Spinel NiCo$_2$O$_4$ Nanorods for Supercapacitor Applications

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Abstract: Herein, we report successful synthesis method of spinel NiCo$_2$O$_4$ nanorods by a low-cost and facile hydrothermal route. Cyclic Voltammetry (CV) and galvanostatic Charge-Discharge (CD) measurements deduce ideal supercapacitive performance (823 F/g) of spinel NiCo$_2$O$_4$ nanorods at a nominal current density of 0.823 A/g with excellent cyclic stability and energy density of 28.51 Wh/Kg.

Keywords: NiCo$_2$O$_4$, Ternary Metal Oxide, Nanorods, Energy Storage, Supercapacitor

Introduction

Advancement of science, technology and rapid industrial progress in the 21st century have already played a pivotal role in causing some serious environment related issues like pollution, global warming, climate change and scarcity of fossil fuels and other non-renewable energy sources. Also the huge demand for energy and power has further complicated the situation. There is an urgent requirement for more cleaner and environment friendly alternate energy resources/devices which could possibly meet up to the expected energy demand, globally and will have negligible/zero contribution towards environment related pollution issues (Dubal et al., 2015; Garg et al., 2014). As alternative energy conversion/storage options, solar cells, (Green et al., 2015) fuel cells, (Galeano et al., 2014; Dusastre 2013; Kafafi, 2015) supercapacitors (Jokar et al., 2015; Lu et al., 2013) have exhibited profound attention in recent years. Supercapacitors are an emerging energy storage option having the combined property of both capacitor and battery. For an energy storage device, it is highly expected that there should be no time lag during charging (similar to a typical capacitor) and also the self-discharge should be much lower (as in case of a typical electrochemical battery) which would result in a higher power density and energy density, respectively. Therefore supercapacitors possess this unique hybrid property of being able to charge within a very short time period and keep it as long as possible without any significant loss. With the rapid growth in areas like portable electronics with light weight and flexible designs, research on these storage devices is of immense significance. The key research on supercapacitor is to enhance the specific capacitance as well as energy density (Garg et al., 2014; Miller and Simon, 2008; Simon and Gogotsi, 2008). Hybrid supercapacitors show both electrochemical double layer capacitance (EDLC) and pseudocapacitance (due to reversible faradaic redox reaction) because EDLC alone is not enough to deliver sufficient amount of energy/power (Lu et al., 2013; Jokar et al., 2015). Also pseudocapacitance is much higher as compared to EDLC. So for practical applications, requirement of better pseudocapacitive materials is obvious.

Recently, there has been growing interest in nanostructured materials with specific morphology like three dimensional (3D) urchins, (Wang et al., 2012b) two dimensional (2D) nanosheets (Zhang and Lou, 2013) and one dimensional (1D) nanoneedles, (Zhang et al., 2012) nanowires (Zhu et al., 2013) and nanorods (Salunkhe et al., 2011) for their possible application as supercapacitor electrodes due to their enhanced electrochemical properties, high specific surface area and availability of short electron and ion transport pathways (Zou et al., 2013). Two dimensional transition metal oxides (TMOs) like RuO$_2$, (Zang et al., 2008) Co$_3$O$_4$, (Xia et al., 2011) NiO (Zhang et al., 2010) and Mn$_3$O$_4$ (Dubal et al., 2009) have been widely studied as electrodes for supercapacitors. Among all, RuO$_2$ has been considered as an influential material because of its high specific capacitance and much better cyclic stability (Bi et al., 2010). But the high cost and toxicity associated with it makes its commercialization improbable (Lu et al., 2012; Zhao et al., 2009; Ghodbane et al., 2009). Several attempts have been made to find other alternate cost-effective, non-toxic, environment friendly electrode materials. Among all, oxides of first row transition-metals like Mn, Fe, Co, Ni etc. have shown promising results as active materials suitable for supercapacitor electrodes. Oxides of both cobalt and nickel have shown unique electrochemical.
behavior owing to the high redox activity of their respective metal ions (Ghosh et al., 2014; Yuan et al., 2009). Mixed transition metal oxides (MTMOs), typically ternary metal oxides with two different metal cations have got large attention in recent years due to their spectacular roles in many energy related applications (Dubal et al., 2015). Many spinel oxides fall into this category having a compositional formula of ABX₄, in which A and B are two different transition metals such as Fe, Ni, Co, Mn, Zn etc (Dubal et al., 2015). Among different MTMOs, nickel cobalt oxide (NiCo₂O₄) is currently emerging as one of the most intriguing material in the field of super capacitors (Xiao and Yang, 2011; Ratha et al., 2015). Similar synthesis procedure was carried out at different temperatures, i.e., 90°C, 120°C, 150°C and 180°C. After the hydrothermal reaction for 12 h, the autoclaves were allowed to cool naturally to room temperature. The precipitates were collected by centrifugation and then dried at 100°C for 4 h and was further annealed at 200°C for 6 h in a vacuum oven. The NiCo₂O₄ samples prepared at 90°C, 120°C, 150°C and 180°C are being labeled as NCO-90, NCO-120, NCO-150, NCO-180 and NCO-200 respectively.

