Investigation of graphene oxide nanogel and carbon nanorods as electrode for electrochemical supercapacitor

K.O. Oyedotun, M.J. Madito, A. Bello, D.Y. Momodu, A.A. Mirghni, N. Manyala*

Department of Physics, Institute of Applied Materials, SARCHI Chair in Carbon Technology and Materials, University of Pretoria, Pretoria 0028, South Africa

ABSTRACT

In this study, a gel of graphene oxide (GO) and carbon nanorods obtained from the GO gel were synthesized via a modified Hummer's method and a force-driven reflux process respectively. Scanning electron microscopy (SEM) was used to analyse the morphology of the as-synthesized materials showing gelatinous and nanorods structures for the graphene oxide and carbon materials respectively. X-ray diffraction (XRD) suggests that the synthesized materials have a hexagonal crystal structure and an increased interlayer spacing due to the interlaced molecules of oxygen-containing functional groups. X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX) analysis were employed to confirm the presence of carbon and oxygen functionalities in the synthesized materials. Electrodes fabricated from both materials prove a limit specific capacitance of 436.5 F g^{-1} and 719.5 F g^{-1} corresponding to specific capacities of 48.5 mAh g^{-1} and 80.8 mAh g^{-1} at a current density of 0.5 A g^{-1} in a three electrode system with 6 M KOH electrolyte for both the graphene oxide gel and carbon nanorods respectively. The materials show good cycle stability after 3000 cycling at a current density of 5 Ag^{-1}, which implies a great promise as electrodes for supercapacitor applications.

© 2017 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Due to high energy consumption and depleting natural resources globally, the necessity for alternative energy has become evident. Electrochemical energy storage (batteries and supercapacitors) have been one of the main focus of storage system for renewable and sustainable energy sources since most of these sources require a storage component [1–4]. Most of these combined systems are already being used in new advanced technologies to store power due to their sustainability and suitability for both stationary and mobile systems [5,6].

The requirement for micro-power units have increased in recent time, and this has put high demands on micro-power devices manufacturing [7]. Micro-power components are needed to become continuously smaller and operate faster to meet technological inventions but not at the expense of its reliability and price. The future requirement for energy generation and storage cannot be easily achieved without innovative design of electrode materials. Therefore, an enormous effort has to be spent on research and development of new materials in order to develop high performance and reliable energy storage devices.

Supercapacitors (SCs) are classified as emerging high power-delivery storage devices which are known to be able to hold much more electrical charge than standard parallel-plate capacitors [3,8]. They are also easily able to discharge at a very fast rate in delivering the necessary high power as compared to batteries and thus can complement batteries in many domestic, commercial and industrial applications [2,3]. SCs also work in very low temperatures; an operating condition that prevents the adoption of many types of electrochemical batteries [5]. They can be divided into three categories, specifically, (1) electric double-layer capacitors (EDLCs) which arise as a result of charge separation at an electrode/electrolyte interface (electric double-layer capacitive behaviour), (2) pseudocapacitors and redox SCs which use the charge-transfer arising from redox reactions occurring on the surface of the electrode (Faradaic behaviour) and (3) hybrid capacitors which combine both the EDLCs properties with a battery-type electrode material to form asymmetric SCs or hybrid systems [3].

Graphene is a hexagonal planar allotrope of carbon and the most representative single-atom-thick two-dimensional (2D) material which exhibits distinct properties which are radically different from its bulk three-dimensional (3D) counterpart of graphite due to its freestanding 2D nature and are suitable for diverse applications due to their fascinating properties such as superior chemical/thermal stability, excellent electrical properties, mechanical properties, high specific surface area (SSA) and good

* Corresponding author. Tel.:+ + 27 12 420 3549; fax: + 27 12 420 2516.
E-mail address: ncholu.manyala@up.ac.za (N. Manyala).

flexibility [1,2,10]. The high theoretical SSA and excellent electrical conductivity has made them attractive as electrode material for energy storage, providing new possibilities for improvement in performance with high rate capability accompanied with minimal cost [3,11,12–15]. Despite these excellent properties, graphene-based electrode materials are still plagued with low energy densities when adopted in energy storage devices such as supercapacitors.

Graphene oxide (GO) or exfoliated graphene oxide has been chiefly prepared by the oxidation of graphite powder and prevalent research has been done to uncover its chemical structure or surface chemistry [16–20]. GO produced by the oxidation of graphite mainly shows sheet-like morphology and the electrochemical performance of this material has been evaluated as SC electrodes. For instance, functionalized exfoliated graphene oxide [18], electrochemically reduced graphene oxide [16], poly(ionic liquid)-modified reduced graphene oxide [21] and GO [20] show specific capacitance values in the range of 146–223.6 F g^{-1} at 5 mV s^{-1}. These specific capacitance values of GO could be enhanced by improving the surface chemistry (i.e. optimize the oxygen-containing surface functionalities) and the morphological properties of the material. Similarly, the energy density of the supercapacitor could be enhanced by either increasing the device specific capacitance by modifying the electrode material or increasing operating potential window by using organic and ionic liquids electrolytes [22,23].

