



Characteristics of thermally reduced graphene oxide and applied for dye-sensitized solar cell counter electrode



Ching-Yuan Ho^{a,b,*}, Hong-Wen Wang^{b,c}

^a Department of Mechanical Engineering, Chung Yuan Christian University, Chung-Li, Taiwan

^b Department of Chemistry, Center for Nanotechnology and Institute of Biomedical Technology, Chung Yuan Christian University, Chung-Li, Taiwan

^c Department of Chemistry, Chung Yuan Christian University, Chung-Li, Taiwan

ARTICLE INFO

Article history:

Received 3 July 2015

Received in revised form 21 August 2015

Accepted 1 September 2015

Available online 3 September 2015

Keywords:

Graphene oxide

Dye sensitized solar cell

Thermal reduction

Raman and infrared spectra

Electrochemical impedance spectra

ABSTRACT

Graphene oxide (GO) was synthesized from a flake-type of graphite powder, which was then reduced to a few layers of graphene sheets using the thermal reduction method. The surface morphology, phase crystallization, and defect states of the reduced graphene were determined from an electron microscope equipped with an energy dispersion spectrometer, X-ray diffraction, Raman spectroscopy, and infrared spectra. After graphene formation, the intercalated defects that existed in the GO were removed, and it became crystalline by observing impurity changes and d-spacing. Dye-sensitized solar cells, using reduced graphene as the counter electrode, were fabricated to evaluate the electrolyte activity and charge transport performance. The electrochemical impedance spectra showed that increasing the thermal reduction temperature could achieve faster electron transport and longer electron lifetime, and result in an energy conversion efficiency of approximately 3.4%. Compared to the Pt counter electrode, the low cost of the thermal reduction method suggests that graphene will enjoy a wide range of potential applications in the field of electronic devices.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Since 2004 when Andre Geim and Konstantin Novoselov successfully synthesized the two-dimensional material, graphene, many researches have attracted much attention to its versatile properties and potential use in synthesis, physical/chemical analysis and electrical application. Generally, a two-dimensional (2D) graphene (GP) structure consists of hybridized bonding of in-plane sp² bonds and π electrons [1], which play a critical role in determining the unique features of GP, such as high electron mobility [2,3], a high heat transfer coefficient, and better tribological properties [4]. Because synthesizing a single layer of GP is challenging, approaches for synthesizing fewer GP layers have been devised using methods such as solvation-assisted exfoliation of graphite [5], chemical vapor deposition (CVD) [6], chemical reduction, and thermal reduction [7]. Among these approaches, the CVD growth method can provide high-quality GP through complete decomposition of ethylene or methane precursors at a high temperature; however, cost-efficiency and environmental concerns of this approach are major issues. In contrast, a low-cost method involving

thermally reducing graphene oxide (GO) has attracted considerable attention in various experimental fields, such as photovoltaic cells, sensors, and electrode applications, despite the resultant GP properties being less favorable than those obtained through CVD. Generally, there are many intercalated impurities, which include moisture and oxide groups, such as carboxyl and hydroxyl groups, embedded in the GP material that must be removed through thermal energy reduction processes prior to the industrial use of the GP material. Therefore, various thermal reduction conditions for GO have been investigated in detail.

Graetzel et al. (1985) presented the sensitization of a polycrystalline TiO₂ (anatase phase) electrode by using a Ru-bipyridine complex; the mechanism of dye sensitized solar cells (DSSCs) has been the subject of substantial academic and technological research over the subsequent three decades. The basic DSSC's structure is composed of three principal parts: dye adhered to nanocrystalline TiO₂ photoanode, an electrolyte solution with a redox mediator, and a Pt counter cathode. The low cost and acceptable energy conversion efficiency of DSSCs allow them to compete with Si-based photovoltaics. However, expensive Pt is used in all DSSC cathodes; thus, there is a motivation to eliminate Pt to reduce the device's cost. Recently, carbon materials, including graphite, amorphous carbon, nano- and microcarbon, and carbon nanotubes, have been considered candidates as counter electrodes for DSSCs [8,9].

