Available online at www.sciencedirect.com
ScienceDirect
Solar Energy Materials & Solar Cells 91 (2007) 1282–1288
Solar Energy Materials and Solar Cells
www.elsevier.com/locate/solmat

Electrochromic properties of nanocomposite WO_3 films

Chia-Ching Liao*, Fu-Rong Chen, Ji-Jung Kai

Department of Engineering and System Science, National Tsing Hua University, Hsinchu 300, Taiwan, ROC

Received 27 July 2006; received in revised form 24 October 2006; accepted 20 November 2006
Available online 1 June 2007

Abstract

A new nanocomposite WO_3 (NWO) film-based electrochromic layer was fabricated by a spray and electroplating technique in sequence. An indium–tin oxide (ITO) nanoparticle layer was employed as a permanent template to generate the particular nanostructure. The structure and morphology of the NWO film were characterized. The optical and electrochromic properties of the NWO films under lithium intercalation are described and compared to the regular WO_3 film. The NWO films showed an improved cycling life and an improved contrast with compatible bleach-coloration transition time, owing to the larger reactive surface area. The nanocomposite WO_3 film-based electrochromic device (NWO-ECD) was also successfully fabricated. Most importantly, the NWO film can be prepared on a large scale directly onto a transparent conductive substrate, which demonstrates its potential for many electrochromic applications, especially, smart windows, sunroof and displays.

Keywords: Nanocomposite WO_3 film; Electrodeposition; Electrochromic applications; Smart windows; Sunroof; Displays

1. Introduction

The transition metal oxides with electrochromic properties have attracted much interests in recent years, since their potential applications in many important technological areas, such as in smart windows [1], self-dimming rear mirrors [2], electrochromic displays [3], sensors [4], etc., have been realized. Among the various transition metal oxides, tungsten oxide is found to be the most efficient candidate. However, the electrochromic performance and the reversible coloration under double injection of ions and electrons of tungsten oxide depend strongly on its nature and structure. In general, WO_3 thin films with high coloration efficiency are mostly obtained by vacuum evaporation [5]. Sputtering is one of the physical methods for WO_3 oxide films, which has been largely used [5,6]. Unfortunately, these methods are expensive, slow, and difficult to adopt for the deposition onto large-area substrates. Among the wet and low-cost methods, spray and electrodeposition seem to be very promising routes [6].

Several researchers have attempted to employ the concept of nanotechnology to improve the drawbacks of thin-film-based electrochromic devices (ECDs) such as contrast, cycling life stability and slow switching time between the colored and bleached states. For example, Gratzel [7] used TiO_2 nanoparticles and absorbed organic monomers to improve the switching speed. Kim and co-workers [8] developed arrays of structured PEDOT nanotubes to provide an attractive solution to improve the slow switching rate and the contrast. ECDs based on transition metal oxide nanowires (NWs, WO_3 and V_2O_5) were developed in our laboratory [9,10]. These new systems all show promising switching rate, life stability and contrast. These works prompted us to further develop ECDs based on nanostructured films.

In this paper, we developed a new nanocomposite WO_3 (NWO) film-based ECD (NWO-ECD) containing the nanostructured WO_3 film as an electrochromic layer. The NWO film was produced by the process involves two steps and each step involved a different procedure. First, the conductive tin-doped indium oxide (ITO) nanoparticles were sprayed onto commercial transparent conductive substrates. The WO_3 was then deposited by an electrochemical method to cover the pre-sprayed ITO

*Corresponding author. Tel.: +886 3 5715131 34282; fax: +886 3 5734066.
E-mail address: d927105@oz.nthu.edu.tw (C.-C. Liao).

0927-0248/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2006.11.020

nanoparticles to form the NWO film. A schematic diagram of conceptual structure of the NWO film is depicted in Fig. 1. The optical and electrochromic properties of the NWO films under lithium intercalation were studied in detail by UV–vis–NIR spectrophotometry and cyclic voltammetry.

2. Experimental

The spray solution was prepared by dissolving a commercial tin-doped indium oxide powder (LHC, particle size less than 40 nm, and resistivity $\rho = 1.7 \times 10^{-4}\,\Omega\,\mathrm{cm}$) in ethyl alcohol. The solution was ultrasonically vibrated to let larger agglomerates fall apart and then placed undisturbed for several hours. The size of the sprayed ITO particles was controlled by the gravity effect. We took the upper part of the solution to spray the ITO nanoparticles onto transparent conductive substrates maintaining at 200 °C. The transparent conductive substrates consisted of tin-doped indium oxide coated on glass that had a sheet resistance of $15\,\Omega/\square$.

