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Electronic Supplementary Information

Synthesis of 3D Cauliflower-fungus-like Graphene from CO_2 as Highly Efficient Counter Electrode Material for Dye-sensitized Solar Cells

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1. Thermodynamic calculation:

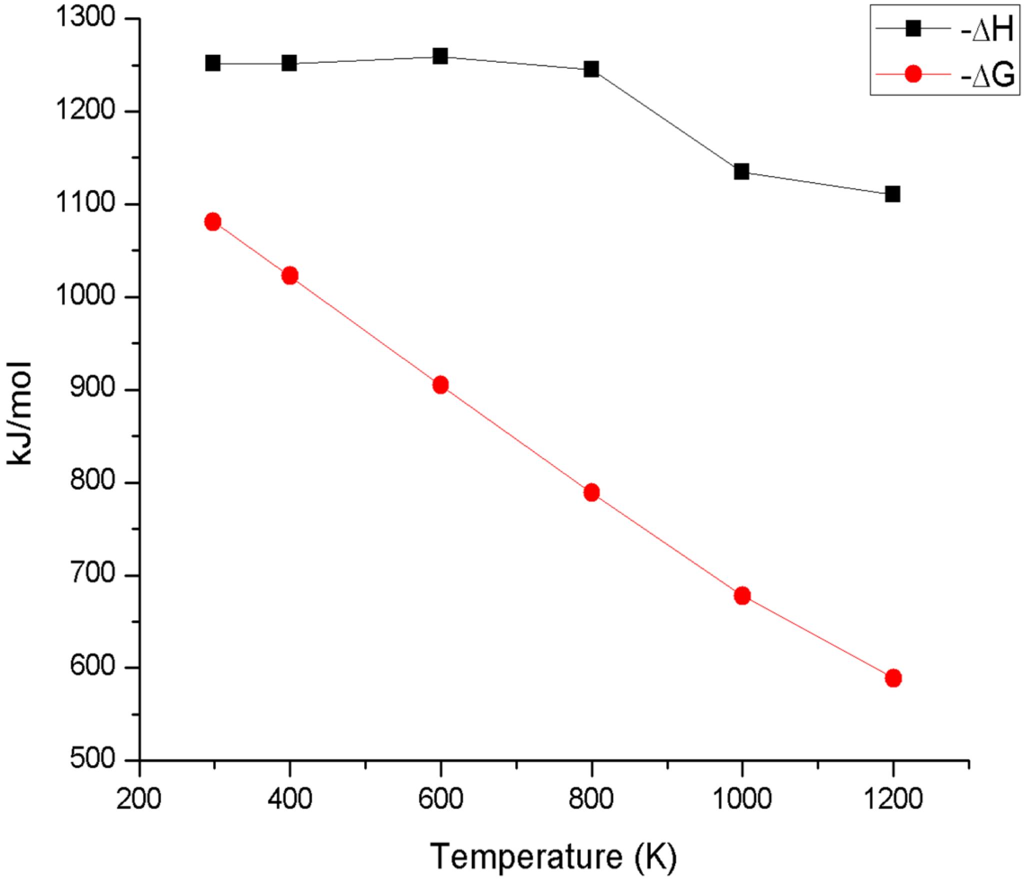

Figure S1. Relationships of reaction Gibbs free energy (ΔG) and reaction enthalpy (ΔH) with temperature for reaction between Li and CO_2 to graphene and Li_2CO_3.

2. Experimental Methods

2.1 Synthesis and characterization of graphene samples

Lithium (Li) particle (Aldrich) was loaded into a ceramic tube batch reactor and CO_2 was introduced into the reactor with initial pressure of 50 psi at room temperature, followed by heating the reactor to a selected temperature (ranged from 500 to 650 ^{o}C) at a rate of 10 ^{o}C/min and then remaining at the target temperature for 48H. The obtained graphene was separated from other solid products by the treatment of 36.5 wt% hydrochloric acid (HCl), de-ionized (DI) water washing (more than 10 times), and centrifugation separation. The obtained graphene was dried overnight at 80 ^{o}C to obtain graphene samples. All solid products before and after the 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. Structures of the graphene samples were characterized by Hitachi-4700 field emission scanning electron microscope (FESEM) with energy dispersive spectroscopy (EDS), JEOL JEM2010F transmission electron microscopy (TEM), and electron energy loss spectroscopy (EELS), X-ray Photoelectron Spectroscopy (XPS) at University of Michigan, and Olympus BX41 Raman spectrometer. Furthermore, RM3 test unit was used to measure sheet resistances of graphene films.

