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Novel eco-friendly synthesis of graphene directly from graphite using 2,2,6,6-tetramethylpiperidine 1-oxyl and study of its electrochemical properties

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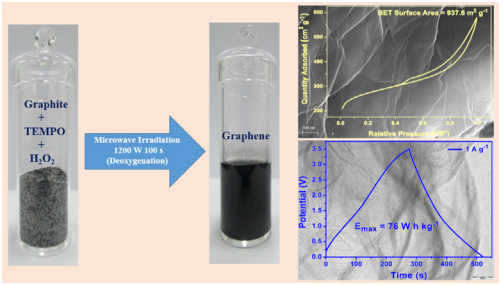
HIGHLIGHTS

- Novel eco-friendly one-pot method for the high yield synthesis of graphene.
- Direct synthesis of high quality graphene from graphite under mild conditions.
- Fabricated symmetrical supercapacitor has high energy and power densities.
- Excellent cycling stability with 90% capacitance retention even after 1000 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein we report a simple, low cost, highly efficient and environment friendly one-pot method for the high throughput synthesis of graphene directly from graphite using 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) and H_2O_2 under microwave irradiation. The formation mechanism of graphene nanosheets (GNS) as investigated by Raman spectroscopy and electron microscopy techniques reveal surface defect generation, intercalation and exfoliation as the main steps. The rapid and local Joule heating of graphite by microwave radiation results in simultaneous deoxygenation and exfoliation forming GNS. The as-synthesized GNS are a few layer thick with a high surface area of 937.6 $m^2\ g^{-1}$ and a high C/O ratio of 9.2. These results open the perspective of replacing toxic oxidizing and reducing agents by environment friendly chemicals of similar efficacy, thus facilitating the large-scale production of GNS by a greener method. Furthermore, GNS exhibits good electrochemical performance with a large specific capacitance (197 F g^{-1}), excellent rate capability and a long cycle life (1000 cycles) in neat 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) electrolyte. It also has a high energy density of 76.03 W h kg^{-1} while simultaneously possessing a high power density of 1.12 kW kg^{-1}.

1. Introduction

Graphene is a one-atom thick planar 2D sheet of sp^2-bonded carbon atoms tightly packed into a hexagonal lattice [1]. Due to the excellent mechanical strength [2], high electrical conductivity [3] and large surface area of over 2630 $m^2\ g^{-1}$ [4] graphene finds applications in nanoelectronics [5,6], sensors [7,8] and energy storage devices [4,9]. These applications require huge quantities of graphene in the form of nanosheets, nanoparticles or nanoplatelets at a reasonable cost. Therefore, economically viable processes for its mass production have to be developed. Up to now, diverse strategies have been applied for the production of graphene, mainly

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including micromechanical cleavage [3], chemical vapour deposition [10], epitaxial growth [11], liquid phase exfoliation [12], thermal/chemical reduction of graphene oxide (GO) [13,14] etc. Among the various methods, chemical reduction of GO seems to be the most promising route because it enables large-scale production of graphene at low cost. But the drawback is that the method requires the use of harsh oxidizers and toxic reducing agents. As a consequence, continuous endeavours have been directed towards the development and optimization of eco-friendly chemicals for the synthesis of graphene. It is therefore desirable to identify a high yield method that can directly exfoliate graphite into graphene sheets. Lu et al. [15] have reported the rapid exfoliation of graphite powder using a mixture of chlorosulfonic acid (CSA) and H_2O_2 for the synthesis of few-layer graphene but the usage of large quantities of CSA is hazardous and thus highly incompatible with health and environmental standards. Use of microwave radiation for intercalation-exfoliation is a green and efficient process as microwave radiation can heat graphite to a high temperature in a short time. The microwave method is based on the dielectric microwave heating of the reactants through selective transfer of energy to microwave sensitive polar solvents resulting in a simultaneous increase in self-generated pressure inside the sealed reaction vessel. This results in the shortening of the reaction time from several hours to a few minutes with an effective energy economy.

Considering all of these, we report a facile one-pot method for the synthesis of graphene directly from graphite using TEMPO and H_2O_2 under high power microwave irradiation within a short reaction time of 2 min with benefits of high yield and mass production. H_2O_2 is used in the exfoliation process due to its remarkable advantages, such as low cost, eco-friendly, versatility, selectivity, wide availability, safety and effectiveness as a reagent. TEMPO, a stable nitroxyl radical is a catalytic oxidant which along with H_2O_2 assists in defect generation and intercalation of oxygen moieties along the c-axis of graphite. It is environmental friendly and can be regenerated in the reaction system. The as-synthesized graphene was studied as an electrode material for supercapacitors in neat $EMIMBF_4$ electrolyte. Due to the high surface area and ideal pore size distribution GNS shows a superior capacitive performance with a large specific capacitance of 197 F g^{-1} and a high energy density of 76.03 W h kg^{-1}.

