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Facial synthesis of nanostructured $ZnCo_2O_4$ on carbon cloth for supercapacitor application

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Abstract. In this work, we have synthesized the $ZnCo_2O_4$ electrode by a facial one-step hydrothermal method on a carbon cloth for the supercapacitor application. The structural and phase purity of the prepared electrode material was confirmed by X-ray diffraction (XRD) technique. The surface morphology and elemental stoichiometry were studied using field emission scanning electron microscopy (FE-SEM). The FE-SEM micrograph illustrates that the $ZnCo_2O_4$ material is composed of microstrips with a ~0.5 μm width and length in micron uniformly covered the carbon cloth surface. The $ZnCo_2O_4$ electrode material further investigated for electrochemical analyses. The cyclic voltammetry results showed that the $ZnCo_2O_4$ microstrips electrode exhibited the highest specific capacitance of 1084 F/g at 2 mV/s scan rate. Remarkably, a maximum energy density of 12.5 Wh/kg was attained at a current density of 2 mA/cm^2 with the power density of 3.6 kW/kg for the $ZnCo_2O_4$ microstrips electrode. Furthermore, the 96.2 % capacitive retention is obtained at a higher scan rate of 100 mV/s after 1000 CV cycles, indicating excellent cycling stability of the $ZnCo_2O_4$ microstrips electrode. The frequency-dependent rate capability and an ideal capacitive behaviour of the $ZnCo_2O_4$ microstrips electrode were analyzed using impedance analyses; a representing the ion diffusion structure of the material. These results show that the $ZnCo_2O_4$ microstrips electrode could be a promising material for supercapacitor application.

1. Introduction

Supercapacitors with extraordinary features including high power density, high energy density, and long term cyclic lifespan are attracted and it can use for advanced green energy storage applications such as electric vehicles, portable electronic devices, etc [1]. Supercapacitors can divide into mainly two types: electrical double layer capacitors (EDLCs) and pseudocapacitors that based on the charge storage mechanism. EDLCs type of capacitor, the electrostatic store charges *via* reversible adsorption of electrolytic ions at the electrode and electrolyte interface to form electric double layer capacitors. While pseudo capacitor store charge *via* reversible faradic redox reaction [2]. Mostly, carbon-based materials are assisted as electrode materials of EDLCs type. Typically metal oxides/hydroxides and polymers served as pseudo-capacitive materials. Recently, Spinel oxide type of transition metal oxides is much attracted for electrochemical application with differing nanostructure architecture. Compared with the monometallic oxides, Spinel oxides exhibiting synergetic effect from two metal ions and effectively achieves the good electrochemical rate performance [3]. Transition metal substituted Spinel structures of cobaltite oxide MCo_2O_4 (M = Mn, Ni, Cu, and Zn) are most promising for current charge

storage applications [4-7]. These types of mixed transition metal oxides offer higher electronic conductivity as compared to single metal oxides. Among the Spinel type transition metal oxide, zinc cobaltite ($ZnCo_2O_4$) electrode material is one of the attractive Spinel structure offer richer redox activities, good electrical conductivity, low cost and environmentally friendly [8]. Moreover, the cobalt and zinc two metal cations provide the higher capacity and an effective electron transport pathway, respectively in the $ZnCo_2O_4$ material [9].

In this work, the one-step hydrothermal method was employed for the preparation of nanostructured the $ZnCo_2O_4$ microstrips on a carbon cloth. The structural, morphological and chemical composition characteristics were systematically examined using XRD and FE-SEM techniques, respectively. Further, electrochemical measurements were investigated using cyclic voltammetry (CV) and charge/discharge (CD) study. Electrochemical impedance spectroscopy (EIS) was used to study the interface behavior of electrode. The $ZnCo_2O_4$ microstrips electrode exhibited excellent electrochemical performance with superior cycling stability of 96.2 % up to 1000 CV cycles.

2. Experimental studies

All the chemicals were used without further any purification. The $ZnCo_2O_4$ material was prepared by facial hydrothermal method on carbon cloth. For a preparation of $ZnCo_2O_4$, 4 mmol ammonium fluoride, 1 mmol Zinc acetate, and 2 mmol cobalt nitrate were dissolved into the 45 ml deionized (DI) water. After stirring for 45 min, the resulting solution was moved to a Teflon-lined stainless steel autoclave followed by maintaining at 150 °C for 12 h. Then the precipitates were collected, cleaned with DI water and ethanol alternatively and dried in a vacuum oven at 70 °C for overnight. Finally, the resultant product was calcinated at 400 °C for 2 h to remove the organic residue in the furnace and then used for characterizations.

