



Preparation and electrochemical property of ionic liquid-attached graphene nanosheets for an application of supercapacitor electrode



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ARTICLE INFO

Article history:

Received 10 July 2013

Received in revised form 29 October 2013

Accepted 24 November 2013

Available online 14 December 2013

Keywords:

Graphene nanosheets

Ionic liquids

Electrochemical property

Supercapacitor

ABSTRACT

In this study, graphene nanosheets (GNS) were modified by 1-Butyl-3-methylimidazolium hexafluorophosphate, which is one of Ionic Liquid (IL). Owing to the modification of graphene with ionic liquids, graphene can not only be structurally stabilized, but also showed the higher charge transfer that is favor to exhibit an enhanced electrochemical performance. Also, a graphene aggregation by the intersheet van der Waals interaction can be prevented because ionic liquids act as an effective agent for the exfoliation of graphene sheets. The structural analysis of prepared composites was confirmed by transmission electron microscopy (TEM), Fourier transform infrared spectra (FT-IR) and X-ray diffractometer (XRD). The electrochemical properties are studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The GNS/IL composites show a high specific capacitance (114 Fg^{-1}) compared to pristine graphene (99 Fg^{-1}) at 10 mVs^{-1} in 6 M KOH electrolyte. Also, the prepared composites showed the enhanced electrochemical performance such as high rate capability and excellent cycle performance. Therefore, the prepared composites could be a candidate of electrode materials for supercapacitors.

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1. Introduction

Supercapacitors are known as the new energy storage devices due to their high power density, a long cycle life and fast charging-discharging rates compared to conventional capacitors [1]. They have received much attention as a broad range of application in electric vehicles, memory backup systems and mobile communications [2–4].

Supercapacitors are classified by two energy storage mechanisms: Electrical double-layer capacitors (EDLC) and Pseudocapacitors. EDLC stores energy by charge separation at the electrochemical interface between an electrode and an electrolyte. Carbon materials with high surface area such as activated carbon, carbon nanotubes, and graphene are the examples of EDLC electrode [5,6]. Transition metal oxides and conducting polymers are corresponded to pseudocapacitor electrode materials that undergo reversible faradaic redox reactions [7].

Graphene nanosheets (GNS), one-atom-thick two-dimensional layers of sp^2 -bonded carbon, are promising materials for supercapacitor electrodes due to their high surface area, excellent electronic conductivity and good mechanical flexibility [8–10]. GNS is an ideal carbon electrode material for EDLC because of their high surface area ($2675 \text{ m}^2/\text{g}$) that is capable of storing a much capacitance on the surface [11,12]. However, GNS tends to aggregate

when obtained by chemical reduction method because of intersheets van der Waals interaction. It results not only a lower specific capacitance because of the decrease of effective surface area but also poor stability and electrical conductivity. So it is very important to prevent the aggregation of GNS for improving the electrochemical performance of supercapacitors [13,14]. Many studies have been reported for preventing agglomeration of GNS such as stabilization of reduced graphite oxide (GO) sheets with polymeric or surfactant dispersant [15], pH controlled reduction of GO dispersion [16] and addition of single walled carbon nanotubes or carbon blacks [17,18].

Recently, ionic liquids (IL) have been attracted as an effective media for the exfoliation of graphene sheets directly from graphite anode [19]. The properties of ionic liquids (IL) include low vapor pressure, non-flammability, excellent mechanical and thermal stability, wide electrochemical stability and high ionic conductivity [20,21]. By modifying surface of graphene with ionic liquids, each graphene sheets effectively stabilized via electrostatic and cation- π interactions [22].

Herein, graphene nanosheets (GNS) were modified by 1-butyl-3-methylimidazolium hexafluorophosphate (Ionic liquids, IL). The GNS/IL composites were prepared very simply by adding the IL in graphite oxide (GO) suspension prior to reduction procedure of GO into graphene. Due to the modification of graphene surface with ionic liquids, it is expected that graphene can not only be structurally stabilized, but also show high conductivity that is favor to exhibit an enhanced electrochemical performance such as good rate capability and long cycle stability. Also, the aggregation

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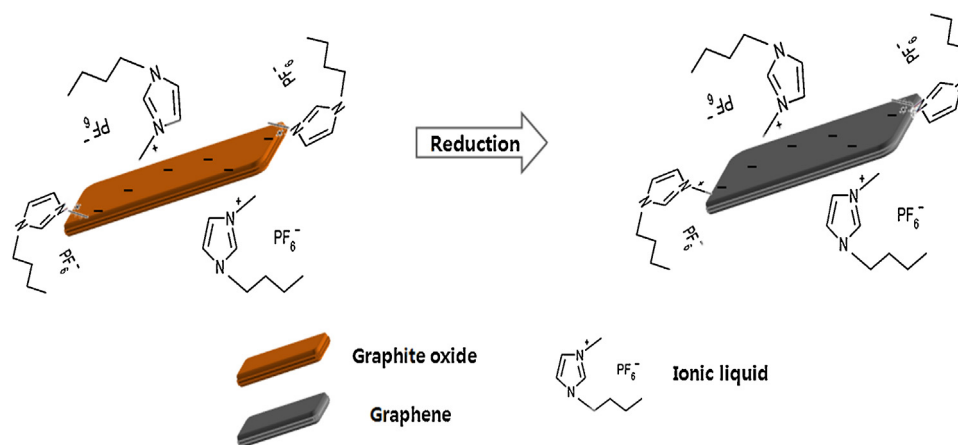


Fig. 1. Schematic representation of the preparation process of GNS/IL composites.

or stacking of graphene by the intersheet van der Waals interaction can be prevented because ionic liquids act as an effective media for the exfoliation of graphene sheets. To find an influence of the surface modification of graphene with ionic liquids, structural and electrochemical performance of the prepared composites were investigated in this study.

