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Electro-exfoliating graphene from graphite for direct fabrication of supercapacitor

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ABSTRACT

A facile production of graphene via electro-exfoliation is demonstrated using different types of oxidizing agent (HNO_3, $NaNO_3$, H_2SO_4 and H_2O_2) in the presence of sodium dodecylbenzenesulfonate as a surfactant. Different types of surfactant–oxidizing agent solutions in different concentrations significantly influenced the electrochemical exfoliation of graphite rod. The surface morphology, layer thickness and defects of the as-produced graphene are further evaluated. Additionally, the as-produced graphene is fabricated as a supercapacitor electrode via direct vacuum filtration. Nylon membrane and polymer gel, each containing 2.0 M of potassium hydroxide, are utilized to investigate the influence of the electrolyte type on the capacitance performance. Upon 1000 charge/discharge cycles, the nylon membrane electrolyte recorded capacitance retention of 94%, whereas the polymer gel electrolyte recorded an impressive capacitance retention that exceeded 100%. The potential of the fabricated supercapacitor for real applications is manifested by its ability to light up a light-emitting diode upon charging.

1. Introduction

Graphene is a thin layer of pure carbon with a two-dimensional (2D) carbon allotrope bonded through sp^2 hybridization [1]. With the extraordinary structure of carbon atoms tightly packed and bonded together in a hexagonal honeycomb lattice [2], graphene possesses an extremely high Young's modulus [3], an outstanding electrical conductivity [4], a high surface area [5], and a unique optical transparency [6]. The unique properties of graphene allow revolutionary applications in various fields, including electronic devices [7], optical devices [8], electrochemical sensing [9], biosensing [10], energy conversion [11], energy storage [12], super lubricant in water-based drilling fluids [13], medicine [14], water treatment [15], desalination [16] and transportation vehicles [17].

Graphene can be synthesized using different methods, starting with the simplest mechanical exfoliation of graphite using scotch tape [18], to the epitaxial growth of graphene by the thermal graphitization of silicon carbide (SiC) [19], liquid-phase exfoliation [20], substrate-free gas-phase synthesis [21], chemical vapor deposition (CVD) [22], and the unzipping of carbon nanotubes [23]. Although numerous kinds of methods have been reported to be successful for graphene production, there is no ideal method for synthesizing defect-free graphene. The reported methods are generally unfavorable because of the need for high energy consumption (high temperature), expensive equipment, and hazardous solvents. They also use of reducing agents that can contaminate the resulting products and have low production yields.

Graphene can also be synthesized via the reduction of graphene oxide (GO) produced from Hummers' method [24]. In a typical Hummers' method, graphite is oxidized by sodium nitrate ($NaNO_3$) with potassium permanganate ($KMnO_4$) and then washed with hydrogen peroxide (H_2O_2) to reduce the residual permanganate and manganese dioxide [25]. Various methods have been developed based on modifications of Hummers' method [26]. However, in practice, these form structural defects that will alter the electronic structure of the graphene and give it a semiconducting nature. Furthermore, large quantities of strong oxidants and acids were required [27].

Electrochemical exfoliation has been reported to be a simple, economic, and fast technique [28] to produce graphene compared to other methods, as previously mentioned. Electrochemical exfoliation is also a nonpolluting technique, because it is based on a mild chemical process without the need for strong oxidizing agents [29]. There are two types of electrolytes that can be used in electrochemical exfoliation: ionic-liquid (IL)-based electrolytes

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and aqueous solutions (surfactant, acid, and sulfate salt). In 2008, a one-pot electrochemical exfoliation approach for the preparation of IL-functionalized graphene sheets using a 1:1 IL/water volume ratio as an electrolyte was investigated [30]. Even though IL can promote green chemistry applications by reducing the use of toxic (hydrazine) and polluting organic solvents (e.g., dimethylformamide or tetrahydrofuran) in the production of graphene [31], it is relatively expensive when used for the production of graphene on a large scale. In 2012, an electrochemical exfoliation method was reported to obtain graphene sheets with the assistance of an aqueous solution of a surfactant-based electrolyte, which was 0.1 M sodium dodecylsulfonate (SDS) [32]. Surfactants have both hydrophilic heads and hydrophobic tails, which can lower the surface tension between two liquids or between a solid and a liquid. The hydrophobic tails of surfactant molecules can be adsorbed onto non-polar objects of graphene flakes by the van der Waals force and lower the binding and interlayer forces within the graphite [33]. Thus, the exfoliation of graphite rods will occur easily. Moreover, the anionic sites of the surfactant can prevent the agglomeration of the exfoliated flakes [34].

Supercapacitors can efficiently store more energy and give a higher power density with a better life cycle than batteries or conventional capacitors [35]. Recently, a graphene-based electrode was reported to give a good electrochemical performance because of its excellent characteristics compared to other carbon allotropes, including chemical stability, high electrical conductivity, and a large surface area [6]. There are many techniques for the fabrication of supercapacitor electrodes, including electrophoretic deposition (EPD) [36], the drop-drying method [37], spray deposition [38] and vacuum filtration deposition (VFD) [39]. In addition, some methods introduce a binder like polytetrafluoroethylene (PTFE) [12] and poly(vinylidenefluoride) (PVDF) [39] for the pre-treatment of graphene before the fabrication of a supercapacitor electrode to ensure that the graphene is strongly attached to the current collector.

