Supporting Information

Direct Conversion of CO₂ to 3D Graphene and its Excellent Performance for Dye-

sensitized Solar Cells with 10% Efficiency

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<u>1. Experimental section</u>

1.1 Synthesis and characterization of carbon nanomaterials.

Sodium (purchased from Aldrich) was loaded into a ceramic tube reactor and CO2 was introduced into the reactor with initial pressure of 50 psi at room temperature, followed by heating to 600 °C at a rate of 10 °C/min and then held for 24H. This reaction was further confirmed by other condition, 550°C for 24h with initial pressure of 50 psi, 600°C for 24h with initial pressure of 35 psi, and 600°C for 12h with initial pressure of 50 psi, respectively. The obtained 3D 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 3D graphene material was dried overnight at 80 °C. All solid products were subjected to X-ray diffraction (XRD) measurements using a Scintag XDS-2000 powder diffract meter with Cu K α (λ =1.5406Å) radiation. Their structures were characterized by Hitachi-4700 field emission scanning electron microscope (FESEM) with energy dispersive spectroscopy (EDS) and JEOL JEM-3100R05 transmission electron microscope (TEM). X-ray photoelectron spectra (XPS) were collected using a Kratos Ulta AXIS DLD XPS with a monochromated Al source. Raman spectra were obtained using an Olympus BX41 spectrometer with a helium-neon laser to excite the samples. Elemental Analysis was carried out using the Control equipment corporation Model 240XA. Surface areas were measured using nitrogen adsorption at liquidnitrogen temperature (77K) with a Micromeritics ASAP 2000 adsorption instrument. The sheet resistance of graphene film was measured by Jandel four-point system with RM3 test unit.

1.2 Preparation and characterization of counter electrodes.

The mixture of 3D graphene with alcohol was stirred for 5 min to form a homogeneous paste. The obtained paste was deposited on a clean FTO glass plate to form a film by the doctorblade method, followed by drying at 80°C for 4 hours. The thickness of the film, which was measured by Model 6000 micromanipulator testing station, is about 20um. Cyclic voltammetry measurements were carried out using an electrochemical workstation (EG&G Princeton Applied Research) with a three-electrode system (carbon nanomaterial 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 I₂, and 0.1 M LiClO₄.

1.3 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 TiO₂ film on a FTO by the doctor-blade method. The TiO₂ 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 TiO₂/FTO glass plate was post-treated with the 0.4 mM TiCl₄ solvent at 70 °C, followed by heating in air at 500 °C for 30min. 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 hours to achieve dye sensitization.

1.4 Fabrication and performance evaluation of DSSCs.

The sandwich solar cells were assembled using the dye-sensitized TiO_2 photoelectrode and the carbon nanomaterials counter electrode with liquid electrolyte (I^-/I_3^- redox) between them. The electrolyte consists of 0.025 M LiI, 0.04 M I₂, 0.28 M tert-butyl pyridine (TBP), 0.6 M 1butyl-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 cm². The photovoltaic performances of DSSCs were evaluated by Kithley 2400 under illumination of 100mW/cm² at the range of 320nm-1100nm using a solar simulator (Newport). 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 kHz using CHI 660D electrochemical workstation under dark condition.

2. Thermodynamic evaluation



Fig. S1 Gibbs free energy change and reaction enthalpy change vs temperature for reaction between Na and CO_2 to carbon and Na_2CO_3 .

3. Schematic for the reactor and conversion of CO₂



Fig. S2 a) Schematic for the reactor and b) Schematic of conversion of CO₂ to graphene.

4. Effects of synthesis conditions on properties of graphene



Fig. S3 Pressure profiles with different programmed-temperature heating processes: a) sample 550-24-50 (which is graphene obtained at 550°C for 24h with initial pressure of 50 psi); b) sample 600-24-35 (which is graphene obtained at 600°C for 24h with initial pressure of 35 psi); c) sample 600-12-50 (which is graphene obtained at 600°C for 12h with initial pressure of 50 psi); d) sample 600-24-50 (which is graphene obtained at 600°C for 24h with initial pressure of 50 psi); d) sample 600-24-50 (which is graphene obtained at 600°C for 24h with initial pressure of 50 psi); d) sample 600-24-50 (which is graphene obtained at 600°C for 24h with initial pressure of 50 psi); d) sample 600-24-50 (which is graphene obtained at 600°C for 24h with initial pressure of 50 psi) (Note: gas compositions after the reactions were analyzed by gas chromatography. No CO was detected).

Sample	Elementary Analysis		BET Surface Area	Sheet Resistance
			(m ² /g)	$(k\Omega/sq)$
	C (mol%)	O (mol%)		
550-24-50	93.12	6.88	481	9.89
600-24-35	94.23	5.77	563	6.12
600-12-50	94.02	5.98	775	8.31
600-24-50	98.87	1.13	575	5.44

 Table S1. Composition and properties of graphene materials.



Fig. S4 FESEM images of 550-24-50 (a), 600-24-35 (b), and 600-12-50 (c); d) Photocurrent density-voltage curves and performance parameters of DSSCs with graphene CEs; e) CV curves of I_3^-/I^- redox pairs; f) EIS curves for solar cells fabricated with graphene CEs (the inset presents the equivalent circuit).

As shown in Fig. S4a, S4b and S4c, graphene samples obtained at different temperature, pressure and times all possess three dimensional layered structure, which further confirmed the strategy of this research as well as the feasibility of the invented reaction. To further verify the excellent performance of graphene CEs, DSSCs were fabricated with N719 dye-sensitized TiO₂ film as photoelectrodes, I⁻/I₃⁻ redox couple as electrolyte, and graphene as CEs. As shown in Fig. S4d, the DSSC with sample 600-24-50 shows the highest efficiency of 10.09%. It is well known that the performance of graphene as a counter electrode for DSSCs is dependent on its two properties: catalytic activity and electrical conductivity. Sample 600-24-50 exhibited the lowest sheet resistance which indicates its highest electrical conductivity. Furthermore, the catalytic

activity of CEs was evaluated by cyclic voltammograms (CV). Sample 600-24-50 shows the smallest peak to peak separation which is inversely proportional to catalytic activity in Fig. S4e, which indicates its excellent catalytic activity of the redox reaction of I_3^-/I^- . It also shows a higher peak current density which indicates its good electrical conductivity. DSSCs with graphene CEs were also subjected to EIS characterization. As shown in Fig. S5f, one can see two well-defined semicircles, providing series resistance (R_s), charge transfer resistance (R_{ct}) at the CE/electrolyte interface, and charge transfer resistance (R_{ct2}) at the TiO₂/dye/electrolyte interface. All of the samples show similar R_s and R_{ct} which could be neglected. The sample 600-24-50 shows the smallest R_{ct2} , which depends on the catalytic reduction of I_3^- to I^- . This further confirmed the excellent electrocatalytic performance of sample 600-24-50.

5. Stability performance of producing photocurrent



Fig. S5 Photocurrent produced under 1.5G (100 mW cm⁻²) and chopped illumination (67 mW cm⁻²)