



Investigation of low thermal reduction of graphene oxide for dye-sensitized solar cell counter electrode



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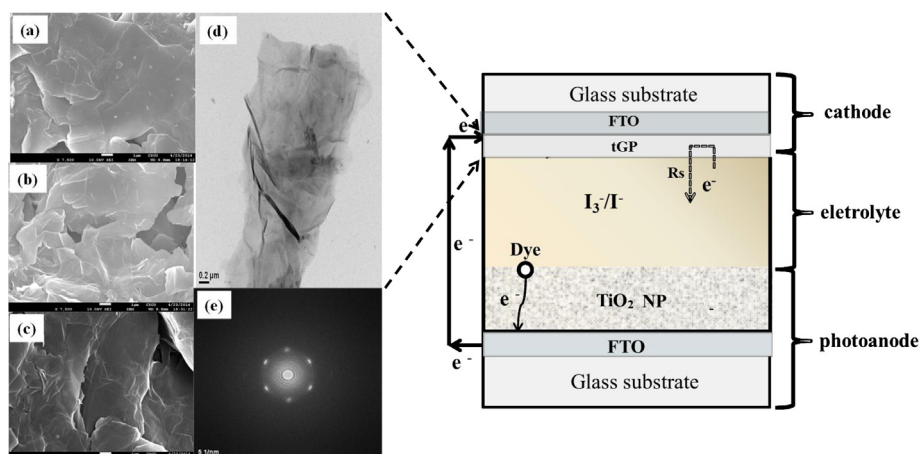
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HIGHLIGHTS

- Intercalated defects were eliminated by increasing reduction temperature of GO.
- High reduction temperature tGP has lower resistance and higher electron lifetime.
- cGP is amorphous due to substitutional Ti^{+} ions disrupted the graphene order.
- Dye-sensitized solar cell with the synthesized graphene as the counter electrode.
- High reduction temperature has an energy conversion efficiency of 3.22%.

GRAPHICAL ABSTRACT

(a) FESEM image of GO, (b) FESEM images of tGP150 and (c) tGP450, (d) TEM image of tGP450 shows folding and overlapping in grapheme sheet, and (e) SAED pattern indicating long range ordering in tGP450.



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ABSTRACT

Flake-type graphite was used for synthesizing graphene oxide (GO), which was then reduced to a few layers of graphene sheets by using a chemical or thermal reduction method. The surface morphology, phase crystallization, and defect states of the reduced graphene were determined using electron microscopy and X-ray diffraction and by using Raman and infrared spectra. Dye-sensitized solar cells with the synthesized graphene as the counter electrode were fabricated to evaluate the electrolyte activity and charge transport performance. Intercalated defects that are generally formed during the thermal reduction of GO were eliminated by increasing the reduction temperature. Furthermore, the product of the chemical reduction of GO was in the amorphous phase because substitutional Ti^{+} ions disrupted the graphene order. Electrochemical impedance spectra showed that increasing the thermal reduction temperature could yield thermally reduced GO with a lower charge transfer resistance, increase the electron lifetime, and result in an energy conversion efficiency of approximately 3.2%.

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1. Introduction

A two-dimensional (2D) graphene (GP) structure shows hybridized bonding of in-plane sp^2 bonds and consists of Π electrons, which not only suggest the coupling of several layers of GP but also play a critical role in determining the unique features of GP, such as high electron mobility, a high thermal transfer coefficient, and high mechanical strength. Because synthesizing a single layer of GP is challenging, approaches for synthesizing GP focus on using exfoliated GP consisting of a few layers (two or three, or even up to 10). Such GP has been produced using methods such as chemical vapor deposition (CVD) [1], solvation-assisted exfoliation of graphite [2], “top-down” physical exfoliation [3], thermally exfoliating reduction [4], and thermal reduction [5]. CVD can provide high-quality GP through complete decomposition of ethylene or methane precursors at a high temperature; however, the cost and environmental effect of this approach are major concerns. Because of its low cost, a method that involves 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. Because intercalated impurities, which include moisture and oxide groups such as carboxyl and hydroxyl groups, embedded in the GP material must be removed through thermal energy reduction processes prior to the industrial use of the GP material, various thermal reduction conditions for GO should be investigated in detail. It is also necessary to devise an economical method for chemically reducing GO sheets in the solution phase by using a strong chemical base [6].

