Gel Combustion Synthesis and Characterization of ZnO/NiO Nanocomposite for Supercapacitor Application

R. Packiaraj, K.S. Venkatesh, P. Devendran, S. Asath Bahadur, N. Nallamuthu

Abstract**: *Energy demand is a major concern around the globe of the world. Electrochemical supercapacitors are one among various alternative and green energy devices. The performances of supercapacitors depend mainly on the enhanced properties of electrode materials. In the present work, ZnO/NiO nanocomposite (NCs) was synthesized by a simple and facile citrate-based gel combustion procedure. The crystal structure and phase identification, surface morphology and functional groups of the samples were analyzed by X-ray diffraction (XRD) pattern, scanning electron microscope (SEM) and Fourier-transform infrared spectroscopy (FTIR), respectively. X-ray Diffraction pattern is observed that the crystalline peaks are broader and confirmed nanoparticles. The mean size of the particle is found to be ~25 nm. The prepared sample is analyzed an electrochemical studies such as cyclic Voltammetry, charge discharge and electrochemical impedance spectrum, respectively. The maximum specific capacitance (Scp) is 450 Fg-1 at 0.5 mA/cm2.***

Keywords**: *ZnO/NiO, gel combustion method, supercapacitors, XRD, FTIR, SEM.***

I. INTRODUCTION

In recent decades supercapacitors based devices have paid must attention in energy storage applications. The supercapacitors used in rapid charge-discharge rate, large operation temperature range and more cycle stability as compared with secondary battery [1-3]. Low Scp and low energy density degrades such potential applications of supercapacitors in energy storage area. In the search of new electrode materials, lot of researches has been implemented to overcome the drawbacks. Recently, transition metal oxides are widely used in electrode material for supercapacitors. In supercapacitors, the transition metal oxides attribute fast faradaic redox reactions [4-6]. Supercapacitors are describe as two kinds of effect such as pseudo capacitor and electric double layer capacitor. Based on the electrochemical reactions supercapacitors are divided into two types one is electrical double layer capacitor (EDLC) and another one is pseudocapacitor (PSc). Compared with EDLC, the transition metal oxides based PSc has better Scp and elevated energy density [7, 8]. There are many reports are available for binary metal oxides based supercapacitors due to their wealthier redox reactions and synergistic effects with different metal ions.

The pure NiO NPs possesses an excellent electrochemical properties which are including its remarkable theoretical supercapacitance value (2584 Fg^{-1}), inexpensiveness and good chemical stability [9-11]. However, the low surface area of a electrode material leads to less capacitance value than the theoretical one. Preparing of nanomaterials ought to be advanced in light of the fact that it will positively affect the materials electrochemical property [12]. By comprises the different kind of nanocrystalline transition metal oxides, improving of capacitance can be achieved through these structure of nanocomposite based electrode. Zinc oxide (ZnO), a significant semiconductor material is mostly preferred due its particular highlights. In addition, ZnO utilizing as a terminal substance, has evident focal points for supercapacitors. These properties incorporate high electron versatility, electrochemical stability, capacity and lower expensive [13- 15]. Encouragingly, a nanocomposite electrode which means by combined NiO and ZnO, has incredible value of voltage. Because of modification by ZnO, the capacitance value is also enhanced in the nanocomposite. Effective synthesis of nanocomposite is also one of the reason for the improvement. Hence, in this approach, the nanocomposite of transition metal oxides are developed as electrode materials for electrochemical storage device applications. [16, 17].

In the present work deals, the ZnO/NiO nanocomposite (NCs) was prepared by a Gel-combustion method with subsequent calcination. The structural, spectroscopic, surface morphological and electrochemical properties are examined through XRD, FTIR, SEM and cyclic voltametry and discharge with charge analysis, respectively.

II. EXPERIMENTAL SECTION

A. Experimental methods and characterization techniques

Citrate-based gel combustion method is adopted to obtain ZnO/NiO NCs. Analytical grade of zinc nitrate, nickel nitrate are

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acting as starting materials and citric acid is used as a chelating agent in gel combustion method. Appropriate amount of zinc nitrate, nickel nitrate and citric acid (2:6 molar ratio) are dissolved in double distilled (DD) water in separate beakers. Initially zinc nitrate and nickel nitrate precursors are dissolved in DD water. The citric acid solution was poured into above solution drop-wise at 80 ^oC. Later, the temperature of the above mixture was increased to 130 ^oC. Then, solution was kept overnight to convert into gel and dried gel was formed. The dried gel is calcined at 500 ^oC for 3 hrs. The entire reaction has shown in scheme.1.The samples are well characterized using XRD, FTIR and SEM analysis.

