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ScienceDirect
Applied Surface Science 254 (2008) 2017–2022
applied surface science
www.elsevier.com/locate/apsusc

Electrochromic properties of nano-structured nickel oxide thin film prepared by spray pyrolysis method

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Received 5 June 2007; received in revised form 7 August 2007; accepted 9 August 2007
Available online 15 August 2007

Abstract

In this study, we present a simple method to improve the electrochromic properties of a nickel oxide thin film. The method involves a three-step process—(a) conducting indium tin oxide (ITO) nano-particles were first sprayed onto a conducting substrate to form a porous nano-structured ITO layer, (b) nickel oxide film was then deposited onto the nano-structured ITO layer by a spray pyrolysis technique, and (c) the substrate, ITO nano-particles layer and nickel oxide film were annealed at high temperature of 300 °C to improve adhesion of these three layers. The microstructure of the resulting electrochromic cell was investigated using scanning electron microscopy. It is evident that the nickel oxide film covers the surface of the ITO nano-particle layer and forms a nano-structured nickel oxide (NSNO) film. The switching time and contrast were characterized by Autolab PGSTAT12 potentiostat and Jasco V-570 spectrophotometer. The results suggest that the transmittance contrast and switching time of NSNO are slightly superior to those of a conventional nickel oxide (CNO) film. However, the cycling durability of NSNO can be much better than that of CNO.

PACS : 61.46.Df; 78.40.Ha

Keywords: Nickel oxide; Nano-structured; Electrochromic; Spray pyrolysis

1. Introduction

Electrochromic (EC) materials, which can change color while an electric voltage is applied, have potential applications in smart windows, car rear-view mirrors, e-paper and high-contrast dynamic displays [1,2]. Among inorganic EC materials, nickel oxide is considered to be a good anodic candidate because it has low material cost and an excellent contrast. Usually, nickel oxide is used as a counter-electrode in complementary EC devices assembled with a cathodic EC electrode, such as tungsten oxide [3].

For practical use in commercial applications, many efforts have been made to improve the EC performances for nickel oxide-based EC devices. For example, Avendaño et al. showed that the optical modulation of nickel oxide-based films was enhanced by co-sputtering with Mg, Al, Si, Zr, Nb or Ta [4]. Ahn et al. used Ta_2O_5 as a protective layer in WO_3/electrolyte/$Ni(OH)_2$ system to improve the durability, transmittance modulation and response speed [5]. Rougier and co-workers improved the durability of nickel oxide thin films by adding W, Co or Ta [6,7].

Recently, nano-structured EC materials have been applied to electrochromic devices due to their unique electrical, physical and chemical properties. Cho et al. made an array structure of poly(3, 4-ethylenedioxythiophene) (PEDOT) nano-tubes to improve slow switching speed and insufficient coloration [8]. Ahn et al. showed that EC devices fabricated with the NiO–Ta_2O_5 nano-composite electrode had better durability, higher coloration efficiency and higher optical modulation than those assembled with the single NiO electrode [9].

Our laboratory successfully demonstrated WO_3 and V_2O_5 nano-wires based EC devices, which showed good performances in switching time, transmittance contrast and durability [10,11]. In our prior work, we have also made nano-composite

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doi:10.1016/j.apsusc.2007.08.029

EC electrodes composed of Prussian blue (PB) or tungsten oxide coated on ITO nano-particles as a medium layer, respectively [12,13]. The EC devices consisted of such nano-composite electrodes showed noticeable improvement in the transmittance contrast and switching speed due to the larger surface area for proceeding redox reaction.

In this paper, we adapted the same idea to construct a nano-structured nickel oxide electrode by using high-conductivity ITO nano-particles as a porous layer and nickel oxide as the EC material. We explored the EC properties, including durability, switching time and optical contrast, of the nickel oxide nano-structured film.

2. Experiment

Commercial indium tin oxide (ITO) coated glass (GemTec Corp. 30 Ω/sq, 1.5 × 3 cm^2) was used as the substrate. Nano-structured nickel oxide (NSNO) film was produced by a three-step process.

(a) One gram of ITO nano-particles (Lihochem Inc. 99.99%, 40 ± 5 nm, 1.7×10^{-4} Ω cm) was added into 0.5 l ethyl alcohol (99.5%). A well-dispersed alcoholic solution of ITO nano-particles was prepared in an ultrasonic tank, and then sprayed onto ITO coated glass substrates at 150 °C. This process was intended to make the ITO nano-particle layer act as a conductive network with a wavy and porous surface in the nano-scale.
(b) A 0.1 M alcoholic solution of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) was then deposited onto the porous surface of the ITO nano-particle layer by a spray pyrolysis technique [14] at 200 °C.
(c) The nano-structured film was heated at 300 °C for 20 min. It is desired that the nickel oxide film would grow conformably to the surface morphology of an ITO nano-particle layer to form a NSNO layer.

