



Electrodeposition of NiO Films and Inverse Opal Organized Layers from Polar Aprotic Solvent-Based Electrolyte



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ABSTRACT

The implementation of polar aprotic organic solvents remains almost unexplored for the direct electrochemical deposition (ECD) of nickel oxide dense or mesoporous thin films and organized macroporous structures. In the present work, the electrochemical deposition of this oxide in dimethyl sulfoxide (DMSO) medium by cathodic reduction of nickel nitrate hexahydrate is investigated. The electrochemical phenomena involved in the deposition process have been analyzed by cyclic voltammetry (CV). It is shown that the ECD process occurs below -0.80 V/SCE. The gas atmosphere for the deposition and salt dissolution was found important parameters for the electroactivity of the system and the best conditions for ECD have been defined. Raman spectroscopy has shown the direct NiO deposition. Moreover, the crystallization and higher ordering occurring through thermal annealing has been followed by the 2-magnon Raman band of NiO. The difficulty of obtaining well-crystallized pure phase without metallic nickel was stressed by the X-ray diffraction study and thermogravimetry of the layers. We have shown that annealing the sample at 450 °C resulted in oxidation and crystallization and in the formation of a mesoporous morphology. The electrochemical activity and electrochromism of the layers has been investigated by CV in alkaline aqueous solution. Finally, we have prepared opal inverse organized structures with a perfectly defined macropore organization and size using a macrosphere polystyrene template. It has illustrated the high interest of the present electrodeposition technique for the preparation of nickel oxide layers with enhanced properties for advanced applications.

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1. Introduction

NiO, as a p-type semiconductor with a wide bandgap ranging between 3.6 and 3.8 eV at room temperature, has attracted a great attention for applications in various fields. Many physical and chemical methods have been described in the literature for the synthesis of NiO thin films and nanostructures such as sputtering [1,2], pulsed laser deposition [3], chemical precipitation [4], hydrothermal processes [5], sol-gel methods [6–8] and electrochemical deposition (ECD) [9–11]. Among them, ECD is of great interest because it allows the accurate adjustment of the layer composition, thickness and morphology by controlling the bath composition, temperature, use of template and applied electrochemical potential or current [12–15]. Also ECD ensures an excellent electrical contact between the conducting substrate and the deposited layer due to electrical charge exchange upon the

deposition process. This technique provides films with many morphologies which have been implemented in various systems such as alkaline batteries [16], electrochemical capacitors [17] and electrochromic devices [18–20].

Higher performances are expected from the optimizing of the oxide layers and then use of new methods of preparation for a better control of their chemical, morphological, electrical and optical properties. In most of the researches on nickel oxide electrodeposition, aqueous growth solutions have been used, leading to the formation of precursor layers made of nickel hydroxides and/or oxy-hydroxides that required a subsequent heat treatment to produce the NiO semiconductor compound [16,17,19–21]. The use of aprotic media has been described by few authors to avoid hydrogen incorporation and favor the direct formation of oxide [18,22–26]. Some authors have investigated the use of ionic liquid based electrolytes whose main drawback is the high cost [22–26]. On the other hand, the implementation of polar aprotic organic solvents remains almost unexplored. To the best of our knowledge this approach has only been reported by Su et al. [18] who used a dimethyl formamide and nickel chloride precursor

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bath to directly cathodically deposit nickel oxide films. ECD in aprotic solvent appears as a very attractive approach to limit the post-deposition treatments, avoid the film cracking and improve its adherence on the substrate. Other potential interests include the possibility of working at temperatures above 100 °C to get better crystallized deposited layers and the enlargement of the electrochemical potential window for the layer deposition.

In recent years, the use of self-assembled colloidal crystal templates for the fabrication of organized hierarchical structures [27] or porous films [28,29] has grown rapidly due to its simplicity and high degree of periodicity that can be achieved in two or three dimensions. The calibrated colloidal crystals (typically polystyrene or silica spheres) can be easily self-assembled on large area and removed completely by dissolution in appropriate solvents or by calcination. The nanosphere lithography method has been used for the preparation of ordered macroporous materials of many compositions, notably of transition metal oxides. Ordered macroporous inverse opal structures made of NiO have been prepared and studied by some authors [30–35]. These structures have been shown to exhibit enhanced optical and electrochemical properties [30–35].

In the present paper, we investigate the use of DMSO, a polar aprotic solvent, as a medium for the cathodic electrodeposition of NiO layers. We have studied the effect of cathodic electrodeposition potential and of post-deposition annealing treatment on the layer structure, composition and morphology. NiO layers have been directly deposited at low overvoltage and well-crystallized and porous films have been produced after an *ad-hoc* annealing treatment. We also report the facile self-assembled polystyrene (PS) spheres template-assisted deposition of NiO using these ECD conditions. The technique is shown suitable for the preparation of organized macroporous layers with an inverse opal hexagonal structure.

