

Supplementary Information

A Facile Preparation Route of Boron-doped Graphene and Its CdTe Solar Cell Application

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Synthesis of chemically reduced graphene oxide

Graphene oxide (GO) preparation started by exfoliating expandable graphite power (100 mesh) using a modified Hummers' method^{S1-2} at 1000 °C in forming gas for 60 s. In a typical reaction, 1.0 g graphite, 0.5 g NaNO₃, and 23 mL H₂SO₄ were stirred together in an ice bath until homogenized. After 3 g KMnO₄ was slowly added to the solution while stirring, the solution was transferred to a 40 °C water bath, stirred for about 2 h to form a thick paste. 100 mL water was added and stirred for 1 h, and then 2 mL H₂O₂ (30 wt. % aqueous solution) was added and stirred for 2 h. Inorganic anions and other impurities were removed through 15 washing cycles that included centrifugation, discarding supernatant liquid, and resuspending the solid in an aqueous mixture using stirring and ultrasonication. After drying, the loose and brown GO powder was obtained.

Hydrazine monohydrate was used to reduce GO to achieve graphene.^{S3} In the chemical reduction procedure, 100 mg graphene oxide was dispersed directly into a hydrazine monohydrate solution (100 mL, 80 wt. %), and stirred at 60 °C for 48 h. The final harvested product was graphene powder. The SEM and AFM images were shown in Figure S2.

Size determination of PG and BG

We calculated the in-plane sizes (L_a) of the undoped and doped graphene samples based on Raman data by the Equation (1) established in Ref.^{S4-5}

$$L_a (nm) = (2.4 \times 10^{-10}) \cdot \lambda_i^4 \left(\frac{I_D}{I_G}\right)^{-1} \quad (1)$$

Here λ_i is the wavelength of the excitation laser used in the Raman experiment in nm units, while I_D and I_G represent the intensity of the D and G peaks, respectively. In our Raman measurements, λ_i is 514.5 nm, and the (I_D/I_G) values of PG and BG are 0.3 and 0.48, respectively. The calculated average sizes of PG and BG are 56 and 35 nm, respectively.

Electrode fabrication of graphene film and AC electrochemical impedance spectra (EIS)

For the EIS measurement, the BG, PG and CRG were fabricated as the film electrodes by the method reported.^{S6} Poly(vinyl difluoride) (PVDF) was dissolved into N-methyl-2-pyrrolidone (NMP) to form a 0.01 g mL⁻¹ homogeneous solution. The graphene and solution were mixed homogeneously (20 mg mL⁻¹), and the obtained paste was then spread on the conducting fluorine-doped SnO₂ glass substrate (FTO) with a glass rod, using adhesive tapes as spacers. The films with a ca. 5 μm thickness and 1 × cm² active area were obtained at 80 °C for 10 h.

The EIS measurements were carried out on a CHI660B electrochemistry station by using three-electrode system. The film electrodes served as the working electrodes, while the platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode, which was performed in the presence of a 10 mmol L⁻¹ K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) mixture as a redox probe in 0.1 mol L⁻¹ KCl solution.

Measurement and characterization

TEM images were obtained with a JEOL JEM 2010 instrument, operated at 200 kV.

SEM measurements were performed using a JEOL JSM 6510 instrument. AFM images in topography were recorded using Seiko SPI 3800 N probe station. Raman spectroscopy was performed on an inVia Renishaw Raman microscope using green ($\lambda = 514.5$ nm) laser excitation. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg $K\alpha$ radiation ($h\nu = 1253.6$ eV). Device efficiency measurements were performed under standard conditions of 100 mW/cm² intensity using a Keithley Model 2440 source meter under AM 1.5 illuminations. EIS was measured by a computer-controlled electrochemical workstation (CHI660B, CH Instruments) in the frequency range of 10 mHz –100 kHz, and with an alternating current amplitude of 5 mV.

Table S1. Elemental abundances determined by XPS in PG and BG samples.

	C		B		Cl	O
	Peak position (eV)	Composition at. %	Peak position (eV)	Composition at. %	Composition at. %	Composition at. %
PG	284.7	89.91	-	-	2.59	7.22
BG	284.4	88.84	191.5	1.08	2.29	7.66

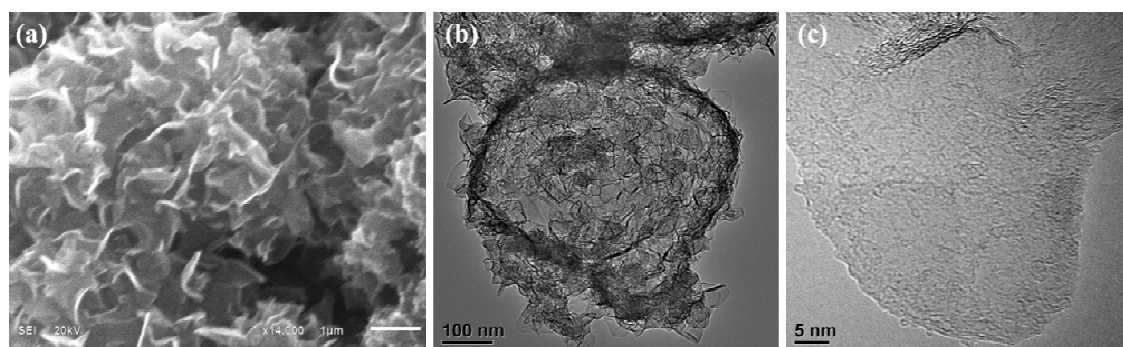


Figure S1. (a) SEM, (b) TEM and (c) HRTEM images of the boron-doped graphene.