2.2 Synthesis of chemical-exfoliation graphene (CEG) from graphite

Chemical-exfoliation graphene sheets were prepared as follows: Graphite oxide was prepared from graphite powder with modified Hummers method.[S1] The obtained graphite oxide was dissolved in di-ionized (DI) water and exfoliated to graphene oxide by ultra-sonic treatment. Then, the graphene oxide was chemically reduced to graphene sheets by $NaBH_4$. The obtained graphene sheets were washed by DI water and dried at 80 ^{o}C.

2.3 Fabrication and performance evaluation of DSSCs

A graphene-based counter electrode was prepared by mixing graphene powder with alcohol then coating on a clean FTO glass plate using the doctor-blade method, and finally drying at 80 ^{o}C for 4 hours.

A TiO_2 photoelectrode was made as follows: FTO glass plates were subjected to ultrasonically washing with water, followed by the treatment of its conducting surface with a 0.4mM $TiCl_4$ aqueous solution at 70 ^{o}C for 30 min. The treated FTO glass plate was coated by commercial TiO_2 sol (Solaronix, Ti-Nanoxide T/SP) using the doctor-blade method. The formed TiO_2 film was thermally treated in air at 325, 375, 450, and 500 ^{o}C for 5, 5, 15, and 15 min, respectively. The obtained TiO_2/FTO glass plate was post-treated with 0.4 mM $TiCl_4$ solvent at 70 ^{o}C and then heated at 500 ^{o}C in air for 30min. Finally, the obtained film was sensitized by immersing it in a cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)-bis-tetrabutyl-ammonium (N719, 0.3 mM in ethanol) dye solution for 24 hours.

The sandwich solar cells were fabricated using the dye-sensitized TiO_2 photoelectrode and the graphene counter electrode with liquid electrolyte (I^-/I_3^- redox couple) 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 0.5 cm^2. The photovoltaic performance of the obtained graphene-based cells was evaluated by Kithley 2400 under illumination of AM 1.5 (1 sun, 100 mW/cm^2) using a solar simulator (Newport).

Incident photon-to-current conversion efficiency (IPCE) curves were obtained using after Newport IPCE instrument. Electrochemical impedance spectroscopy (EIS) data of DSSCs were obtained at open circuit voltage and 10 mV amplitude over the frequency range of 0.1-100k Hz using 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 $LiClO_4$.

3. Photovoltaic performance comparison of three counter electrodes:

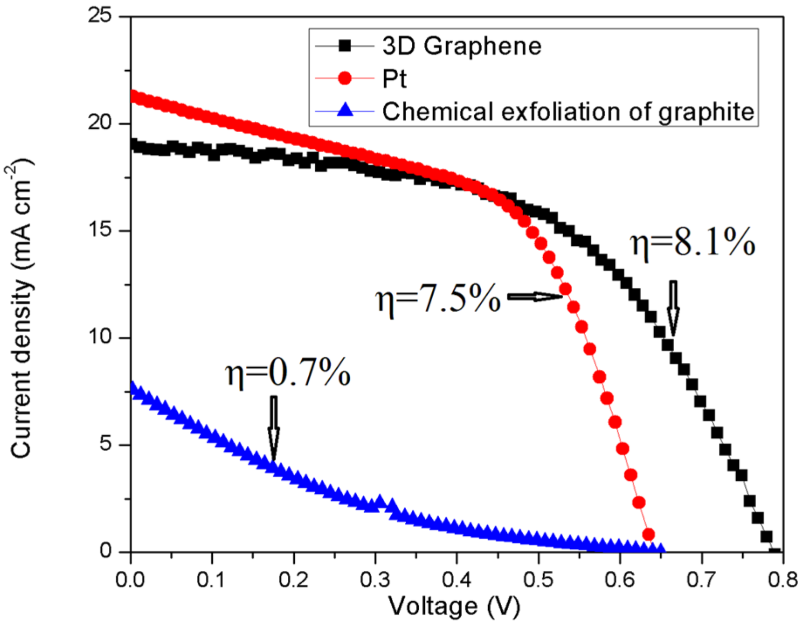

Figure S2. J-V curves of DSSCs with counter electrodes of CFG-600, platinum, and CEG graphene.

4. X-ray photoelectron spectroscopy (XPS) analysis:

Table S1. SP^2 and SP^3 carbon content of CFG from XPS analysis.

Samples	sp^2 (%)	sp^3 (%)
CFG-500	80.83	19.17
CFG-550	83.67	16.33
CFG-600	84.76	15.24
CFG-650	83.81	16.19

The sp^2 carbon corresponds to the highly ordered graphite-like structure, whereas the sp^3 carbon is associated with disorders of a graphene sheet. The higher sp^2 content (the lower sp^3 content) would generate the higher electrical conductivity.

References

S1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.