Supporting Information

Potassium-Chemical Synthesis of 3D Graphene from CO_2 and Its Excellent Performance

for HTM-free Perovskite Solar Cells

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1. Experimental Methods

1.1 Preparation of graphene samples

Potassiun (K) particle (Aldrich) was loaded into a ceramic tube reactor and exposed to CO_2 at pressure of 50 psi. The reactor temperature increased from room temperature to 550 ^{o}C at a rate of 10 ^{o}C/min and then kept at target temperature for a selected time (12h, 24h, 48h), 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 ^{o}C to get graphene powder.

1.2 Characterization of graphene materials

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. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) were performed in a JEM-2010 transmission electron microscope. 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 PSC assemble and characterization

1.3.1 Synthesis of CH₃NH₃I

1.3.1 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.

1.3.2 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 20 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_3NH_3I solution, in which CH_3NH_3I was dissolved in 2-propanol with 3D honeycomb-like structured graphene (3DHG) using ultrasonic techniques, to form $CH_3NH_3PbI_3$ perovskite on TiO_2 layer, and dried in air. Finally, a perovskite solar cell was obtained by preparing a carbon counter electrode on the film by doctor-blade coating 3DHG, 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). Electrochemical impedance spectroscopy (EIS) data of PSC was obtained at 0.9 V and 10 mV amplitude over the frequency range of 1-100k Hz by CHI 760E electrochemical workstation under dark condition. Mott Schottky plot was also obtained by CHI 760E electrochemical workstation under dark condition.
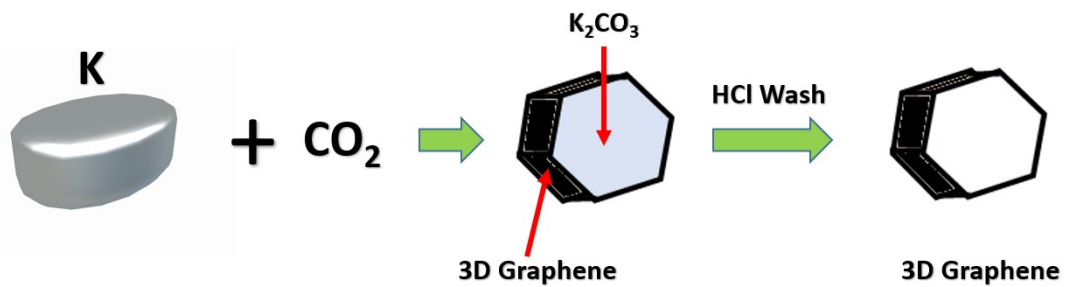
2. Schematic of Reaction

Fig. S1. Schematic of conversion of CO_2 to graphene.