2. Experimental

2.1. Materials

Graphite flakes (CAS Number 7782-42-5), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (CAS Number 2564-83-2), nafion (CAS Number 31175-20-9) and isopropanol (CAS Number 67-63-0) were procured from Sigma Aldrich. Hydrogen peroxide (CAS Number 7722-84-1) was procured from Merck India.

2.2. Synthesis

Graphene nanosheets were synthesized from natural graphite flakes under microwave irradiation as follows: In a typical experiment 0.5 g of graphite flakes (100 mesh) and 0.05 g of TEMPO were added to 1 mL of hydrogen peroxide and sonicated for 10 min. Then the mixture was refluxed in a high temperature microwave sintering furnace (2.45 GHz, 0–1.95 kW) at a power of 1200 W for 100 s. Under microwave irradiation, the precursors exfoliated rapidly, accompanied by sparks and violent fuming. After the microwave treatment, the suspension was ultrasonicated and centrifuged to remove the unreacted graphite (21 wt.%). The supernatant was filtered and the solid obtained was washed repeatedly with distilled water and freeze dried, obtaining 0.25 g of the product.

2.3. Characterization

The morphological analysis of GNS was done by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) using Zeiss Ultra 55 field emission scanning electron microscope and JEOL TEM-2100 respectively. X-ray diffraction (XRD) measurements were conducted using a D8 Advance (Bruker) X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Brunauer–Emmett–Teller (BET) surface area analysis was done by recording nitrogen adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020 apparatus. Prior to analysis, samples were degassed at 200 °C in vacuum for 24 h. The specific surface area (SSA) was calculated by the BET method based on adsorption data in the relative pressure (P/P^o) range of 0.05–0.3. The total pore volume was measured from the amount of nitrogen adsorbed at a relative pressure (P/P^o) of 0.99. The pore size distribution (PSD) was analyzed using a non-local density functional theory (NLDFT) method with a slit pore model from the nitrogen desorption data. Raman spectra were collected using Seki Technotron STR 300 laser Raman spectrometer using laser excitation at 514.5 nm. X-ray photoelectron spectroscopy (XPS) data were taken on an AXIS Ultra instrument from Kratos Analytical in the range of 1–1300 eV to investigate the surface chemical composition of the obtained product.

2.4. Fabrication of the supercapacitor

The supercapacitor electrodes have been fabricated as follows: As-synthesized GNS and ionic liquid (1:1 w/w) were dispersed in isopropanol by ultrasonication with 5% nafion solution as a binder. The electrodes were prepared by coating graphene dispersion (~6.0 mg of active material/electrode) on 2 cm × 2 cm sized Toray Carbon Paper (Alfa Aesar) using layer-by-layer brush coating technique. Coated carbon paper was heated in vacuum oven at 80 °C for 6 h to reduce the effect of binder used. The supercapacitor setup consists of GNS-coated carbon paper as electrodes, polypropylene membrane (Celgard) as separator, $EMIMBF_4$ as electrolyte and the stainless steel sheets as current collectors. Separator rinsed with $EMIMBF_4$ was sandwiched between two electrodes. This assembly was further sandwiched between current collectors. All the electrode preparation steps were carried out under glovebox conditions of < 0.1 ppm of water and oxygen content.

2.5. Electrochemical measurements

Electrochemical performances of the supercapacitor cells were tested by cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) on a computer controlled VERSA STAT 3 (Princeton Applied Research) potentiostat/galvanostat. All of the experiments were carried out in a two-electrode system. The potential range for CV measurements and galvanostatic charge/discharge tests was 0–3.5 V. EIS tests were carried out in the frequency range of 100 kHz–1 mHz by impressing a small 10 mV amplitude of ac signal.

3. Results and discussion

3.1. Synthesis of GNS

Despite of investigating varied reactant ratios, best results were obtained at reaction mixture consisting of graphite flakes, TEMPO and 30 wt.% hydrogen peroxide in the ratio of 1:0.1:2. TEMPO radical plays a dual role in the synthesis of GNS directly from graphite. First, under microwave irradiation it initiates radical induced cutting along the edges and c-axis of graphite producing