Nanostructured Nickel-Cobalt Hydroxide Nanoflakes Thin Film Electrodes as High Performance Pseudocapacitor Electrodes

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ABSTRACT

Vertically aligned Ni-Co hybrid nanoflakes composite was deposited on stainless steel substrate through simple, scalable, cost efficient, flexible successive ionic adsorption and reaction method (SILAR) method. Their morphology and distribution on substrate were examined by FESEM. Effect of cobalt insertion and their effect on capacitive behaviour were also studied thoroughly. This method gives an effective way to enhance capacitance behaviour because of binder-free deposition, uniform pore size, porous morphology and constant material distribution. Porous vertically aligned interconnected nanosheet array morphology obtained from this method is preferred for supercapacitor application. Their electrochemical properties were measured by cyclic Voltammetry and highest specific capacitance of 680 Fg^{-1} obtained at 5mVs^{-1} and composites also exhibit excellent cyclic stability, which suggests the pertinence of this method for next generation supercapacitors.

Keywords*: Ni-Co hybrid, nanoflake, redox, charge storage, supercapacitor.*

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1. Introduction

Pollution is turning out and the shortage of nonrenewable energy sources to be a serious concern among all over the world. It is calling for consideration to find clean and new ways of energy source. Supercapacitors (SC) or electrochemical capacitors or ultracapacitor would represent a significant advance in energy storage technology.[1] Supercapacitor have creating great attention in nowadays due to their various advantages like high power density, enduringness, high specific energy, fast recharge capacity, environmental friendly, and excellent cyclic stability.[2][3][4] It can employ balanced and the combined advantages of both the capacitor and batteries. On the material basis SC can be classified in two catagories, first electric double layer capacitor (EDLC) and pseudocapacitor.[5][6][7] Transition metal oxides/hydroxides and conducting polymer comes under pseudocapacitor classes. They store charge on them through fast and reversible faridic redox reactions.[8] Among them, Ni-Co nanocomposites are going to use popularly as electrode material for supercapacitor applications, because of their high theoretical capacitance, easy processability approach, well defined redox behavior and chemical stability.[9] But their less experimental capacitive value and retention value restricts their application as efficient electrode material. To overcome such restriction there is need to enhance their capacitive properties by synthesis process,controlled morphology, enhancement of effective surface area and introduce more conductive region in electrode material.[10][11] Now the research in energy storage are moving towards bi-metal matrix of nickel and cobalt to utilize their conjugative redox behavior and improvedmorphology with conductivity. Meher et al. prepared porous NiOflakelike electrode material through controlled Microwave-Mediated Synthesis process and found the highest specific capacitance of 370 Fg^{-1} at 2 Ag^{-1}.[12] Deng et al. synthesized 2-D ultrathin mesoporous

$NiCo_2O_4$nanosheets via facile solvothermal method and found 999 Fg^{-1} and 15.6% capacitance loss after 3000 cycles.[9] It is believed that the incorporated electrodes structure can reduce the inactive surface in conventional electrode and provide more effective charge and mass transfer. Thus, it will have highly need to prepare efficient and facile way to develop electrode materials on substrates for high performance supercapacitors.

Herein, we demonstrate facile fabrication of vertically aligned nanoflakes of Ni-Co hydroxide on stainless steel substrate for the application of supercapacitors electrodes. Remarkably, developed electrode materials shows hierarchical nanflake architectures which increased electrochemical performance as high specific capacitance and better cycling retention, making it a favorable electrode material for supercapacitors application.

2. Experimental section

2.1 Synthesis and reaction mechanism

Deposition of electrode material on substrate is follows the adsorption and reaction mechanism from the cationic and anionic solution ions. In this two-step deposition technique, electrode film is deposited on substrate called as SILAR (Successive ionic layer adsorption and reaction) method. Substrate was dipped in deionized water between every cycle to avoid loosely bonded materials and impurities. Film was developed on the substrate surface due to ion by-ion deposition at nucleation sites allowing to the growth kinetics. Immersion in cationic and anionic solution takes place for 30 sec and the cycle continue upto the optimum deposition. At a room temperature the Co/Ni hydroxide film was deposited on a stainless steel substrate by the SILAR method. Electrode samples are labelled as NH and CNH for nickel and cobalt-nickel films.

