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Supporting Information

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3D Honeycomb-Like Structured Graphene and Its High Efficiency as a Counter-Electrode Catalyst for Dye-Sensitized Solar Cells**

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SUPPORTING INFORMATION

1. Experimental Methods

1.1 Synthesis of honeycomb-structured graphene (HSG)

Lithium oxide (Li_2O) power (Aldrich) was loaded into a ceramic tube reactor and exposed to CO at pressure of 35 psi. The reactor temperature increased from room temperature to 550 ºC at a rate of 10 ºC/min and then kept at 550 ºC for a selected time, followed by cooling down to room temperature. This solid product was treated by 36.5 wt% hydrocholoric 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 ºC to get graphene powder.

1.2 Characterization

All solid products before and after acid wash were subjected to X-ray diffraction (XRD) measurements by a Scintag XDS 2000 Powder Diffractometer with Cu Kα (λ=1.5406 Å) radiation in the range of $10 \leq 2\theta \leq 70^{o}$. The morphology of synthesized graphene was investigated by a Hitachi-4700 field emission scanning electron microscope (FESEM) with energy dispersive spectroscopy (EDS). Transmission electron microscopy (TEM) images, selected area electron diffraction (SAED), and electron energy loss spectroscopy (EELS) were performed in a JEOL JEM2010F electron microscope that can be performed in both TEM and scanning transmission electron microscopy (STEM) modes. EELS was performed in STEM mode with a 0.2 nm probe size and a 12mrad beam convergent angle and 32mrad collection angle, respectively. 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. Raman spectra of graphene were obtained using an Olympus BX41 spectrometer with a helium-neon laser to excite the samples. Sheet resistance of graphene film was measured by Jandel four-point probe system with RM3 test unit.

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

Chemical-exfoliation graphene sheets were prepared as follows: Graphite oxide was obtained from graphite powder with modified Hummers method[S1,S2]. 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 °C.

1.4 DSSC assemble and characterization

Fluorine-doped tin oxide (FTO) glass plates were cleaned and immersed in 40 mM $TiCl_4$ at 70 ºC for 30 min. TiO_2 paste (P25 TiO_2 in EtOH) was deposited on FTO glass to prepare a TiO_2-based photoelectrode. The photoelectrodes were heated at 325, 375, 450, and 500 ºC for 5, 5, 15, and 15 min, respectively. Then the TiO_2 deposition and heat-treatment processes were repeated one more time. After that, the TiO_2 photoelectrodes were treated again with 40 mM $TiCl_4$ at 70 ºC for 30 min and sintered at 500 ºC for 30 min. The obtained photoelectrodes were immersed in an ethanol solution of 0.3 mM N719 dye (Aldrich) for 24 h to achieve sensitization. The counter electrode was prepared by depositing graphene (HSG or CEG) on FTO glass plates. The electrolyte in the DSSCs consists of 0.025 M LiI, 0.04 M I_2, 0.28 M tert-butylpyridine (TBP), 0.05 M guanidinium thiocyanate, and 0.6 M 1-Buty-3-methylimazolium iodide (BMII) in acetonitrile/valeronitrile with 85/15 volume ratio. The sandwich-type DSSCs were assembled by combining the photoelectrode and the counter electrode together with the electrolyte. The active area of a fabricated DSSC was 0.5 × 1.0 cm^2. The Photocurrent−voltage (I−V) measurements were performed using a Keithley Model 2400 measurement unit. The light source (AM 1.5 solar illumination, 100 mW/cm^2) was generated by a Newport solar simulator equipped with a 1.5G air mass filter. Incident photon-to-current conversion efficiency (IPCE) curves were obtained after the simulated sunlight was focused through a monochromator (Newport). The electrochemical impedance spectra (EIS) measurement was performed using CHI600D Electrochemical workstation in the frequency range of 0.1 to 100k Hz under dark condition. Cycle voltammetry (CV) was carried out in a three-electrode system (containing a acetonitrile solution of 0.1 M $LiClO_4$, 10 mM LiI, and 1 mM I_2 at a scan

rate of 20 mV^{-1}): a Pt wire as the counter electrode, an Ag/AgCl electrode as the reference electrode, and the graphene-based electrode as the working electrode.

2. Supplementary Table

Table S1. EDS analysis of honeycomb-structured graphene

Samples*	Carbon (atomic ratio)	Oxygen (atomic ratio)
HSG-12h	94.56 %	5.44 %
HSG-24h	96.91 %	3.09 %
HSG-48h	97.44 %	2.56 %

* HSG-12h, HSG-24, and HSG-48 denote the honeycomb-like-structured graphene with synthesis time of 12, 24, and 48h, respectively.