In this research, we synthesized two phases of carbon-based materials namely; graphene oxide (GO) gel and carbon nanorods obtained from the GO gel via a modified Hummer's method and a force-driven reflux process respectively, using powdered graphite as the main precursor. The as-prepared electrode materials were extensively characterized using various techniques and the electrochemical performance of the materials was evaluated via a three electrode cell configuration. The prepared materials demonstrated good electrochemical properties which suggest their promising contribution to the supercapacitors field.

2. EXPERIMENTAL

2.1. Synthesis of graphene oxide (GO) gel

Graphene oxide gel was prepared at room temperature using a modified Hummers method [24]. In the preparation process, 1.0 g of graphite powder and 6.0 g of KMnO$_4$ were poured into a beaker containing 120 mL of concentrated sulphuric acid (H$_2$SO$_4$) (95–99.9%). The mixture was stirred for 15 min to secure a homogeneous dispersion of the solution which resulted in a yellowish-green dark suspension. This was then transferred into a silicone oil

bath and further stirred at 50 °C for 180 min to obtain a thick dark-grey solution which was left to cool down to room temperature. A stoichiometric volume of 30% H$_2$O$_2$ and distilled water was subsequently poured into the solution to subdue residual permanganate and manganese (IV) oxide mixture to a colourless soluble manganese sulphate. This caused a large heat evolution due to the dehydration of the tetraoxo sulphate (VI) ions. The reacted solution became very hot with distinct agitation, which was then stirred for 1 min and then centrifuged for 10 min with the supernatant decanted away. The recovered gelatinous solution was re-dispersed in distilled water by mechanical shaking (250 oscillations/minute) for 1 h, with additional centrifugation for 30 min and thereafter was kept for 10 days in ambient conditions at room temperature to solidify. The recovered solid (graphene oxide) was dried in an electric furnace under normal pressure at a temperature of 90 °C for 2 h.

2.2. Synthesis of carbon nanorods

In the synthesis of carbon nanorods, 0.3 g of the as-prepared GO gel was re-dispersed into 45 ml of 10 M aqueous NaOH solution with continuous stirring for 5 min, and then transferred into reflux set-up upon magnetic stirring. The reflux flask was put in a silicone oil bath on a hot plate at 100 °C which is close to the boiling point of the high-concentration alkaline solution (ca. 120 °C) for 24 h at a stirring rate of 500 revolutions per minute, as demonstrated in Scheme 1. This synthesis was carried out under the refluxing condition so that the pressure within the system during synthesis is kept constant at ambient atmospheric pressure. After the reaction, the reflux flask was taken out of the bath and allowed to cool naturally to room temperature. The resulting sample was collected via centrifugation, washed repeatedly with deionized water to obtain a pH of 7. The recovered sample was re-dispersed in water with 2 ml HCl (32%) added drop wise and heated at 100 °C for 20 min to further neutralize the solution. The supernatant was decanted away and the resulting sample was washed several times with deionized water. The recovered product (i.e. carbon nanorods shown in Scheme 1) was put in an oven to dry at a temperature of 80 °C.

2.3. Materials characterizations

Scanning electron micrographs were obtained at 1 kV on a Zeiss Ultra Plus 55 field emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive X-ray spectrometer (EDX). The X-ray diffraction (XRD) patterns were obtained by employing an XPERT-PRO diffractometer (PANalytical BV, Netherlands) with reflection geometry at 2θ values in the range
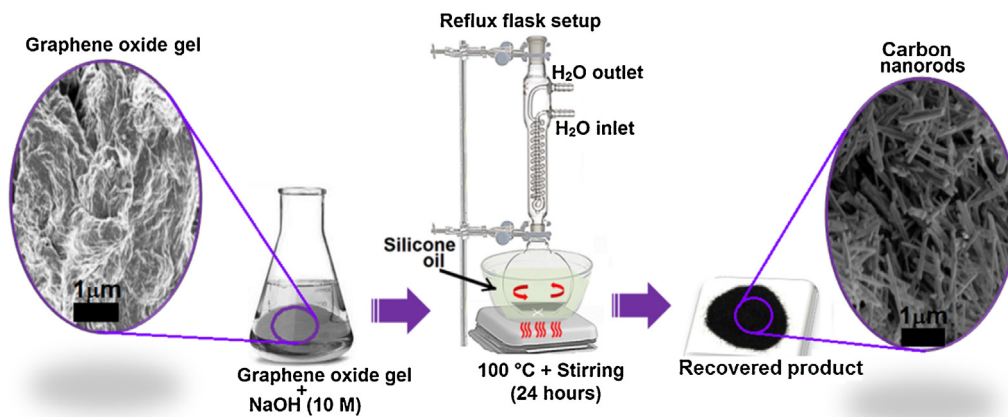
Scheme 1. Schematic of the synthesis process of carbon nanorods from as-prepared graphene oxide gel.