Solar Energy Materials & Solar Cells 99 (2012) 43–49

Contents lists available at SciVerse ScienceDirect

Solar Energy Materials & Solar Cells

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

Electrochromic properties of electrochemically fabricated nanostructure nickel oxide and manganese oxide films

Takako Yoshino *, Kanae Kobayashi, Shingo Araki, Kazuki Nakamura, Norihisa Kobayashi

Graduate School of Advanced Integration Science, Chiba University, 1-33 Yayoi-chou, Inage-ku, Chiba-Shi, Chiba 263-8522, Japan

ARTICLE INFO

Available online 5 October 2011

Keywords:
Electrochromism
Nanostructure
Nickel oxide film
Nanotube
Manganese oxide film

ABSTRACT

Thin films of mesoporous lamellar nickel oxides and nanotube manganese oxides were electrochemically fabricated on indium tin oxide (ITO) glass using sodium n-dodecyl sulfate (SDS) as a template agent under different controlled potentials in 10 mM $Ni(NO_3)_2$ and 100 mM $MnSO_4$ solutions. Electrochromic characterization together with the morphological observation by transmission electron microscopy (TEM), structure analysis by X-ray diffraction (XRD) and electron diffraction (ED) was made. Nickel and manganese oxide films of nanostructures, compared with conventional structure ones, showed marked changes in optical transmittance and electric charge with regard to the electrochromic reactions in aqueous solution of 100 mM LiOH. However, in a non-aqueous γ-butyrolactone (GBL) solution of 100 mM Bis(trifluoromethane)sulfonimide lithium, the nickel oxide films did not show any notable electrochromic reactions, while the manganese oxide films of both nanostructure and conventional structure are electrochromically active and the effect of nanostructure on the electrochromic properties was remarkable.

1. Introduction

Researches on the fabrication of nanostructure films to be used as electrochromic materials [1–4] are recently very active. In electrochromic reactions, ions migrate in the films to compensate the charge produced as a result of the color/bleach reaction. Therefore, if the specific surface area of the electrochromic materials increases by providing the oxide films with nanostructure, migration of ions will be promoted and consequently redox reactions will become faster. This idea will lead to the development of the electrochromic display devices of high performance.

Majewski et al. [5] demonstrated that the potential-controlled transformation of hemimicellar aggregates of SDS formed a condensed monolayer on a gold electrode surface. Choi et al. [1] reported that these potential controlled surfactant assemblies on the electrode can be utilized as a template for the production of metal and metal oxide nanostructure films when they are combined by electrodeposition processes. The authors [4] have electrochemically fabricated nanotube structure cobalt oxide films using a template of potentially controlled surfactant aggregates of cylindrical micelle.

Applying these findings to our present study, we have attempted to fabricate nanostructure nickel oxides [6–9] and manganese oxides [10–13] by electrodeposition using SDS surfactant as a template agent.

Electrochromic characterization by cyclic voltammetry and optical transmission measurement was made. The morphological observation by TEM and structure analysis by XRD and ED were also made. The effects of nanostructures on the electrochromic properties of these films were examined by comparing the nanostructure and conventional structure films both in aqueous solution of 100 mM LiOH and in non-aqueous GBL solution of 100 mM Bis(trifluoromethane)sulfonimide lithium.

2. Experimental

Nickel nitrate, manganese sulfate and SDS were all the products of Kanto Chemical Co. Inc., and used without any further purification. An indium tin oxide (ITO) coated glass was first ultrasonicated in water containing a detergent, rinsed with deionized water twice and finally immersed in acetone for 20 min. The ITO glass was used as the working electrode over which metal oxide was electrodeposited. A glassy carbon plate and a standard Ag/AgCl electrode were used as the counter electrode and as the reference electrode, respectively. The films obtained were washed with water and ethanol and also heat-treated at 280 °C for 30–60 min to remove the remaining surfactant.

All the films used for this study were adjusted to have almost the same amount of oxide by controlling the quantity of electricity flowing during potentiostatic electrodeposition. This was

* Corresponding author.
E-mail address: takakoyoshino@kvj.biglobe.ne.jp (T. Yoshino).