3. Supplementary Figures (with additional discussion in caption)

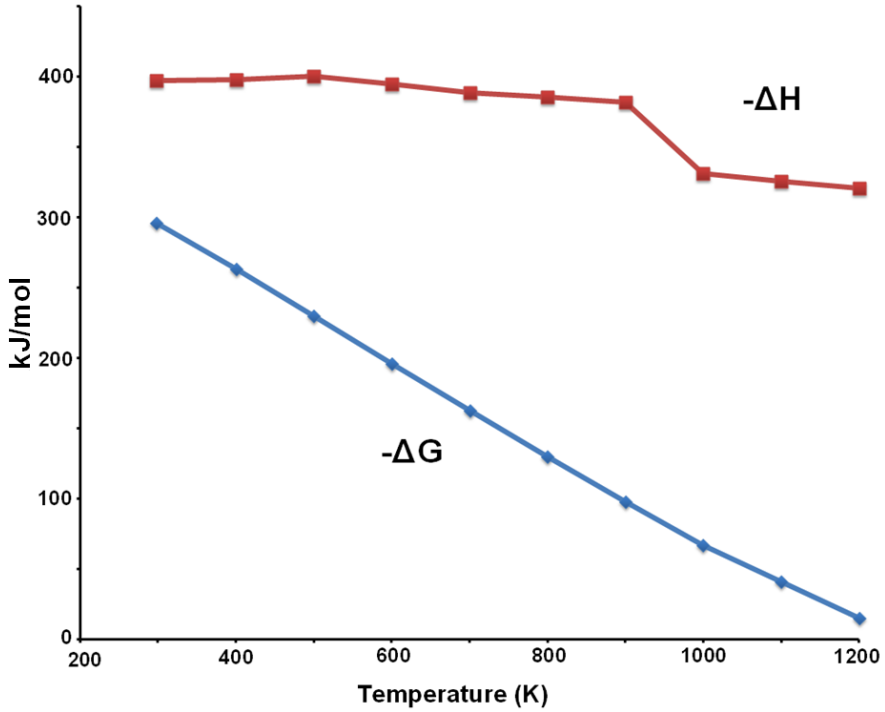

Figure S1. Relationships of Gibbs free energy change (ΔG) and reaction enthalpy change (ΔH) with temperature for reaction between Li_2O and CO to graphene and Li_2CO_3. One can see the Gibbs free energy change and the enthalpy change are both negative in a large temperature range from room temperature to 1000 ^oC (The drop appeared in enthalpy change is due to phase transformation.). The negative features indicate that this reaction is thermodynamically favorable.

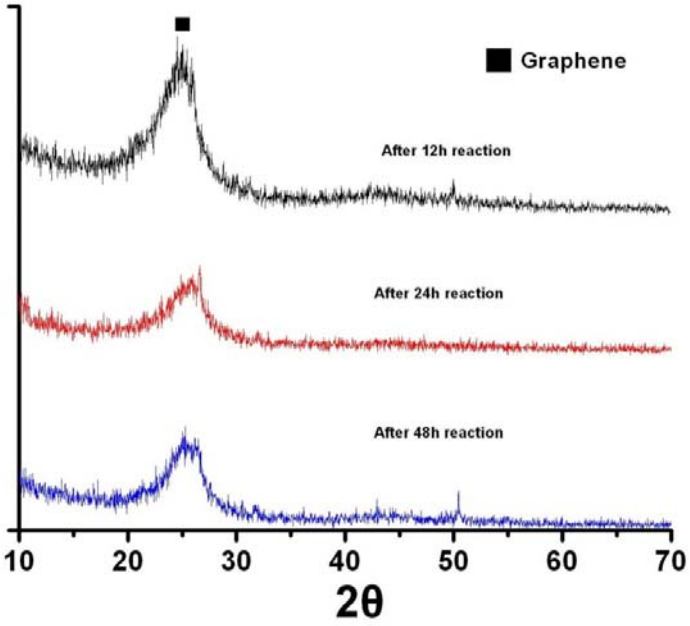

Figure S2. XRD patterns of HSG powder obtained from reaction between Li_2O and CO at 550 ºC (followed by hydrochloride acid wash).

