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Full Length Research Paper

Electrochemical investigation and capacitance properties of a novel electrodeposited ordered mesoporous cobalt hydroxide films

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The present work explored a novel, simple and low cost electrochemical route for the investigation of ordered mesoporous cobalt hydroxide films electrodeposited onto gold substrate from cobalt acetate in pluronic lyotropic liquid crystal (P84). This method produces thin films of cobalt hyhdroxid mesostructures on gold substrate by combination of potentiostatic and voltammetric electrodeposition techniques. The prepared nanomaterials were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and x-ray diffraction (XRD). Electrochemical capacitance properties of cobalt hydroxide films were evaluated via cyclic voltammetry method. The film showed maximum specific capacitance of 727 F/g in 1 M sodium hydroxide electrolyte at scan rate of 5 mV/s. This indicates the potential application of cobalt films in electrochemical supercapacitors.

Key words: Electrodeposition, mesostructures, electrochemical measurements, specific capacitance, supercapacitors.

INTRODUCTION

Electrochemical supercapacitors are unique electrochemical devices with high power, high charge-discharge cycle life and high energy efficiency. They are considered for all kinds of power source applications such as auxiliary power source for mobile electronic devices (CaO et al., 2004; Zhao et al., 2007). According to the mechanisms of charge storage delivery, supercapacitors can be divided into the electric double –layer capacitors (EDLCs) and redox pseudocapacitors (Conway, 1991; Sarangapani et al., 1996). The development of inexpensive electrode materials with high performance such as NiO (Kalu et al., 2001), CoO_x (Lin et al., 1998), MnO_2 (Prasad and Miura, 2004), $Ni(OH)_2$ (Zhao et al., 2007), $Co(OH)_3$ (CaO et al., 2004) etc. has been one of the most active research areas of electrochemistry during the last few years. Among them, $Co(OH)_2$ materials are attractive in view of their layered structure with large interlayer spacing (Jayashree and Kamath, 1999) their well defined electrochemical redox activity and the possibility of the enhanced performance through different preparative methods (Ganesh et al., 2005). It was established that, the pervoskite BiFeO3 nanocrystalline thin film electrode showed comparable specific capacitance of 81 F g 1 and electrochemical super-capacitive performance and stability in an aqueous NaOH electrolyte to that of commonly used ruthenium based pervoskites (Lokhande et al., 2007).

Among the existing synthetic approaches to the nanostructures materials (Sun et al., 2006) electrochemical techniques are of great interest due to their relatively easy and accurate control of the surface microstructure of deposited films by changing deposition variables, such as electrolyte, deposition potential, bathing temperature, and so forth (Nelson et al., 2002).

The porous films of nanoflakes $Co(OH)_2$ were successfully deposited electrochemically in water-ethanol and water solutions. The electrodeposited $Co(OH)_2$ films exhibit excellent supercapacitor properties. It is ascribed to the nanoflakes porous structure, which can enhance the utilization and capacitance of the $Co(OH)_2$ films.

In addition, it could be found that the $Co(OH)_2$ films deposited in water-ethanol solution have much higher

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specific capacitance than in water solution. It is attributed to the ethanol enter into the layered $Co(OH)_2$ films, which increase the layer distance between crystal lattices, improve the motion of the ions and the reversibility of Co^{2+}/Co^{3+} at the charge-discharge processes (Yu et al., 2010). This method could also be used to improve the electrochemical properties of the other metal hydrate for supercapacitors application.

Over recent years, the fabrication of nanostructured materials using surfactant mesophases as templates has been proved to be a very promising research area. One particularly versatile approach is the use of pluronic lyotropic liquid crystalline templates (Delling and Braun, 2004) which maintains the topology of the phase throughout the progress of the reaction and holds the ability to fabricate thin films with high surface area via electrode position.

