EFFECT OF ELECTROLYTE CONCENTRATION ON SUPERCAPACITOR PERFORMANCE OF GRAPHENE-NIO COMPOSITE

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ABSTRACT

Graphene-NiOcomposite was synthesized employing hydrothermal method. The composite was characterized using X-ray diffraction, Field emission scanning electron microscopy, thermo-gravimetric analysis, N_2 adsorption-desorption measurement and Raman spectroscopy. The capacitive performance of the composite as electrode material in aqueous KOH electrolyte of various different concentration (1,5 and 6M) was systematically studied using cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge-discharge techniques. The results reveal that the composite electrode achieves its highest capacitance in 5M KOH. This has potential applications in further research.

Keywords : Capacitance, Electrolyte, Graphene, Nickel oxide, Supercapacitor.

I INTRODUCTION

The problem of ever-increasing environmental pollution and growth in demand of fossil fuels has motivated people to search for alternative sources of energy. Supercapacitors offer a possibilty. They have high specific capacitance [1], long cyclic life[2] and low maintenance cost.They may be profitably used for energy storage.Supercapacitors, also known as electrochemical capacitors are classified on the basis of their charge storage mechanism into two categories. They are electric-double layer capacitors (EDLCs) and pseudocapacitors. In EDLCs, energy is stored through charge accumulation at the electrode-electrolyte interface. This results in high power density and large cyclic life, howeverthe magnitude of capacitance is limited. Pseudocapacitors, on the other hand, are dominated by reversible and fast- faradaic reaction on the surface of electrode materials. Hence compared with EDLCs, pseudocapacitors exhibit better specific capacitance and energy densities. In EDLCs, carbon and its allotropes are used as active electrodematerials, while inpseudocapacitorsone makes use of metal oxides and conducting polymers as active electrode materials.

To integrate the advantages of EDLCs and pseudocapacitors, composites of carbon materials (such as CNT, graphene), and metal oxides (such as RuO_2, MnO_2, CuO) have been investigated as possible electrode materials. Among various metal oxides, NiO has drawn considerable attention of researchers due to its low cost. Graphene, on

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the other hand, due to its high surface area has been the prefferedchoice material for EDLCs. Different routes such as chemical vapour deposition[3],hydrothermal precipitation [4], microwave assisted synthesis[5], electrochemical deposition[6] have been used for fabrication of graphene metal-oxide composite electrode. However, in the present work we have used hydrothermal method to synthesize Graphene-NiOcomposite (GNC).

II EXPERIMENTAL

2.1 Materials

All chemicals were of analytical grade and used as received, without further purification. All aqueous solution were prepared in DI water.

2.2 Synthesis of Graphene

Graphene oxide (GO) was synthesized according to modified Hummers method [7]. Later, GO was thermally exfoliated according to previously reported method [8].

2.3 Synthesis of Graphene-NiO composite

Initially, 0.03 M nickel nitrate ($Ni(NO_3)_2.6H_2O$) solution in 50 mlof isopropylalcohol: DI water (1:1 v/v) was prepared. Graphene (50 mg) was added to above solution, and ultrasonication was done for 1 h. To this suspension, 1 ml of ammonia solution ($NH_3.H_2O$, 25 wt %) was added and stirred for 2 h. Themixed suspension was then sealed in a 50 mL Teflon-lined stainlesssteel autoclave (for hydrothermal reaction) at 170 °C for 18 h. The product was collected after filtering, and dried at 80 °C in oven. Finally, the samples were calcined at 350 °C for 3h under N_2 atmosphere to obtain the Graphene-NiO composite.

2.4 Material characterization

The surface morphology of the synthesized product (GNC) was determined by field-emission scanning electron microscopy (FESEM. MIRA3 TESCAN). Phase structure of composite wascharacterized by X-ray diffraction (XRD, Bruker). Raman spectra were recorded at room temperature on Raman spectrometer (Horiba Scientific). Thermal stability was studied using thermo-gravimetric analyzer (TGA, Perkin Elmer). N_2 adsorption/desorption isotherms were determined by Surface Analyzer (Micrometrics, Gemini V).

