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Study of graphene nanoflake as counter electrode in dye sensitized solar cells

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ABSTRACT

Graphene nanoflake (GNF) films have been fabricated on a fluorine doped tin oxide (FTO) glass using a doctor blade method and thermally annealed in air and argon ambient at various temperatures. The GNF/FTO thin films were employed as a counter electrode for dye sensitized solar cells (DSSCs). Results showed the GNF/FTO film could enhance the power conversion efficiency (PCE) of DSSC devices more effectively when annealed in argon ambient rather than in air and at annealing temperatures higher than 380 °C. The PCE enhancement was mainly due to the lowered oxygen concentration in the film and the elevated electrical conductance. A PCE of 6.08% or 88% of that with a Pt counter electrode has been achieved for DSSCs with a GNF counter electrode, suggesting that GNF is a highly potential candidate to replace Pt catalyst.

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1. Introduction

Graphene has excellent electrical and physical properties such as extremely low electrical resistivity [1], high thermal conductivity [2,3] and high optical transparency to visible light [4]. In addition, its unique chemical properties have attracted many interests. For instance, the high active surface area [5] allows graphene to apply for secondary batteries or super-capacitors. Its superior catalytic properties are also advantages for being an electrode in the fields of fuel cells [6] and electrochemical dye-sensitized solar cells (DSSC) [7–10].

Indeed, the excellent physical and chemical properties of graphene have attracted a great number of researchers to investigate its electrochemical mechanism for being an anode or cathode material. One of high interests is to replace the platinum (Pt) cathode in a dye-sensitized solar cell. Studies have shown that the power conversion efficiency (PCE) of DSSC with graphene cathode varies widely from 0.74% to 9.05% depending on its structures and processing conditions [10,11], and nitrogen-doped graphene nano-platelets appeared to be the most efficient counter electrode (CE) in regard to electron transfer ability and electrocatalytic activity in $Co(bpy)_3^{3+/2+}$ redox couple [12]. However, as the catalytic effect occurs only on the active sites of graphene [10,11], a perfect and large area of graphene sheets may not provide enough active sites for being a catalyst. Hence, many efforts have focused on increasing active sites by generating graphene defects such as graphene oxide [13], functionalized graphene [14], and graphene nano-platelet [15]. The existence of these graphene defects nevertheless would degrade the electrical conductivity as a result of the increase in internal resistance in DSSC. Thus, it is important to keep a balance between the electrical conductivity and catalytic activity for graphene CE.

Graphene conductive ink has been commercially available and widely applied for printing electronics such as electrodes of transistor [16], antennas of RFID tags [17], thermally conductive film [18], *etc*. Using the commercial graphene ink for preparing CE of DSSC can simplify the material preparation processes, ensure the stability of source quality, and be more cost-effective. Hence, in this article we employed the commercial binder-free graphene ink consisting of few-layer graphene nanoflakes (GNFs) with low defect ratio, dispersants and solvents, and demonstrated that the ink is suitable for preparation of GNF CE in DSSCs. To be particularly highlighted is that the GNF film could provide high active sites and at the same time remain highly electrically conductive. The films were thermally annealed in argon (Ar) and air ambient to investigate how the PCE of DSSCs would be influenced by the defect states of the GNF films at various annealing conditions.

2. Experimental

The fabrication of the GNF film was conducted using a doctor blade process where graphene nanoflake ink was first applied onto fluorine-doped tin oxide (FTO) glass (Solaronix TCO22-7, 7 Ω/sq) and then homogeneously roller-printed over the glass to form a GNF film with a loading of around 20–30 μg/cm^2. The ink (Grat-Ink™ 101 N, Blue Stone Materials) consists of ~5 *wt.%* graphene nanoflake. The GNF film was then dried at 120 °C for 10 minsand thermally annealed in air and Ar ambient at temperatures of 280, 380, and 480 °C for 30 mins.

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Fabrication of DSSC devices was carried out based on the process reported elsewhere [19]. On another FTO glass, a TiO_2 film of 4 mm × 4 mm was screen-printed using TiO_2 nanoparticle pastes provided by Eternal Materials. The TiO_2 film was dried at 120 °C for 10 mins before a scattering layer was screen-printed. The stacked film was then annealed at 480 °C in air for 60 mins. The final thickness of TiO_2 nanoparticle layer and the scattering layer was ~12 μm and ~4 μm, respectively. The TiO_2 electrode was then immersed overnight in a 0.3 mM Eversolar D720 dye solution (acetonitrile/tert-butyl alcohol = 1:1). Eversolar D720 (Everlight Chemical) is a ruthenium-based sensitizer with a chemical structure similar to N719, but on the ammonium cation it contains various alkyls groups which are different from the butyl groups of N719. Packaging of the TiO_2 and GNF substrates followed using a 125-μm-thick Surlyn thermoplastic film (Solaronix) melt at 90 °C for 30 s. A low viscosity acetonitrile-solvent-based I^-/I_3^- redox couple electrolyte (EL-200, Everlight Chemical), was finally injected into the cell and sealed to complete the device. A DSSC device with a screen-printed Pt electrode was also prepared with the same process except that the Pt film (Eversolar Pt-200) was annealed at 480 °C in air and the packaging was conducted at 130 °C for 90 s.

