Electrochimica Acta 55 (2010) 2344–2351

Contents lists available at ScienceDirect

Electrochimica Acta

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

Simple and rapid synthesis of NiO/PPy thin films with improved electrochromic performance

A.C. Sonavane[a], A.I. Inamdar[a,b], D.S. Dalavi[a], H.P. Deshmukh[c], P.S. Patil[a,*]

[a] Thin Film Materials Laboratory, Department of Physics, Shivaji University, Kolhapur 416 004, India
[b] Department of Semiconductor Science, Dongguk University, Seoul 100-715, Republic of Korea
[c] Department of Physics, Y.M. College, Bharati Vidyapeeth, Erandwane, Pune, India

ARTICLE INFO

Article history:
Received 22 August 2009
Received in revised form
24 November 2009
Accepted 26 November 2009
Available online 2 December 2009

Keywords:
Nickel oxide thin films
Polypyrrole (PPy)
Electrodeposition
Chemical bath deposition (CBD)
EC properties

ABSTRACT

Nickel oxide/polypyrrole (NiO/PPy) thin films were deposited by a two step process in which the NiO layer was electrodeposited potentiostatically from an aqueous solution of $NiCl_2 \cdot 6H_2O$ at pH 7.5 on fluorine doped tin oxide (FTO) coated conducting glass substrates, followed by the deposition of polypyrrole (PPy) thin films by chemical bath deposition (CBD) from pyrrole mixed with ammonium persulfate (APS). The NiO/PPy films were further characterized for their structural, optical, morphological and electrochromic properties. X-ray diffraction study indicates that the films composed of polycrystalline NiO and amorphous PPy. Infrared transmission spectrum reveals chemical bonding between NiO and PPy. Rectangular faceted grains were observed from scanning electron microscopy results. The electrochromic (EC) property of the film was studied using cyclic voltammogram (CV), chronoamperometry (CA) and optical modulation. The NiO/PPy presents superior EC properties than their individual counterparts. The coloration/bleaching kinetics (response time of few ms) and coloration efficiency (358 cm^2/C) were found to be improved appreciably. The dramatic improvement in electrochemical stability (from about 500 c/b cycles for PPy to 10,000 c/b cycles for NiO/PPy) was observed. This work therefore demonstrates a cost-effective and simple way of depositing highly efficient, faster and stable NiO/PPy electrodes for EC devices.

1. Introduction

Organic–inorganic hybrid materials represent a new class of materials as they can combine the advantages of both the components and offer special properties through modification of each other [1]. It is therefore anticipated that the improved electrochromic device based on hybrid material would deploy a material with high coloration efficiency, faster response time and an outstanding operation lifetime. The organic polymers have good mechanical flexibility, toughness, and formability, while inorganic ceramics have excellent durability to chemical attacks, high thermal stability, and surface hardness. Inorganic–organic composite materials thus have combined interesting properties and hence gained much attention [2]. However, further studies are necessary to unveil the still unexplored properties of hybrid materials. The successful implementation of these materials in to the devices would further require facile synthetic strategies. At present organic polymer/inorganic nanocomposites have been synthesized by adopting several chemical routes [3–5].

Conjugated polymers by virtue of their high electrical conductivity and easy processibility have attracted a great attention and consequently have been extensively explored as an alternative to metals or inorganic semiconductors in fabrication of optoelectronic, microelectronic and microelectrochemical devices [6–8]. Amongst the important conducting polymers, polypyrrole (PPy) has potential applications in drug delivery [9,10], sensors [11], biomolecules [12], adhesives [13], actuators [14], immunosensors [15] and corrosion protection [16]. Due to the intrinsic semiconducting properties, PPy has been used as an electronic component in electronic devices, e.g., photoelectrochemical devices [17], organic light-emitting diodes [18], and rectifying devices [19].