**Characterization**

All the NiCo₂O₄ samples were characterized by FESEM (MERLIN Compact with GEMINI I electron column, Zeiss Pvt. Ltd., Germany) and by elemental mapping with EDAX. X-Ray Diffraction (XRD) patterns of the samples were obtained by a Bruker D8 Advanced diffractometer using Cu-Kα radiation (λ = 1.54184 Å).

**Electrode Fabrication**

First the surface of a bare glassy carbon electrode (GCE) was sequentially polished with micro polishing powder (Al₂O₃ powder having different grain sizes such as 1.0 µm, 0.3 µm and 0.05 µm) to get a mirror finish and it was subsequently sonicated with DI water for about 15 min in order to remove any adsorbed species on the electrode surface. About 1mg of the as synthesized sample was dispersed in a mixture of 95 µL of ethanol and 5 µL of nafion which was further ultrasonicated for 10 min to give a homogeneous mixture solution. Then 2.5 µL of the mixture solution was drop casted on to the surface of the freshly polished glassy carbon electrode and then it was dried in a vacuum desiccator for 1 h. By comparing the weight of the glassy carbon electrode before sample loading and after sample loading, the mass of the sample deposited on the GCE surface was found to be 0.034 mg.

**Electrochemical Measurements**

The electrochemical performance of the NiCo₂O₄ nanorods modified electrode was evaluated in a three electrode electrochemical cell using a Potentiostat/Galvanostat (PG-16125, Techno science instrument, Bangalore, India) in 2 M aqueous solution of KOH working as the electrolyte. A basic schematic of the three electrode cell arrangement is shown Fig. 2. The CV and CD measurments were carried out at room temperature at different scan rates and different current densities keeping the potential window between -0.1V to 0.4V Vs. Ag/AgCl electrode. The specific/gravimetric
Capacitance ($C_{sp}$) was calculated from cyclic voltammetry curves using the following Equation 1:

$$C_{sp} = \frac{\int_0^{V_f} I(V)dV}{m.s[V_f - V_i]}$$

where, the integral part in the numerator gives the area under the CV curve, $m$ is the mass of the sample loaded onto the GCE surface, $s$ is the scan rate and $[V_f - V_i]$ is the potential window ($V_f$ and $V_i$ are the final and initial potential values, respectively). From charge-discharge curves, the specific capacitance of the material was calculated using the following Equation 2:

$$C_{sp} = \frac{I}{m \left(\frac{dV}{dt}\right)}$$

where, $I$ is the discharge current, $m$ is the mass of the sample loaded onto the GCE surface and $dV/dt$ is the slope of the discharge curve. To calculate the Energy density ($E_d$) and Power density ($P_d$) for the sample, following Equation 3 and 4 were used:

$$E_d = \frac{1}{2} C_{sp} V^2$$

$$P_d = \frac{1}{2} C_{sp} V.s$$

Fig. 1. Schematic showing an illustrative representation of synthesis procedure and growth mechanism of NiCo$_2$O$_4$ nanorods

Fig. 2 Schematic showing a typical three-electrode cell configuration used for the electrochemical measurements
Results and Discussion

Morphological Study

Figure 3 shows the FESEM images of the samples prepared at different temperatures in which the formation of nanorod shaped NCO is clearly depicted. Similarly, Fig. 4a and b show the FESEM images of the sample prepared at 200°C which confirms the formation of nanorod like NCO. On an average, these nanorods are having a diameter of 50-60 nm and a length in the range of ~0.2-1 µm. The EDAX spectrum and elemental composition data is shown in Fig. 4c. Elemental analysis show the Ni and Co ratio of ~1:2, confirming formation of NiCo$_2$O$_4$ phase. Figure 5 shows the elemental mapping data for the NCO-200 sample. In Fig. 6, X-ray diffraction patterns of NCO samples prepared at different temperatures have been shown. From the XRD patterns, it is confirmed that the sample synthesized at 200°C is of high crystallinity compared to the samples prepared at lower temperatures. All the diffraction peaks match with JCPDS file No. 20-0781 and showed a prominent growth along (311) direction. All the peaks can be assigned to a face centered cubic lattice of spinel NCO.

