Thin Solid Films 584 (2015) 52–60

Contents lists available at ScienceDirect

Thin Solid Films

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

Electrochemical deposition of molybdenum sulfide thin films on conductive plastic substrates as platinum-free flexible counter electrodes for dye-sensitized solar cells

Chao-Kuang Cheng, Chien-Kuo Hsieh *

Department of Materials Engineering, Ming Chi University of Technology, New Taipei City 24301, Taiwan, ROC

ARTICLE INFO

Available online 16 February 2015

Keywords:
Molybdenum sulfide
Dye-sensitized solar cells
Pulsed electrochemical deposition
Flexible
Counter electrode

ABSTRACT

In this study, pulsed electrochemical deposition (pulsed ECD) was used to deposit molybdenum sulfide (MoS_x) thin films on indium tin oxide/polyethylene naphthalate (ITO/PEN) substrates as flexible counter electrodes (CEs) for dye-sensitized solar cells (DSSCs). The surface morphologies and elemental distributions of the prepared MoS_x thin films were examined using field-emission scanning electron microscope (FE-SEM) equipped with energy-dispersive X-ray spectroscopy. The chemical states and crystallinities of the prepared MoS_x thin films were examined by X-ray photoelectron spectroscopy and X-ray diffraction, respectively. The optical transmission (T (%)) properties of the prepared MoS_x samples were determined by ultraviolet–visible spectrophotometry. Cyclic voltammetry (CV) and Tafel-polarization measurements were performed to analyze the electrochemical properties and catalytic activities of the thin films for redox reactions. The FE-SEM results showed that the MoS_x thin films were deposited uniformly on the ITO/PEN flexible substrates via the pulsed ECD method. The CV and Tafel-polarization curve measurements demonstrated that the deposited MoS_x thin films exhibited excellent performances for the reduction of triiodide ions. The photoelectric conversion efficiency (PCE) of the DSSC produced with the pulsed ECD MoS_x thin-film CE was examined by a solar simulator. In combination with a dye-sensitized TiO_2 working electrode and an iodine-based electrolyte, the DSSC with the MoS_x flexible CE showed a PCE of 4.39% under an illumination of AM 1.5 (100 mW cm^{-2}). Thus, we report that the MoS_x thin films are active catalysts for triiodide reduction. The MoS_x thin films are prepared at room temperature and atmospheric pressure and in a simple and rapid manner. This is an important practical contribution to the production of flexible low-cost thin-film CEs based on plastic substrates. The MoS_x thin films produced by pulsed ECD are good candidates for catalysts in flexible DSSCs.

1. Introduction

In recent years, because of the depletion of traditional fossil fuels and of the increasing demand for renewable energy, electrocatalytic materials that are used in electrochemical energy applications, including hydrogen production [1–3], supercapacitors [4], lithium-ion batteries [5–7], fuel cells [8], and photoelectrochemical cells [9], have received considerable attention from scientists.

Dye-sensitized solar cells (DSSCs) are a type of photoelectrochemical cells that are used for photoelectric conversion to obtain electric power. Since DSSCs were first demonstrated by Oregan and Gratzel [10], many scientists have studied DSSCs as attractive candidates for third-generation solar cells. DSSCs exhibit many advantages such as low cost, easy fabrication, and high photoelectric conversion efficiency (PCE). As DSSCs are electrochemical devices, the electrocatalytic materials used in DSSC assembly play important roles in the redox reactions to transfer charge and generate electric power [9]. Pt and its composites are the most active catalysts for DSSCs [9,11,12]. However, the large-scale application of Pt catalysts is limited by their high cost and low abundance.

