# Nickel–Cobalt Layered Double Hydroxide Anchored Zinc Oxide Nanowires grown on Carbon Fiber Cloth for High-Performance Flexible Pseudocapacitive Energy Storage Devices

Imran Shakir [a,b,*], Muhammad Shahid [c], Usman Ali Rana [a],
Inas M. Al Nashef [d], Rafaqat Hussain [e]

[a] *The Sustainable Energy Technologies Center,College of Engineering, KIng Saud University, PO-BOX 800, Riyadh 11421, Kingdom of Saudi Arabia*
[b] *Interdisciplinary Research Centre in Biomedical Materials (IRCBM), COMSATS Institute of Information Technology (CIIT), Lahore, Pakistan*
[c] *Material Science and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia*
[d] *Department of Chemical Engineering King Saud University, PO-BOX 800, Riyadh 11421, Kingdom of Saudi Arabia*
[e] *Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor Darul Ta'zim, Malaysia*

## ARTICLE INFO

## ABSTRACT

Nickel-cobalt layered double hydroxide (Ni-Co LDH) nanoflakes–ZnO nanowires hybrid array has been directly synthesized on a carbon cloth substrate by a facile cost-effective two-step hydrothermal route. As electrode materials for flexible pseudocapacitors, Ni-Co LDH nanoflakes–ZnO nanowires hybrid array exhibits a significantly enhanced specific capacitance of 1927 Fg$^{-1}$, which is a ∼1.8 time greater than pristine Ni-Co LDH nanoflakes. The synthesized Ni-Co LDH nanoflakes–ZnO nanowires hybrid array shows a maximum energy density of 45.55 Whkg$^{-1}$ at a power density of 46.15 kWkg$^{-1}$, which is 35% higher than the pristine Ni-Co LDH nanoflakes electrode. Moreover, Ni-Co LDH nanoflakes–ZnO nanowires hybrid array exhibit excellent excellent rate capability (80.3% capacity retention at 30 Ag$^{-1}$) and cycling stability (only 3.98% loss after 3000 cycles), due to the significantly improved faradaic redox reaction.

## 1. Introduction

The successful commercialization of flexible, portable and textile electronic devices is limited by the lack of fully integrated high performance energy storage, as the conventional capacitors and batteries are too bulky in size and heavy in weight [1–4]. The development of various flexible energy storage devices such as batteries and supercapacitors are much slower than that of the flexible electronic devices themselves. Among various flexible energy storage devices, electrochemical supercapacitors have gain ample attention, as they can provide an instantaneous higher power density, fast charging, long life cycles when compared to flexible batteries [2,5–8]. Flexible supercapacitors based on storage mechanisms are classified into two major classes, electrical double layered capacitors (carbon materials) and Faradic redox reaction pseudocapacitors (metal oxides/hydroxides and conducting polymers) [9–12]. Electrical double layered capacitors ((EDLCs) possess excellent cycle stability and high maximum power

density, but suffer from low specific capacitance and energy density, while pseudocapacitors have very high specific capacitance and energy density because of the reversible redox reaction during charging and discharging to store energy [13]. Among various explored pseudocapacitor materials for flexible supercapacitor, Ni-Co LDH have drawn extensive research attention due to its low cost, flexible ion exchangeability, better redox activity and electrical conductivity as compared to the corresponding (Ni(OH)$_2$ and Co(OH)$_2$) and environmentally friendly nature [14–16]. Although, Ni-Co LDH shows better electrochemical performance as compared to crosspronding single hydroxides but it is not good enough to meet the demand of new energy storage devices as low power performance and long cycle life still remains the major issues with Ni-Co LDH which must be resolved prior to the applications being viable. In order to resolve these major technical challenges a convenient and scalable hydrothermal based approach to deposit nanoflakes of Ni-Co LDH on ZnO nanowires arrays grown directly on carbon fiber substrate as a binder-free electrode for high-performance flexible supercapacitors. The coating of Ni-Co LDH nanoflakes onto ZnO nanowires arrays enlarges the contact area with electrolyte, maximum utilization of Ni-Co LDH and fast redox reaction. As an electrode for flexible electrochemical supercapacitor, Ni-Co LDH