Scheme.1. Preparation of ZnO/NiO NCs

III. RESULTS AND DISCUSSION

A. Powder X-Ray Diffraction Analysis

X – Ray diffractogram for ZnO/NiO NCs is displayed in Fig. 1. In the crystal structure, ZnO and NiO are hexagonal and cubic geometry, respectively. Fig.1 diffractogram of the calcinated sample, characteristic diffraction peaks could shows X – Ray every part of the be matched to hexagonal ZnO (JCPDS No. 361451) and cubic NiO (JCPDS No. 897130) [18]. No diffraction peaks belonging to impurities could be found, indicating that the precursor was completely transformed into ZnO/NiO mixed metal oxides. The size of the crystallite is estimated by Scherrer's equation. The estimated average crystallite size is obtained about ~25 nm.

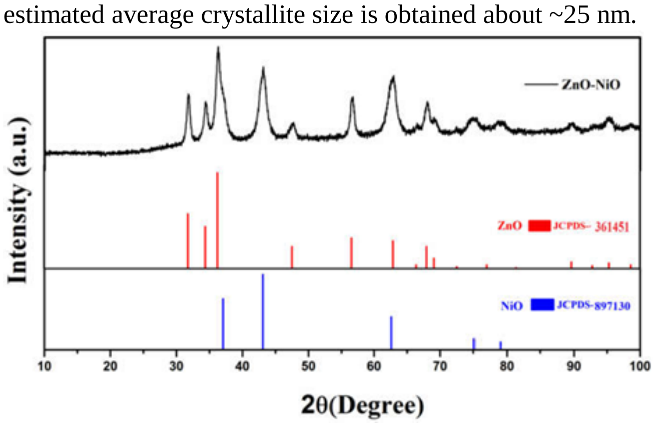

Fig. 1.XRD pattern of ZnO/NiO NCs

B. FTIR

The Fig.2, described FTIR spectra of ZnO/NiO nanocomposites, heated for 3h at 500 ^oC. Four new IR bands are found to be observed at 1602, 1478, 1100 and 417 cm-1[19]. A broad band around 3346 cm^{-1} attributes the stretching mode of OH group which is contributed by adsorbed water molecules. The peak around 2367 cm^{-1} was observed indicating CO2 group. Band formed at 1602 cm^{-1} can be contributed due to OH group in the sample. IR peak at 1478 cm^{-1} is obtained corresponds to C=O bond in asymmetric stretching mode and at 1100 cm^{-1} are obtained

due to C-O bonding. IR band at 417 cm^{-1} is observed indexing the confirmation of the occurrence of crystalline Ni–O bond formation [20].

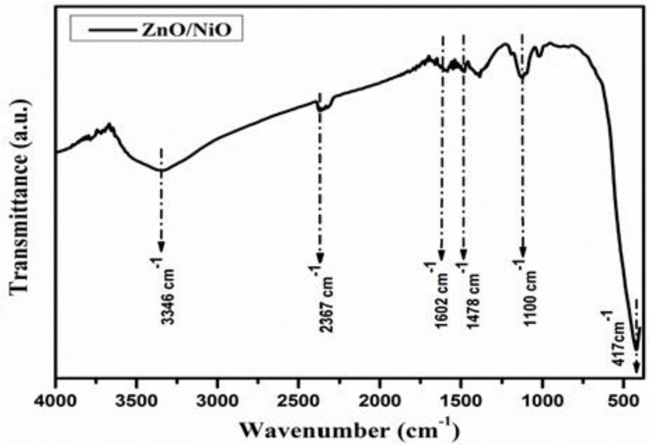

Fig. 2.FTIR spectrum of ZnO/NiO NCs

C. SEM

The morphological analysis of the ZnO/NiO composite is examined using SEM. The different magnification of SEM images of the ZnO/NiO composite is presented as shown in Fig. 3. (a and b). It is illustrated that the sample is composed nano spheres like agglomerated particles. The average size of the particles is measured as ~61 nm.

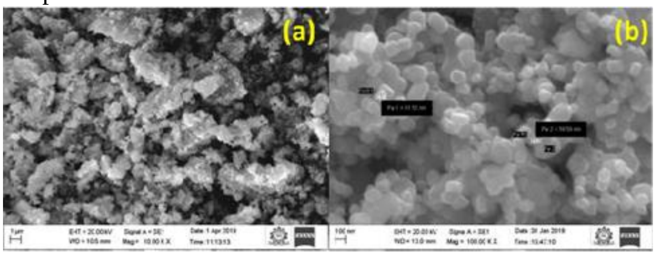

Fig. 3.(a, b) SEM images of ZnO/NiO NCs

D. Electrochemical characterizations

The microstructural analysis and ion transport behavior of the ZnO/NiO nanospheres is analyzed through cyclic voltammeteric studies. It is investigated by GCD, CV and EIS with KOH solution of electrolyte in three-electrode cell setup. The curves described in Cyclic voltammetry at the range of scan rates between 5mVs^{-1} and 100 mVs^{-1} which characteristically pseudocapacitive behaviour in the way of delineating redox peaks. It is ascribed in Fig. 4a. Because of the scan rate increments to the higher rates, cathodic curve drop down towards lower potential whereas the anodic peak shifts towards higher voltage

proposing a superior electrochemical reversibility [21, 22]. The determined Csp values are 111, 124, 136, 166, 146 and 198 F g^{-1} for 100, 50, 25, 10 and 5 mV s^{-1} respectively. In Fig. 4. b., the GCD plot of the material demonstrates the curves applied in the range of 4 to 0.5 mA/cm^2 current densities. The GCD graphs are profoundly

regular in nature proposing the great capacitive profile. The deliberate Scp esteems from the