In this work, graphene was produced through the electrochemical exfoliation of graphite rod using a combination of sodium dodecylbenzenesulfonate (SDBS) as a surfactant and oxidizing agents of various concentrations. The surface morphology and layer thickness of the as-produced graphene were further analyzed using a field emission scanning electron microscope (FESEM), atomic force microscope (AFM) and transmission electron microscope (TEM). The as-produced graphene was subjected to vacuum filtration on a nylon membrane to form a graphene film, in which the graphene was subsequently used as supercapacitor electrode. The nylon membrane and polymer gel acted as a carrier of electrolyte where each one contained 2.0 M potassium hydroxide (KOH) electrolyte, in which the ions that took part in an electric double layer capacitance (EDLC) mechanism. Polymer gel was compared to this nylon membrane to investigate the influence of the types of electrolyte on the capacitance performance. Cyclic voltammetry and charge/discharge analyses of the as-produced graphene samples were performed to obtain specific capacitance values and measure the stabilities, which were compared to those of graphene nanoplatelets (GNPs) and activated carbon (AC).

2. Experimental

2.1. Materials

Commercial natural graphite rod was obtained from Alfa Aesar®. Sodium dodecylbenzenesulfonate (SDBS) powder was purchased from Acros Organics, NJ, USA. Hydrogen peroxide (H_2O_2), sulphuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), nitric acid (HNO_3), denatured ethanol (95%), and activated carbon were purchased from Systerm, Malaysia. Poly(vinyl alcohol) and glycerine were provided from Merck, Malaysia. Potassium hydroxide (KOH) was purchased from R&M Marketing. Nickel foam was purchased from Goodfellow Cambridge Ltd. Nylon membrane filter was obtained from Membrane Solutions, LLC, USA.

2.2. Electrochemical exfoliation of graphite

The procedure reported in our previous work was modified [40]. The electrochemical exfoliation of graphite rod was carried out using an Autolab PGSTAT204 electrochemical workstation. For three-electrode systems, a graphite rod acts as a working electrode, a platinum (Pt) wire is the counter electrode, and a saturated calomel electrode (SCE) is used as the reference electrode. In contrast, in two-electrode systems, graphite rods act as both the working and counter electrodes. The electrochemical process was carried out in a 0.1 M SDBS aqueous solution, and a static potential of +10 V was applied. After 1100 s, a black precipitate of the exfoliated graphite was obtained and denoted as 1 cycle. The precipitate was sonicated for 15 min, and a surfactant–graphene mixture was formed. The mixture was washed with a 1:1 volume of ethanol to facilitate the filtration process. Vacuum filtration was carried out on the resulting dark solution using a piece of nylon membrane filter, and it was washed using copious amounts of water and ethanol. The filtered graphene was placed in the oven to evaporate excess moisture, and the final mass of the product was recorded. Then, the steps were repeated using a three-electrode system with different electrolytes. The electrolyte system used was a mixture of 0.1 M SDBS with different types and concentrations of oxidizing agents (HNO_3, $NaNO_3$, H_2SO_4, and H_2O_2). The two highest production of graphene using different oxidizing agents (1.0 M HNO_3 and 1.5 M $NaNO_3$) were chosen for further experiments with various electrochemical exfoliation cycles; 1 cycle (1100 s), 5 cycles (5500 s), and 10 cycles (11000 s). The as-produced graphene samples were named using acronyms of G-HNO_3, G-$NaNO_3$, G-H_2SO_4, G-H_2O_2, depending on the oxidizing agents used to produce them.

2.3. Synthesis of graphene nanoplatelets (GNPs)

GNPs were produced by the thermal exfoliation of expandable graphite (3772, Asbury, Inc.). The expandable graphite was subjected to a thermal shock at 950 °C for 10 s. The obtained thermally exfoliated graphite was sonicated for 1 h using a probe sonicator to obtain GNPs.

2.4. Preparation of polymer gel electrolyte

Ten percent (w/v) of poly(vinyl alcohol) (PVA) in water was stirred continuously at 90 °C until complete solvation. 1.12 g of KOH pellets was added into the solution and was stirred thoroughly. Ten percent (wt/wt) of glycerine was added as a plasticizer to prevent the loss of electrolyte. The mixture was poured onto a Petri dish and left to evaporate to form a polymer gel electrolyte at room temperature.

2.5. Preparation of graphene films for supercapacitor electrodes

The as-produced graphene was mixed with deionized water and sonicated for 5 min to form a water–graphene mixture. Then, this water–graphene mixture was vacuum-filtered onto a nylon membrane and allowed to dry at room temperature to form a graphene film, which was used as a supercapacitor electrode. Next, the nickel foam that acted as a current collector and two supercapacitor electrodes were stacked together, with the polymer gel electrolyte placed between the electrodes, whereas, for the nylon