* Corresponding author.
*E-mail addresses:* shakir@skku.edu, mshakir@ksu.edu.sa (I. Shakir).

nanoflakes–ZnO nanowires hybrid array exhibits a high specific capacitance of 1927 F g$^{-1}$, with excellent rate capability, long-term cycle stability and high energy and power densities. These results suggest that Ni-Co LDH nanoflakes–ZnO nanowire hybrid array is a potential candidate for next generation flexible energy storages devices.

## 2. Experimental Methods

All the reagents Zn(CH$_3$COO)$_2$·2H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, NH$_4$OH and hexamethylenete-tramine (HMTA) used in the experiment were of analytical grade (Sigma-Aldrich) and were used without further purification. For the synthesis of ZnO nanowires, carbon fabric cloth was dip coated with 5 mM of Zn(CH$_3$COO)$_2$·2H$_2$O solution in ethanol for three to four times and then heated on a hot plate at 150 °C for 10 minutes. Next, the seeded carbon fabric cloth substrate was hung in a glass bottle containing 200 ml aqueous solution of 12 mM Zn(NO$_3$)$_2$·6H$_2$O and 12 mM HMTA. The bottle was then heated in a furnace at 95 °C for 10 h and then cooled to ambient temperature. After the hydrothermal reaction, the carbon fabric cloth substrate was rinsed with deionized (DI) water and dried on a hot plate. For the coating of Ni-Co LDH on ZnO nanowires 10 mmol of Co(NO$_3$)$_2$·6H$_2$O and 5 mmol of Ni(NO$_3$)$_2$·6H$_2$O were dissolved in 100 ml of H$_2$O to form a solution. After being magnetically stirred for 30 min in air at room temperature, NH$_4$OH was added drop wise and resulting suspension was kept stirring for another 3 hrs in air. In the final step, ZnO nanowires on carbon fiber cloth substrate was placed at the bottom of Teflon-lined stainless steel autoclave and above solution was added for the hydrothermal growth of Ni-Co LDH on ZnO nanowires. The synthesis of Ni-Co LDH on ZnO nanowires was carried out heated at 90 °C for 6 h. After the hydrothermal reaction, the carbon fabric cloth substrate washed several times with DI water and dried at 70 °C in oven overnight. Pristine Ni-Co LDH was prepared with the same procedure as described above.

## 3. Material and Electrode Characterization

The morphological and structural properties were examined by field emission scanning electron microscopy (FE-SEM, JEOL JSM–7401F), and X-ray diffraction (XRD, D8 FOCUS 2200 V, Bruker AXS, Cu Kα radiation ($\lambda$) 1.5418 Å). All the electrochemical measurements were carried out in a conventional three-electrode cell with a CHI-660B electrochemical station (CH Instruments Inc., TX, USA). Ni-Co LDH nanoflakes–ZnO nanowires hybrid array as a working electrode while Ag/AgCl (saturated with KCl) electrode and a Pt foil were used as reference and counter electrode, respectively, in an aqueous electrolyte solution of 6 M KOH. The mass of the active electrode material on carbon fabric cloth was determined by subtracting the weight before the deposition of nanoflakes from the weight after the coating of Ni-Co LDH nanoflakes. The loading mass of each electrode was approximately 0.98 ± 0.02 mg cm$^{-2}$.

The specific capacitance (C$_s$, Fg$^{-1}$) of the electrode was calculated from the CVs (taking into account weight of entire electrode) and the discharge capacitance from galvanostatic charge–discharge curve according to the following equations:

$$C_s = i/(V \times m)$$

Where i is the current density (A) in the CV anodic branch; V is the scanning rate (V s$^{-1}$) and m is the mass of active material on the electrode.

C$_s$ = (i × t)/(ΔV × m), where i is the discharge current, t is the discharge time, ΔV is the potential window, m is the mass of the active materials.