Also, a conventional nickel oxide (CNO) film was prepared by the same method on the flat ITO coated glass substrate without using ITO nano-particles. The procedure of preparation for these two samples is shown in Fig. 1. Although the nickel oxide film was deposited with the same conditions by spray pyrolysis process for NSNO and CNO, it is worth noting that the NSNO and CNO layers are expected to have different thicknesses due to difference in the density of these two structures. The NSNO shall contain high density of porosity as discussed in our previous publications [12,13].

The structure of nickel oxide film was examined by X-ray diffraction (XRD, MAC Science, MXP18). The film morphology was investigated by scanning electron microscopy (SEM, JEOL JSM-6330F). The electrochromic properties were measured by cyclic voltammetry (Autolab model PGSTAT12). The electrochemical redox was carried out in a three-electrode cell using 0.5 M KOH as the electrolyte. An Ag/AgCl electrode was used as the reference electrode, and a platinum plate as the counter-electrode. The transmittance spectra were measured using Jasco V-570 spectrophotometer in a wavelength range

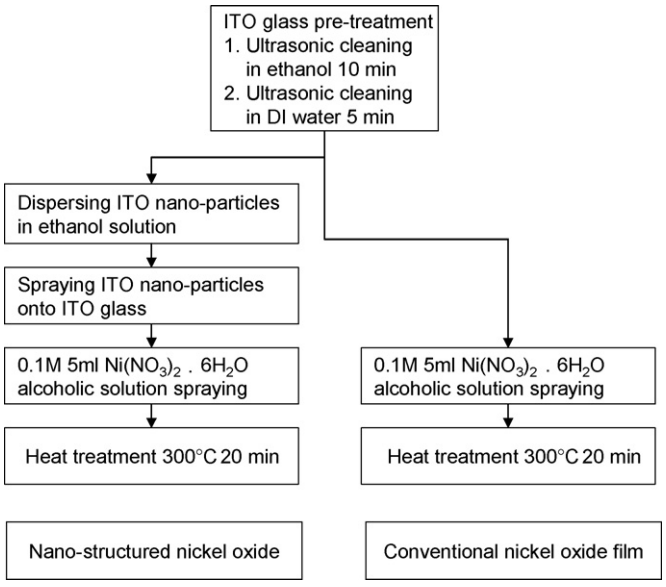

Fig. 1. Procedure to prepare nano-structured nickel oxide (NSNO) and conventional nickel oxide (CNO) films.

from 340 to 850 nm. The switching time was measured in situ by the response of transmittance with applied pulse potential of +1 V (color) and 0 V (bleach). The cycling durability of both NSNO and CNO films was tested by applying a rectangular pulse potential set between 1.5 and −1.5 V. The period of each pulse was set to be 5 s. Furthermore, the test results of cyclic voltammogram (CV) and transmittance were recorded every 100 cycles and up to 3000 cycles totally.

3. Results and discussion

3.1. XRD and SEM characterizations

Fig. 2 shows the XRD pattern of the NSNO film. Besides peaks associated with ITO structure, there are three major diffraction peaks at $2\theta = 37.2°$, 43° and 63°, which are identified to be {1 1 1}, {2 0 0} and {2 2 0} reflections of a cubic NiO structure, respectively.

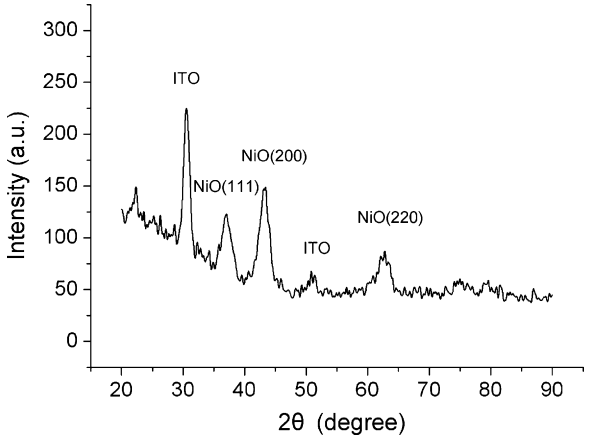

Fig. 2. X-ray diffraction (XRD) pattern of the NSNO film on the ITO coated glass substrate.