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Short communication

Mechanochemical preparation of graphene nanosheets and their supercapacitor applications

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ABSTRACT

A facile method for the preparation of graphene nanosheets via mechanochemical reduction of graphene oxide (GO) has been reported. XPS and Raman analyses revealed the removal of oxygenated functional groups and the restoration of sp^2 domains in graphene after the mechanochemical reaction. Cyclic voltammetry curves showed a rectangular behavior suggesting the presence of double layer capacitance in the graphene electrodes. Graphene electrodes delivered a specific capacitance of 169 F/g as observed from the charge–discharge analysis at a current density of 1 mA/cm^2. The cyclic stability analysis revealed that about 98% of its initial capacitance was retained after 1000 cycles.

Introduction

Graphene nanosheets are attracted much attention during this decade owing to their wide spread applications in various fields such as nanoelectronics, nanophotonics, energy storage devices, and biomedical sectors [1,2]. This is due to the excellent physico-chemical properties and remarkable electronic properties of graphene which facilitates them as an ideal candidate for several applications [3]. Among the various synthetic routes for graphene, chemical methods involving the reduction of graphene oxide (GO) into graphene nanosheets are promising due to their high scalability compared to mechanical exfoliation and CVD methods [4]. Several approaches viz. wet-chemical method, sonochemical, hydrothermal, microwave reaction, etc., are used for the preparation of graphene from GO [5,6]. However, it is still necessary to develop a novel method for the gram scale preparation of graphene. In this regards, mechanochemical method is one of the well known methods for preparation of several nanomaterials, and composites, with high yield [7,8]. This method employs a mechanical stress during the milling process, in addition to the chemical reaction which enables to obtain high quality products in gram scale [9]. Considering the efforts until taken on the graphene preparation using milling methods, scalable preparation of thin graphite sheets and graphene via mechanical delamination has been reported [10,11]. Another study demonstrated that ball milled graphite powders (with different reaction time) produces GO with tunable lateral size [12]. Recently, a solvent free reduction of GO into graphene via ball milling under H_2 atmosphere has been reported [13]. In this study, we demonstrated a mechanochemical route for the preparation of graphene via deoxygenation of GO using hydrazine (reducing agent) and investigated its use as an electrode material for supercapacitors.

Experimental

Materials used

Graphite powder was purchased from Sigma–Aldrich Ltd, South Korea. Potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), hydrazine hydrate, and ethanol, were obtained from Dae Jung Chemicals and Metal Co., Ltd., South Korea. The ball milling process has been carried out on a Pulverisette 6 planetary mill (Fritsch instruments) using a tungsten carbide bowl and tungsten carbide balls with diameter of 5 mm.

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Preparation of graphene oxide nanosheets

The GO nanosheets were synthesized according to the modified Hummers method using graphite powder, H_2SO_4, and $KMnO_4$ as the starting precursors. The detailed procedure is reported elsewhere [5,8].

Mechanochemical preparation of graphene nanosheets

The graphene nanosheets are prepared via mechanochemical method in wet conditions using GO as the starting material, ethanol as a solvent and hydrazine as the reducing agent. Breifly, GO nanosheets (10 g) was dissolved ethanol (50 mL) followed by the addition of hydrazine (5 mL) and are allowed to wet milling using tungsten carbide balls in a tungsten carbide bowl at a 300 rpm for 30 min. After the completion of the reaction, the obtained black colored graphene nanosheets were washed with ethanol and water. Finally, the obtained graphene nanosheets are allowed to dry at 80 °C for overnight.

Characterization techniques

The crystal structure was determined by X-ray diffraction analysis performed on a Rigaku X-ray diffractometer operated at 40 kV and 40 mA with Cu Kα radiation. The surface morphology of the samples was studied using a high resolution transmission electron microscope (HR-TEM, FEI Titan 80-300) instrument. The chemical composition and state of elements present in the outermost part of the prepared samples were studied by X-ray photoelectron spectroscopy (XPS) techniques using ESCA-2000, VG Microtech Ltd. Here a monochromatic X-ray beam source at 1486.6 eV (Aluminum anode) and 14 kV was used to scan the sample surface. A high flux X-ray source with an Aluminum anode was used for X-ray generation, and a quartz crystal monochromator was used to focus and scan the X-ray beam on the sample. Raman spectra of the samples were measured using a LabRam HR800 micro-Raman spectroscope (Horiba Jobin-Yvon, France). The Raman system was operated at 10 mV laser power and an excitation wavelength of 514 nm with an Ar^+ ion laser.