To the best of our knowledge, there is no report for the measurement of the capacitance of electrodeposited mesoporous cobalt hydroxide films using pluronic lyotropic liquid crystalline template. In this article, we report for the first time a simple method to directly electrodeposited ordered mesoporous H_I-e Co $(OH)_2$ films from the hexagonal lyotropic liquid crystal template of pluronic 84. The capacitive properties of the cobalt hydroxide thin films were investigated using cyclic voltammetry method. The effect of potential sweep rates on the electrochemical capacitance of H_I–e Co $(OH)_2$ films were analyzed for the purpose of achieving optimum parameters for the deposition of the H_I–e Co $(OH)_2$ film with the best capacitive performance.

EXPERIMENTAL

Materials

All chemicals were analytical grade and used as obtained without further purification. Cobalt acetate ($CoAc_2.4H_2O$ 99.5%), potassium acetate (KAc 99%) and P-xylene (99%) were obtained from Fluka. Plouronic 84 is a trade name for poly (ethylene oxide)-block-poly-(propylene oxide)-block-poly (ethylene oxide) copolymer. All solutions and liquid crystalline template (LCT) were prepared using reagent grade (18 MΩ cm). All glassware was cleaned by soaking in 5% Decon 90 (Aldrich solution) for few days followed by rinsing with deionized water and dried in an oven at 50°C.

The plating mixtures used in this work were ternary system consisting of P84 non –ionic surfactant [(EO)19(PO)43(EO)19], aqueous solution of $CoAc_2.4H_2O$, KAc and p-xylene. The H_1 phase of ternary mixture containing 53.13 wt% aqueous Co salt and potassium acetate 44.6% weight of P_{84} and 2.23% weight of p-xylene which is stable at room temperature for more than a month.

Instrumentation

The electrochemical deposition and cyclic voltammetry (CV) measurements were performed on EG and G 283 Potentiostat and a conventional three electrode cell (15 ml volume capacity).

Electrodeposition process

The $Co(OH)_2$ films were electrodeposited in a three-electrode cell at room temperature. The working electrode was a 1 mm diameter gold disk electrode, while for the structural characterization of the electrodeposited films, the working electrode was flat gold substrate with geometrical surface area 1 cm^2 (made by evaporating 10 nm of a chromium adhesion layer followed by 200 nm thick of gold onto thin glass microscope.

Platinum gauze of area 1 cm^2 was used as counter electrode and saturated calomel electrode (SCE) as the reference electrode. 1 mm disk electrode was polished by polishing paper (grade 1200) followed by alumina (Buehler) of two grades: 1.0 and 0.3 µm then rinsed with deionized water. The electrolyte was the plating mixture described previously, the electrochemical deposition experiments were carried out at a constant potential of -0.82 V vs. SCE. The deposition of $Co(OH)_2$ film was carried out via passing 1 C cm^2 of charge in the electrochemical cell.

The process of electrochemical deposition of the $Co(OH)_2$ films could involve an electrochemical reaction and a precipitation reaction suggested as follows:

$$2\ CH_3COO^- + 2\ H_2O + 2e^- \rightarrow 2\ CH_3COOH + 2\ OH^-$$

$$Co^{2+} + 2OH \rightarrow Co(OH)_2$$

After deposition, the electrodes were rinsed with excess amounts of deionized water to remove the surfactant. The gold electrode was cleaned by sonication in propanol (BDH) for 1 h followed by rinsing with deionized water.

An analytical scanning electron microscope (JEOL 6400) was used to study the morphology and thickness of the electrodeposited cobalt films. XRD with Cu Kα radiation was used to prove primary evidence for the formation of a nanostructured film. The regularity of the nanostructure was investigated using JEOL 2000FX transmission electron microscope operating at an accelerating voltage of 200 KV.

X-ray diffraction characterization

XRD measurements of electrodeposited $Co(OH)_2$ films were carried out on a Bruker D8 x-ray diffractometer using Cu K α radiation (λ = 0.154 nm). The XRD spectra were obtained using high resolution in the step-scanning mode with a narrow receiving slit (0.4o) with a counting time of 15 s per 0.1°

RESULTS

In this study, pluronic 84 (P84) containing hydrophobic blocks and connected ethylene oxide moieties as hydrophilic head groups has been employed as the surfactant. When mixed with the aqueous solution of the metal salt, the hydrophobic blocks cluster together and the hydrophilic blocks dissolve in the water, forming the lyotropic liquid crystal phases.

