Electrochimica Acta 132 (2014) 58–66

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Tungsten Trioxide/Zinc Tungstate Bilayers: Electrochromic Behaviors, Energy Storage and Electron Transfer

Huige Wei[a,b], Daowei Ding[a], Xingru Yan[a,b], Jiang Guo[a], Lu Shao[c], Haoran Chen[d], Luyi Sun[e], Henry A. Colorado[f], Suying Wei[a,b,*], Zhanhu Guo[a,*]

[a] Integrated Composites Laboratory (ICL), Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, TX 77710 USA
[b] Department of Chemistry and Biochemistry, Lamar University, Beaumont, TX 77710 USA
[c] School of Chemical Engineering and Technology, State Key Laboratory of Urban Water Resource and Environment (SKLUWRE), Harbin Institute of Technology, 150001, China
[d] Department of Chemistry and Biochemistry & Materials Science, Engineering, and Commercialization Program, Texas State University-San Marcos, San Macros, TX 78666 USA
[e] Department of Chemical & Biomolecular Engineering and Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT 06269 USA
[f] Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín, Colombia

ARTICLE INFO

Article history:
Received 17 December 2013
Received in revised form 3 March 2014
Accepted 11 March 2014
Available online 22 March 2014

Keywords:
Bilayers
electrochromism
energy storage
electron transfer.

ABSTRACT

Pair-sequentially spin-coated tungsten trioxide (WO_3) and zinc tungstate ($ZnWO_4$) bilayer films onto indium tin oxide (ITO) coated glass slides have been prepared via sol-gel methods followed by annealing. The bilayers ($ZnWO_4/WO_3$ denoting the bilayer film with the inner layer of $ZnWO_4$ and the outer layer of WO_3 on the ITO while $WO_3/ZnWO_4$ standing for the bilayer film with the inner layer of WO_3 and the outer layer of $ZnWO_4$ on the ITO) exhibit integrated functions of electrochromic and energy storage behaviors as indicated by the *in situ* spectroelectrochemistry and cyclic voltammetry (CV) results. Accordingly, blue color was observed for the bilayer films at -1 V in 0.5 M H_2SO_4 solution. An areal capacitance of 140 and 230 $\mu F/cm^2$ was obtained for the $ZnWO_4/WO_3$, and $WO_3/ZnWO_4$ film, respectively, at a scan rate of 0.05 V/s in the CV measurements. The CV results also unveiled the electron transfer behavior between the semiconductor films in the oxidation process, suggesting a sequence-dependent electrochemical response in the bilayer films. Meanwhile, methylene blue (MB) was used as an indicator to study the electron transfer phenomenon during the reduction process at negative potentials of -0.4 and -0.8 V, in 0.5 M Na_2SO_4. The results indicated that the electrons transfer across the bilayers was enhanced at more negative potentials.

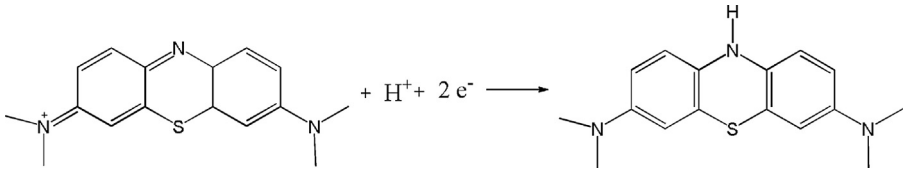
1. Introduction

Thin films have attracted significant attention due to their wide potential applications for electronic semiconductor devices [1–3], optical coatings [4,5], batteries [6,7], and photovoltaic cells [8,9]. A bilayer of two distinct thin films may form interesting junctions, leading to multifunctional devices [10]. The electron transfer process across different layers of a film is one of the key issues to understand the fabrications and operational fundamentals of these devices. The understanding of electron transfer and trapping in the bilayer film can optimize the structure design and improve the performances of bilayer film-based devices.

Tungsten trioxide, WO_3, is a wide bandgap semiconductor with versatile applications. It has become one of the most investigated functional materials due to its unique properties, for example, electrochromism, photochromism, electrocatalysis and photocatalysis [11–13]. WO_3 thin films are capable of exhibiting a reversible optical coloration during the electrochemical intercalation/deintercalation with cations such as H^+, Li^+, Na^+ and K^+ [14]. As a typical and most studied electrochromic material, WO_3 remains one of the promising candidates for electrochromic devices since its electrochromic behavior was first discovered in 1969 [15–17]. $ZnWO_4$, another important type of tungstate, has received considerable attention due to its particular physical and chemical properties [18–23] and wide applications for photocatalysis [24–26], photoelectrocatalysis [27] and photoluminescence devices [28,29]. Moreover, it has been reported that the combination of WO_3 and other materials may enhance the electrochromic behaviors of WO_3. Given the excellent chemical stability and a

* Corresponding authors.
E-mail addresses: suying.wei@lamar.edu (S. Wei), zhanhu.guo@lamar.edu (Z. Guo).

http://dx.doi.org/10.1016/j.electacta.2014.03.056
0013-4686/



Scheme 1. Reduction of methylene blue to leuco-methylene blue at negative potentials.

similar energy band structure to that of WO_3, the introduction of $ZnWO_4$ is expected to improve the chemical stability and electrochromic behaviors of WO_3. However, the electron transfer process between WO_3 and $ZnWO_4$ bilayer films has not been reported.

Methylene blue (MB) is a thiazine dye with quinonoimine group and has been widely used as a photosensitizer and as a model pollutant for photocatalysis study. MB can be reduced to its leuco form (colorless leuco methylene blue, LMB, Scheme 1) when it accepts electrons [30], enabling it extensively employed as a redox indicator in the chemical analysis. However, its application for electron transfer study has not been reported especially for bilayer structures.