GCD curves are 450, 390, 312, 270 and 174 F g^{-1} for current densities 0.5, 1, 2, 3 and 4 mA/cm^2, individually. By the electrochemical investigation, the outcome is presumed that the expansion of current densities and scan rate diminish the execution of capacitance effect in nanocomposite materials. At the intension of lower current densities, the ionic charge carriers has efficient time to diffuse the layer in the interfacial region of electrode and electrolyte which provide the illustration of high capacitance value. Then again, at high current density the flow of ions is very quick and the accumulation of ions is very minimum on the surface of the working electrode henceforth the S_{cp} value reduces [23].

The EIS study of the ZnO/NiO nanospheres (Fig.4.4d) shows a semi-circle at the high frequencies with inclined spike with Y-axis obtained at lower frequencies, displaying great electrochemical behavior in modified working electrode. The appearance of small semi-circle indicates the miniature of charge transfer resistance which is remarkable for quick ion charge exchange and prompted predominant [22, 24]. The retentively of S_{cp} study for different cyclic performance is also much interesting property to analyze the cycle time of working electrode.

From fig.4.c displays cyclic durability for ZnO/NiO NCs were analyzed for 5000 cycles with applied current density of 3mA/cm2. After 5000 cycles, the retention of the ZnO/NiO NCs is about 74.7 % was observed. In the present study the retention graph reveals the long life of the ZnO/NiO NCs.

The electrochemical reaction mechanism of the prepared ZnO/NiO nanospheres as follows [24]

$ZnO + OH^- \leftrightarrow ZnOOH + e^-$ (1)

$NiO + OH^- \leftrightarrow NiOOH + e^-$ (2)

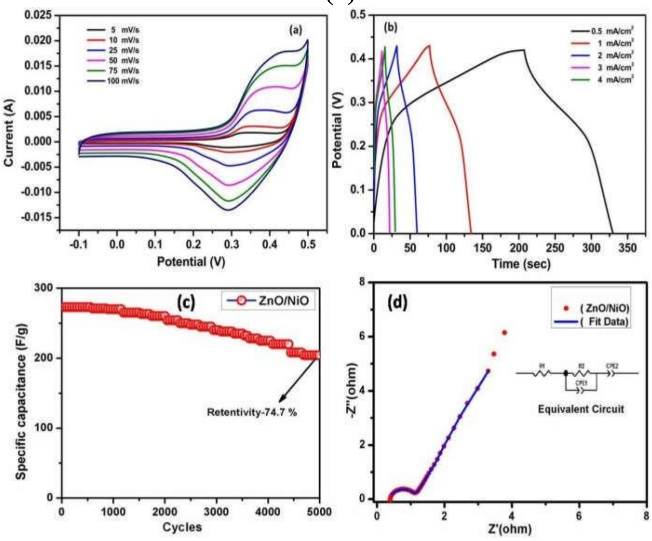

Fig. 4.(a) Cyclic Voltammetry curve (b) Charge discharge curve (c) Cyclic stability graph (d) Electrochemical impedance spectrum of ZnO/NiO NCs

IV. CONCLUSION

ZnO/NiO nanocomposite has been successfully synthesized by Gel-combustion process. The XRD revealed the mixed phases of ZnO/NiO nanocomposite. In the crystal structure, ZnO and NiO are hexagonal and cubic geometry, respectively. No diffraction peaks belonging to impurities could be found, indicating that the precursor was completely transformed into ZnO/NiO mixed metal oxides. The FTIR spectrum confirmed the formation pure metal oxides ZnO/NiO. The SEM study divulged sphere like particles. By the electrochemical study, the S_{cp} value of 198 F g^{-1} at a scan rate of $5mVs^{-1}$. From charge discharge graph the calculated the maximum S_{cp} value is 450 F g^{-1} at 0.5 mA/cm^2.

The ZnO/NiO composite modified electrode has higher S_{cp} and also exhibited an excellent cyclic stability performance of 74.7 % retained up to 5000 cycles. The result obtained from these electrochemical performances suggests that the pristine ZnO/NiO nanosphere is considered as active- material for applications of electrochemical storage devices.

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