2.1. Material characterization techniques

The structural and phase purity of the prepared material was examined by powder X-ray diffraction (XRD) with Cu Kα radiation. The surface morphological and elemental compositions of the prepared material were investigated by field emission scanning electron microscope (FE-SEM). The electrochemical properties of the prepared electrode were carried out using cyclic voltammetry, galvanostatic charge/discharge and impedance analysis by the compatible IVIUM technologies electrochemical workstation. The electrochemical measurements were investigated in three-electrode cell configuration (saturated calomel electrode as reference and platinum as a counter electrode) in 1 M KOH electrolyte with 0 to 0.5 V/SCE scanning sweep potential ranges.

The areal and specific capacitances of the $ZnCo_2O_4$ microstrips electrode was calculated using equation (1). Where, Ca and Cs are the areal (F/cm^2) and specific capacitance (F/g), respectively of electrode material. I, ν and (V2−V1) are the current response (mA), scan rate (mV/s) and the working potential window (V/SCE) of in the unit area (1 cm^2). m is the areal mass of electrode material deposited on carbon cloth. Further, the discharging capacitance (Ccd, F/g), specific energy (E, Wh/kg), and specific power density (P, W/kg) were calculated using equation (2), as follows [10];

$$C_a = \frac{\int_{V_1}^{V_2} I(V)dV}{\nu \times (V_2 - V_1)} \quad \text{and} \quad C_s = \frac{C_a}{m} \tag{1}$$

$$C_{cd} = \frac{I \times Td}{(V_2 - V_1) \times m}, \qquad E = \frac{0.5 \times C_{cd} \times (V_2^2 - V_1^2)}{3.6} \quad \text{and} \quad P = \frac{E \times 3600}{Td} \tag{2}$$

3. Results and discussion

3.1. Structural and morphological studies

Figure. 1(a) displays the XRD pattern of $ZnCo_2O_4$ material prepared on carbon cloth. The major diffraction peaks observed at 31.47 º, 36.96 º, 45.06 º, 59.59 º and 65.18 º are indexed as (220), (311), (400), (511) and (440) planes of the cubic $ZnCo_2O_4$ structure. The obtained XRD peaks best matches with standard diffraction pattern of $ZnCo_2O_4$ (JCPDS card: 00-001-1149) as shown in figure 1(a) bottom. Moreover, the broad peak was found at the peak position of 25 º related to activated carbon [11]. From XRD study it is clear that $ZnCo_2O_4$ material exhibits a polycrystalline nature. To identify the elemental composition, Energy-dispersive X-ray spectroscopy (EDX) was used. Figure. 1(b) shows the elemental spectrum and inset table displays elemental compositions of $ZnCo_2O_4$ material. From the EDX analysis, it demonstrates the existence of Zn, Co and O elements with the elemental composition ratio of 1:2:4, respectively. Further surface microstructural images were analyzed using FE-SEM technique. Figure 1 (c, d) show the typical FE-SEM images of $ZnCo_2O_4$ material on carbon cloth at ×10 k and ×50 k magnifications. Figure 1 (d) clearly reveling that microstrip-like surface morphology with strip width nearly 0.5 µm covered the carbon cloth surface uniformly. The microstrips have a porous surface with nanocrystalline grains. Such porous morphological surface important is for ion adsorption in the redox reaction to store more charge（5）.