2.5 Electrochemical characterization

The electrochemical properties of composite were studied in two-electrode assembly using Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) and Galvanostatic Charge-discharge (GCD) techniques. Working electrodes were prepared by mixing composite with acetylene black and PVdF-HFP in a wt. ratio of

80:10:10.The mixture was dispersed in acetone to form a slurry and coated on graphite sheets (~1cm^2). The fabricated electrodes were then dried in vacuum oven at 80 °C for 24 h. Electrolyte used for measurement was 1, 5 and 6 M KOH aqueous solution. CV and EIS analysis were carried out with a CHI660D electrochemical workstation, and charge-discharge tests were done on Arbin instruments.

III RESULTS AND DISCUSSION

3.1 Physiochemical Characterization

Fig. 1 (A-B) shows FESEM image of GNC at different magnification. It is evident that Graphene sheets are uniformly covered with NiO particles. Graphene sheet coated with NiO particles overlap each other to form a three-dimensional network structure. This increases the effective liquid-solid interfacial area, and provides a fast path for insertion and extraction of electrolyte ions, resulting in increase of faradaic reactions.
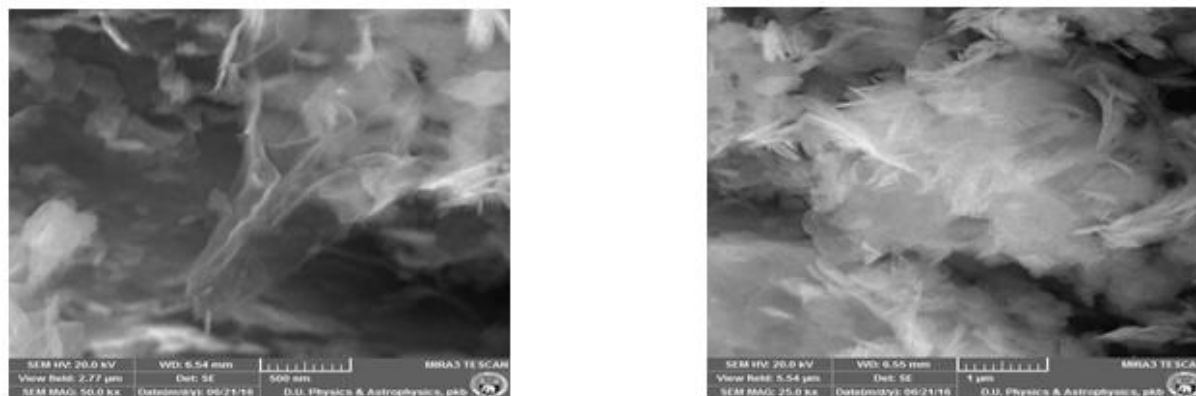
Figures

Figure 1(A-B) FESEM images of Graphene-NiO composite at different magnification.

Fig. 2 (A) shows XRD pattern of synthesized composite. Diffraction peaks at 2θ = 24.1, 37.1, 43.1, 62.4° are observed. These peaks can be attributed to <002>, <111>, <200>, <200> crystal planes respectively. Peak at 37.1, 43.1 and 62.4° are due to NiO nanoparticles while peak at 24.1° corresponds to carbon peak. Fig. 2 (B) displays Raman spectra for synthesized product. Three peaks positioned at about 483.1, 1354.9 and 1590.9 cm^{-1}are detected. Raman peaks at 1590.9 and 1354.9 corresponds to G and D band lines. G band line is allotted to E$_{2g}$phonon of carbon sp^2 atoms while D band line is living mode of k-point phase of A$_{1g}$ symmetry [9]. Additional peak at ~483.1 cm^{-1} is observed due to NiO nanoparticles. Fig. 2 (C) shows TGA curve of GNC. As temperature is increased from room temperature to 150 °C, the composite shows a slow mass loss. This is probably due to removal of physisorbed