The most interesting phase of this work is the hexagonal liquid crystal (H_I) phase where the surfactant molecules aggregate into parallel cylin-drical rods arranged in a hexagonal pattern (Figure 1). The interior of the surfactant rod is hydrophobic while the aqueous component resides in the interspaces between individual rods (Bender et al., 2007). Electrodeposited films were investigated via cyclic voltammetry, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and x-ray diffraction (XRD) techniques.

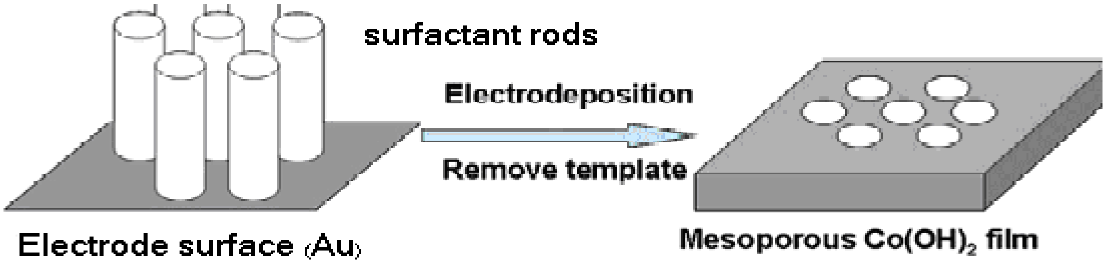

Figure 1. Schematic mechanism of the growth process of the mesoporous H_1-e Co $(OH)_2$ films electrodeposited in the presence of hexagonal liquid crystal template.