Many efforts have been devoted to the development of alternative catalysts to replace Pt that are used in many electrochemical energy applications. Recently, molybdenum sulfide (MoS_x; x = 2, 3) has been identified as a promising electrochemical catalyst for many electrochemical applications, including hydrogen production [1–3], supercapacitors [4,13], solar cells [14,15], fuel cells [8], and lithium-ion batteries [5,6]. Amorphous MoS_2, MoS_3, and MoS_x films have been reported as heterogeneous catalysts for the hydrogen evolution reaction (HER) [1,3]. A two-dimensional (2D) MoS_2 nanostructure has been reported, and its activities for HER and triiodide reduction are correlated with the quantity of exposed basal plane edge sites [2,15]. The good crystallinity of the 2D MoS_2 nanostructure with stacked atom layers (S–Mo–S) enables the easy intercalation of metal ions for lithium-ion batteries [6]. MoS_2 nanowall films have also been used in supercapacitors because of their sheet-like morphologies, which provide large surface areas for double-layer charge storage [13]. The emergence

* Corresponding author. Tel.: +886 2 2908 9899x4438; fax: +886 2 2908 4091.
E-mail address: jack_hsieh@mail.mcut.edu.tw (C.-K. Hsieh).

http://dx.doi.org/10.1016/j.tsf.2015.02.025
0040-6090/

of these materials has sparked new interest in developing and using MoS_x thin films. Such MoS_x catalysts are attractive because they are made of abundant and inexpensive elements, which can improve the efficiency and lower the cost for electrochemical applications in energy fields.

In this study, we investigated the deposition and properties of MoS_x thin films used as catalytic counter electrodes (CEs) in DSSCs. As flexible DSSCs have become an important research topic, we deposited the MoS_x thin films on indium tin oxide/polyethylene naphthalate (ITO/PEN) conductive plastic flexible substrates using pulsed electrochemical deposition (pulsed ECD). The as-deposited MoS_x/ITO/PEN was used as a flexible CE for DSSCs. The electrochemical deposition method showed many advantages; it provided an economical method to deposit thin films without using expensive vacuum equipment, can be used for deposition at room temperature, and allows thin film deposition on all types of conductive substrates with good adhesion.

The surface morphologies of the pulsed ECD MoS_x thin films were examined by field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). Energy-dispersive X-ray spectroscopy (EDX) and ultraviolet–visible (UV–vis) spectroscopy were performed to examine the surface elemental composition and optical transmission (T (%)) of the MoS_x/ITO/PEN specimen, respectively. The chemical state and crystallinity of the MoS_x/ITO/PEN specimen were examined by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), respectively. The electrochemical catalytic properties were studied by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Tafel polarization. The PCE of a DSSC containing the MoS_x/ITO/PEN flexible CE was examined by a solar simulator under an illumination of AM 1.5 (100 mW cm^{-2}).

2. Experimental methods

2.1. Preparation of the MoS_x thin-film counter electrodes

The ITO/PEN flexible substrates were cut into pieces with dimensions of 2.5 × 1 cm^2 and cleaned ultrasonically using acetone, deionized (DI) water, and ethanol. The ITO/PEN was subjected to a pulsed ECD in a plating bath containing an Ar-saturated aqueous precursor solution (2 mM solution of $(NH_4)_2(MoS_4)$ in 0.1 M KCl in DI water) at room temperature. The pulsed ECD of MoS_x was performed using a potentiostat/galvanostat (PGSAT 302N, Autolab, EcoChemie) in a conventional three-electrode cell at a controlled temperature of 30 °C under ambient pressure. A Pt plate and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. In each scan cycle, voltages of −0.15 V and −0.9 V vs. SCE were applied for durations of 1.5 s and 2.5 s, respectively. The MoS_x/ITO/PEN CE was then baked under vacuum at 80 °C to remove moisture. Various scan cycles were used to deposit the MoS_x thin films on the ITO/PEN flexible substrates. A CE consisting of Pt-coated ITO/PEN was prepared by electron beam evaporation and used as a reference. To ensure the high PCE of the Pt film, the film was deposited on ITO/PEN with a thickness of 50 nm.

2.2. Fabrication of TiO_2 working electrode

To fabricate the working electrode (WE), a print-screen method was used to coat nanocrystalline TiO_2 thin films on fluorine-doped tin oxide conducting glass (FTO, 8 Ω/sq., 2.2 mm in thickness, TEC-7, Hartford). The active area of the TiO_2 film was approximately 0.049 cm^2. We used two types of TiO_2 nanoparticle layers to prepare the WEs. The first layer (10 μm in thickness) served as the interlayer; on this interlayer, a layer of light-scattering anatase TiO_2 particles (2 μm in thickness) was coated on the FTO glass. The TiO_2-coated WEs were then gradually heated to 550 °C in ambient air for 30 min and then cooled slowly to room temperature. After sintering, the TiO_2 WEs were then immersed in a solution containing N719 dye (3 mM in a mixture of acetonitrile and tert-butyl alcohol (volume ratio 1:1)) at room temperature for 24 h. After the dye-adsorption process, the dye-adsorbed TiO_2 WEs were then washed with acetonitrile to remove the remaining dye and dried at room temperature for a few seconds.