Energy and power density (E, P) of the electrodes were calculated according to the following equations

$$E = 1/2 C_{total} V^2$$

and

P= 2E/unit time, where C$_{total}$ is the total capacitance of the cell.

## 4. Results And Discussion

The morphology of the ZnO nanowires, Ni-Co LDH nanoflakes–ZnO nanowires and Ni-Co LDH nanoflakes was examined with field emission scanning electron microscopy (FE-SEM) and the results are presented in the Figs. 1 and 2(a). Fig. 1(a) presents a low-magnification field emission scanning electron microscopy image showing conducting carbon fabric cloth substrate fully covered with ZnO nanowires array, with a close-up view in Fig. 1(b). The carbon fabric cloth substrate is highly flexible and the ZnO nanowires array synthesized on the textile fiber have a typical hexagonal flat-ended morphology. Fig. 1(c-d) shows that ZnO nanowires are fully covered with Ni-Co LDH nanoflakes film and FE-SEM analysis revealed that the deposition of a Ni-Co LDH nanoflakes onto the ZnO nanowires by this simple hydrothermal approach has no influence on the original shape and morphology of the ZnO nanowires (Fig. 1(c-d)). The high resolution FE-SEM image of Ni-Co LDH nanoflakes–ZnO nanowires hybrid array (Fig. 1(d)) shows that nanoflakes have a typical thickness of ∼5 nm. The deposited ultrathin Ni-Co LDH nano-flakes on ZnO nanowires array are interconnected with each other and create pores and crevices which ensure large surface area for fast diffusion rate within the redox phase, an easier electrolyte ion transport and more superficial electroactive species. The crystallographic information of conformally coated Ni-Co LDH nanoflakes–ZnO nanowires hybrid array was examined by X-ray diffraction and the XRD patterns of pristine carbon cloth, ZnO nanowires coated carbon cloth and Ni-Co LDH nanoflakes–ZnO nanowires hybrid array coated carbon cloth are shown in Fig. 2(b). It can be observed that the spinel Ni-Co LDH phase is completely formed after the hydrothermal growth at 95 C for 6 h as the XRD patterns are in good agreement with the standard peaks for Ni-Co LDH as reported in the literature [17].

Furthermore, the peaks originated from the substrate are marked with asterisk (*) as can be seen in the Fig. 2(b). The chemical composition of the Ni-Co LDH nanoflakes–ZnO nanowires hybrid array was determined by Energy dispersive X-ray analysis (EDXA). In the inset of Fig. 1(c), EDXA spectrum of the Ni-Co LDH nanoflakes–ZnO nanowires hybrid array shows that it contains only Ni, Co, Zn, C and O with no trace of by-products and the atomic ratio of each constituent in the structure is shown in table in the inset of Fig. 1 (d). To examine the capacitive performance of Ni-Co LDH nanoflakes–ZnO nanowires hybrid array and pristine Ni-Co LDH nanoflakes, cycle voltammetry (CV) and galvanostatic charge–discharge (CD) measurements were carried out in 6 M KOH. The CV of Ni-Co LDH nanoflakes–ZnO nanowires hybrid array and pristine Ni-Co LDH nanoflakes electrode at a scan rate of 20 mVs$^{-1}$ in Fig. 2(c) consists of well-defined pair of strong redox peaks within the potential range from 0 to 0.6 V, which reveals that the capacitive characteristics Ni-Co LDH nanoflakes–ZnO nanowires hybrid array are mainly governed by Faradaic redox reactions related to M–O/M–O·OH, where the M represents both Ni and Co ions [18–22]. It is imperative to nota that Ni-Co LDH nanoflakes–ZnO nanowires hybrid array electrode exhibit a large area under the CV curve as compared to that of pristine Ni-Co LDH nanoflakes, implying that Ni-Co LDH nanoflakes–ZnO nanowires hybrid array have a much higher capacitance. This enhancement in the electrochemical properties of Ni-Co LDH nanoflakes–ZnO nanowires hybrid array