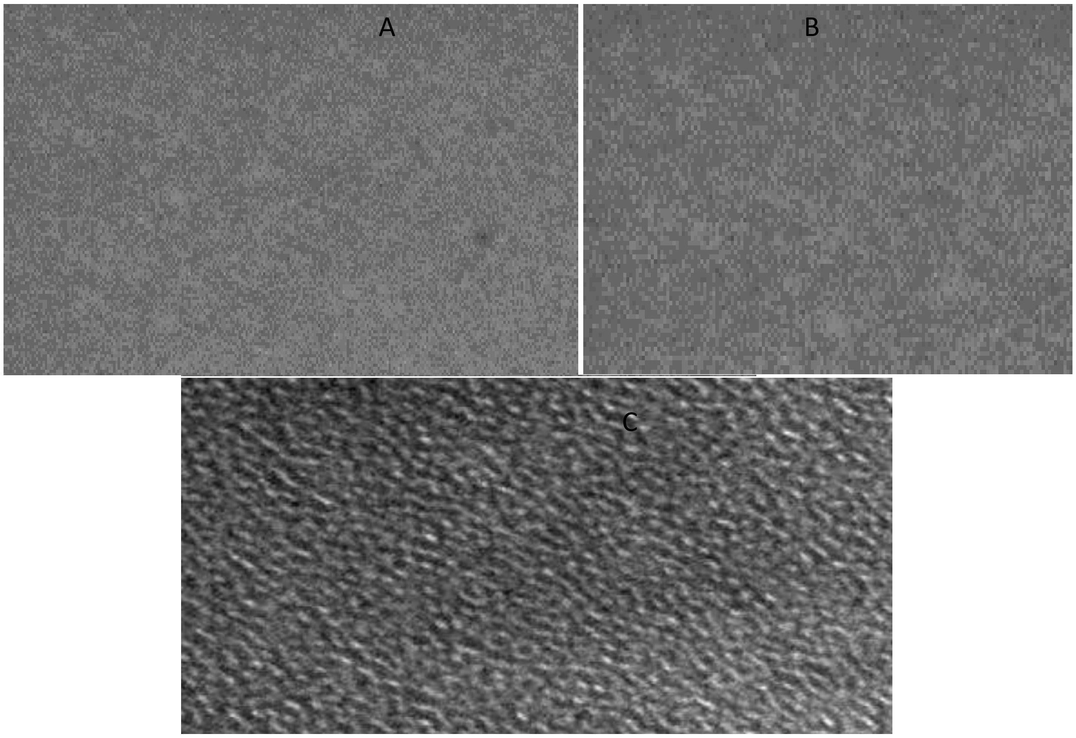

Figure 2. SEM photographs of the H_1-eCo $(OH)_2$ films deposited at -0.75 V (A) and -0.95 V (B). (C). TEM image of the H_1-e $Co(OH)_2$ films deposited at deposition potential -0.95 V.

DISCUSSION

SEM and TEM characterization of H_I-e Co hydroxide films

The SEM images of the H_I–e Co hydroxide films deposited at different potentials of -0.75, and -0.95 V are displayed in Figure 2. The surface morphology of mesostructured $Co(OH)_2$ films is found to be unchanged with the deposition potentials. Figure 2A and B shows that smooth and compact films form at deposition potentials of -0.75 and -0.95 V. Figure 2C shows typical TEM images of the H_I–e Co $(OH)_2$ film electrodeposited at -0.95 V. The $Co(OH)_2$ film on gold electrode (Figure 2C) consisting of cylindrical pores of about 9.01 nm in diameter arranged on a hexagonal lattice with the center to center pore distance of about 9.23 nm.

It is apparent that all the films have uniform and well – ordered mesoprous structures. It was noted that the mesostructures of the H_I–e–Co almost remain unchanged under different deposition potentials, which is consistent with the result reported in literature (Tan et al., 2005). This type of morphology can lead to high surface area and a mesoporous volume, which provides the structural foundation for the high specific capacitance. Such surface morphology with mesoporous structures may feasible for supercapacitor applications. The porosity indicates that the electrolyte can penetrate throughout the plating and it can be effectively utilized for charge storage. On the basis of the pore size and well thickness, a high specific area inside these pores would be expected.

Cyclic voltammetry characterization

In this work the cobalt hydroxide electrodes were used in the supercapacitor and their performance was tested using cyclic voltammogram technique. Figure 3A displays the characteristic CV curves of the H_I–e Co $(OH)_2$ film electrode at different scan rates. For Co-electrode material, it is well accepted that the surface faradiac reaction can be expressed as follows:

$$Co \longleftrightarrow Co^{2+} + 2e$$

It is clear to see that a pair of redox peaks is visible in each CV curve, indicating that the measured pseudo capacitance is mainly based on the redox mechanism. Furthermore, the shape of the CV curves reveals that the capacitance characteristic of $Co(OH)_2$ is distinct from that of the electric double-layer capacitance, which would produce a CV curve close to an ideal rectangular shape. Moreover, the shape of the CV curves for the H_I – e$Co(OH)_2$ film is not significantly influenced with increasing the scan rates. This can be attributed to the improved mass transportation and electron conduction within the material as a result of its regularly ordered mesoporous.

The effect of scan rate on the cobalt hydroxide electrode supercapacitor was studied in 0.1 M NaOH and voltage range was -1.2 to -0.4 V vs SCE (Figure 3A). The voltammetric curves show that the current densities are directly proportional to the scan rate of CV, indicating ideally capacitive behaviour. It can also be seen that when the scan rate increased, the current densities increased rapidly and the separation between the reduction and oxidation peaks becomes larger, which is mainly due to the polarization of the cell under the relatively high scan rate.

It is well accepted that the anodic and cathodic waves are assigned to the oxidation of $Co(OH)_2$ to CoOOH and the reverse process, respectively:

$$Co(OH)_2 + OH^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} CoOOH + H_2O + e^-$$

It was established that the electrodeposited cobalt compounds involves various oxidation-state cobalt compounds as well as cobaltous hydroxide and cobalt metal. X-ray photoelectron spectroscopy (XPS), Energy-dispersive X-ray and x-ray diffraction revealed that the cobalt compounds surface is covered with $Co(OH)_2$, while the cobalt compound bulk involves cobalt metal (Hoshino and Hitsuoka, 2005).