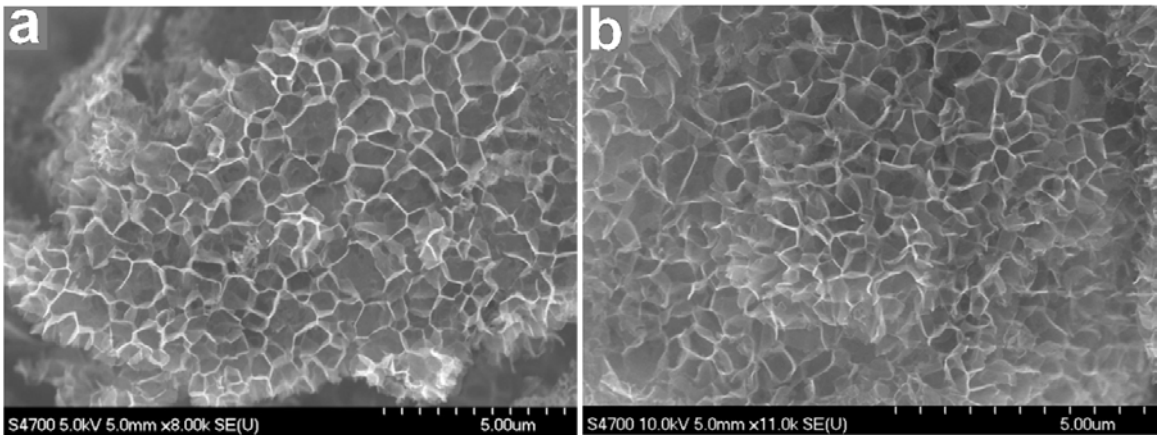

Figure S3. FESEM images of HSG sheets obtained from reaction between CO and Li_2O at 550 ºC for (a) 12h and (b) 24h (followed by hydrochloride acid wash). Similar with micrograph in Fig.2a, curved graphene sheets connect to each other to form a three-dimensional honeycomb-like structure, with the cell size of graphene honeycombs in the range of 50-500 nm.

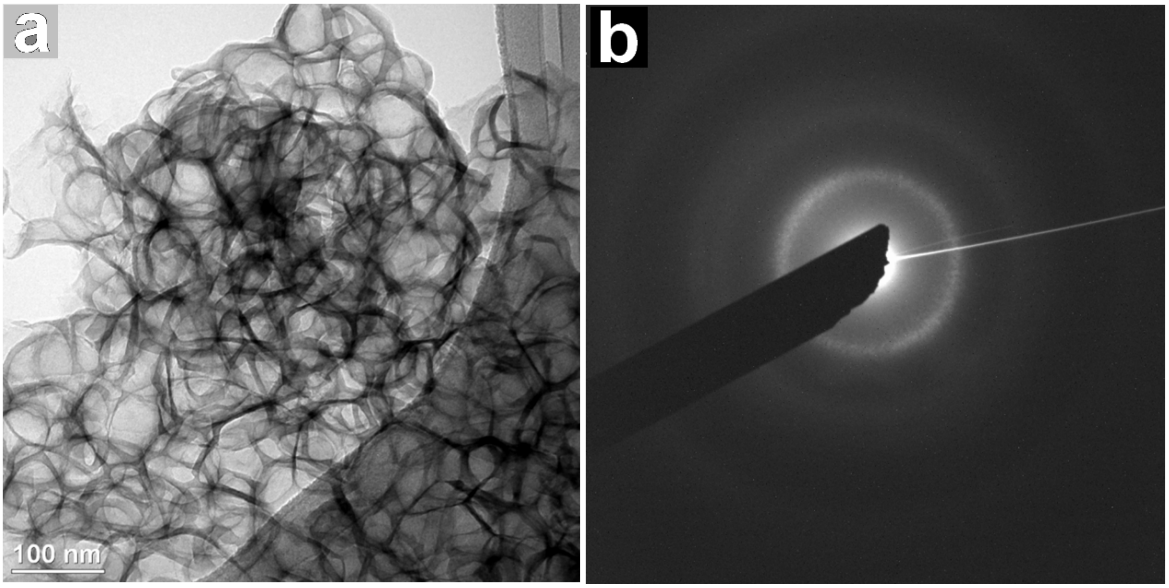

Figure S4. TEM image (a) and electron diffraction pattern (b) of HSG sheets produced from reaction between CO and Li_2O for 12h at 550^oC (followed by hydrochloride acid wash). As can be seen in the TEM image, micro-structure of honeycomb cells connect to each other to form large curved graphene sheets. The cell size of graphene honeycombs is around 50-200 nm, which is consistent with FESEM images. Furthermore, poly-crystalline ring patterns were observed for this sample due to scrolled graphene sheets, which is the same as observed in Fig.2.