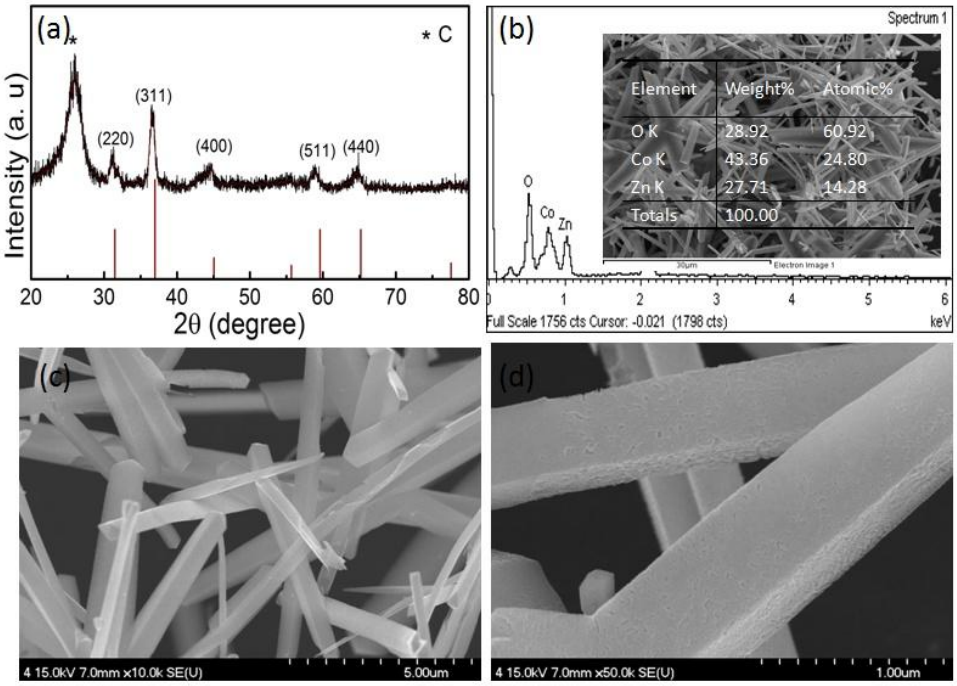

Figure 1. (a) XRD pattern of the $ZnCo_2O_4$ electrode grown on carbon cloth and bottom part shows stick pattern corresponding to JCPDS card (00-001-1149). **(b)** EDX spectrum with inset shows the elemental composition of the $ZnCo_2O_4$ electrode. **(c)** and **(d)** FESEM images of the $ZnCo_2O_4$ electrode at × 10 k and ×50 k magnifications, respectively.

3.2. Electrochemical studies

The cyclic voltammetry measurements were carried out at various scan rates (2, 5, 10, 20, 50, 70, 100, 150 to 200 mV/s) and results as shown in figure 2. From the CV curves, it can be noticed that the shape of CV curves remain unchanged at different scan rates. As scan rate increase, the peak current increases. The areal and specific capacitance of the $ZnCo_2O_4$ electrode area calculated from equation (1). Figure 2(a) and (b) shows that areal and specific capacitance decreased with increasing scan rate. The highest areal and specific capacitances at 2 mV/s scan rate are found to be 0.13 F/cm^2 and 1084 F/g, respectively. Even at higher scan rates of 100 and 200 mV/s, the specific capacitance is of 225 and 173 F/g, respectively indicating a good rate capability of the $ZnCo_2O_4$ electrode in the aqueous electrolyte. The specific capacitance decreased from 751 to 225 F/g at 10 to 100 mV/s scan rate may

be due to the effective inner surface adsorption of ions was reduced at higher scan rate accordingly. At higher scan rates, the decrease of the specific capacitance is attributed to the diffusion ion charge transports lagging behind the electronic mobility [12]. Venkatachalam et al [13] reported the specific capacitance of 845.7 F/g for the double hydroxide treated the $ZnCo_2O_4$. The electrochemical cyclic stability rate performance of the $ZnCo_2O_4$ electrode carried out at a 100 mV/s scan rate over 1000 CV cycles. As seen in figure. 2(d), area under the curve little decreased showing the good cyclic stability of the $ZnCo_2O_4$ electrode in KOH electrode. It is seen that capacitive retention of the $ZnCo_2O_4$ electrode as a function of cycle number. The capacitive retention of 96.2 % retained after 1000 cycles for the $ZnCo_2O_4$ electrode that is better than coral-$ZnCo_2O_4$ nanowires with 85% capacitance retention after 2000 cycles [8]. The capacitive retention of the $ZnCo_2O_4$ microstrips electrode decreased after hundred of CV cycles possibly due to the initial CV cycles that induce a lower rate of ion adsorption.