2. Experimental

2.1. Synthesis of the graphite oxide

All the chemicals were of analytical grade and were used as received without further purification. Graphite oxide (GO) was synthesized from natural graphite (SP-1, Bay carbon) by a modified hummer's method [23]. Briefly, 1 g of graphite powder was added into a mixture of 46 mL of 98% sulfuric acid, 1 g of sodium nitrate, 5 g of potassium permanganate, and the solution was maintained at 45 °C for 2 hrs. Then, 7 mL of 30% H₂O₂ and 80 mL of H₂O were slowly added into the solution. The oxidized solution was filtered and washed with HCl (10%) and a bright yellow precipitation was washed with water through a centrifugation (3600 rpm, 5 min) and GO powders were obtained after freeze drying.

2.2. Synthesis of GNS/IL composites

GNS/IL composites were synthesized by following steps. 0.1 g GO was dispersed in 100 mL DI water and then 1-butyl-3-methylimidazolium hexafluorophosphate (IL) was added into GO suspension. After 1 hr sonication, the mixture was reduced with sodium borohydride (NaBH₄) as described elsewhere [24]. It was stirred at 90 °C for 4 hrs and then the reaction mixture was filtered and washed several times with ethanol and DI water. Finally, it was dried in vacuum-oven at 60 °C for 12 hrs. The resultant powder was collected for the following characterizations. For comparison, pristine graphene was also synthesized by the same procedure as described above in the absence of IL.

2.3. Characterization methods

The nanostructures of the samples were investigated by using transmission electron microscope (TEM, JEOL JEM-2010). Fourier transform infrared (FT-IR) spectra were performed in the wavelength range of 4000–400 cm⁻¹ with KBr pellet method. Structural properties of the composites were collected with X-ray diffractometer (XRD, Philips X'Pert-MPD system) with Cu K α radiation in 2 θ range from 10° to 80°.

2.4. Electrochemical Characterization

All electrochemical measurements were carried out using Iviumstat (Ivium Technologies, Netherlands) in a three electrode cell system at room temperature. Working electrodes were prepared according to following method. 85 wt.% of prepared powder was mixed with 10 wt.% of carbon black (Super-P, Alfa-Aesar) and 5 wt.% polyvinylidene fluoride (PVDF) as binder in an agate mortar. The N-methyl-2-pyrrolidene (NMP) was used as solvent. The homogeneous slurry was coated on a nickel foam substrate (1 cm x 1 cm). Then, the resulting samples were dried in vacuum oven at 100 °C for 12 hrs. Pt wire and Ag/AgCl electrode were used as a counter electrode and a reference electrode, respectively. The measurements were done in a 6 M KOH aqueous electrolyte. The cyclic voltammetry (CV) test were measured between -0.8 ~ 0.2 V at different scan rates of 10, 20, 50 and 100 mVs⁻¹. Besides, galvanostatic charge/discharge curves were measured in the same potential range of at a current density of 1 Ag⁻¹. The electrochemical impedance spectroscopy (EIS) measurements were tested in the frequency range from 50000 Hz to 0.01 Hz at open circuit potential with an alternating current (AC) perturbation of 5 mV.

3. Results and discussion

3.1. Structure characterizations

Fig. 1 represents the preparation procedures of GNS/IL composites. As shown in the schematic illustration, GNS/IL composites were simply synthesized from GO in the reduction step. The assembly of GNS and IL comes from the cation- π interaction and electrostatic force [22]. In the GNS/IL composites, the 1-butyl-3-methylimidazolium hexafluorophosphate (IL) was easily attached on GNS and played a crucial role in modification the surface of GNS. It is expected that the modified GNS could have enhanced electrochemical properties and help the exfoliation of graphene sheets effectively [25].

Morphological properties of the prepared composites were identified by TEM images. Fig. 2 shows the morphology of pristine GNS and GNS/IL composites. Fig. 2a showed the wrinkled and ultrathin transparent graphene nanosheets resulted from the exfoliation of graphite. In the GNS/IL composites, IL was dispersed as many opaque spots on the surface of GNS as shown in Fig. 2b. Also, it was observed as thin nanosheets with some folded area and several fragments.

The vibrational characterization of the pristine GNS and GNS/IL composites was investigated by fourier transform infrared (FT-IR) spectroscopy as shown in Fig. 3. The bands referring to hydroxyl

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