiation at room temperature in a standard q–2θ mode.

The optical band gap value for each coating composition was measured by photoluminescence (PL) spectroscopy employing a 266-nm excitation laser and by UV/Vis spectrometry (Thermo Scientific Evolution 300).

2.3. Degradation of phenol red dye

The photoelectrocatalytic activity of as-prepared coatings was tested for the degradation of phenol red (PR) dye solution in a cylindrical batch reactor (Pyrex glass) under UV light irradiation