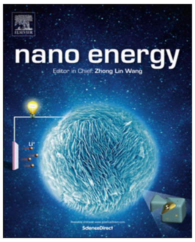
Nano Energy (2015) 13, 336–345

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy



RAPID COMMUNICATION

High-performance dye-sensitized solar cells using edge-halogenated graphene nanoplatelets as counter electrodes

In-Yup Jeon[d,1], Hong Mo Kim[a,1], In Taek Choi[a,1], Kimin Lim[b], Jaejung Ko[b], Jae Cheon Kim[c], Hyun-Jung Choi[d], Myung Jong Ju[a,*], Jae-Joon Lee[c,*], Hwan Kyu Kim[a,*], Jong-Beom Baek[d,*]

[a]*Global GET-Future Lab., Department of Advanced Materials Chemistry, Korea University, 2511 Sejong-ro, Sejong 339-700, South Korea*
[b]*Department of Advanced Materials Chemistry, Korea University, 2511 Sejong-ro, Sejong 339-700, South Korea*
[c]*Nanotechnology Research Center, Department of Applied Life Science, College of Biomedical and Health Science, Konkuk University, Chungju 380-701, South Korea*
[d]*School of Energy Engineering/Low-Dimensional Carbon Materials Center, Ulsan National Institute of Science and Technology (UNIST), 100 Banyeon, Ulsan 689-798, South Korea*

Received 13 October 2014; received in revised form 20 November 2014; accepted 27 February 2015
Available online 9 March 2015

KEYWORDS
Ball-milling;
Halogenations;
Graphene nanoplatelets;
Dye-sensitized solar cells;
Counter electrode

Abstract

Edge-selectively halogenated graphene nanoplatelets (XGnPs, X=Cl, Br, and I) were prepared by the mechanochemically driven reaction between graphite and diatomic halogen molecules (Cl_2, Br_2 or I_2). The contents of halogens (Cl, Br, and I) in XGnPs were 3.18, 1.77, and 0.66 at%, respectively, by X-ray photoelectron spectroscopy. The XGnPs as counter electrodes (CEs) showed remarkably enhanced electrocatalytic activities toward $Co(bpy)_3^{3+}$ reduction reaction in dye-sensitized solar cells (DSSCs) with an excellent electrochemical stability. Amongst XGnPs, IGnP-CE demonstrated the lowest charge-transfer resistance (R_{ct}) of 0.46 Ω cm^2 at the CE/electrolyte interface. This value is much lower than that of Pt-CE (0.81 Ω cm^2). In addition, the DSSC with IGnP-CE had the highest fill factor (71.3%) and cell efficiency (10.31%), whereas those of DSSCs with Pt-CE were only 70.6% and 9.92%, respectively.

---

*Corresponding authors.
E-mail addresses: jmj12@korea.ac.kr (M.J. Ju), jjlee@kku.ac.kr (J.-J. Lee), hkk777@korea.ac.kr (H.K. Kim), jbbaek@unist.ac.kr (J.-B. Baek).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.nanoen.2015.02.037
2211-2855/

Introduction

Photovoltaic technology has been realized as a suitable means of generating electrical power by converting solar energy into direct current electricity for the fulfillment of the increasing demand for energy consumption with the least impact on the environment. Since it was first developed by O'Regan and Grätzel, the dye-sensitized solar cell (DSSC) has been developed into a powerful photovoltaic technology because of its high efficiency and simple fabrication process [1,2]. Its record high power conversion efficiency (PCE) is 13.1% after two decades of concentrated efforts [3]. However, this emerging photovoltaic technology seems to be always associated with unsatisfactory problems for practical use. For example, a platinum (Pt) catalyst is still the most efficient and widely used counter electrode (CE) in DSSCs. Obviously, this high-cost metallic Pt and its poor electrochemical stability is a common pitfall for commercial production of DSSCs. Therefore, it is essential to search for non-precious metal and/or metal-free electrocatalysts with a high catalytic activity and long-term electrochemical stability for practical use of DSSCs. Since Kay and Grätzel first reported a DSSC employing a carbon black/graphite composite CE instead of Pt and obtained a promising PCE of 6.7% [4], there have been extensive efforts towards the development of metal-free CEs in energy conversion devices using heteroatom-doped carbon-based materials, e.g., boron (B) [5,6], nitrogen (N) [7-11], phosphorus (P) [12,13], sulfur (S) [14] and their co-doping [15].