2. Experimental

The chronoamperometry and cyclic voltammetry (CV) experiments were conducted with a PGSTAT 30 potentiostat-gavanostat from Autolab controlled by the NOVA software. For the cyclic voltammetry curves and the layer depositions, fluorine-doped tin oxide (FTO) coated glass substrates (TEC-10) were used as a working electrode. The substrates were first cleaned with soap, rinsed with distilled water, then sonicated 5 min in acetone and 5 min in ethanol. The electrode surface area was $1.5 \times 1.5 \text{ cm}^2$. The substrate was placed vertically in the cell. The counter-electrode was a platinum wire and the applied potential was controlled versus a saturated calomel reference electrode (SCE).

The bath for the layer deposition was a DMSO solution containing 0.2 M nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Alfa Aesar, 98%). The nickel salt and DMSO solvent were poured in a vial which was filled with argon before to be capped. The vial was then placed in a water bath set at 90 °C. The solution was stirred for 2 min for full salt dissolution before to be used. The depositions were performed at 90 °C and the solution was stirred using a magnetic barrel rotated at 250 rpm. After deposition, the samples were dried 10 mins at 200 °C. For annealing, the samples were placed in a carbolite tubular furnace. The annealing temperature was reached using a ramp of 15 °C/min.

For the nanosphere lithography experiments carboxyl-functionalized polystyrene particles with a mean diameter of 527 nm (Microparticles-GmbH) were used. The substrate was sonicated in a water, ethanol and H_2O_2 (5:1:1 volume mixture) solution for 2 h in order to increase the hydrophilic properties of their surface. The cleaned substrates were stored in deionized water prior use. The functionalized PS spheres were dispersed on the surface of a water/ethanol mixed solution containing sodium

dodecyl sulfate (SDS) surfactant. The nanospheres were then deposited on the conducting glass slide by a floating transferring method. The slide was kept at an angle of 45°, at room temperature, until full drying. Then, it was placed in an oven at 100 °C for 10 min to ensure a good adherence of the spheres on the substrate. The NiO layer was deposited at -0.85 V/SCE for 250 s. For this experiment the deposition temperature was lowered to 80 °C to ensure the template integrity in the deposition bath. The spheres were eliminated by a thermal treatment at 200 °C for 10 min.

The film electrochemical activity was measured in a 0.5 M NaOH solution. The CV scan rate was $10 \text{ mV} \cdot \text{s}^{-1}$. The morphology of the samples was examined with a high resolution Zeiss LEO 1530 scanning electron microscope (FE-SEM) using the in-lens mode and an acceleration voltage of 5 kV. The layer crystal structure was characterized by a PANalytical X-Pert high-resolution X-ray diffractometer (XRD) operated at 45 kV and 40 mA and using $\text{CuK}\alpha$ radiation with $\lambda = 1.5406 \text{ \AA}$. Raman scattering spectra were measured at room temperature with a Renishaw INVIA apparatus equipped with a microscope and a CCD detector. A 532 nm solid-state green laser was used for off-resonance excitation with 10 mW power. The instrument was calibrated using a silicon standard. The TD-ATG measurements were conducted using a SETSYS evolution 16 apparatus from SETARAM. 24.1 mg of deposit material was scratched from several electrodes for the measurement. The sample was heated from room temperature to 800 °C in air (1 bar, $30 \text{ mL} \cdot \text{min}^{-1}$). The temperature scan rate was $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$.

3. Results and discussion

The electrochemical behavior of the organic deposition bath and electroactive species were investigated and analyzed by cyclic voltammetry (CV). In Fig. 1A the effect of the negative potential scan boundary is shown. The potential was first scanned from the rest potential (0 V/SCE) towards the negative direction. A cathodic current wave started at -0.65 V/SCE . When the negative limit was -0.80 V , the reverse scan curve overlaid the direct one and no anodic peak was observed. For more negative scan boundaries, a cathodic current onset was observed and the reverse current was higher compared to the direct one (Curve b and c, Fig. 1A) and the electrode then darkened. This shows the deposition of a layer which favored the electrochemical cathodic reaction. To better understand the phenomenon, a blank curve was recorded using a glass/FTO electrode and a 0.4 M KNO_3 in DMSO solution. (Curve a, Fig. 1B). The same onset was observed but the current increase was limited due to the poor reaction kinetics on FTO. This reaction is assigned to the electrochemical reduction of nitrate. On the reverse scan, for the $\text{Ni}(\text{NO}_3)_2$ solution, an anodic current peak appeared centered at about 0.2 V/SCE in curve b and c, Fig. 1A due to the oxidation of the deposited layer. Moreover, the amplitude of this anodic peak increased with the negative scan boundary limit. We have also noted that the corresponding anodic reaction led to a bleaching of the electrode surface.

The effect of the atmosphere in the vial upon nickel salt dissolution was found to influence the electrochemical behavior of the system. In Fig. 1B we compare CVs measured for dissolutions performed in air and under argon atmospheres. The curves show that the cathodic current onset occurs in the case of air but the recorded current is lower. On the positive going scan, the anodic peak is of low intensity and shifted toward higher potential. More reactivity is found in the case of the dissolution in the argon purged vial. It suggests that using Ar atmosphere results in a better solubilisation of the reactant. Fig. 1C shows the effect of gas bubbling on CV curves. In the case of oxygen bubbling (curve-a), no anodic peak was observed even if the cathodic current wave was of higher intensity than for the potassium nitrate blank. It shows the additional electrochemical reduction of molecular oxygen.

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