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Cost effective synthesis of spinel $NiCo_2O_4$ nanocrystal by sol-gel citrate method and its application for supercapacitor

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Abstract

In the present investigation, nanocrystalline spinel $NiCo_2O_4$ was synthesised by simple and cost effective sol-gel citrate method. Synthesized $NiCo_2O_4$ was characterized by using different characterization techniques. The electrochemical supercapacitive performance study shows that $NiCo_2O_4$ exhibits high specific capacitance of 342 Fg^{-1} in 1 M Na_2SO_4 electrolyte with good stability. The further EIS analysis implies low ESR value with excellent frequency response of nanocrystalline $NiCo_2O_4$.Thus present study successfully conveys the applicability of easy and cost effective sol- gel citrate method for synthesis of nanocrystalline $NiCo_2O_4$ to be utilised for supercapacitor.

Keywords: supercapacitor, specific surface area, impedance spectroscopy, specific capacitance

1. INTRODUCTION

Due to the concerns about the depletion of fossil fuel, global warming issues and increasing demand of energy, the development of alternate energy storage resources with high power and energy capacity is of particular interest [1,2]. Among the various energy storage resources, supercapacitor, have attracted immense attention because many attractive properties, such as high energy density, fast charging-discharging and long cycle life [1]. The electrode material is an important part of supercapacitor. At present, the use of nanomaterials as the electrode of supercapacitors has attracted

great interest since they have shown higher power, energy densities and specific surface area than the respective bulk material [3]. The conductivity of the material directly influences the charge stored on the electrodes [4]. The binary transition metal oxides have a much higher electrical conductivity as compared to single transition metal oxides. The binary metal oxides such as $NiCo_2O_4$, $MnCo_2O_4$, $ZnCo_2O_4$, $CuFe_2O_4$, $CoFe_2O_4$, $ZnMn_2O_4$ have been extensively studied for the electrode material in supercapacitor [5].Among the binary metal oxides, $NiCo_2O_4$ is considered as a very promising electrode material for supercapacitor because of its good electrical conductivity, low cost, non toxicity and great flexibility in the structures and morphology [6,7].

This letter is aimed at presenting a more systematic report on the applicability of easy and cost effective sol- gel citrate method for synthesis of nanocrystalline $NiCo_2O_4$ to be utilised for supercapacitor. The specific capacitance of the supercapacitor can be enhanced by increasing the surface area of synthesized material. There are different methods of synthesis of $NiCo_2O_4$ [8,9], out of these different methods of synthesis of nanocrystalline $NiCo_2O_4$, sol- gel citrate method is simple, cost effective and results in high surface area nanocrystals with desire morphology[10].

2. EXPERIMENTAL

Nanocrystalline $NiCo_2O_4$ was synthesised by using sol-gel citrate method. Nickel nitrate and cobalt nitrate were used as starting materials. A stoichiometric mixture of nitrates was mixed with citric acid and ethanol and stirred magnetically at 80^oC for 3 h to obtain a homogenous mixture. The solution was further heated at the pressure vessel at about 130^oC for 3h. The dried powder was then calcined at temperatures from 350^oC to 750^oC. Electrode was fabricated by dispersing the nanocrystalline powder of 95 weight % $NiCo_2O_4$ in dimethyl formamide as a solvent and 5 wt % Poly (Vinylidene fluoride) (PVDF) as binder, homogeneous gel formed deposited on stainless still as a substrate via bath deposition method. The electrochemical test of the sample was conducted using a three electrode system in 1 M Na_2So_4 using a CHI 604e electrochemical workstation. The stainless still supported composite was directly used as working electrode with platinum plate counter electrode and Ag/AgCl as a reference electrode.

3. RESULT AND DISCUSSION

Fig 1(a) shows XRD pattern of nanocrystalline $NiCo_2O_4$ synthesised by sol- gel citrate method. It is seen that XRD pattern exhibits major peaks reflecting along the (311), other peaks corresponding to (111), (220), (400), (401), (422), (511) and (440) planes observed with a lower intensity. The XRD pattern of nanocrystalline $NiCo_2O_4$

is in good agreement with that of the standard pattern for $NiCo_2O_4$ (JCPDF File 20-0781) [11].The result indicates that as prepared $NiCo_2O_4$ has spinel structure with polycrystalline in nature. The average crystalline size of $NiCo_2O_4$ is calculated by Deby-Scherrer formula [12] (1) and it is found to be 19 nm.

