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Defected graphene nano-platelets for enhanced hydrophilic nature and visible light-induced photoelectrochemical performances

Mohammad Ehtisham Khan[a], Mohammad Mansoob Khan[b,*], Moo Hwan Cho[a,*]

[a] School of Chemical Engineering, Yeungnam University, Gyeongsan-si, Gyeongbuk 38541, South Korea
[b] Chemical Sciences, Faculty of Science, Universiti Brunei Darussalam, Jalan Tungku Link, Gadong BE1410, Brunei Darussalam

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ABSTRACT

This paper reports an optimized electron beam irradiation (60 kGy and 90 kGy) approach for defects-related engineering of graphene nano-platelets for optical and structural properties dependent photoelectrochemical performances. The defects in the electron beam irradiated pristine graphene nano-platelets were studied, analyzed and confirmed using standard characterization techniques such as, diffuse reflectance spectroscopy (DRS), X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET), high resolution-transmission electron microscopy (HR-TEM) and contact angle measurements. DRS clearly revealed the increment in the absorption band using electron beam irradiation doses of 60 kGy and 90 kGy. Contact angle measurements confirm the additional hydrophilic nature of the defects engineered graphene nano-platelets in comparison with pristine graphene. The photoelectrochemical performances such as linear sweep voltammetry and electrochemical impedance spectroscopy further confirms the enhancement in the optical, spectroscopic, and photoelectrochemical properties of the 90 kGy defected graphene in comparison to pristine graphene nano-platelets. Therefore, the proposed method is a reliable way of fine-tuning the properties (optical, spectroscopic and photoelectrochemical) of pristine graphene nano-platelets using electron beam irradiation for enhanced photoelectrochemical performance.

1. Introduction

Graphene nano-platelets is a one-atom thin two-dimensional (2D) structure of carbon atoms that is highly conducting (~2.02 x 10^2 S cm^{-1}). In addition, it has an extremely high charge carrier mobility (200000 cm^2 V^{-1} s^{-1}), enormous specific surface area, high transparency, and great mechanical strength [1,2]. This substance is considered one of the most promising materials for the next generation of optoelectronic materials on account of its extremely high charge carrier mobility. On the other hand, graphene nano-platelets lack a suitable band gap around the Fermi level, which is a defining feature of semiconducting materials and essential for controlling the conductivity by electronic means [2,3]. Therefore, graphene nano-platelets are expected to be an ideal material for photo-electronic applications, energy storage and conversions [1–4]. The unique sheet like structure gives graphene a range of superior properties, such as high charge carrier transport and thermal conductivity [1,5,6] good transparency, great mechanical strength, inherent flexibility, and huge specific surface area (SSA) [7–9]. Therefore, graphene nano-platelets has attracted considerable attention in recent years in the fields of optoelectronics and micro/nanoelectronics devices [4,10,11] energy storage materials [9,12,13] electrocatalysts [14,15] polymer composites [16] and ultra-strong paper-like materials [17–20].

Up-to-date studies have shown that pristine (defect-free) graphene nano-platelets exhibit an ultra-high elastic modulus and unsurpassed strength [1,2]. Recently, it was reported that the electrical conductivity of pristine graphene nano-platelets can be modified by metal ion doping, adding impurities, noncovalent modifications, and chemical functionalization [21–23]. Pristine graphene nano-platelets have a Young's modulus of ~1 TPa and a tensile strength of more than 100 GPa [24,25]. Graphene nano-platelets and its composites are used for a range of potential applications, such as chemical sensors, ultra-capacitors, transparent electrodes, photovoltaic cells and biodevices [26–34]. On the other hand, the emergence of defects in the graphene nano-platelets lattice is inevitable either because of the production process or because of the environmental and operating conditions under which the graphene material based device operates [35–37]. Very few studies have shown that electron beam irradiation can be used for the synthesis of different metal nanoparticles and thin films of metal oxides with the desired properties [38,39]. This approach has

* Corresponding authors.
E-mail addresses: mmansoobkhan@yahoo.com (M.M. Khan), mhcho@ynu.ac.kr (M.H. Cho).

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several advantages over other methods as a defects engineer, such as an ability to interact effectively with the materials through coulomb interactions produced by charged particles, i.e., electrons [38–40].

Defects engineering in pristine graphene nano-platelets is performed not only to modify its properties, but also to extend its functionality by providing sites for chemical reactions, which involves the intentional self-doping at specific points [1,41–43]. If a large number of atoms are missing from the pristine graphene nano-platelets lattice, the defect configurations could become more complicated, and the graphene nano-platelets could be energetically unstable. If the number of missing atoms is even, the carbon atoms could be reconstructed completely, leaving no dangling bonds. In contrast, if an odd number of atoms are missing, there will be dangling bonds that make the graphene more unstable and provide reactive sites [44]. These dangling bonds in the graphene nano-platelets layers could be useful sites for doping with impurities or functionalizing them with different atoms or molecules for other types of graphene nano-platelets based applications. Defective graphene nano-platelets are also used in nanoelectronic applications for opening a band gap [45]. Band gap opening can be interpreted in terms of either the hybridization of the electronic state at the K and K' points in the Brillion zone or symmetry breaking of the A and B sublattices by external or internal perturbation [46]. Given that defects are ubiquitous in the operational environment of graphene nano-platelets based devices, it is important to understand how the defects in graphene nano-platelets affect its elastic properties and intrinsic strength. Several studies have revealed the formation and structural evolution of defects in graphene using both experimental and theoretical tools [47–49]. On the experimental side, however, few studies have examined how the density and type of defects affect the mechanical properties of graphene using an electron beam as a defects engineer [48,49]. Therefore, it is important from a fundamental standpoint and for practical applications to understand how the optoelectronic properties of graphene nano-platelets can be influenced by defects formed by electron beam irradiation. The contact angle measurement could be an effective technique to check the hydrophobic/hydrophilic nature of pristine graphene nano-platelets or graphene related material [22]. The interaction of pristine graphene nano-platelets with aqueous solution of salts strongly depends on the wetting properties of graphene nano-platelets. Pristine graphene has already been recognized as a hydrophobic material [50]. However, quantitative knowledge of its wetting properties is still missing. Therefore, the specific standard characterization of these properties is of crucial importance and became a topic of investigation recently [22,50]. Electron beam irradiation offers the possibility to improve the aqueous dispersibility of pristine graphene nano-platelets, which means an improvement in hydrophilicity.

