Supporting Information

Lithium-Chemical Synthesis of Highly Conductive 3D Mesoporous Graphene for Highly Efficient New Generation Solar Cells

Wei Wei,† Dario Stacchiola,‡ Nusnin Akter,§ J Anibal Boscoboinik,‡ and Yun Hang Hu *†

†Department of Materials Science and Engineering, Michigan Technological University, 1400 Townsend Dr., Houghton, MI, 49931, USA.

‡Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA

§Department of Materials Science and Chemical Engineering, Stony Book University, Stony Brook, New York 11790, USA

*Corresponding author: yunhangh@mtu.edu

1. Experimental Methods

1.1 Preparation of graphene samples

Lithium (Li) particle (Aldrich) was loaded into a ceramic tube reactor and exposed to CO at pressure of 50 psi. The reactor temperature increased from room temperature to 600 °C at a rate of 10 °C/min and then kept at target temperature for a selected time (12 h, 24 h, 48 h), followed by cooling down to room temperature. This solid product was treated by 36.5 wt% hydrochloric acid (HCl) and washed with de-ionized (DI) water for more than 10 times. The remained solid was separated from water by centrifugation (3600 rpm) and then dried overnight at 80 °C to get graphene powder.
1.2 Characterization

All solid products before and after acid wash were subjected to X-ray diffraction (XRD) measurements using a Scintag XDS-2000 powder diffract meter with Cu Kα (λ=1.5406Å) radiation in the range of 10° < 2θ < 70°. Hitachi-4700 field emission scanning electron microscope (FESEM) with energy dispersive spectroscopy (EDS) was employed to evaluate the structure of the carbon powder. Raman spectra of graphene were obtained using an Olympus BX41 spectrometer with a helium-neon laser to excite the samples. X-ray photoelectron spectroscopy (XPS) was exploited to analyze the structure of graphene sheets using SPECS surface nano analysis GbmH instrument equipped with Al Kα monochromator. Sheet resistance of graphene film was measure by Jandel four-point probe system with RM3 test unit. Surface areas were measured using nitrogen adsorption at liquid nitrogen temperature (77K) with a Micromeritics ASAP 2000 adsorption instrument.

1.3 DSSC assemble and characterization

1.3.1 Preparation of counter electrodes

The black powder was mixed with alcohol and the obtained mixture was stirred for 5 min to form a homogeneous paste. The mixture paste was deposited on a clean FTO glass plate to form a film by the doctor-blade method, followed by drying at 80°C for 4 hours.

1.3.2 Preparation of photo electrodes

FTO glass plates were ultrasonically washed with water and the conducting surface of the FTO was treated with a 40 mM TiCl₄ aqueous solution at 70 °C for 30 min. A commercial TiO₂ sol
(Solaronix, Ti-Nanoxide T/SP) was used to form a TiO$_2$ film on a FTO by the doctor-blade method. The TiO$_2$ film was thermally treated in air at 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min, and 500 °C for 15 min. The obtained TiO$_2$/FTO glass plate was post-treated with the 40 mM TiCl$_4$ solvent at 70 °C, followed by heating in air at 500 °C for 30 min. Finally, the obtained film was immersed in a cis-bis(isothiocyanato) bis(2,2’-bipyridyl-4,4’-dicarboxylato)-ruthenium(II)-bis-tetrabutylammonium (N719, 0.3 mM in ethanol) dye solution for 24 h to achieve dye sensitization.

1.3.3 Fabrication and performance evaluation of DSSCs

The sandwich solar cells were assembled using the dye-sensitized TiO$_2$ photoelectrode and the graphene counter electrode with liquid electrolyte (I$_3^-$/I$_2$ redox) between them. The electrolyte consists of 0.025 M LiI, 0.04 M I$_2$, 0.28 M tert-butyl pyridine (TBP), 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), and 0.05 M guanidinium thiocyanate in acetonitrile/valeronitrile solvent with 85/15 volume ratio. The effective cell area is 0.25 cm$^2$. The photovoltaic performance of the obtained graphene-based cells was evaluated by electrochemical workstation (EG&G Princeton Applied Research) under illumination of 100 mW cm$^{-2}$ at the range of 320-1100 nm using a solar simulator (Newport).