* Corresponding author at: 200, Chung Pei Rd., Chung-Li 32023, Taiwan.
E-mail address: cyho@cycu.edu.tw (C.-Y. Ho).

Ladislav et al. measured the electrocatalytic activity of a carbon-based cathode and mass transport in an electrolyte solution by using the electrochemical impedance spectra (EIS). Many carbon-based electrodes exhibited catalytic activity and long-term stability comparable with those of Pt [10]. Among these carbon-based electrodes, GP materials are widely used because of their low charge transfer resistance, high surface-to-volume ratio, high chemical resistance, high carrier mobility, and high catalytic activity [11,12]. However, impurities existed at the synthesized GP base, influencing the material's properties, reducing the mass transport of the mediator in the electrolyte, and ultimately affecting the overall energy conversion efficiency of the DSSCs. Adarsh et al. evaluated various GP-based materials used as counter electrodes in DSSCs, and the thermally exfoliated graphite oxide/fluorine-doped tin oxide (FTO) exhibited an efficiency of approximately 2.8% [13]. In addition, pasting GP on transparent conducting oxide (TCO) films requires heat treatment, and peeling between the GP coating and the TCO film interface inevitably occurs during high-temperature thermal treatment. Therefore, employing high-temperature thermal reduction of GO entails a tradeoff between the quality of the GP material and the extent of GP peeling on the TCO substrate. Currently, achieving low cost, high chemical resistance, and electrical conductivity associated with the high electrocatalytic activity of GP applied as a counter electrode in DSSCs is a major objective.

A modified version of Hummers' chemical oxidation was used for oxidizing graphite to GO in this study. The thermal reduction process was used to produce GP by reducing the GO. The characteristics of GP produced through thermal reduction are extensively discussed in this paper. The reduction of GO, intercalated defect removal, and phase crystallization were analyzed. Moreover, to determine the electrical characteristics and catalytic activity, GP produced through low-temperature thermal reduction served as a counter electrode in the DSSC that was fabricated, and the EIS and photovoltaic characteristics of the DSSC were measured. We demonstrated that the considerably simplified method of low-temperature thermal reduction of GO was feasible for producing GP that is appropriate for use as a DSSC counter electrode. This GP exhibits higher energy conversion efficiency than that of graphite.

2. Experimental details

Flake type of graphite (Alfa, 99.9%, 7–10 μm) was used to form the graphene oxide (GO) and subsequently synthesized to create a few layers of graphene by lower thermal reduction method in N_2 ambient. 1 g of graphite, 0.75 g of Na_2SO_4 mixed with 30 mL of concentrated H_2SO_4 was placed into the flask and ice cooling for 30 min. Subsequently, 2.25 g of KMnO_4 (99%) added into the ice cold solution was stirred for 30 min and then reacted at room temperature for 48 h. Deionized water was added for an additional half hour and then a 30 mL of H_2O_2 (35%) was added and stirred for another 1 h to wash the GO residuals. The residuals were then collected using centrifugation and re-washed again. The synthesized GO was freeze-dried at -47.7°C under pressure of 69.3 Pa for 2 days. Subsequently, the freeze-dried GO materials were then dispersed into mixed solvent of ethanol/DI water (1:1) with concentration of 0.1 g/mL for one day to form GO paste. Second step contained the thermal reduction of GO under a flow of laminar N_2 gas (99.999%) was divided into three groups for graphene sheet formation which were denoted as tGP. Three groups of GO paste coated on FTO were put into furnace at different temperature conditions (150°C , 300°C and 450°C) to reduced GO and formed graphene films (tGP), respectively. These thermal reduction graphene are denoted as tGP₁₅₀, tGP₃₀₀ and tGP₄₅₀, respectively. Material characteristics of these graphene films synthesized via reduced GO methods will be

investigated, subsequently applying to counter electrode for dye-sensitized solar and comparing the catalytic activity.