Graphene, one of carbon-based allotropes consisting of a single-layer sp^2 carbon with a two-dimensional honeycomb lattice structure, has demonstrated many interesting properties, including superb electrical conductivity and structural stability. In this regard, defect-free graphene is hardly suitable as the CEs in DSSCs; therefore, it is important to develop heteroatom-doped graphene-based CEs to balance electrical conductivity for efficient charge transfer and charge polarization for enhanced reduction activity of redox couples simultaneously [16]. However, the neutral polarity of graphene often restricts efficient charge transfer at the graphene/liquid interface, despite the high in-plane charge mobility [17]. Thus, edge-selective heteroatom doping of graphene is quite challenging to impart both efficient in-plane charge transfer and to improve polarity, and hence to enhance electrocatalytic activity [18]. Furthermore, quantum mechanics calculations revealed that the electron accepting/donating ability of heteroatom-doped graphene creates net positive/negative charges on adjacent carbon atoms in the graphitic lattice to efficiently facilitate reduction catalytic activity [19]. Therefore, edge-selective heteroatom-doping of the graphitic framework could be a pivotal factor for the overall enhancement of electrocatalytic activity. In this regard, we prepared edge-selectively halogenated graphene nanoplatelets (collectively designated as XGnPs, X=Cl, Br and I) by a simple yet efficient mechanochemically driven reaction between graphite and diatomic halogen molecules (Cl_2, Br_2 or I_2) and tested them as potential alternatives to precious Pt CE [20].

Experimental section

Materials

Graphite was obtained from Alfa Aesar (Natural, −100 mesh, 99.9995% metals basis, 14735) and used as received. chlorine (Cl_2), bromine (Br_2) and iodine (I_2) were purchased from Aldrich Chemical Inc. and used as received. All other solvents were supplied by Aldrich Chemical Inc. and used without further purification, unless otherwise specified.

Synthesis of XGnPs

In a typical experiment, pristine graphite (5.0 g) was placed with a reactant, such as chlorine (Cl_2, 1.2 bar), bromine (Br_2, 20 g), and iodine (I_2, 20 g) in a stainless steel capsule containing stainless steel balls (500 g, diameter 5 mm). The capsule was sealed and degassed after application of reduced pressure (0.05 mmHg) to remove air and then fixed in a planetary ball-mill machine and agitated at 500 rpm for 48 h. The resultant products were Soxhlet extracted with acetone to get rid of unreactive materials and washed with 1 M aq. HCl solution to remove metallic impurities, if any. The final products were then freeze-dried for 48 h to yield a dark black powder of ClGnPs (5.93 g), BrGnPs (6.59 g), and IGnPs (6.65 g).

Instrumentations

Elemental analysis (EA) was conducted with a Thermo Scientific Flash 2000. The surface area was measured by nitrogen adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) method on a Micromeritics ASAP 2504N. Field emission scanning electron microscopy (FE-SEM) was performed on an FEI Nanonova 230 while high-resolution transmission electron microscopy (HR-TEM) was carried out on a JEOL JEM-2100F (Cs) microscope operating at 200 kV. TEM specimens were prepared by dipping carbon micro-grids (Ted Pella Inc., 200-mesh copper grid) into well-dispersed samples in ethanol. X-ray photoelectron spectra (XPS) were recorded on a Thermo Fisher K-alpha XPS spectrometer. X-Ray diffraction (XRD) patterns were recorded with a Rigaku D/MAZX 2500 V/PC with Cu-Kα radiation (35 kV, 20 mA, λ=1.5418 Å). Micro-Raman measurements were made with a WiTec Alpha300S system with 532 nm wavelength laser light and a 50 × objective.

Results and discussion

As schematically shown in Figure 1, pristine graphite can be easily edge-selectively halogenated and exfoliated by mechanochemical ball-milling. For a mechanochemical reaction to take place, high-speed traveling stainless steel balls must deliver enough kinetic energy to the graphitic frameworks to cause unzipping of graphitic C–C bonds. As a result, the generated active carbon species (mostly carboradicals) react with halogens to produce edge-halogenated graphene nanoplatelets (XGnPs).

Scanning electron microscopy (SEM) images demonstrate obvious grain-size reduction of XGnPs (Figure 2a-c)