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Synthesis of graphene via ultra-sonic exfoliation of graphite oxide and its electrochemical characterization

Hassnain Asgar [a], K.M. Deen [b], Usman Riaz [a], Zia Ur Rahman [c], Umair Hussain Shah [a], Waseem Haider [a, c, *]

[a] School of Engineering and Technology, Central Michigan University, Mt. Pleasant, MI 48859, USA
[b] Department of Materials Engineering, University of British Columbia, Vancouver, BC V6T 1Z4, Canada
[c] Science of Advanced Materials, Central Michigan University, Mt. Pleasant, MI 48859, USA

HIGHLIGHTS

- A relatively direct synthesis method for production of graphene is presented.
- IR, Raman and XRD analyses confirmed formation of graphene starting from graphite.
- XPS and TEM characterization validated the formation of graphene.
- Electrochemical response of GO and graphene was evaluated in de-aerated 0.5M KOH.
- Presence of functional groups in GO resulted in improved values of R_{ct} and $C_{eff,p}$.

ABSTRACT

A direct method of producing graphene from graphite oxide (GO) via ultra-sonication is presented in this work. The synthesis of graphene was validated through IR, XRD, Raman, and XPS analyses. Moreover, the diffraction pattern obtained from TEM also validated the formation of graphene with characteristics (002) plane. The electrochemical behavior of GO and graphene was evaluated by electrochemical impedance spectroscopy and linear sweep voltammetry in 0.5M KOH solution. The relatively larger effective pseudocapacitance and broad current peak exhibited by GO in the LSV plots was related with the dominant adsorption of 'H_{ads}' during reduction of water. It has been considered that large overpotential and relatively higher current response exhibited by GO compared to graphene was associated with the preferential adsorption of H_{ads} in the presence of surface functional groups.

1. Introduction

Graphene and its related materials have unique physicochemical properties to support several electrochemical processes involving electro-catalysis [1], electrochemical sensing [2], supercapacitance [3] etc. It is well established that the heterogeneous electron transfer, required for these processes, from/to a graphene sheet takes place on the edges and is affected by the attached functional groups. The presence of functional groups also facilitates the adsorption/desorption of molecules on the graphene planes [4]. The production method for graphene greatly influences these properties. A lot of work is going on with graphene as core interest and its production is being reported continuously via various processes [5–7]. But the large-scale use of graphene is still hindered due to extensive and time-consuming production methods.

In this work, a relatively direct and efficient route is presented to produce graphene from graphite and the effect of surface functional groups on electrochemical properties has been investigated.

2. Experimental

Graphite powder (Asbury Carbon Inc.) was oxidized to graphite oxide (GO) using improved Hummer's method as explained in Ref. [8]. After the reaction, GO was dried overnight at 80 °C. To produce graphene, GO was ultra-sonicated in DI water for 12 h using Branson® M2800H ultrasonic bath operating at the frequency of 40 kHz. The powder from the suspension was obtained via centrifugation with a g-force of ~2285 using the Rotofix 32A Benchtop Centrifuge by Helmer® Scientific.

Infrared (IR) spectra of graphite, GO and graphene was acquired from FTIR-ATR spectrometer (NicoletTMiSTM 50) in Attenuated

* Corresponding author. School of Engineering and Technology, Central Michigan University, Mt. Pleasant, MI 48859, USA.
E-mail address: haide1w@cmich.edu (W. Haider).

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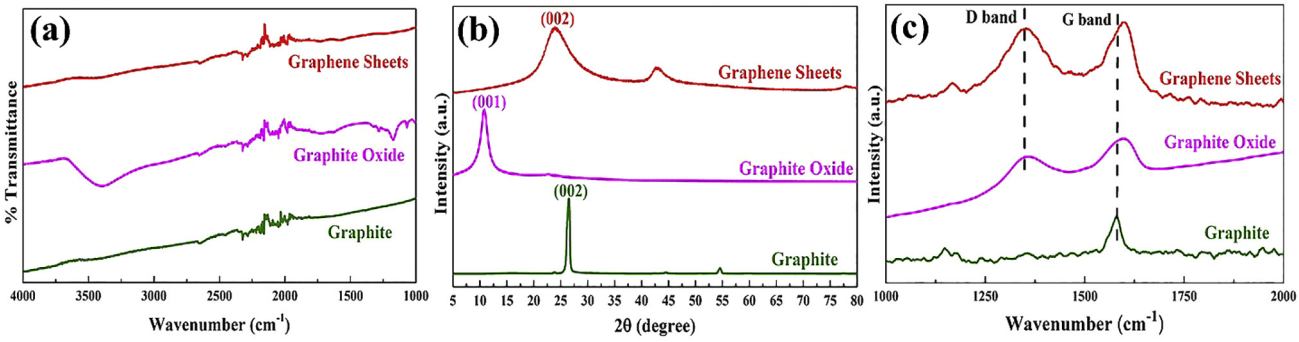

Fig. 1. IR (a), XRD (b), and Raman (c) trends of graphite, graphite oxide, and graphene.