Prior to the DSSC assembling, FTO conductive glasses were cleaned in an acetone and isopropyl alcohol mixture in an ultrasonic water bath for 1 h to remove contaminants and then dried under N_2 . TiO_2 colloidal solution was prepared by adding 3 mL of acetic acid and distilled water (v/v = 1/1) mixture solution to 0.5 g of P25 powder (Degussa-P25) and 0.15 g of polyethylene glycol (PEG). The purpose of PEG is to create porous TiO_2 anode for dye contact improvement. The 14 μm thickness of synthesized TiO_2 colloidal solution photoanodes was prepared by layer-by-layer coating on the FTO glass and annealed at 450°C for 30 min in air atmosphere. An active area of $0.5\text{ cm} \times 0.5\text{ cm}$ TiO_2 photoanode was immersed in a $3.0 \times 10^{-3}\text{ M}$ solution of the ruthenium based dye $[\text{RuL}_2(\text{NCS})_2]\text{TBA}_2$, where Ru is ruthenium, L stands for 2,2-bipyridyl-4,4-dicarboxylic acid, NCS represents isothiocyanate and TBA is tetra-n-butylammonium (N719 dye, Everlight Chemical, Taiwan) for overnight. The specimens were washed with ethanol after immersing in N719 dye solution. The iodide/triiodide (I^-/I_3^-) electrolyte (Iodolyte R-150) was cast onto the dye absorbed TiO_2 electrodes. The colloidal graphene was coated on ITO substrate using screen printer (YULISHIH Industrial, nimble screen printer, NSP-1t) to retain same thickness. The TiO_2 electrode and counter electrodes coating different thermally reduced graphene films were clamped together in order to assemble the DSSC devices. Besides, the Pt on FTO glass was applied for counterpart.

The surface morphologies and oxygen/carbon elements were characterized by field emission scanning electron microscopy (FESEM, FEI QUANTA) equipped with EDS (energy dispersion spectrometer). For TEM measurements, the graphene powder was dispersed in absolute ethanol using mild ultrasonication and casted onto carbon coated Cu grids (SPI supplies) transmission electron microscopy (TEM) was carried out using a DELONG instrument LVEM5 (Low Voltage Electron Microscopy) at an accelerating voltage of 50 kV. Surface roughness of various reduced tGP specimens was observed via atomic force microscope (AFM) with a SEIKO SPA 400 in the tapping mode. The crystalline phases of the obtained graphene electrodes were analyzed by X-ray diffraction (XRD, PANalytical X'Pert PRO). The excitation source of Nd:YAG laser (532 nm) was carried out using WITec alpha 300 Confocal Raman system for Raman spectra measurement. The minimum intensity was kept to avoid laser induced heating and defects. The impurities embedded in graphene was confirmed via a Perkin Elmer Fourier transform infrared spectroscopy (FTIR) spectrometer in the range $500\text{--}4000\text{ cm}^{-1}$. Electrochemical impedance spectra (EIS) and photovoltaic characteristics were measured from an illuminated area of $0.5\text{ cm} \times 0.5\text{ cm}$ by an electrochemical analyzer (CHI C611B, CH Instruments Co., USA) under a standard AM 1.5 sunlight illumination (XES-151S, San-Ei, Japan) with 100 mW/cm^2 light source. The electrochemical impedance spectra (EIS) were also measured in the range of 0.01 Hz to 100 kHz and at a potential pulse magnitude of 10 mV. Incident photon-to-current conversion efficiency (IPCE) of the N719 adsorbed TiO_2 photoelectrode was measured with the monochromatic excitation from xenon arc lamp using a setup from PV Measurements, Inc Boulder, Colorado.

3. Results and discussion

Fig. 1(a)–(c) depicts the experimental process involving graphene oxide formation by impurity intercalation and graphene synthesis by the removal of impurities. The former includes graphite oxidation using Hummers' method and the latter adopts the thermal reduction method to form two-dimensional graphene sheets. The morphological types of graphene sheets, including wrinkling, fluffiness, and disorder, are strongly associated with the

Download English Version:

<https://daneshyari.com/en/article/5348311>

Download Persian Version:

<https://daneshyari.com/article/5348311>

[Daneshyari.com](https://daneshyari.com)