Tungsten oxide films were cathodically electrodeposited onto two types of the transparent conductive substrates using a peroxytungstate deposition bath [11]. These two substrates were the ITO nanoparticles/ITO film/glass and a regular ITO glass (ITO film/glass), respectively. The bath was prepared by dissolving the $Na_2WO_4 \cdot 2H_2O$ salt (Sigma-Aldrich) in distilled water and adding concentrated hydrogen peroxide. Briefly, the bath consisted of 25 mM $Na_2WO_4 \cdot 2H_2O$ and the same concentration H_2O_2 with the pH adjusted to 1.2–1.5 with HNO_3. It is necessary that the tungsten oxide film covers on the surface of the ITO nanoparticles to form a so-called NWO film as shown in Fig. 2(b). The NWO film was referred to as sample #1 and WO_3 film on the regular ITO-coated glass was referred to as sample #2. Electrodeposition experiment was performed at a potential of −0.45 V (vs. Ag|AgCl|saturated KCl reference; all potentials in this study were quoted with respect to this reference) for a nominal duration of 3 min and the deposition was performed in air. The sample #1 was annealed of 250 °C during 1 h in order to establish good contact between the ITO nanoparticles and the electrodeposited WO_3. An analysis shows that the deposition rate of WO_3 films onto the ITO nanoparticles layer was faster than that onto the regular ITO-coated glass. It results that sample #1 may contain more WO_3 with the same deposition time of 3 min. This result is reasonable, since reaction current in the cell may concentrate around the ITO nanoparticles. The total thickness of both ITO layer and WO_3 film in the sample #1 are thicker than those in sample #2. It is expected that the electrochromic properties of these two samples shall be different.

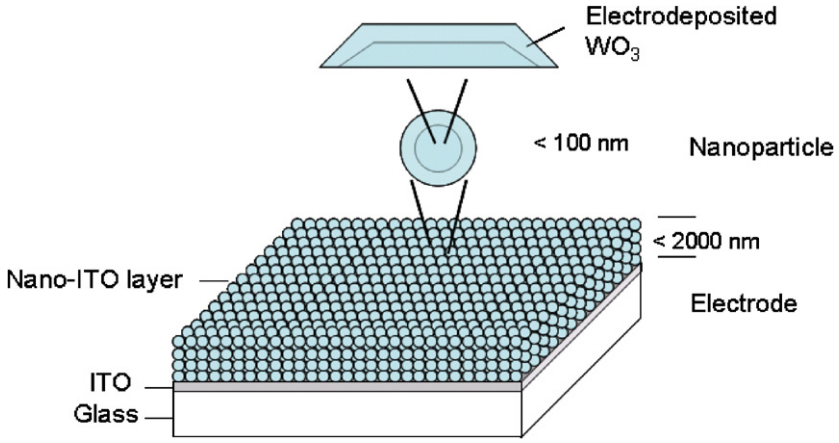

Fig. 1. Schematic illustration showing the conceptual structure of the nanocomposite WO_3 (NWO) film. In the NWO film, the ITO nanoparticles are completely covered by WO_3 film.

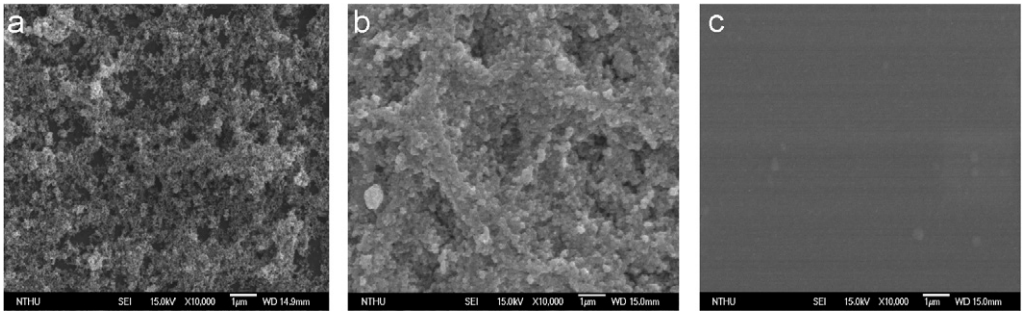

Fig. 2. SEM images of (a) sprayed ITO nanoparticles on an ITO/glass, (b) sample #1: NWO film/ITO/glass and (c) sample #2: WO_3 film/ITO/glass.