Total Reflection (ATR) mode. X-ray diffraction (XRD) patterns (Rigaku Mini Flex II) were obtained by using Cu Kα (λ = 1.54 Å) radiation source. For Raman spectra, the laser beam excitation of 532 nm (Kaiser Optical Systems Inc.) was used. The XPS spectra (Thermo Scientific K-Alpha) of graphene were gathered by using Al Kα irradiation source. The morphology and structure of graphene sheets were observed in transmission electron microscope (TEM) (HT7700).

For electrochemical studies, the working electrodes were prepared by casting the paste made of an active material; GO and/or graphene (85 wt%), carbon black (5 wt%), binder; poly(-vinylidene fluoride) (10 wt%) and curing agent; 1-methyl-2-pyrrolidinone into the electrode cavity. The as-cast paste was cured overnight at room temperature before electrochemical investigations. Electrodes containing GO and graphene are termed as graphite oxide paste electrodes (GOPE) and graphene paste electrodes (GrPE), respectively in the following discussion. Electrochemical analyses of GOPE and GrPE were carried out by using Gamry-Potentiostat (R-3000) coupled with three-electrodes cell assembly in 0.5M KOH solution of pH 9.5 ± 0.5. GOPE/GrPE were working electrodes, saturated calomel electrode (SCE) was the reference, whereas, a platinum wire was used as a counter electrode. Nitrogen gas was sparged for 30 min before each test to eliminate the effect of dissolved oxygen. Electrochemical impedance spectroscopy (EIS) was done with 5 mV AC potential perturbation within 10 mHz–100 kHz frequency range at 0 V DC bias potential versus OCP. Linear sweep voltammetry (LSV) scans were obtained at sweep rates of 10, 5 and 2 mV/s in the reverse (cathodic) direction from 0 to −1.5 V vs. OCP.

3. Results and discussion

IR, XRD and Raman spectra of graphite, GO and graphene are shown in Fig. 1. Graphite exhibited an insensitive behavior in the infrared range (Fig. 1a). The transmittance peaks at 2325-1981 cm^{-1} could be associated with the diamond crystal used in ATR mode [9]. A broad peak at 3405 cm^{-1} presented by GO could be attributed to the -OH bond stretching vibrations belonging to C-OH and/or adsorbed moisture. Similarly, the peak at 1173 cm^{-1} could be related to the stretching of C-O bond [10]. Graphene demonstrated similar behavior as graphite in the IR range; no signatures for functional groups which could be removed during ultra-sonic cleavage of GO. The XRD patterns (Fig. 1b), represented the characteristic peak of graphite (2 <theta> = 26.5°) corresponding to (002) plane. This peak was shifted to lower 2 <theta> values of 10.8° and 23.9° in case of GO and graphene, respectively. In GO this corresponded to (001) plane which also suggests the successful oxidation of graphite [11]. Whilst for graphene the peak at 23.9° was related to the (002) plane of sp^2 hybridized carbon atoms [12]. The Raman spectra of graphite (Fig. 1c) showed a G band peak at 1579 cm^{-1} which was affiliated with the stretching vibrations of in-plane carbon atoms. In GO and graphene, the G band vibrations originated at relatively higher wavenumbers 1597 cm^{-1} and 1601 cm^{-1}, respectively, compared to graphite. Another band, known as D band, was also observed at 1359 cm^{-1} (GO) and 1352 cm^{-1} (graphene) which may be related with the defects or irregularities in the plane of carbon chains and/or may be due to the formation of grain boundaries [13]. XPS survey and high-resolution spectra of graphene are presented in Fig. 2a. All the peaks were

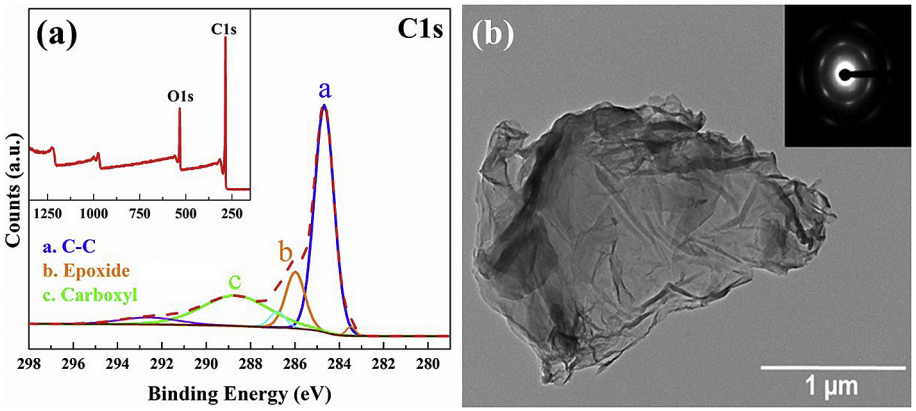

Fig. 2. XPS high-resolution (inset; survey) spectra (a) and TEM micrograph (inset; diffraction pattern) (b) of graphene.