The specific capacitance (C) of the electrodeposited films can be calculated according to the following equation (Jayalakshmi et al., 2006):

$$C = Q / m\,v\ \Delta V$$

Where Q is the half of the investigated area of the CV curves, m is the mass of the deposited film (g), v is the sweep rate (V/s) and ΔV is the potential window (V). The values of specific capacitance calculated from the cyclic voltammograms curves were listed in Table 1. The specific capacitance obtained would be due to the fact that the surface morphology of deposited films significantly affects the capacitance of an electrochemical capacitor.

The effects of potential scan rates (10 to 200 mVs-1) on the capacitive of electrodeposited films are shown in Figure 3B. The decrease in capacitance with the scan rate is attributed to the presence of inner active sites, which cannot precede the redox transitions completely at higher scan rates of cyclic voltammograms, probably due to the diffusion effect of proton within the electrode (Lei et al., 2008).

The specific capacitance obtained at the slowest scan rat is believed to be close to that of full utilization of the electrode material (Lei et al., 2008). The lower sweep rates allow more time for the proton to access the bulk of the oxide. Such large values of capacitance are attributed to the typical morphology and amorphous nature of the film (Lei et al., 2008).

X-ray characterization

Figure 4A depicts the low – angle XRD patterns of the liquid crystal template (curve a) and the deposited H_I-e Co hydroxide film (curve b), separately. Both plots present peaks at small angles, which indicate the existence of a size – controlled nanoporosity. The hexagonal liquid crystalline mixture displays a clear diffraction peak with d – spacing of 9.0 nm at around 2Ө = 1.11° (curve a), which can be indexed as the (100) plane.

The pore – to pore distance for this hexagonal array, given by d_{100}/ cos 30, is 9.2 nm. The H_I – e $Co(OH)_2$ film also shows a well defined peak at around 2Ө = 1.13 (curve b), which is expected to be from d100 diffraction plane of the hexagonal nanostructure corresponding to a d – spacing of 9.01 nm and a pore to pore distance of 9.23 nm, suggesting a porous nanostructure derived from the structure of the template solution.

Figure 4B illustrates the wide – angle XRD spectra of the as – deposited H_I –e Co hydroxide film on gold substrate.

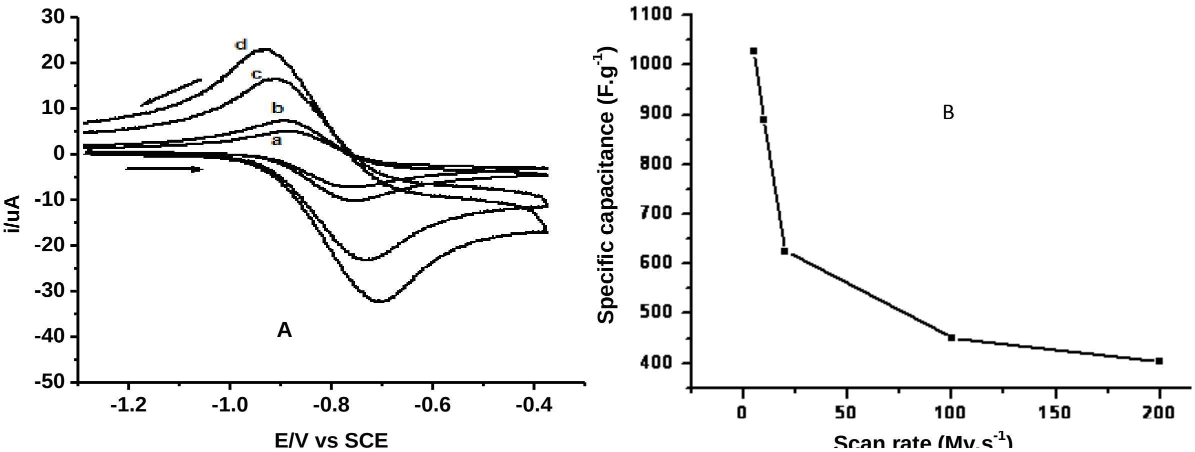

Figure 3. A. Cyclic voltammograms of deposited cobalt hydroxide film from pluronic lyotropic liquid crystal in 1M NaOH at different scan rates, 10 mV s-1(a) , 20 mV s-1(b), 50 mv s-1 (c) and 100 mV s-1 (d). B. Indicates the variation of specific capacitance of the electrodeposited films versus the scan rates.