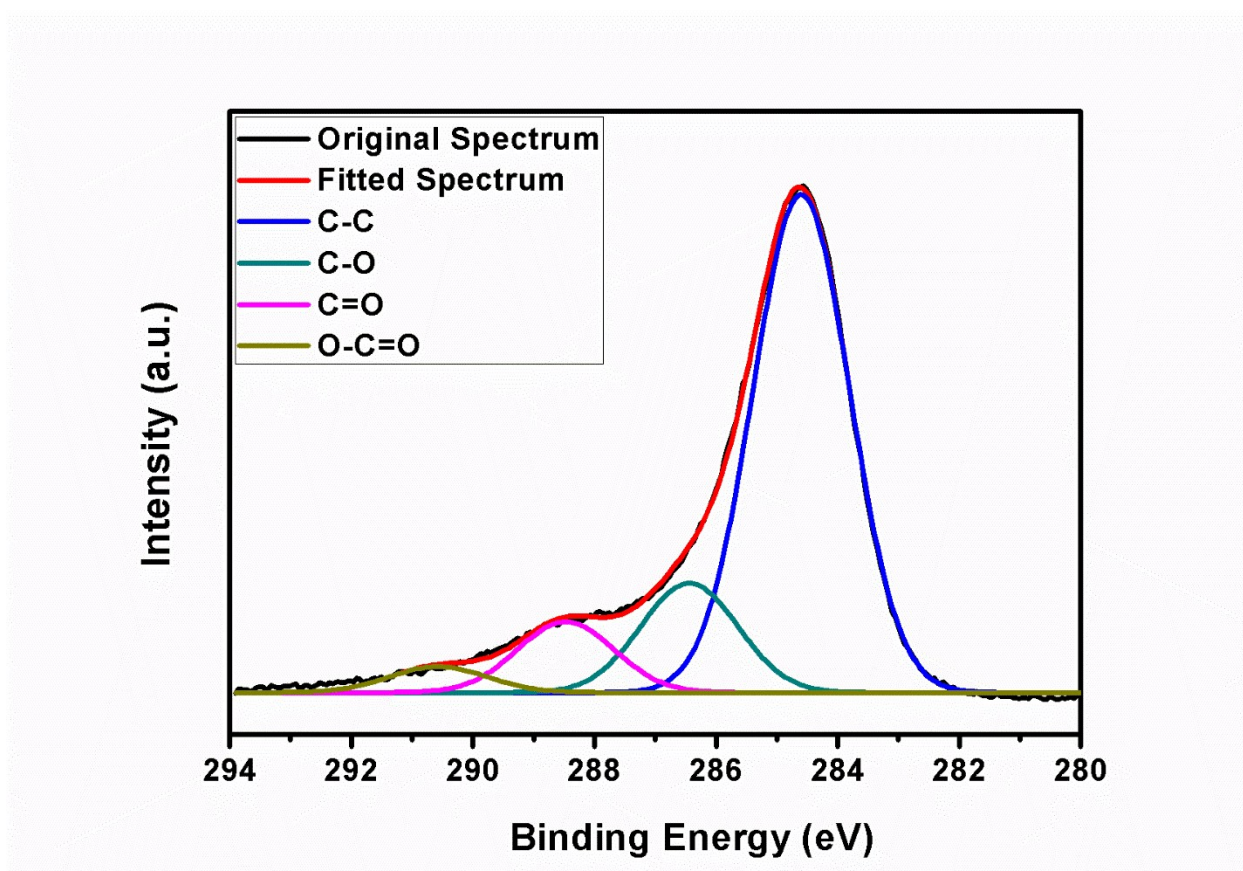## 3. XPS Spectrum

Fig. S2 XPS spectrum of 3DHG-48.