water molecules. A large mass loss is observed between 525 and 725 °C, which can be attributed to the removal of graphene from the composite.After 725 °C, no sharp decrease in mass is observed indicating thatgraphene has been removed from composite. The nitrogen adsorption/desorption isotherm of the synthesized composite has been shown in Fig. 2 (D). According to International Union of Pure and Applied Chemistry (IUPAC) classification, isotherm displayed by GNC is a type IV isotherm [10]. In medium relative pressure region, the adsorbed N_2 increases steadily with the increase in relative pressure. This is probably due to capillary condensation and multilayer absorption in mesopores. However, in high pressure region, a sudden climb is observed indicating absorption in the void among nanoflakes. This type of isotherm reveals the existence of imperfect and complex cylindrical channel of uniform size. The BET surface area and average pore size observed are 143.14 m^2/g and 56.65 nm respectively, indicating mesoporous structure in product.
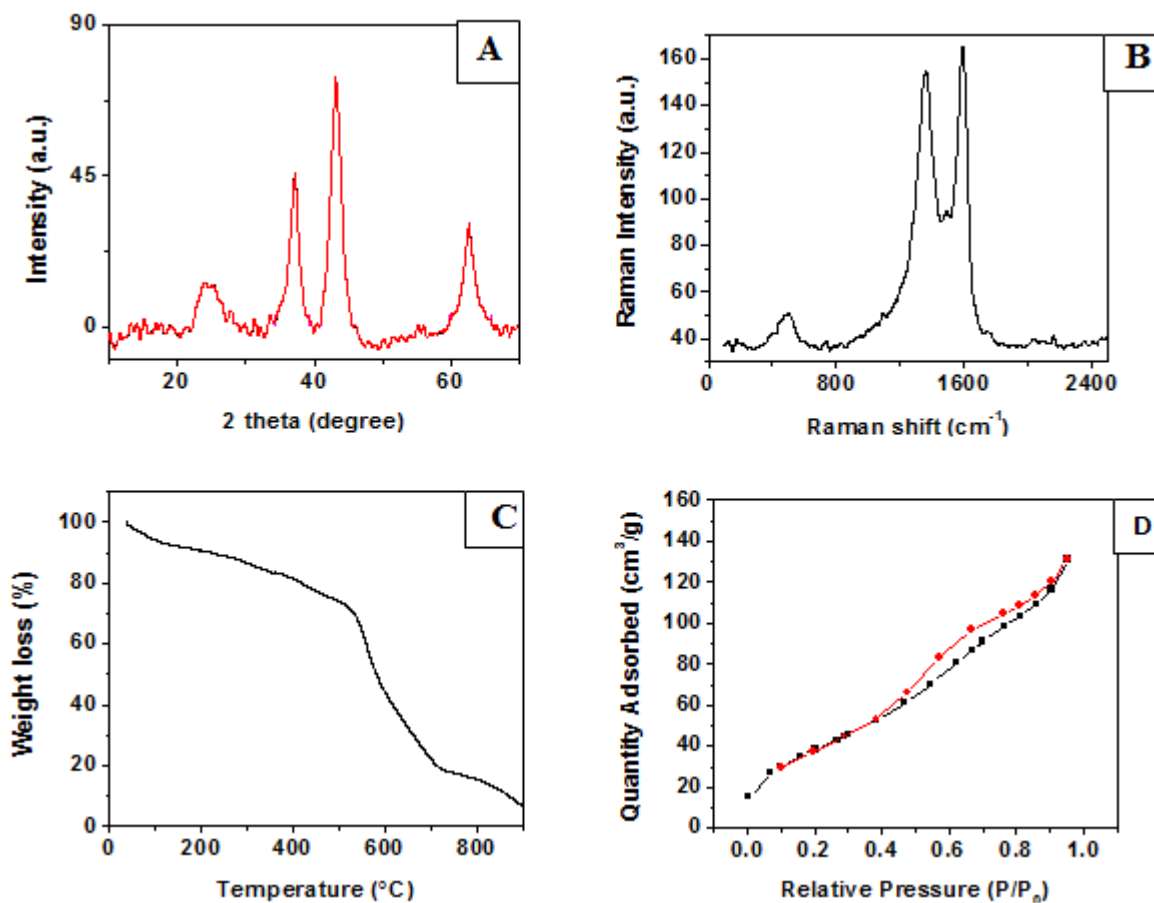

Figure 2. (A) XRD, (B) Raman, (C) TGA and (D) N_2 Adsorption-desorption spectra of Graphene-NiO composite.

3.2 Electrochemical Characterization

To evaluate the effect of KOH concentration on capacitive performanceof GNC electrode, CV and EIS studies were done. Fig. 3 (A) shows CV curves at scan rate of 10 mV/s in various concentration of KOH. No notable change is observed in rectangular shape for three values of concentration. However, the magnitude of capacitance calculated in case of 5 M KOH is 60.87 F/g, which is greater than the respective values of 44.09 and 52.42 F/g, obtained for 1 M and 6 M KOH. EIS spectra for GNC electrode in different KOH concentration has been displayed in Fig. 3 (B). As seen from figure, value of Z" observed for 5 M KOH is less than the values for other two concentrations. This indicates agreement with the above CV results.