Table 1. Capacitance values derived from cyclic voltammograms of electrodeposited nanostructured cobalt hydroxide films at various sweep rates.

Sweep rate (mVs^{-1})	Capacitance (F g^{-1})
5	1027
10	890
20	625
100	450
200	403
500	350

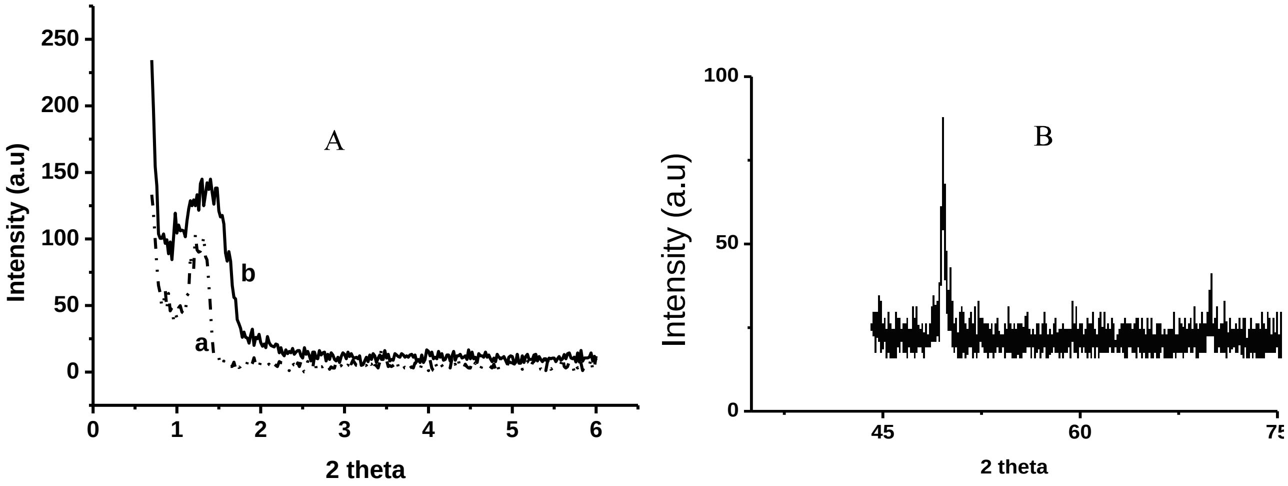

Figure 4. (A) Low –angle XRD for the H1-eCo film from pluronic lyotropic liquid crystal template (a), for electrodeposited H1-eCo film on gold substrate (b) and (B) wide – angle XRD for electrodeposited H_1-e Co film on gold substrate.

It can be seen that all the peaks are in accordance with the patterns of Co. The XRD pattern consists of sharp peak at 45°, except the substrate peaks, the XRD result corresponds to the well-known layered of Co (Dan-Dan et al., 2007).

Conclusion

In the present work, we present a simple and a novel method for the electrode position of the mesoporous $Co(OH)_2$ film on gold electrode from the hexagonal lyotropic liquid crystalline phase of inexpensive nonionic surfactant P84. The CV, SEM, TEM and XRD were employed to characterize electrodeposited films. The electrodeposited films exhibited the maximum specific capacitance of 1027 F.g-1 at scan rate of 5 mV s^{-1}. The specific capacitance may be attributed to a larger effective surface area within the mesoporous films. All the results indicate that the experimental conditions have significant effects on the structure and electrochemical capacitance of the prepared H_I–e Co hydroxide films.

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