0927-0248/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2011.08.024

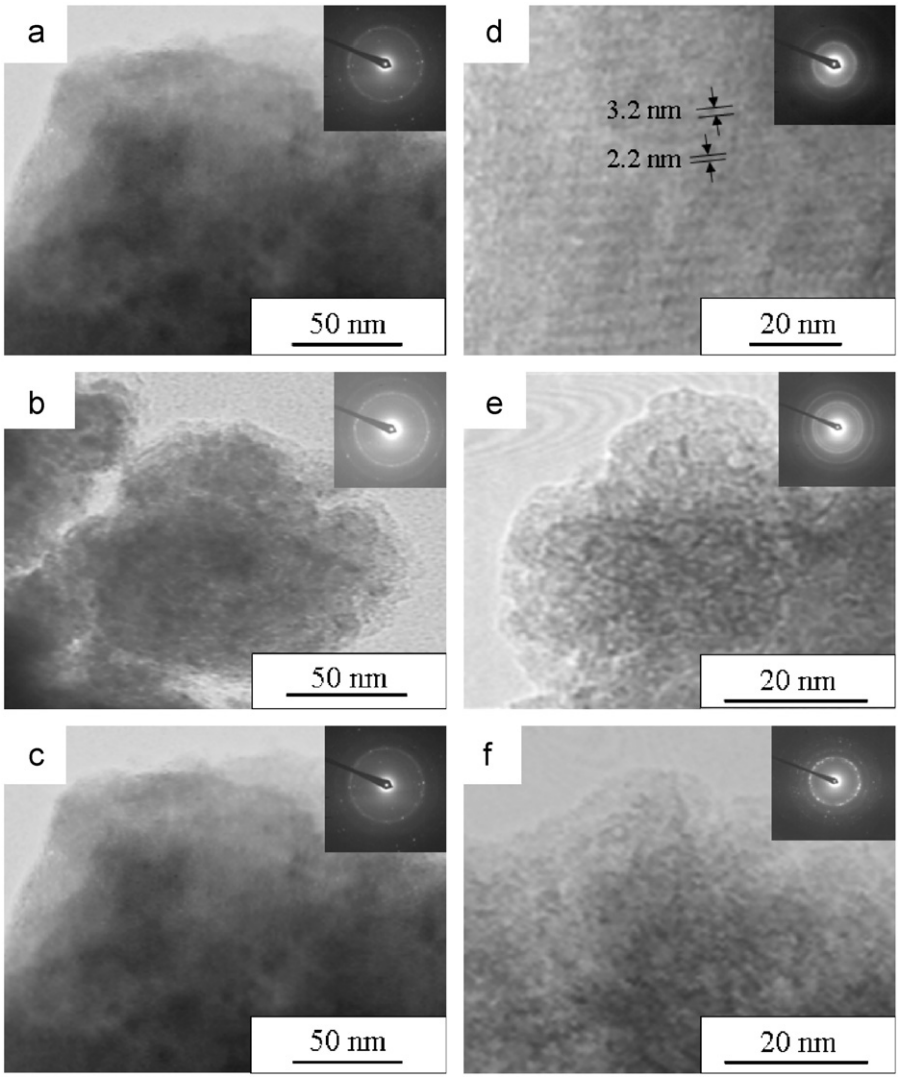

Fig. 1. TEM images of nickel oxide films deposited at (a) −0.8 V, (b) −0.9 V and (c) −1.0 V without SDS, and (d) −0.8 V, (e) −0.9 V and (f) −1.0 V with SDS.

intended for quantitative comparison of electrochromic properties of each thin oxide film.

Structural and morphological characterizations were made by a TEM (JEM 2000FX). TEM sample preparation for the observation of nanostructured thin oxide films was done by the following procedures:

1) The film was scraped off from the ITO glass with a spatula into an agate mortar.
2) The finely milled oxide powder was dispersed in 1:1 mixed solution of water and alcohol for an hour.
3) A small amount of the liquid taken from the surface of oxide dispersed solution was dropped on the microgrid of each TEM sample holder, which was then dried.

The structure analysis of nickel oxide films was made by small angle XRD (MAC Science M21 × 9).

The solutions used for the electrochromic measurement of cyclic voltammetry and optical transmissions of the samples were two:

1) aqueous solution of 100 mM LiOH (Kanto Chemical Co. Inc.);
2) non-aqueous γ-butyrolactone (GBL) (Kanto Chemical Co. Inc.) solution of 100 mM Bis(trifluoromethane)sulfonimide lithium ($\{CF_3SO_2\}_2NLi$) (Sigma Aldrich Japan).

The cyclic voltammogram (CV) was recorded using an ALS model 660A potentiostat/galvanostat equipped with a computer. A three-electrode cell was constructed with an ITO glass as the working electrode, a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference. The scan rate was 25 mV/s for nickel oxide film and 50 mV/s for manganese oxide and Mn/Ni oxide films. The transmittance spectrums at 400 nm and at 700 nm were recorded in situ during the potential sweep using an Ocean Optics USB2000 diode array detection system.

2.1. Fabrication of nickel oxide thin films

The films were cathodically deposited from a solution of 10 mM $Ni(NO_3)_2$ at room temperature, without stirring the solution and under a potential range from −0.8 V to −1.0 V. SDS surfactant of 0.1 wt% was added to the electrolytic solution as a template agent to provide the films with nanostructure. Conventional nickel oxide films also were deposited from a solution of 10 mM $Ni(NO_3)_2$ without SDS in order to compare the electrochromic properties of nanostructure oxide films with conventional ones.

The experimental setup has an H-shaped cell with a glass wool partition wall in the middle to prevent the diffusion of solution from the anodic to cathodic rooms, because the cathodic deposition is