Electrochemical measurements

The electrochemical properties of the graphene nanosheets were studied on AUTOLAB PGSTAT302N electrochemical workstation using 1 M Na_2SO_4 solution as an electrolyte. The electrochemical analyses were carried out in three-electrode configuration with graphene modified stainless steel substrate as working electrode, platinum as counter electrode and Ag/AgCl as reference electrode, respectively. The working electrode was prepared by taking active material (graphene), conductive additive (carbon black), and binder (PVDF) in the weight ratio (85:10:5) and mixed together with N-methylpyrrolidone (NMP) as a solvent. The resulting mixture was coated onto the stainless steel substrate (1 cm × 1 cm) and allowed to dry at 80 °C in an oven for overnight. The mass loading of the active material in the working electrode is measured as 1.2 mg.

Results and discussion

In this study, the graphene nanosheets are prepared via mechanochemical reaction in wet conditions using GO s as starting material with ethanol as solvent and hydrazine as reducing agent. After 30 min of milling process, black colored graphene sheets has been obtained in gram scale. The mechanism underlying mechanochemical reduction of GO can be explained as follows: the shear and compressive forces in the reaction medium during the milling process [9,10], can effectively reduces the GO into graphene via hydrazine reaction and results in simultaneous delamination of graphene nanosheets. This mechanochemical method for obtaining graphene is cost-effective, relatively fast with large scalability compared to the conventional methods for preparation of graphene. Fig. 1(a) shows the XRD pattern of graphene nanosheets in comparison with the starting material GO. The XRD pattern of GO shows a broad diffraction at $2\theta = 10.4^\circ$ corresponding to an interlayer spacing of 0.84 nm [8]. The XRD pattern of the mechanochemically prepared graphene showed a broad diffraction peak observed at $2\theta = 24.3^\circ$ with an interlayer spacing of about 0.33 nm [14]. This finding suggested the re-graphitization of graphene nanosheets via mechanochemical reduction of GO. Fig. 1(b) shows the HR-TEM micrograph of

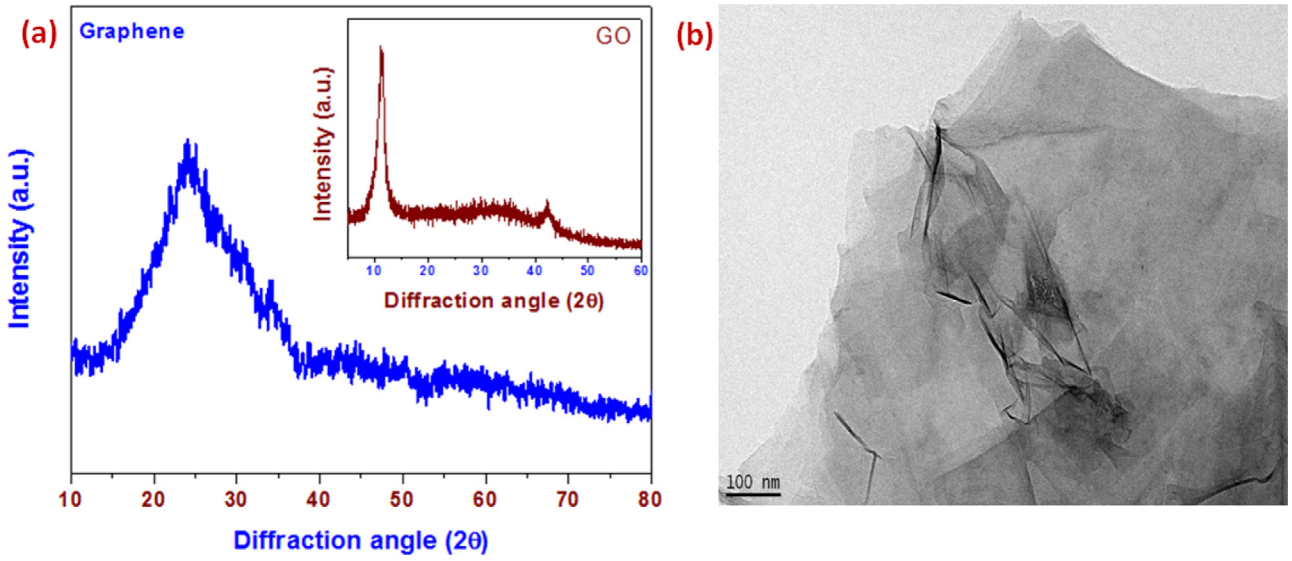

Fig. 1. (a) X-ray diffraction pattern and (b) high resolution transmission electron micrograph of mechanochemically prepared graphene. The inset in (a) shows the XRD pattern of GO.