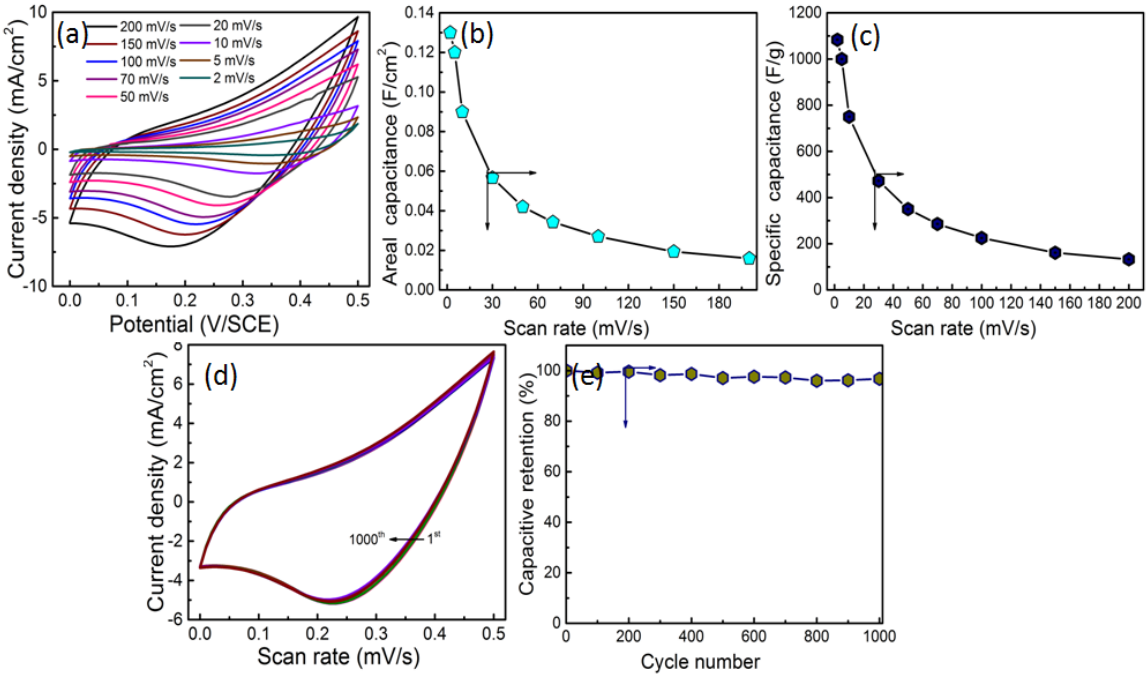

Figure 2. Electrochemical studies of the $ZnCo_2O_4$ microstrips electrode: (**a**) CV curves at different scan rates (from 2 to 200 mV/s) and corresponding plots show the areal **(b)** and specific **(c)** capacitances. **(d)** The electrochemical cyclic stability CV curves of the $ZnCo_2O_4$ microstrips electrode with various cycle numbers, and **(e)** the capacitive retention against a number of cycles.

Figure 3. (a). shows the charge/discharge profiles of the $ZnCo_2O_4$ microstrips electrode measured at 2, 5, 7 and 10 mA/cm^2 current densities. The charge/discharge time reduced with an increase in the current density. From the charge/discharge curves, the semi-symmetric nature of the $ZnCo_2O_4$ electrode reveals that typical pseudo capacitive behavior. The discharge capacitance under different current densities was calculated from equation (2). The discharge capacitance as a function of current density is plotted in figure 3(b). The maximum discharge capacitance is 423 F/g and the corresponding areal capacitance is 0.05 F/cm^2. The discharge capacitance of the $ZnCo_2O_4$ microstrips electrode decreased from 423 at 2 mA/cm^2 to 112 F/g at 10 mA/cm^2 current densities. It means that the capacitance of the $ZnCo_2O_4$ microstrips electrode as a function of current density. Further, using equation (2) the energy and power density were calculated. The Ragone plot as seen in figure 3(c), it suggests that the specific power density increases with decreasing energy density. The calculated maximum energy density of the $ZnCo_2O_4$ microstrips electrode is about 12.5 Wh/kg with the delivered power density of 3.6 kW/kg. The obtained values of energy and the power density of the $ZnCo_2O_4$ microstrips electrode are higher than $ZnFe_2O_4$/NRG composite [14]. It means that, the $ZnCo_2O_4$ store 6.7 Wh/kg energy density with delivering a power of 3000 W/kg.