Some organic/inorganic composites have already been reported in the literatures, such as PPy/TiO_2 [20], PPy/Ti [21], PPy/Au [22], PPy/Ag [23], PPy/Pt [24], PPy/Pd [25], Fe_3O_4/PPy [26], PPy/Ta_2O_5 [27], PPy/$Cu_{1.4}Mn_{1.6}O_4$ [28], RuO_2-PPy [29], FeO-PPy [30], and PPy/ZnO [31] for various applications. Interestingly, PPy has been effectively used to enhance/improve several properties of the inorganic oxides, hence it offers promising organic counterpart in the electronic devices.

Five kinds of uniform metal oxide particles (a-Fe_2O_3, CeO_2, CuO, NiO, and SiO_2) were coated with polypyrrole by reacting the dispersed solids with pyrrole in a water/ethanol medium without

---

[*] Corresponding author. Tel.: +91 231 2609230; fax: +91 231 2691533.
E-mail address: psp_phy@unishivaji.ac.in (P.S. Patil).

0013-4686/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2009.11.087

the use of a soluble oxidant. Fe_2O_3 and SiO_2 were found to be inactive in the polymerization, while CeO_2 and CuO react with the adsorbed pyrrole molecules through a reductive-dissolution process, in which the monomers are oxidized, causing a release of reduced metal ions [32]. An EC window based on PPy/nickel oxide combination in an aqueous electrolyte has been reported by Scrosati and co-workers [33] as a light-modulation window with high cycling efficiency (93%), long life (1000 cycles) and fast switching time (of the order of few seconds). This paper demonstrates a promising way to improve the EC property of inorganic oxide with an organic counterpart. It is quite surprising to note that there are no further reports on this system, to the best of the author's knowledge. Hence we revisited this NiO/PPy system for further exploration, with a slight change in synthetic strategy.

In this paper NiO/PPy samples have been prepared by using simple electrodeposition and CBD techniques. Electrodeposition is of particular interest due to low-cost, environmental friendly process, and feasibility of room temperature growth on large area for the deposition of NiO films. On the other hand, the advantage of chemical synthesis is that it offers mass production at a reasonable cost for polypyrrole films, without compromising on quality. The EC performance of NiO/PPy film was tested in $LiClO_4$-PC. In-situ transmittance with time was used to determine the response time of the coloration-bleaching process of the device. The electrochemical stability was examined, by repeating color/bleach cycles in an electrolyte for prolonged period. The NiO/PPy presents superior EC properties than their individual counterparts. The coloration/bleaching kinetics, coloration efficiency and electrochemical stability were found to be improved appreciably. This work therefore demonstrates a cost-effective and simple way of depositing highly efficient, faster and stable NiO/PPy electrodes for EC devices.

2. Experimental

NiO/PPy films were prepared sequentially by adopting electrodeposition and CBD techniques. In the first part nickel oxide thin films were electrodeposited from an aqueous nickel chloride bath containing 0.5 M nickel chloride (LOBA CHEMIE Extra Pure 97%) and 0.1 M KCl onto FTO (15–20 Ω/□) coated conducting glass substrates. The bath solution was complexed using EDTA (A.R. 99%) and pH was adjusted at 7.5 by addition of KOH. The three-electrode electrochemical cell was used to deposit NiO thin films in potentiostatic mode in which graphite was counter electrode, SCE was reference electrode. The electrochemical quartz crystal (EQCM) measurements were taken using an electrochemical analyzer (model—CHI-400A) made by CH Instrument, USA. The EQCM measurements were performed on a platinum electrode of 1 cm^2 area in a specially designed electrochemical cell.

The cyclic voltammogram was recorded in the range from +0.3 to −0.8 V vs SCE in a precursor solution at 10 mV/s. Fig. 1(a) and (b) is associated with the reduction-oxidation behaviour of nickel species on the Pt electrode (area 1 cm^2) accompanied by a concurrent shift in the frequency of the quartz crystal electrode with the applied voltage. The arrows indicate the scan direction. The scans were initiated at +0.3 V vs SCE, reversed at −0.8 V (vs SCE) and terminated at +0.3 V (SCE). During the cathodic scan, the increment in current density beyond −0.2 V (vs SCE) is due to reduction of Ni^{+2} ions, where slight increase in mass takes place (Fig. 1(b)). The peak at −0.4 V is due to oxygen reduction [34–36]. This causes local pH to increase and a dip at −0.5 V on the *I*–*V* curve. The exponential increase in current density beyond −0.5 V is due to Ni $(OH)_2$ reduction (Fig. 1(a)) [37]. Subsequently, NiO growth takes place via intermediate steps of hydroxide formation as given in Eqs. (1) and (2).