3 Characterization techniques

The morphology of the films was found by a field emission scanning electron microscope (SIGMA, Carl Zeiss) and the elemental composition of the films was examined using energy dispersive X-ray analysis (INCA OXFORD). The porosity of the developed films was calculated by using digital image analysis software. Cyclic Voltammetry, galvanostatic discharge and electrochemical impedance spectroscopy measurements were executed in electrochemical workstation (Novocontrol Alpha-Aanalyzer + POT/GAL). The electrochemical measurement were done in three electrode system, which consist of a platinum wire as a counter electrode, a saturated calomel electrode (SCE) as a reference electrode and the film deposited stainless steel substrate as a working electrode in 1 M KOH solution electrolyte. Cyclic Voltammetry data was examined using WinChem software.

4 Results and discussion

4.1 Morphology and structural study

From figure 1 shows the FESEM micrographs of sample NH and NCH. It can be seen from the figure that the sample NH consists of different size particles combined in aggregate form. Incorporation of nickel in cobalt hydroxide cause to change the morphology in intersected and vertically aligned porous with interconnected nanoflakes array, which is advantageous to the enrichment of active sites and provides better capacitive properties, easy charge transfer, fast ion/electron interaction with short diffusion path for electrochemical kinetics.[13][14]

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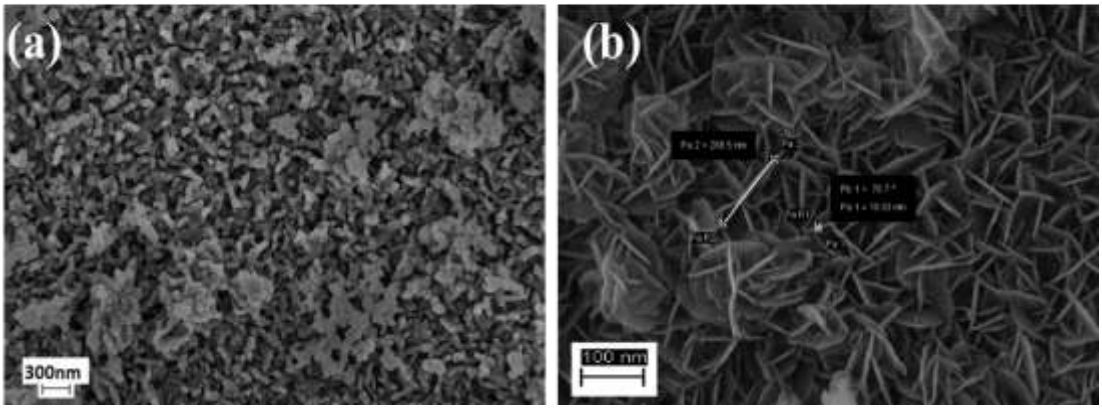

Fig-1: FESEM micrograph of sample NH (a) and NCH (b)

The percentage porosity was computed by employing total optical porosity method with the help of Image-J software. It was figured by generating a porosity threshold image and was found to be 27 and 68% for NH and NCH samples. The obtained Bi-metal composite film NCH shows a highly porous nanoflakes array with cavities, which is preferential structure to the improvement of capacitive properties by allowing for fast charge transfer and more ion/electron access for enhancing electrochemical reactions.[15][16]

Further, EDX elemental mapping in figure 2 gives information on the quantitative elemental values and an estimation of their relative presence on the surface.