2.3. Fabrication of DSSC devices

The as-prepared WE was further assembled with the MoS_x/ITO/PEN flexible CE into a sandwich configuration and then sealed with a 60-μm hot-melt spacer (SX1170-60, Solaronix) by heating at 100 °C for a few seconds. An iodide-based electrolyte (AN-50, Solaronix) was then injected into the space between the WE and CE. Finally, the DSSC devices were illuminated by a solar simulator with a light intensity of

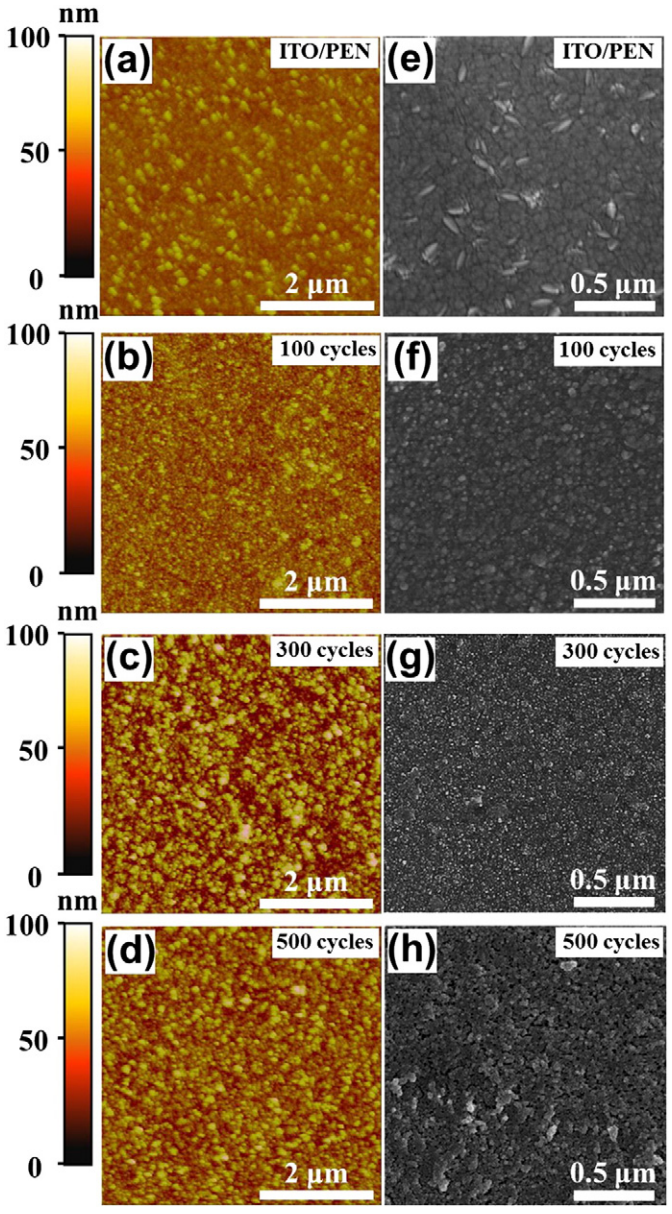

Fig. 1. AFM 2D roughness images of (a) fresh ITO/PEN and pulsed ECD MoS_x thin films deposited on ITO/PEN by (b) 100 cycles, (c) 300 cycles, and (d) 500 cycles of pulsed ECD. FE-SEM surface morphologies of (e) fresh ITO/PEN and pulsed ECD MoS_x thin films deposited on ITO/PEN by (f) 100 cycles, (g) 300 cycles, and (h) 500 cycles of pulsed ECD.