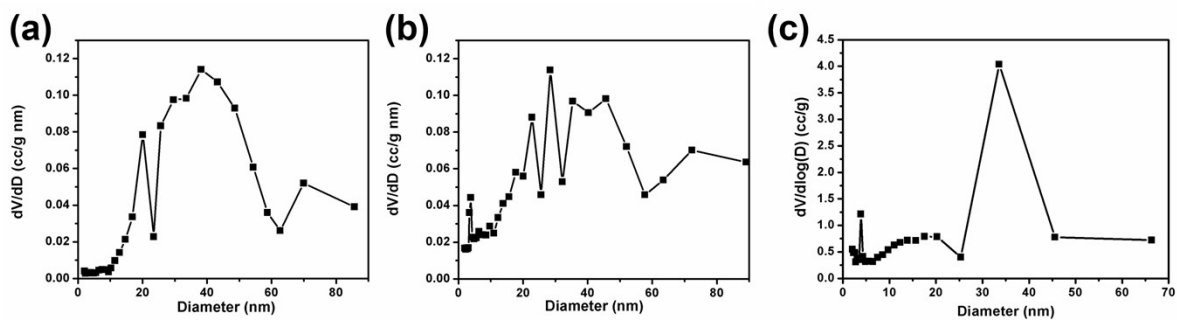## 4. Pore Size Distribution

Fig. S3 Pore size distribution of (a) 3DHG-12, (b) 3DHG-24, and (d) 3DHG-48.
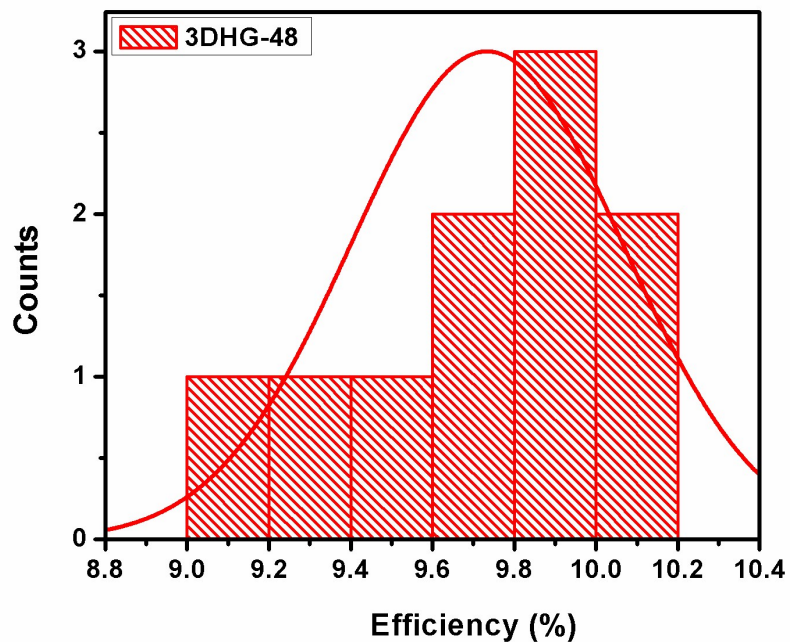
5. Histogram of Efficiency

Fig. S4 Histogram of power conversion efficiencies for 10 PSCs fabricated under the same experimental conditions with 3DHG-48 as counter electrodes.
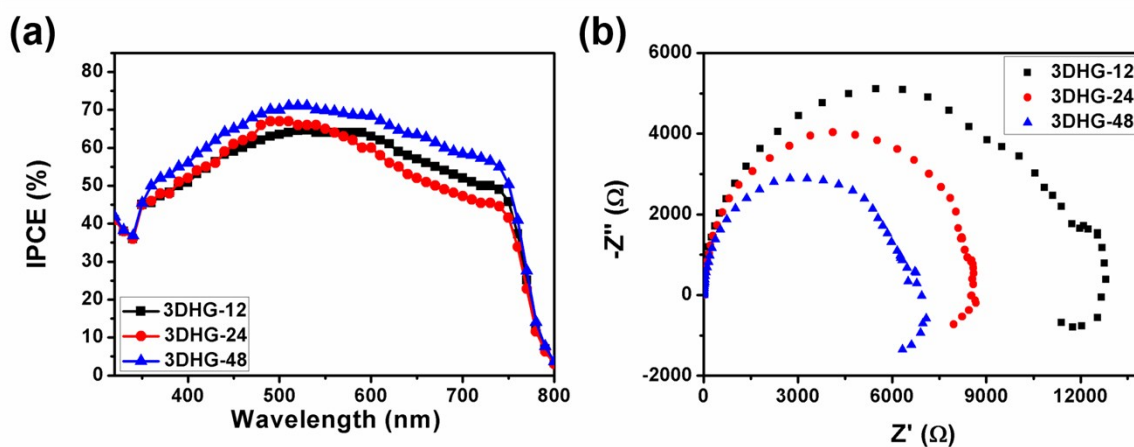
6. Nyquist Plots and IPCE

Fig. S5 Characterization of HTM-free PSCs with 3DHG counter electrodes: (a) IPCE curves and

(b) Nyquist plots.

The IPCE curves show that the incident-photon-to-current conversion efficiency for a wavelength range from 550 to 750nm is the lowest for 3DHG-24-based PSC among 3 PSCs. This happened probably because 3DHG-24 has the largest visible light absorption, leading to the reduction in visible light absorption by the perovskite and thus the reduction in photon-to-current conversion efficiency. As a result, the 3DHG-24-based PSC exhibited the lowest I_{sc}.