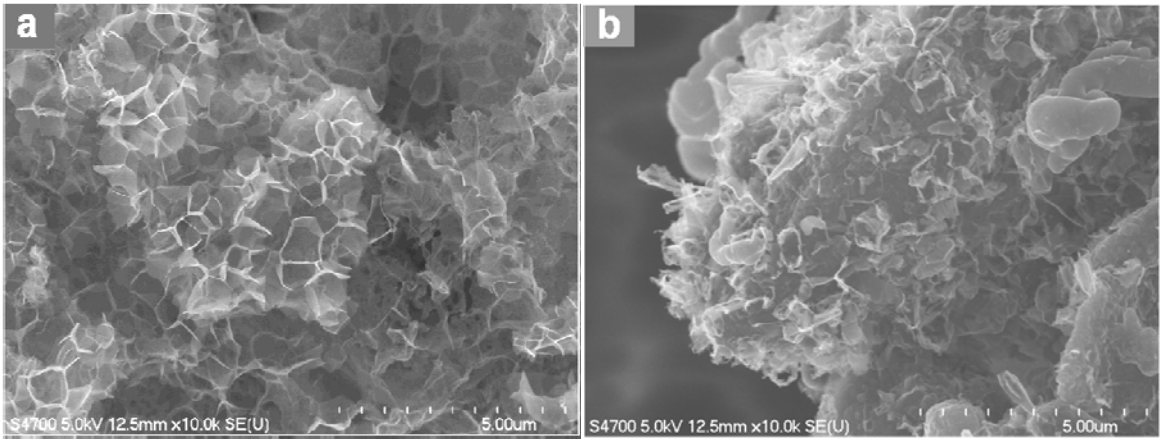

Figure S5. FESEM images of HSG sheets obtained from reaction between CO and Li_2O for 24h at (a) 500 ºC and (b) 600 ºC. As seen in the images, the honeycomb-structured graphene sheets prepared at 500 ^{o}C have the same shape as the HSG synthesized at 550 ^{o}C (Fig.S3). However, some large carbon shells can be observed for the sample prepared at 600 ^{o}C. This indicates that 600 ^{o}C is too high for the synthesis of the honeycomb-structured graphene sheets.

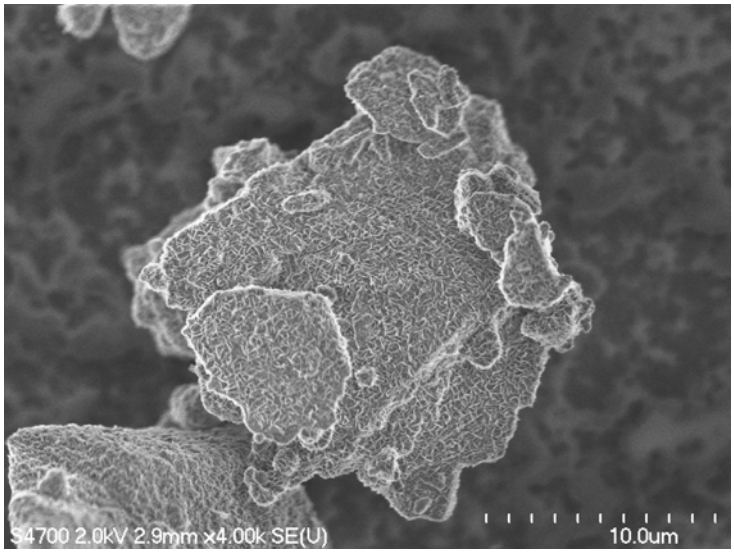

Figure S6. FESEM image of Li_2O. The image shows the particle size range from several nm to about 10 μm with very rough surface.

4. Relationship between the surface areas of HSG sheets and the power conversion efficiencies of HSG CE based DSSCs

HSG-12 and HSG-24 have almost the same surface areas (151 and 153 m^2/g), whereas the power conversion efficiencies (7.80 and 6.53%) of HSG-12 and HSG-24 based DSSCs are different. This indicates that the efficiency is not determined by surface area. This happened because the efficiency is dependent on both the defects (as catalytic sites) and the electronic conductivity of HSG sheets.

5. Properties of Li_2O

Li_2O sample was characterized. The average crystal size of Li_2O from XRD measuremet is 50 nm. Its surface area from BET measurements is 5 m^2/g. Furthermore, the particle size of Li_2O has a broad distribution from several nm to about 10 μm with very rough surface (Fig.S6). However, the cell sizes of synthesized honeycomb-structured graphene sheets are from 50-500 nm, which are much smaller than the large particles of Li_2O.

References

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

S2. S. Stankovich, D.A. Dikin a, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y.Wu, S. T. Nguyen, R. S. Ruoff, *Carbon* **2007**, *45*, 1558.