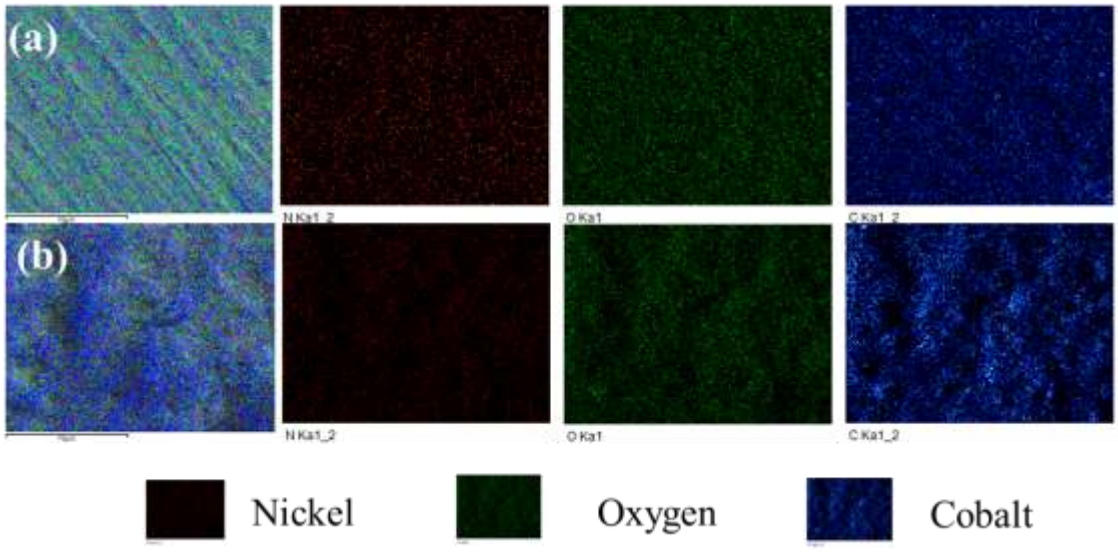

Fig-2:Elemental mapping image of samples NH (a) and NCH (b).

4.2 Electrochemical studies

All electrochemical characterization were carried out in a three electrode cell system in 1 M KOH electrolyte. Cyclic voltammetry (CV) studies were carried out to study and compare the capacitive behavior of the material deposited

on the substrate. Figure 3 presents the CV curves of NH and NCH electrode films at various scan rates with a potential window of -0.2 to +0.8 V. Non-rectangular shape curves of CV spectra indicates the pseudocapacitive

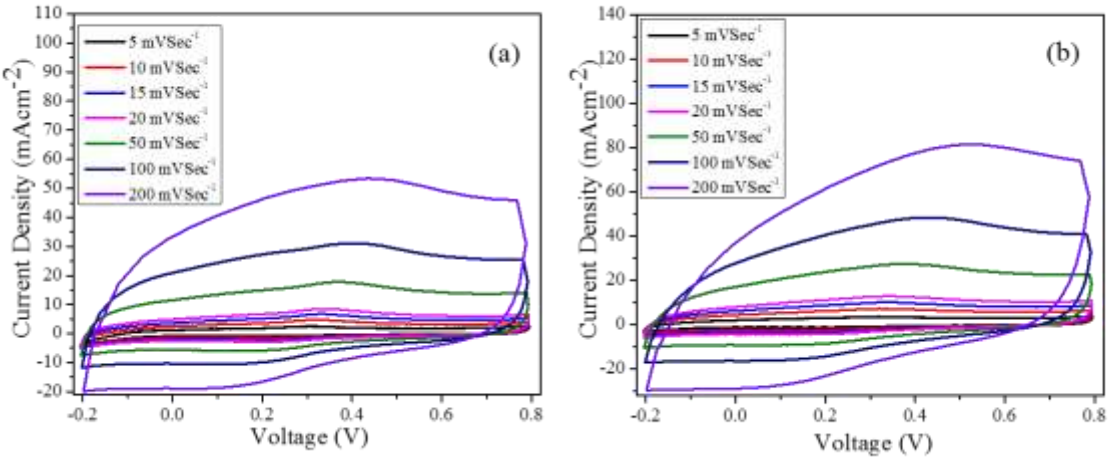

Fig-3:Cyclic curves spectrum of NH (a) and NCH (b) samples.

behaviour of electrode material. Redox peak showed the reversible faradic transfer action as a result of pseudocapacitivebehavior and also demonstrated the symmetrical positive and negative sweep. The anodic peak occurred due to oxidation of Co/Ni hydroxide and the cathodic peak appeared because of the reverse process. This process can be expressed by following the reversible equations (1) and (2).[17][18]

$$Ni(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O + e^- \qquad (1)$$

$$Co(OH)_2 + OH^- \rightleftharpoons CoOOH + H_2O + e^- \qquad (2)$$

The figure also depicts the effect of scan rate from 5 to 200mVs^{-1} on the supercapacitive activities of the nanohybrid composites. Enclosed curve area of CV curve slowly increase with the increasing of scan rate. From the CV study the specific capacitance CS is calculated by following relation:[19]

(3)

Where m is the deposited mass of the material on the substrate, v is the scan rate, I (V) is the response current, V_c-V_a Is the potential window. Integration of response current gives the area of CV curve, which gives the average current. Mass deposition on the substrate is calculated by the mass difference method.