Supercapacitive Study

We performed systematic electrochemical supercapacitor measurements of NCO-200 due to its high crystallinity compared to the NCO prepared at lower temperatures. Systematic electrochemical measurements such as CV and CD were performed in presence of 2 M KOH as electrolyte. For cyclic voltammetry and charge discharge measurements, the potential window was kept within the range -0.1 to 0.4 V. Figure 7a shows the cyclic voltammogram curves of NCO-200 at different scan rates. From Fig. 7d it is observed that the specific capacitance decreases gradually with increase in scan rate. Also from Fig. 7a, it can be inferred that with increase in scan rate, the anodic peak shifts towards positive potential and the cathodic peak shifts towards negative potential. From the specific capacitance calculation from CV curves, the maximum value of specific Capacitance ($C_{sp}$) was found to be 470.58 F/g at 4 mV/s. Similarly, to further quantify the specific Capacitance ($C_{sp}$) of NCO-200, galvanostatic charge-discharge experiments were conducted in the three electrode cell configuration at various current densities with the same potential window between -0.1 to 0.4V. Figure 7b shows the charge discharge curves of NCO-200 at different current densities. Specific capacitance ($C_{sp}$) of values 823 F/g, 460 F/g and 382 F/g were obtained at current densities of 0.8 A/g, 1.38 A/g, 3.44 A/g and 5.58 A/g, respectively. Similarly from Fig. 7c, it is observed that with increase in current density, the specific capacitance decreases gradually.

![Fig. 3. FESEM images of (a) NCO-90 (b) NCO-120 (c) NCO-150 and (d) NCO-180](image-url)
Fig. 4. (a), (b) FESEM images of NCO-200 and (c) EDS spectra with inset showing percentage of composition of constituent elements (Ni,Co,O)

Fig. 5. Elemental mapping of NCO-200 (a) electronic image over which mapping has been performed, presence of oxygen (b) cobalt (c) and nickel (d) is confirmed from the mapping data
Fig. 6. X-ray diffraction patterns of NCO samples prepared at different temperatures and comparison with JCPDS file No. 20-0781 of NiCo$_2$O$_4$

Fig. 7. Electrochemical study of NCO-200 (a) Cyclic voltammetry curves at different scan rates (b) charge-discharge curves obtained at different current densities variation of obtained specific capacitance with respect to (c) current density and (d) scan rates
A long cycling stability performance of any material is the most important criteria for its possible application as supercapacitor electrode (Wang et al., 2012a; 2010). Figure 8a shows the capacitance retention capability of NCO-200 over 1000 cycles with the inset showing 1000 charge-discharge curves. The galvanostatic charge discharge was performed for 1000 cycles at a current density of 5.58 A/g. The sample shows excellent cycling stability which is evident from the fact that even after 1000 cycles, the retention of supercapacitor performance remained close to the initial value which is shown in Fig. 8a. Similarly Fig. 8b shows the charge-discharge curve of last 5 cycles of 1000 cycles. The Ragone plot showing the relationship between energy density and power density has been shown in Fig. 8c. The maximum energy density and power density from the graph was found to be 28.51 Wh/Kg and 49.9 KW/Kg respectively. The specific capacitance for NCO-200 was found to be 823 F/g at current density of 0.8 A/g which is very much comparable to previously reported values. Tang et al. (2013) have shown that NCO nanowires exhibit a specific capacitance of 760 F/g at a current density of 1 A/g. Similarly, urchin shaped NiCo$_2$O$_4$ in sequential crystallization process shows a specific capacitance, 658 F/g at 1 A/g synthesized by Wang et al. (2012). Deng et al. (2014) have synthesized NiCo$_2$O$_4$ nanowires on carbon fiber paper via solvothermal method with specific capacitance, 690 F/g at a current density of 16 A/g. Pu et al. (2013) have synthesized NiCo$_2$O$_4$ nanoplates via hydrothermal method shows specific capacitance 294 F/g at current density of 1 A/g. The NCO-200, reported here shows supercapacitive behavior which is very much comparable to the above reported values and has a potential to be used as a supercapacitor electrode for next generation energy storage devices.

**Conclusion**

In summary, NiCo$_2$O$_4$ nanorods were synthesized by a facile hydrothermal route at different temperatures.
i.e., 90°C, 120°C, 150°C, 180°C and 200°C. The growth mechanism of the NCO nanorods were discussed and its super capacitor performance was tested in a 3- electrode configuration in 2M aqueous KOH solution. The supercapacitive properties of NiCo$_2$O$_4$ synthesized at 200°C were studied in detail. The specific capacitance ($C_{sp}$) of the NCO-200 reached as high as 823 $F_{g}^{-1}$ at a current density of 0.823 $A_{g}^{-1}$ with energy density of 28.51 Wh/Kg and also showed excellent cyclic stability even after 1000 charge-discharge cycles. So these results readily explain the viable application of spinel NiCo$_2$O$_4$ nanorods as high performance electrode material for supercapacitor application.

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Author’s Contributions

All authors equally contributed in this work.

Ethics

The authors declare no competing financial interest.

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