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Full Length Article

Fabrication of one dimensional graphene nanoscrolls for high performance supercapacitor application

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ABSTRACT

One-dimensional (1D) Graphene Nanoscrolls (GNS) is a new topology of carbon-based materials. This structure attracted more researchers towards a new class of energy storage materials due to its unique 1D tubular morphology. Here, the 1D GNS was synthesized by rapid quenching of aqueous suspension of chemically reduced graphene using liquid nitrogen. The electrochemical performances were investigated using cyclic voltammetry, galvanostatic charge/storage and electrochemical impedance spectroscopy techniques. The specific capacitance of 309.8 F/g for GNS was obtained at the constant current density 0.5 A/g. The maximum energy and power densities achieved for GNS are 27.5 Wh/kg and 10800 W/kg, respectively with excellent cyclic stability. These results indicated that GNS with unique morphology could be used in future as a new electrode material for energy storage devices.

1. Introduction

Supercapacitors are the new class of charge storage devices which bridge the gap between high energy battery systems and high power dielectric capacitors. Due to fast charge transport mechanism of supercapacitors, it becomes an essential element where the large amount of energy needed to be released very quickly such as in high power supplies, portable electronics and hybrid electric vehicles [1,2]. Supercapacitors stores charges based on two mechanisms; electrochemical double layer capacitors (EDLC) and pseudocapacitors [3,4]. EDLC stores charge owing to double layer electrostatic interaction between charged electrode and electrolyte ions. On the other hand, pseudocapacitors store energy through fast surface oxidation-reduction reactions of the electrode material with the electrolyte. Although, pseudocapacitors using metal oxides or conducting polymers as electrode materials could deliver a high faradaic capacitive performance, but cannot maintain it after long cycling. In most commercially available supercapacitors are made of inexpensive and corrosion-resistant carbon-based electrode materials. The capacitive performance of this type of charge storage device is mainly dependent on the specific surface area (SSA) and electrical conductivity of electrode materials along with the accessibility of pores to the electrolyte ions. Over the past years, a lot of research focused on porous carbons such as activated carbons (ACs) as an electrode material [5–8]. This traditional material offered high SSA, good electrical conductivity, excellent power density, cyclic stability, low cost and easily available but failed in charge storage capacity.

Carbon nanotubes (CNTs), the other form of carbon material have been synthesized with high electrical conductivity and SSA and used as electrode material for supercapacitors [9,10]. But their capacitance performance has not reached the expected standard. It is worthy to note that the closed architecture of CNTs results in a long path of ion diffusion and the observed high contact resistance between the electrode and current collectors. Later, Graphene sheets, a monolayer of 2D carbon network have been used as electrode material in supercapacitors due to its unique physical and chemical properties [11–13]. However, agglomeration property of graphene sheets kept away its expectation becoming commercialized [14].

Recently, graphene Nanoscrolls (GNS) formed by rolling of graphene sheets have been shown to make new topological structures with unique 1D tubular morphology with open ends. This topology of GNS has the characteristics of scrolled conformation, open ends/edges, porous structure and adjustable interlayer spacing along with the excellent properties of graphene sheets. Therefore, GNS is becoming an interesting carbon conformation, distinct from graphene sheets and CNTs. Some experimental methods have been reported on the synthesis and characterization of GNS in detail [15,16]. Very few reports exhibited the usage of GNS as an electrode material for supercapacitor application. Yafei Kuang and his group designed the scrolled graphene using microexplosion

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and obtained the specific capacitance of 224 F/g at the current density of 1 A/g for supercapacitor application [17]. Recently, Arthur J. Epstein et al. reported the graphene nanoscrolls (GNS) by shock cooling of GO dispersion using liquid nitrogen and reduced it by sodium nitrate to remove the functional groups. The specific capacitance of 156 F/g at 1 A/g had achieved with capacitance retention up to 2000 charge/discharge cycles [18]. Gao et al. reported the mass production of GNS using the similar method and achieved the high reduction degree of GNS [19]. This involves two steps reduction processes ie., before and after the nanocrolls formation. Also, they used giant graphene oxide sheets (GGO) to make the nanoscrolls. GNS prepared shows specific capacitance about 90–100 F/g at 1 A/g. The capacitance value obtained till now using GNS is not upto the mark for its application in energy storage devices.

In this work, we reported the formation of the tubular morphology of 1D GNS and its applicability as an electrode material for supercapacitor application. First, GO was synthesized by simplified Hummers method and reduced by the chemical technique using hydrazine hydrate and named as chemically reduced graphene (CRG). Later, CRG suspension sprayed into liquid nitrogen bath for rapid quenching process to form GNS. The as-prepared GNS used as an electrode material and studied the electrochemical performances in 1 M H_2SO_4 electrolyte.