Fig. 3 (C-D) shows the galvanostatic charge/discharge curve of GNC electrode in 5 M KOH at different values of amplitude and current density. It was found that charge/discharge profiles are mostlylinear and symmetrical. Specific capacitance with a value of 84.32 F/g, at amplitude 1.2 V and current density 1 mA/cm^2 was observed. Power and energy density were also calculated. The respective values found are 8.65 kW/kg and 4.216Wh/kg.
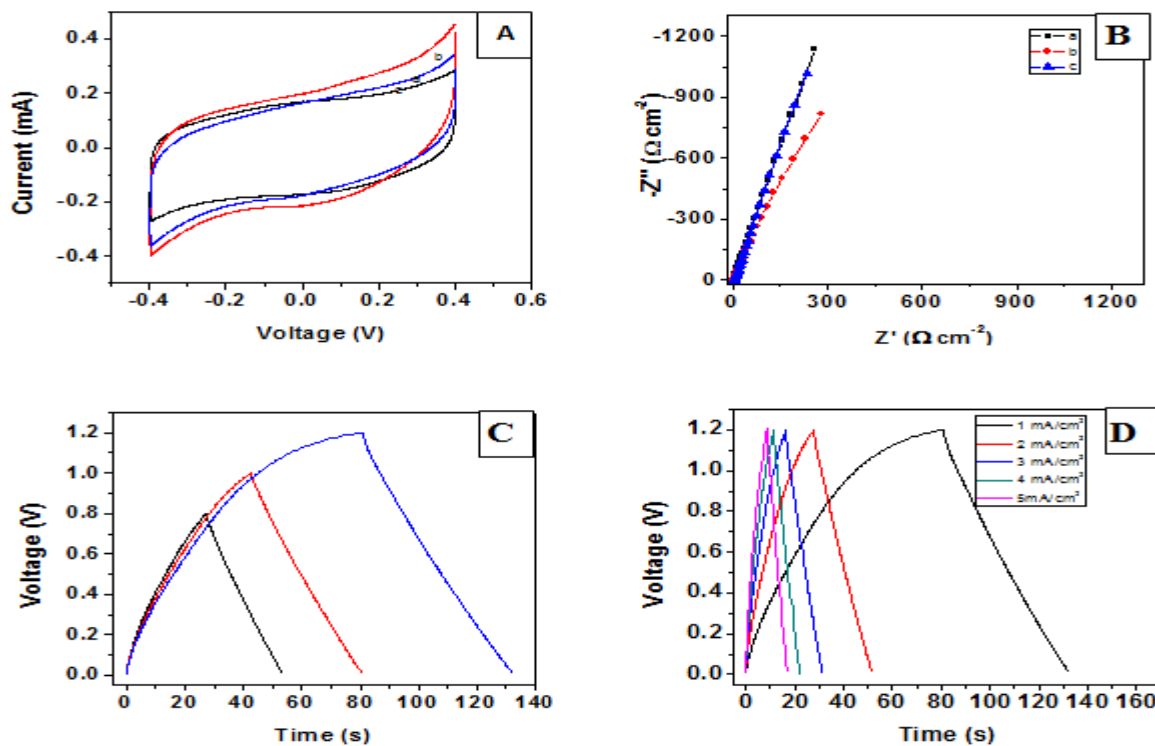

Figure 3. (A) Cyclic Voltammograms at scan rate of 10 mV s^{-1} and (B) EIS plot of Graphene-NiO composite electrode in different concentration of KOH (a 1 M, b 5 M, c 6 M). Galvanostatic charge-discharge curves of Graphene-NiO composite electrode at (C) different amplitude and (D) different current density.

IV CONCLUSIONS

In present investigation, Graphene-NiO composite employing hydrothermal method, has been successfully prepared and characterized. Physiochemical studies show that the product synthesized is indeed Graphene-NiO composite (GNC). Electrochemical tests implythat GNC electrode exhibits higher capacitance in 5 M KOH as compared to 1 and 6 M KOH solution. High values of power and energy density were observed for GNC electrode. All these characteristics of the prepared composite, demonstrate its potential application to design low-cost, high-performance supercapacitor.

V ACKNOWLEDGEMENT

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