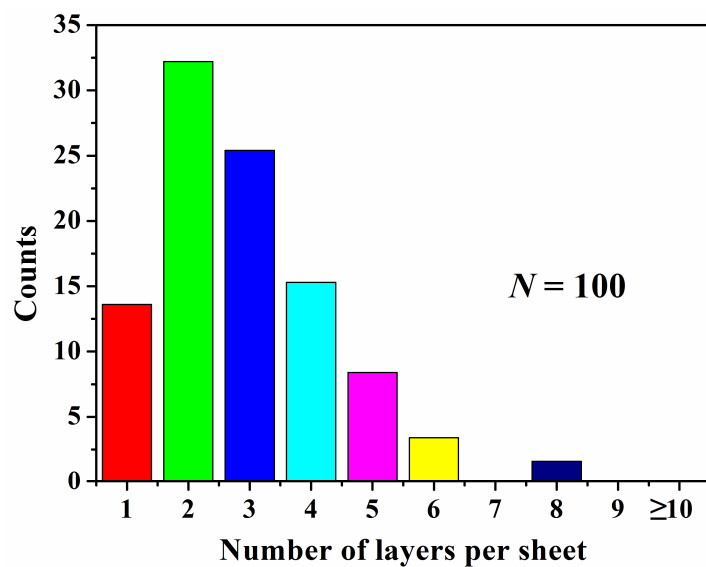


Figure S2. Flake population ($N=100$) as a function of number of layers per flake.

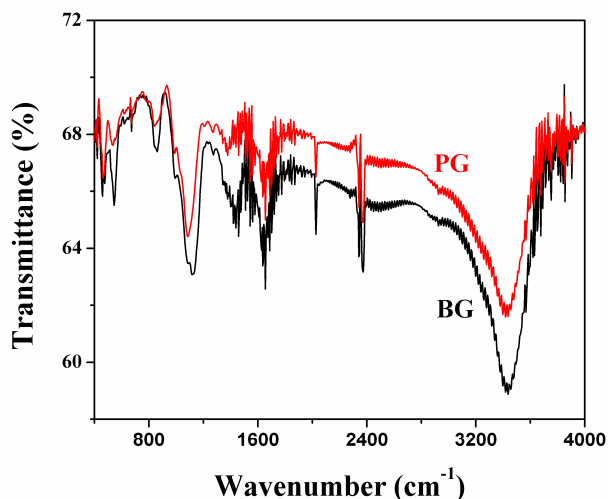


Figure S3. FTIR spectra of the pristine graphene (PG), and boron-doped graphene (BG) samples. The PG and BG samples were ground with KBr (spectrum pure) and pressed into thin discs. The FTIR measurements were carried out on Shimadzu FTIR Prestige-21. As the FTIR spectra are shown in Figure S2, the characteristic vibration bands include a intense peak around 3400 cm^{-1} (assigned to O–H groups), a henylhydroxyl stretching peak around 1100 cm^{-1} arising from tightly bound water molecules, and the vibration peaks around 1640 cm^{-1} from the adsorbed water.

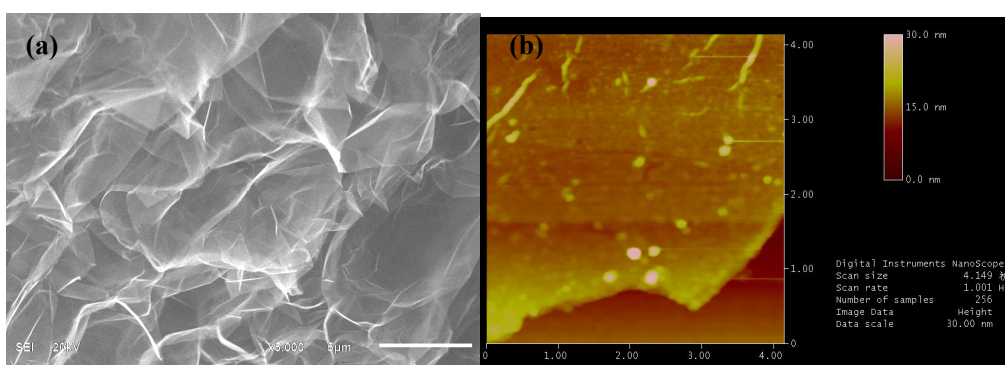


Figure S4. (a) SEM and (b) AFM images of r-GO. The scale bar in (a) is $5\mu\text{m}$.

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