2. Experimental details

2.1. Preparation of graphene oxide (GO)

GO was synthesized using simplified Hummers method in ambient conditions [20]. In a typical synthesis, the oxidation of graphite was carried out by mixing 49.2 ml of H_2SO_4, 5.3 ml of H_3PO_4, 1 g of graphite flakes and 5 g of $KMnO_4$ using magnetic stirrer. After adding all the materials slowly, the mixture left under stirring in ambient conditions for three days to allow the maximum possible oxidation of graphite. At this stage, the color of the mixture changed from dark purplish green to dark brown. Later, the H_2O_2 solution was added, which results in changes the color of the mixture to bright yellow indicating the completion of the oxidation process. The graphite oxide formed was washed three times with 1 M of HCl solution to remove the residual salts and washing process repeatedly done with deionized water until neutral pH of supernatant achieved. The washing process was carried out using simple decantation of supernatant via a centrifugation technique. During this process, the graphite oxide experienced exfoliation thus formed highly viscous graphene oxide suspension. This suspension was poured into a petri dish and kept for drying at atmospheric condition. Once drying process completed, peeled off carefully using tweezers to get GO paper.

2.2. Preparation of 1D graphene nanoscrolls

The GO suspension (0.25 mg/ml) prepared by dispersing 50 mg GO in 200 ml deionized water using bath sonicator for 30 mins. 0.735 ml of hydrazine hydrate ($N_2H_4{\cdot}H_2O$) solution was added drop wise into GO suspension and followed by stirring for 5 mins. The above suspension was transferred into the sealed container to convert into chemically reduced graphene and kept in the oil bath at 60 °C for 30 mins with stirring. The chemically reduced graphene suspension sprayed into liquid nitrogen bath and the product formed in the shape of black colored frozen solid. This product was finally freeze-dried by lyophilizer with a controlled temperature programme to obtained GNS.

2.3. Characterization

The tubular morphology of GNS was studied using scanning electron microscopy (SEM) using JEOL JSM 6380 and high-resolution transmission electron microscopy (HRTEM) at 200 KV (JEOL JEM 2100). The reduction of GO was confirmed by X-Ray diffraction (XRD) for GO and GNS samples using powder X-ray diffractometer (Bruker D8 Advance) using Cu Kα radiation (k = 1.54 Å). The X-ray photoelectron spectroscopic (XPS) measurements performed on a PHI 5000 Versaprobe II equipped with monochromatic Al Kα X-ray source.

2.4. Electrochemical measurements

The electrochemical performance of the GNS electrode measured by a three-electrode system using electrochemical workstation (μAUTOLAB Type III), in which a platinum wire used as counter electrode and Ag/AgCl electrode used as reference electrode. The suspension of electrode material prepared by mixing 5 mg of GNS with 1 ml of ethanol (0.5 ml) and deionized water (0.5 ml) mixture and 50 μl of Nafion solution under ultrasonic treatment for 30 mins and 4 μl of suspension loaded onto a 3 mm diameter of glassy carbon electrode (GCE). The typical mass loading of the electrode material obtained is 0.29 mg/cm2. To study the electrochemical performances of GNS, cyclic voltammetry (CV), galvanostatic charge/discharge (CD) and electrochemical impedance spectroscopy (EIS) measurements were done in 1 M H_2SO_4 electrolyte.

3. Results and discussion

3.1. Physicochemical characterization

The scanning electron microscopy images of GO, chemically reduced graphene (CRG) and GNS have been given in Fig. 1. Fig. 1a shows the cross-sectional view of GO, clearly exhibiting the highly exfoliated and layered structure. After chemical reduction of GO, the CRG sample maintained its layered morphology as shown in Fig. 1b. In case of GNS (Fig. 1c and d), the SEM images showed tubular-like morphology. These reveal that 2D graphene sheets have transformed into 1D rolling structure due to rapid quenching of CRG suspension using liquid nitrogen.

The high-resolution TEM images of CRG and GNS showed in Fig. 2. The CRG reveals that it has flat and sheet-like morphology as shown in Fig. 2a. Fig. 2b shows the conformational changes of CRG sheets into nanoscrolls. The nanoscroll formation process is spontaneous. During the rapid freezing process, the graphene sheets undergo twisting, bending and rolling due to faster growth of ice crystals resulted in crumpled nanoscrolls[21]. The single nanoscroll in Fig. 2c shows a distinct tubular morphology. Fig. 2d reveals the rolled regions of HRTEM image. These images strongly indicate that tubular-like rolling configuration GNS successfully formed by this simple method.

Specific surface area of GNS measured by N_2 absorption-desorption method. The obtained BET surface area value for GNS is 434.7 m^2/g with the total pore volume of 0.83 cc/g, whereas GO showed only 75 m^2/g. The GNS material was confirmed to be mesoporous in nature using Barret-Joyner-Halenda (BJH) method with pore distribution within the range of 2–50 nm and most probable pore diameters are 2–4 nm as shown in Fig. 3. This unique tubular morphology and porous nature of new form of carbon materials is expected to be efficient for adsorption and desorption of electrolyte ions into electrode materials during charging and discharging of supercapacitors.

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