The electrochemical surface interface behavior and ion diffusion rate of the $ZnCo_2O_4$ electrode were evaluated using impedance analysis. Figure 3(d and e) displays impedance measurement results of the $ZnCo_2O_4$ electrode (frequency range: 1 MHz to 0.1 Hz). The Nyquist plot, the real impedance against imaginary impedance of the $ZnCo_2O_4$ microstrips electrode as presented in figure 3(d**)**. Nyquist plot divided into two frequency regions. In the high-frequency region, a semicircle and a straight line occurred in the low-frequency region. The occurrence of a vertical line along with the imaginary axis indicates the ideal capacitive behaviour of the $ZnCo_2O_4$ electrode and the electrode material has a lower ion diffusion resistance [15]. The internal solution resistance (Rs) and charge-transfer resistance (Rct) values of the $ZnCo_2O_4$ electrode are found to be 1.9 Ω and 3.5Ω, respectively indicating that good charge transfer performance of electrode material. The frequency dependent phase angle plot as presented in figure. 3(e). It shows that the phase angle approaches -75 º at 79 Hz frequency. Furthermore, the Bode plot magnitude plot (figure. 3(e)) suggests that in the lower frequency region the $ZnCo_2O_4$ microstrips electrode shows an ideal capacitive behavior.

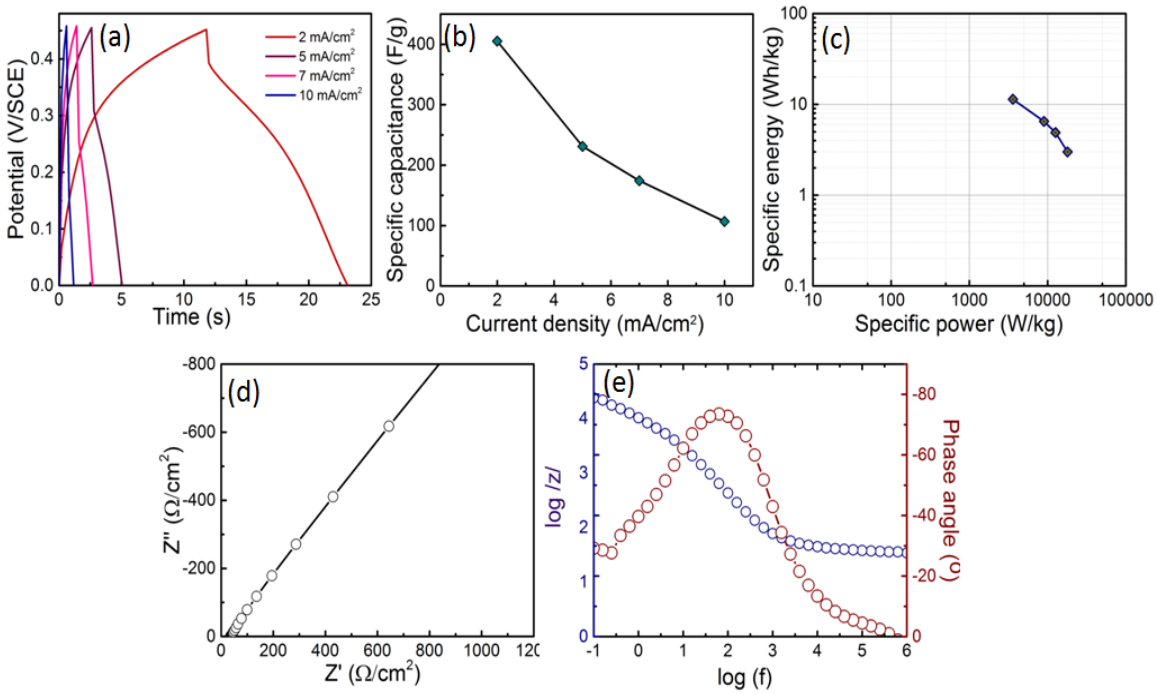

Figure 3(a-b). Charge/discharge profiles with various current and corresponding the specific capacitance of the $ZnCo_2O_4$ microstrips electrode. **(c)** Ragone plot of the $ZnCo_2O_4$ microstrips electrode at various current densities. Impedance analysis: **(d)** Nyquist plot and **(e)** Bode magnitude/ phase plots of the $ZnCo_2O_4$ microstrips electrode.

4. Conclusion

In conclusion, the $ZnCo_2O_4$ have been prepared *via* a hydrothermal method followed by calcination at 400 ℃. Further, structural and morphological studies systematically studied. The electrochemical study proved that $ZnCo_2O_4$ microstrips electrode has good rate capability with 1084 F/g specific capacitance and showed the superior capability of 96.2% capacitive retention in 1 M KOH aqueous electrolyte. These results indicate that the $ZnCo_2O_4$ microstrip architecture desirable for long term cyclic stability rate performance in the electrochemical application.

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