$$D = \frac{0.9\,\lambda}{\beta\,cos\theta} \tag{1}$$

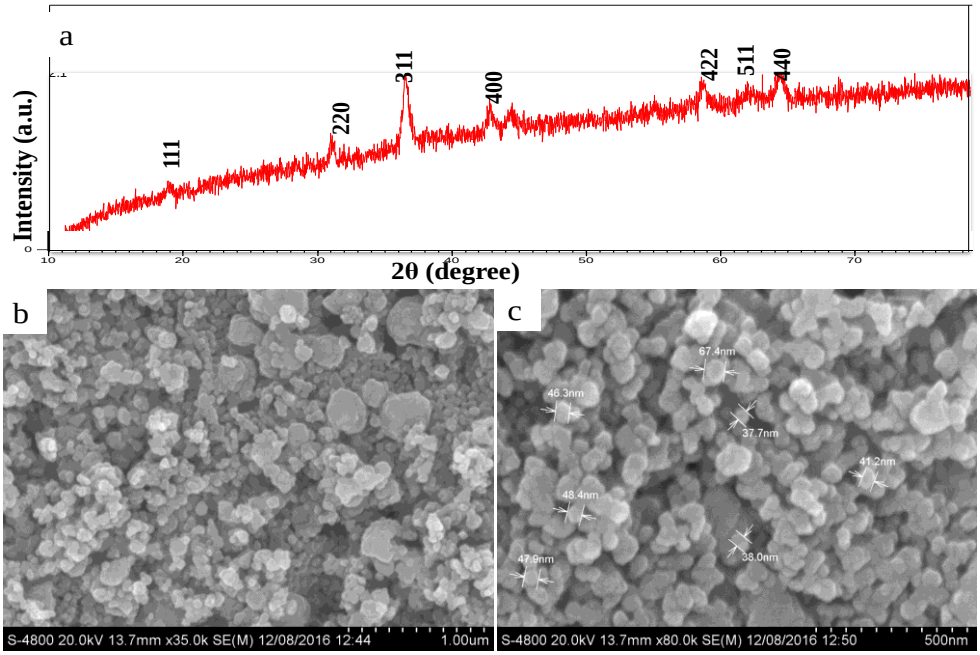

Fig.1. (a) XRD spectra, (b) and (c) FESEM micrograph

The morphology of $NiCo_2O_4$ is investigated by Field emission scanning electron microscopy (FE-SEM). Fig 1 (b) and (c) represent the FE-SEM micrographs of nanocryasalline $NiCo_2O_4$ at two different magnifications. From Fig 1 (b) and (c), it is seen that the random shaped aggregates and agglomeration clusters of $NiCo_2O_4$, the approximate size of which is about 38-68 nm. It is also seen that the size of nanocrystals are uniform, rough and porous with smaller particles suggesting high surface area.

The optical absorption spectrum in the range of 250-280 for $NiCo_2O_4$ is shown in Fig 2 (a). Inset of Fig 2 (a) shows the plot of photon energy (hυ) versus $(\alpha h\upsilon)^2$, which is linear at the absorption edge conforms the material has a direct band gap. The optical band gap value of nanocrystalline $NiCo_2O_4$ estimated from classical relation equation (2) and it is found out to be 4.9 eV.

$$\alpha = \frac{A(h\nu - E_g)}{h\nu} \tag{2}$$

Thermogravimetric and differential thermal analysis (TG-DTA) in the temperature range between room temperature and 700ºC were carried out on the nanocrystals of $NiCo_2O_4$ to investigate their thermal behaviour. The corresponding pattern is illustrated in Fig 2 (b). It is seen that, there is no much weight loss is observed with the increase in temperature. This is due to the material was calcined at 550ºC and the contained impurities like moisture, structural water, nitrate, CO_2 etc. was already decomposed. The total weight loss is found to be 1.6%. This study confirms that the $NiCo_2O_4$ is thermally stable at higher temperatures and can be applied as the electrode material for supercapacitor at variable temperature applications.