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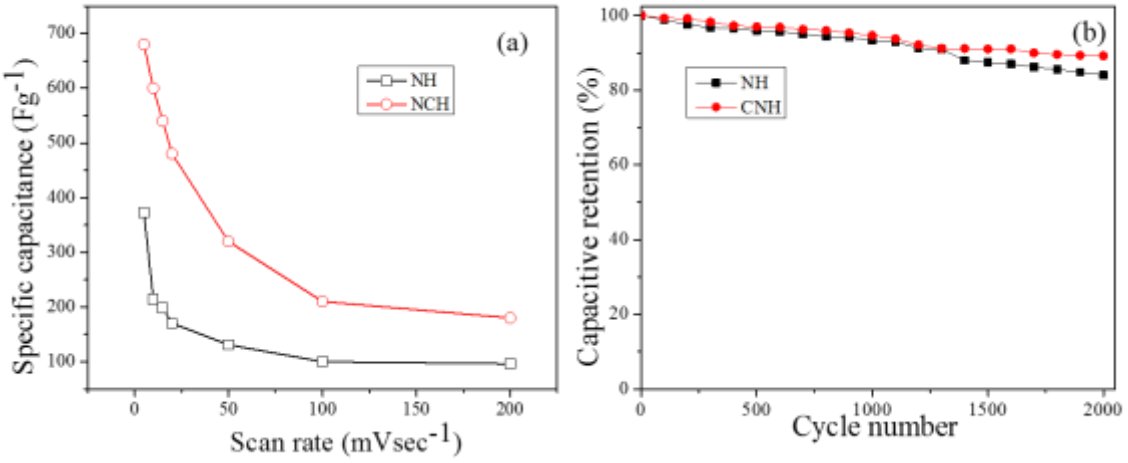

Fig-4:Calculated specific capacitance value at various scan rates (a) and capacitive retention plot for 2000 cycles.

Highest specific capacitance calculated from CV curves are 680 Fg^{-1} for NCH electrode sample at a scan rate of 5 mVs^{-1}. This value is potentially higher than the specific capacitance of a pure nickel hydroxide electrode, NH (372 Fg-1. Inn general case specific capacitance at slow scan rate gives the operational range of the electrode materials. At higher scan rate high rate creates depletion of ions, which increases the ionic resistivity and decreases the capacitance. The improvement of the specific capacitance in the NCH electrode film come due to the improved morphology, porous architecture, greater surface area, easy transfer path and more active sites presence for ion diffusion.[20][21] Fig. 5a demonstrates the plot between specific capacitance and taken various scan rates. Cyclic retention is an important parameter to established long-term usefulness of the developed electrode material for supercapacitor application. The cyclic stability of samples NH and NCH for 2000 cycles is measured at a scan rate of 50 mVs^{-1} and shown in Figure 5b. Sample NH holds 82% and sample NCH retains 89% of its capacitance after 2000 continuous cycles.

Conclusions

In this study, we demonstrate the preparation of porous film of Ni-Co nanohybrid composite by simple, scalable, cost efficient, flexible successive ionic adsorption and reaction method (SILAR) on stainless steel and examine their electrochemical studies for supercapacitor application. This method is an effective method to enhance capacitance behavior because of binder free deposition, uniform pore size, porous morphology and constant material distribution. Porous vertically aligned interconnected nanosheet array morphology obtained from this method is preferred for supercapacitor application. Their electrochemical properties were measured by cyclic Voltammetry in 1 M KOH electrolyte. The maximum specific capacitance of 680 Fg^{-1} obtained at 5mVs^{-1}, and composites also exhibit excellent cyclic stability, which suggests the pertinence of this method for next generation supercapacitors.

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