$$NiCl_2 \cdot 6H_2O + H_2O \rightarrow Ni(OH)_2 + 2HCl + 5H_2O \qquad (1)$$

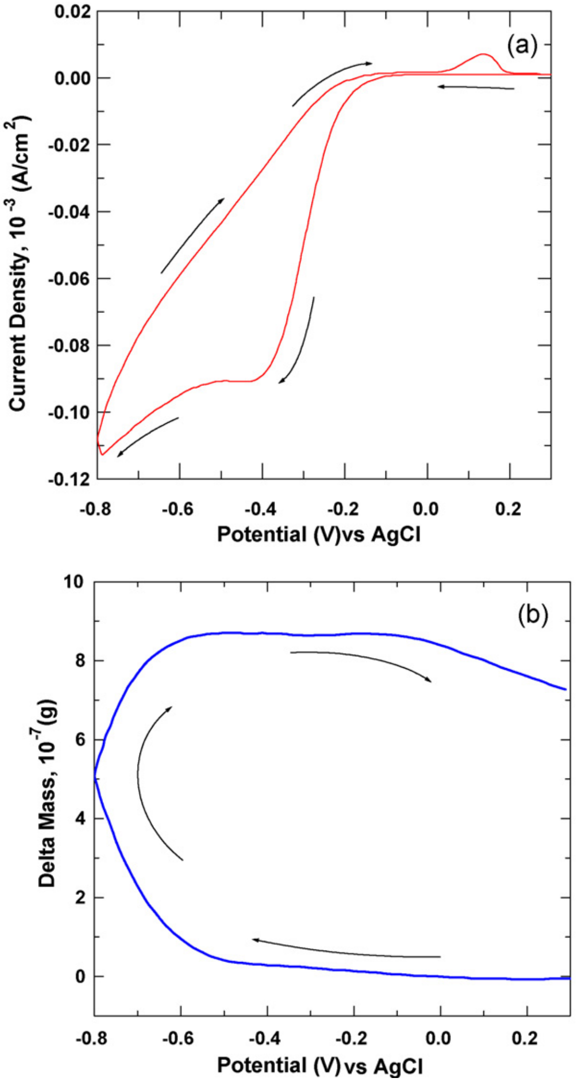

Fig. 1. (a) The reduction–oxidation behaviour of the electrolyte on the Pt electrode (area 1 cm^2) accompanied by (b) a concurrent shift in the delta mass of the quartz crystal electrode with the applied voltage.

$$Ni(OH)_2 \rightarrow NiO + H_2O \qquad (2)$$

Upon reversal of the plot scan, the mass deposited onto the electrode continues to increase up to −0.5 V and leveled off till 0 V (vs AgCl) (Fig. 1(b)). The nickel oxide thin films were deposited at room temperature under potentiostatic condition at −0.75 V [38].

In the second part, polypyrrole (PPy) was synthesized using monomer Pyrrole (0.03 M in 100 ml distilled water) chemically polymerized with ammonium persulfate ($[(NH_4)_2S_2O_8]$ APS 0.06 M in 50 ml distilled water). This reaction mixture was stirred continuously at a constant low temperature (5 °C) to obtain PPy. As soon as the pyrrole is mixed with the APS, the mixture turned to a characteristic black color with change in pH from 5 to 2, indicating that the organic polymerization reaction began immediately. The reaction was allowed to proceed for 10 min. The pre-deposited NiO films were dipped vertically in PPy solution for 10 min, lifted and rinsed with double distilled water. This dip-lift cycle was repeated twice to obtain PPy film of adequate thickness.

The NiO, PPy and NiO/PPy films were prepared for EC investigations with a standard three electrode electrochemical cell of configuration,

$$Glass/FTO/NiO/PPy/1\,M\,LiClO_4 + PC/SCE$$