The specific surface area of nanocrystalline $NiCo_2O_4$ has been measured through employing Brunauer-Emmett-teller (BET) method. To study surface area and porosity of nanocrystalline $NiCo_2O_4$ the N_2 adsorption-desorption isotherm has been carried out. The corresponding pattern is illustrated in Fig 2 (c) and (d). Fig 2 (c) shows the isotherm with a distinct hysteresis loop in the range of 0 to 1 and at relative pressure P/P_o. The observed hysteresis loop shifts to higher relative pressure on approaching $P/P_o = 1$, that suggests the hierarchical mesoporous structure of $NiCo_2O_4$. The pore size distribution and pore volume of $NiCo_2O_4$ are estimated using the Barrett-Joyner-Halenda (BJH) method. Fig 2 (d) shows the pore size distribution of $NiCo_2O_4$ at the amount of nitrogen absorbed at P/P_o =0.98595. BET surface area of the $NiCo_2O_4$ is 22.011 m^2/g and a corresponding pore volume is 0.0303 cm^3/g. These results are in good agreement with the literature

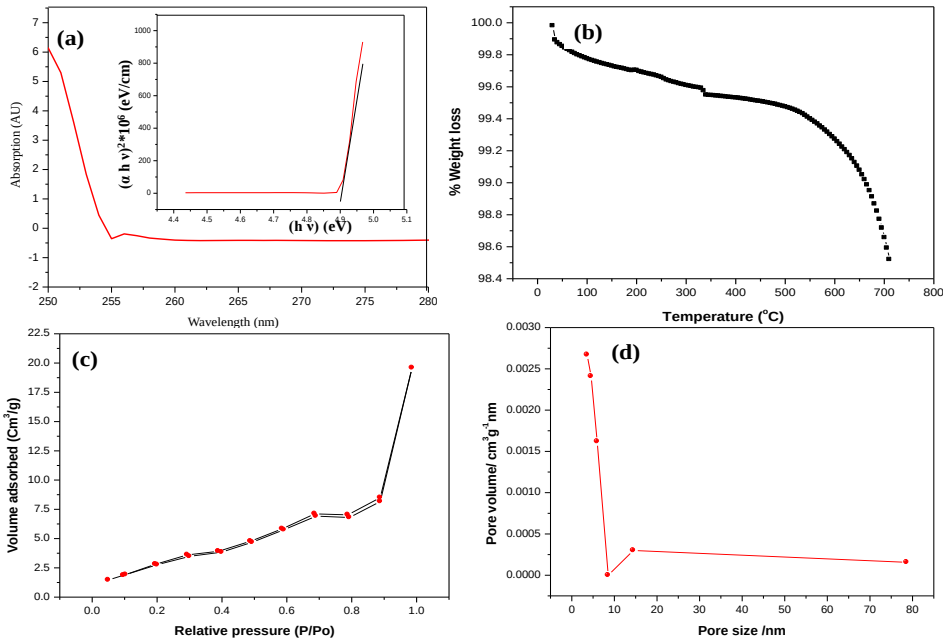

Fig 2 (a) UV- Visible spectra, inset shows the variation of photon energy (hυ) vr $(\alpha h\upsilon)^2$, (b) Thermal analysis (c), N_2 adsorption desorption isotherm and (d) pore size distribution

To estimate the electrochemical behaviour of nanocrystalline $NiCo_2O_4$, Fig 3 (a) gives the cyclic voltrammetric curves for nanocrystalline $NiCo_2O_4$ electrodes in the potential of -0.3 to 0.6V at scan rates 1, 10 and 100 mVs^{-1}in 1M Na_2SO_4 electrolyte. Compared with the curves at different scan rates, all curves shows the pair of oxidation and reduction peaks, which indicates that the current potential response was potential dependant and pseudocapacitance mainly derived from redox reaction of nanocrystalline $NiCo_2O_4$ electrodes. It was found that the current responses as a function of scan rates and the slowly increased with the increase scan rate. This shows that the volatmmetric currents are directly proportional to scan rates of CV. This indicates an ideally capacitive behaviour [13].

The $NiCo_2O_4$ electrode exhibits specific capacitance of 342 Fg^{-1} 248 Fg^{-1} and 13. 3 Fg^{-1} at 1 mVs^{-1} 10 mVs^{-1} and 100 mVs^{-1} scan rates respectively. The maximum specific capacitance and energy density was calculated to be 342 Fg^{-1} and 12.35 W h Kg^{-1} at scan rate 1mVs^{-1}. Fig 3(b) represents the variation of scan rate with the specific capacitance. As the scan rate increases, the specific capacitance decrease, which is distinctive for electrochemically active $NiCo_2O_4$. As shown in fig 3 (b) the specific capacitance decreases from 342 Fg^{-1} to 13.3 Fg^{-1}. Such behaviour of supercapacitor is due to diffusion effects of protons within the electrodes and presence of inner active sites that cannot sustain the redox transition completely at higher scan rates[14].