In this study, according to the author's knowledge, this is the first report of the use of an electron beam technique at optimum doses like, 60 kGy and 90 kGy to produce defects in pristine graphene nano-platelets in an aqueous dispersion in a controlled manner. For example, devices made from a zero band gap material are difficult to switch off, losing the advantage of the slow static power consumption of complementary metal oxide semiconductor (CMOS) technology [51]. Therefore, maintaining sizeable and well-tuned optical properties in pristine graphene is a significant challenge for graphene-based electronic devices, in which introducing defects have shown great potential [52]. Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and high resolution-transmission electron microscopy (HR-TEM) were used to characterize and understand the defects. In addition, X-ray diffraction (XRD) was used to examine the structural changes and the Brunauer-Emmett-Teller (BET) method was used for pore size and surface area analysis. The electron transfer mechanism was tested and confirmed by photoelectrochemical performances, such as linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). The results suggested that the graphene layers with defects are more rugged and structurally robust than the pristine graphene layers, suggesting that they are a promising material for use in the future generation of optoelectronic devices.

2. Experimental section

2.1. Materials

Pristine graphene nano-platelets were purchased from Iljin Nano Tech, Seoul, Korea (7–8 layers graphene with mean length of 500 nm). Ethanol (C_2H_5OH) was acquired from J. T. Baker. Sodium sulfate (Na_2SO_4) was supplied by Duksan Pure Chemicals Co. Ltd., South Korea. Ethyl cellulose and α-terpineol were obtained from KANTO Chemical Co. Fluorine-doped transparent conducting oxide glass (FTO; F-doped SnO_2 glass; 7 Ω/sq) was purchased from Pilkington. The above mentioned reagents used in this study were of analytical grade and used as received. All solutions were prepared from DI water obtained using a PURE ROUP 30 water purification system.

2.2. Methods

An electron beam accelerator (ELV-0.5, BINP, Russia) with a maximum beam power, maximum beam current, and maximum beam energy of 28 kW, 40 mA, and ~0.7 MeV, respectively, was used to modify the pristine graphene. The UV–Vis diffuse reflectance spectra (DRS) of the powdered samples were obtained using a UV–vis–NIR double beam spectrophotometer (VARIAN, Cary 5000, U.S.A.) equipped with a diffuse reflectance accessory. XRD (PANalytical X'pert PRO-MPD, The Netherlands) was performed using Cu Kα radiation (λ=0.15405 nm). Raman spectroscopy was performed on a HR800 UV Raman microscope (Horiba Jobin-Yvon, France). XPS (ESCALAB 250 XPS System, Thermo Fisher Scientific U.K.) was conducted using the following X-ray source: monochromated Al Kα, hν =1486.6 eV, X-ray energy: 15 kV, 150 W and spot size: 500 μm at KBSI. The microstructures of the samples were measured by HRTEM (JEM- 2100 JEOL) at an operating voltage of 200 kV. Selected-area electron diffraction (SAED) images were recorded by HRTEM. The BET specific surface area of the samples was measured using a Belsorp II-mini (BEL, Japan Inc.). The contact angles were measured using a video based contact angle device, OCA-20 (Dataphysics, Germany).

The photoelectrochemical measurements, such as LSV (photocurrent) and EIS (impedance) were conducted using a 400 W lamp with an intensity of 31 mW/cm^2 (3 M, λ > 420 nm, USA). The LSV and EIS measurements were performed using a potentiostat (Versa STAT 3, Princeton Research, USA) comprising of a standard three-electrode system. Ag/AgCl (3 M KCl), a Pt gauge and FTO glass coated with pristine graphene, 60 kGy-graphene and 90 kGy-graphene, were used as the reference, counter and working photoelectrodes, respectively. The experiment was performed in a 0.2 M Na_2SO_4 solution as the electrolyte at room temperature. The projection area of the photoelectrode was 1 cm^2. The working electrodes for CV were prepared as follows: 50 mg of each sample was mixed thoroughly by adding 0.05 g ethyl cellulose as a binder and 0.05 g of α-terpineol as the solvent for preparing a paste. The obtained paste was then coated on carbon paper using the doctor-blade method and dried overnight under a 60 W lamp. The resulting electrode was used as a photoelectrode.

2.3. Defects engineering in pristine graphene nano-platelets using electron beam irradiation

Pristine graphene nano-platelets was modified using an electron beam accelerator in integral mode with electron beam energy of 0.7 MeV and an initial electron beam current of 2 mA/sec in DI water at room temperature and atmospheric pressure. Two 75 mL aqueous dispersions of pristine graphene nano-platelets (0.25g) were prepared using a low sonication system (Branson 2800, low power sonication instrument). The initial pH of the aqueous dispersions was 7.61. The