The surface morphology and film structure of the GNF/FTO film were examined using a FE-SEM (JEOL JSM-6701F) microscopy and a Raman spectrometer (HORIBA Scientific iHR550 Imaging Spectrometer, Laser Source: 532 nm), respectively. The oxygen concentration in GNF film was analyzed using an X-ray photoelectron spectroscopy (VG Scientific Fison (VG) ESCA 210), and the carrier mobility was determined using a Hall Effect (Ecopia HMS-3000) measurement unit. Electrochemical properties such as electrocatalytic and interfacial kinetic effects were measured using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The CV measurement was performed with a 3-electrode system, in which non-aqueous Ag/Ag^+ (10 mM $AgNO_3$ and 0.1 M Tetra-n-butylammonium fluoride in acetonitrile) was used as a reference electrode. Electrolyte containing 10 mM KI, 0.5 mM I_2 and 0.1 M tetrabutylammonium hexafluorophosphate was employed as a supporting electrolyte in acetonitrile. The voltage applied to the electrodes ranged from −1.0 V to +1.0 V with a scan rate of 50 mV/s. The EIS of DSSC was conducted under illumination at the open circuit potential with an alternative potential of 5 mV oscillated from 100 kHz to 10 MHz. Current–voltage (*J*-V) characteristics for power conversion efficiency of DSSC devices were measured using a Newport 94043A AM1.5 solar simulator and a CHI-650B electrochemical potentiostat.

3. Result and discussions

Fig. 1(a), (b), and (c) shows the SEM morphological images of GNF films annealed at 280, 380, and 480 °C, respectively. It reveals that the graphene nanoflakes have no particular shapes and are randomly in-plane oriented. And, no apparent changes in the flake size were observed for films annealed at various annealing temperatures. This indicates there was no crystal growth in the course of the heat treatment. All GNF films were also found to have roughly the same quantity of active area at crystal edges. Besides, majority of the flakes appeared to align horizontally to the FTO substrate, and only a small part of the flakes showed vertical orientation as the bright regions shown in the SEM images. Interestingly, the number of the misaligned vertical flakes was considerably reduced as the annealing temperature was increased. This means the flakes tended to lie horizontally rather than vertically at high temperatures, and as a consequence the film mass density increased. This could be confirmed from the fact that the film thickness decreased at higher annealing temperatures.

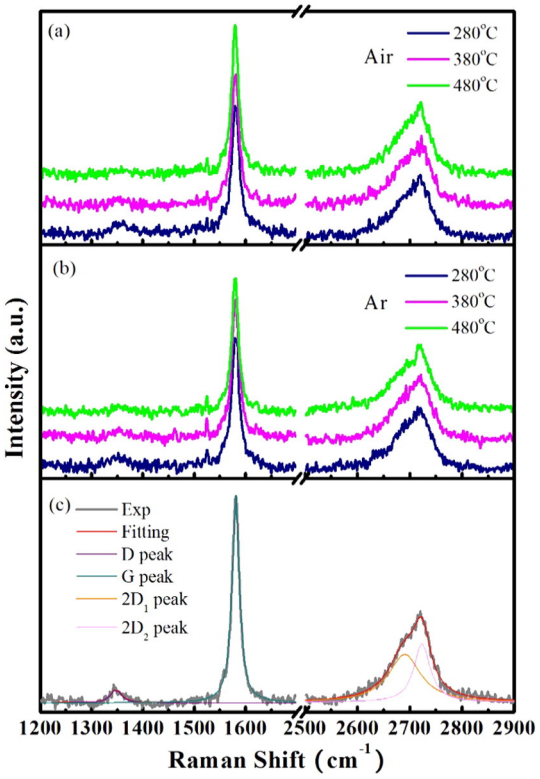

Fig. 2. Raman spectra of GNF films annealed (a) in air and (b) in argon at temperature of 280 (blue line), 380 (pink line), and 480 °C (green line). (c) Fitting curves of Raman spectrum of GNF film annealed in Ar at 280 °C using Lorentzian function. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2(a) and (b) compares the Raman spectra (532 nm excitation) of GNF films annealed in air and argon at various temperatures, respectively. It can be clearly seen the two most intense features appear at the G peak of 1580 cm^{-1} and the 2D peak around 2700 cm^{-1}, indicating that GNFs formed in this work exhibit a typical few-layer graphene characteristic [20]. This can be supported by the high intensity ratio (1.6) of $2D_1$ to $2D_2$ (I_{2D1}/I_{2D2}) of Raman spectrum of GNFs annealed at 280 °C in Ar as shown in Fig. 2(c) where the 2D peak was fitted with $2D_1$ and $2D_2$ components using the Lorentzian function. Ferrari [20] reported that an increase in the number of graphene layer generally leads to a significant decrease in the relative intensity of $2D_1$ peak. In addition to the G and 2D peaks, the D peak around 1350 cm^{-1} representing the crystal defect is also observed for the GNF film annealed at 280 °C. To derive the intensity ratio of D peak to G peak (I_D/I_G), the peaks were

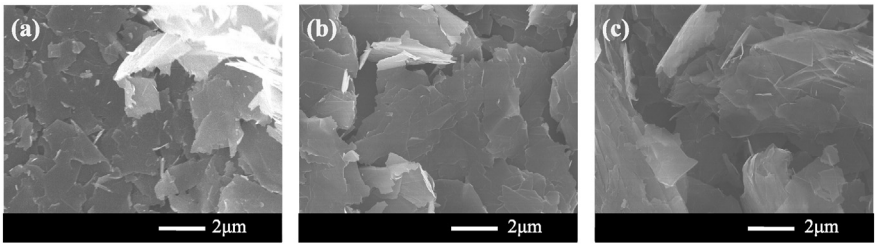

Fig. 1. SEM images of graphene nanoflake films thermally annealed in air at temperature of (a) 280 °C (b) 380 °C and (c) 480 °C.

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