In this work, MB was innovatively used as an indicator to investigate the electron transfer process between the bilayer films of tungsten oxide (WO_3) and zinc tungstate ($ZnWO_4$) on indium tin oxide (ITO) coated glass slides. The amount of electrons transferred can be monitored easily by measuring the concentration changes of MB. The combination of electrochemical measurements with UV-Vis spectroscopy was employed to study the electron transfer process and the structure properties. The electrochemical energy storage and the electrochromic behaviors of the bilayer films were also investigated in a systematic manner.

2. Experimental

2.1. Materials.

Tungsten (VI) ethoxide, diethylenetriaminepentaacetic acid, ammonium tungsten oxide hydrate, and methylene blue were purchased from Alfar-Aesar. Zinc nitrate hexahydrate was supplied by strem chemicals and citric acid was provided by Sigma-Aldrich. The microscope glass slides and indium tin oxide (ITO) coated glass slides were obtained from Fisher and NanoSci Inc, respectively. The ITO coated glass slides were sonicated in ethanol for 10 min, immersed in 5 mL deionized water containing 1 mL 28.86 wt% ammonium hydroxide and 1 mL 30.0 wt% hydrogen peroxide (both from Fisher) for 10 min, and sonicated in deionized water for 10 min before usage.

2.2. Preparation of WO_3 and $ZnWO_4$ Film Electrodes.

The $ZnWO_4$ precursor was prepared via a sol-gel method [31]. Briefly, 0.008 mol $5(NH_4)_2{\cdot}12WO_3{\cdot}5H_2O$ powder was first dissolved in 200 mL distilled water, and white precipitation was observed after a stoichiometric amount of $Zn(NO_3)_2{\cdot}6H_2O$ (0.096 mol) powders was added. Citric acid [n(metal ions): n(critic acid) = 1:1.1] was then added to the solution as a chelating agent to obtain the sol-gel precursor. The WO_3 film was also prepared via a sol-gel method [32,33]. Briefly, 0.5 g tungsten ethoxide was dissolved in 125 mL ethanol under stirring for 3 h at 75 °C. Then 0.5 mL distilled water containing 3.5×10^{-4} g HCl was added in the solution for hydrolysis while kept stirring vigorously at room temperature. The bulk film electrodes were prepared by dropping about 2 mL precursor on the ITO substrates, which have been cleaned using the aforementioned procedures, and spun at 2000 rpm for 20 s. The film was then calcined at 500 °C in the air for 2 h at a heating rate of 10 °C/min and cooled down to room temperature naturally. The bilayer films were prepared using a similar sequentially annealing method. Specifically, for the $WO_3/ZnWO_4$ bilayer film, the WO_3 precursor was spin-coated on the ITO substrate and annealed first, and then the $ZnWO_4$ precursor was spin-coated on the annealed WO_3 electrode, and was annealed again. The $ZnWO_4/WO_3$ bilayer film was prepared in a similar way. The bilayer film consisting of $ZnWO_4$ as the inner layer and WO_3 as the outer layer on the ITO was denoted as $ZnWO_4/WO_3$ while the bilayer film consisting of WO_3 as the inner layer and $ZnWO_4$ as the outer layer on the ITO was denoted as $WO_3/ZnWO_4$.

2.3. Characterizations.

FT-IR spectra of the films were performed on a Bruker Inc. Vector 22 (coupled with an ATR accessory) in the range of 500 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. The morphologies of the thin films grown on the glass slides were characterized by a JEOL field emission scanning electron microscope (SEM, JSM-6700F). The XRD analyses were conducted in a Bruker D8 Advance X-ray diffractometer equipped with a RINT 2000 wide-angle goniometer using Cu Kα radiation and a power of 40 kV × 40 mA. Diffraction patterns of the films were recorded within the range of 2θ = 10-70° with a step size of 0.02°. UV-Vis diffuse reflectance spectroscopy (DRS) was performed on a Jasco V-670 spectrophotometer and $BaSO_4$ was used as a reference.

Cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical working station VersaSTAT 4 potentiostat (Princeton Applied Research) at room temperature and atmospheric pressure. A classical three-electrode electrochemical cell consisting of a working, reference and counter electrode was used. Saturated calomel electrode (SCE) served as the reference electrode and a platinum (Pt) wire as the counter electrode. The film on ITO glass slide was used as the working electrode for optical and electrochemical characterizations. A long path length, home-made spectroelectrochemical cell with Teflon cell body with front and rear windows clapped with two steel plates was used when the film on ITO glass slide served as the working electrode. The CV was conducted between -1.0 and 1.0 V at different scanning rates in 0.5 M H_2SO_4 aqueous solution. EIS was carried out in a frequency range from 100, 000 to 1 Hz at a 10 mV amplitude referring to the open circuit potential. The spectroelectrochemistry (SE) measurements were performed on a Jasco V-670 spectrophotometer coupled with the potentiostat for applying electrochemical potentials. An Ag/AgCl electrode saturated with KCl was employed for SE measurements.

The reduction of MB upon subjecting to different potentials was analyzed to investigate the electron transfer process between WO_3 and $ZnWO_4$ bilayer films. The films were used as the working electrode (Pt wire as counter electrode, and SCE as the reference electrode) in 0.5 M Na_2SO_4 aqueous solution containing 5×10^{-6} M MB. The potentials were set at -0.4 and -0.8 V, respectively, for 3 h with an effective area of 2.5 cm^2 for the films. The MB removal efficiency of the films was calculated from the change in the maximum absorption peak intensity at 664 nm using a Jasco V-670 spectrophotometer.