1.3.4 Solar Cell Characterization

Electrochemical impedance spectroscopy (EIS) data of DSSCs were obtained at open circuit voltage and 10 mV amplitude over the frequency range of 0.1-100 k Hz by CHI 660D electrochemical workstation under dark condition. Cyclic voltammetry measurements were carried out using an electrochemical workstation (EG&G Princeton Applied Research) with a three-electrode system (graphene as a working electrode, Pt wire as a counter electrode, and Ag/AgCl as a reference electrode) containing acetonitrile solution of 10 mM LiI, 1 mM I$_2$, and 0.1 M LiClO$_4$. 

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Incident photon-to-current conversion efficiency (IPCE) curves were obtained after the simulated sunlight was focused through a monochromator (Newport).

1.4 PSC assemble and characterization

1.4.1 Synthesis of CH$_3$NH$_3$I

CH$_3$NH$_3$I was synthesized by reaction of 30 mL of methylamine (40% in methanol, TCI) and 32.3 mL of hydroiodic acid (57 wt% in water, Aldrich) in a 250 mL flask at 0 °C for 2 h with stirring. The precipitate was recovered by putting the solution on a rotary evaporator and carefully removing the solvents at 50 °C. The yellowish raw product of methylammonium iodide (CH$_3$NH$_3$I) was washed with diethyl ether for three times, for each of which the solution was stirred for 30 min. Then, CH$_3$NH$_3$I was recrystallized from a mixed solvent of diethyl ether and ethanol. After filtration, the solid was collected and dried at 60 °C in a vacuum oven for 24 h.

1.4.2 Fabrication and characterization of perovskite solar cells

A fluorine doped SnO$_2$ glass substrate (FTO, TEC-8, Hartford glass CO.) was cleaned with water, acetone, and ethanol, respectively. To prevent direct contact between the FTO and the hole-conducting layer, the compact TiO$_2$ layer was coated on FTO substrate by spinning coating using a precursor solution of 15 mM titanium diisopropoxide bis (acetylacetonate) followed by annealing at 500 °C for 30 min. Then the film was post-treated by 200 mM TiCl$_4$ solution at 70°C for 60 min and washed with distilled water and ethanol, followed by annealing at 500 °C for 30 min in air. PbI$_2$ was dissolved in N,N-dimethylformamide at a concentration of 460 mg mL$^{-1}$ and kept at 70 °C. After the TiO$_2$ coated substrates were pre-heated to 70 °C to remove the water vapor, the PbI$_2$ solution was spin-coated on the top of the TiO$_2$ layer at 3,000 rpm for 30 s, gently dried in air, and heated up to 70 °C for 15min. Then, the top of the film was spin-coated at 3,000 rpm for 20s with
the CH$_3$NH$_3$I solution, in which CH$_3$NH$_3$I was dissolved in 2-propanol with 3D porous graphene using ultrasonic techniques, to form CH$_3$NH$_3$PbI$_3$ perovskite on TiO$_2$ layer, and dried in air. Finally, 3D graphene was mixed with 2-propanol and the obtained mixture was stirred for 5 min to form a homogeneous paste. Graphene counter electrode was prepared by doctor-blade coating the mixture paste, followed by vaporizing the solvent and heating at 120 °C for 1h. The photovoltaic performances of the perovskite solar cells were evaluated by electrochemical workstation (EG&G Princeton Applied Research) under illumination of 100 mW cm$^{-2}$ at the range of 320-1100 nm using a solar simulator (Newport). Incident photon-to-current conversion efficiency (IPCE) curves were obtained after the simulated sunlight was focused through a monochromator (Newport).

2. Performance of DSSC with Pt Counter Electrode

![I-V curve of DSSC with Pt as counter electrode](image)
3. Band Structure of The Device

Figure S2. Band structure of the device.