Graetzel et al. first presented the sensitization of a polycrystalline TiO_2 (anatase phase) electrode by using a Ru-bipyridine complex in 1985, and the mechanism of dye sensitized solar cells (DSSCs) was the subject of substantial academic and technological research over the subsequent two decades. The basic structure of dye DSSCs consists of three principal components: a nanocrystalline TiO_2 photoanode, an electrolyte solution with a redox mediator, and a cathode (counter electrode). The low cost and acceptable energy conversion efficiency of DSSCs have prompted them to rival Si-based photovoltaics. However, expensive Pt is used in all DSSC cathodes; thus, there is a motivation to eliminate Pt to reduce the device cost. Recently, carbon materials including graphite, amorphous carbon, nano- and microcarbon, and carbon nanotubes have been considered candidate counter electrodes for DSSCs [7–10]. Ladislav et al. measured the electrocatalytic activity of a carbon-based cathode and mass transport in an electrolyte solution by using electrochemical impedance spectra (EIS). Many carbon-based electrodes exhibited catalytic activity and long-term stability comparable with those of Pt [11]. Among these 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 [12–14]. However, impurities existed at the synthesized GP base, influencing the material properties, reducing the mass transport of the mediator in the electrolyte, and, ultimately, affecting the overall energy conversion efficiency of DSSCs. Adarsh et al. evaluated various GP-based materials used as counter electrodes in DSSCs, and thermally exfoliated graphite oxide/fluorine-doped tin oxide (FTO) exhibited an efficiency of approximately 2.8% [15]. 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 extent of GP peeling on the TCO substrate. Currently, achieving the 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.

In this study, a modified version of Hummers’ chemical oxidation was used for oxidizing graphite to GO. Subsequently, two approaches – thermal reduction and the chemical Ti^{3+} ion reduction process – were used to produce GP by reducing GO [16,17]. The characteristics of GP produced through thermal and chemical reduction of GO are discussed extensively in this paper. The reduction of GO, intercalated defect removal, phase crystallization, and lattice contraction were analyzed. Moreover, to determine the electrical characteristics and catalytic activity, GP produced through low-temperature thermal reduction served as a counter electrode in a DSSC that was fabricated in this study, 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

A few layers of graphene was synthesized by reduction of graphene oxide (GO) using the modified Hummers’ method. First, natural flake type of graphite (Alfa, 99.9%, 7–10 μm) was employed to synthesize the graphene oxide (GO). 1 g of graphite, 0.75 g of Na_2SO_4 and 30 mL of concentrated H_2SO_4 were mixed in the flask and ice cooling for 30 min. Following, 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. 300 mL of deionized water was added for an additional 30 min 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 collected GO was freeze-dried at $-47.7^\circ C$ under vacuum 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 reduction of GO which was divided into four groups for graphene sheet formation. First group is chemically reduced GO, the GO paste was coated on polyimide tape above fluorine doped tin oxide (FTO) conducted glass, following a drying process at $80^\circ C$. The resultant film/PI was immersed in $TiCl_3$ aqueous solution at $120^\circ C$ for 30 min. In this solution, the GO film was reduced to a graphene film, washing by DI water three times and represented as cGP [17]. Others were thermal reduction of GO sheet and represented as tGP. After coating GO paste on FTO conducted glass, each sample was put into furnace at different temperature conditions ($150^\circ C$, $300^\circ C$ and $450^\circ C$) to reduced GO and formed graphene films (tGP). All thermal reduction graphene are denoted as tGP₁₅₀, tGP₃₀₀ and tGP₄₅₀, respectively. Characteristics of these graphene films synthesized by both reduced GO methods will be investigated, subsequently applying to counter electrode for dye-sensitized solar and comparing the catalytic activity.

FTO conductive glasses were cleaned in an acetone and isopropyl alcohol mixture ($v/v = 1/1$) in an ultrasonic water bath for 30 min. 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 mixture was ultrasonicated for 3 h to form the TiO_2 colloidal solution. The photoanode were prepared by layer-by-layer coating of synthesized TiO_2 colloidal solution on the FTO glass and annealed at $450^\circ C$ for 30 min in air atmosphere. Thickness of TiO_2 photoanode is 14 μm . An adhesive tape was used to control the thickness of the thin layer to make it identical for all the samples. An active area of 0.5 cm \times 0.5 cm TiO_2 photoanode was immersed in a 3.0×10^{-3} M solution of the ruthenium based dye $[RuL_2(NCS)_2]TBA_2$, where

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