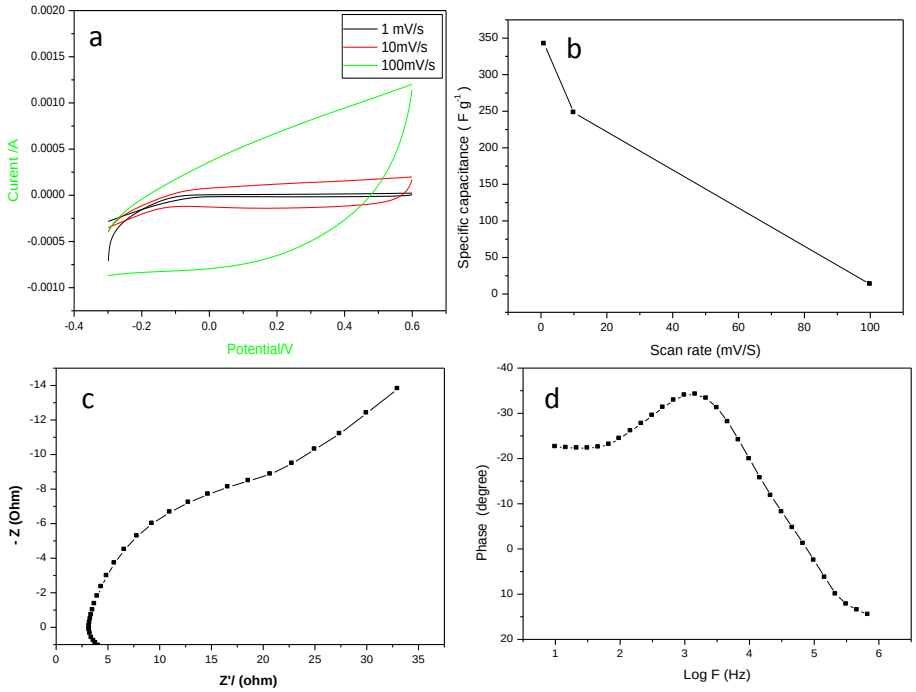

Fig 3 (a) cyclic voltrammogram curve, (b) effect of scan rates on specific capacitance (c) Nyquist plot and (d) Bode plot

Impedance spectroscopic analysis of material was carried out in the frequency range 1Hz to 1MHz. Fig.3 (c) and (d) shows the Nyquist plot (real part vs. imaginary part of impedance) and Bode plots (frequency vs. phase angle) of nanocrystalline $NiCo_2O_4$ respectively. The intercept of the Nyquist plots to the real axis represents equivalent series resistance (R_s) which involves the electrolyte resistance, the intrinsic resistance of the electrode material and the contact resistance of active material to the current collector. The semicircle in the high frequency region gives the charge transfer resistance (R_{ct}), it is related to the internal resistance of the electrode and the double layer capacitance (C_{dl}). The charge transfer resistance (R_{ct}) was calculated by measuring the diameter of the semicircle. [15]. From fig 3 (c) equivalent series resistance (R_s) and charge transfer resistance (R_{ct}) of $NiCo_2O_4$ supercapacitor were found to be 4.7Ω and 15.2Ω respectively. The response-time data are calculated from Bode plot *(frequency Vs Phase).* Fig.3 (d) shows the Bode plot for electrode. These data follow the same trend as internal- resistance values. The ion-diffusion pathway through the layer of porous matrix is responsible for shorter response time [16]. The response time of $NiCo_2O_4$ is found to be less at a constant phase angle.

4. CONCLUSION

In summary, we have successfully synthesised nanocrystalline $NiCo_2O_4$ by cost effective sol-gel citrate method. BET surface area and corresponding pore volume of $NiCo_2O_4$ were found to be 22.011 m^2/g and 0.0303 cm^3/g respectively. The highest specific capacitance and energy density at scan rate 1 mVs^{-1} were achieved to be 342 Fg^{-1} and 12.35 W h Kg^{-1} respectively. ESI study shows the low values of equivalent series resistance and charge transfer resistance are favourable for an increase in the value specific capacitance of $NiCo_2O_4$. Thus the results suggest that the sol-gel citrate method can serve as promising synthesis method for preparation of $NiCo_2O_4$ for high performance supercapacitor.

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