Electronic Supplementary Information

Boron-doped graphene as high-efficiency counter electrode for dye-sensitized solar cells

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1. ***Synthesis of graphite oxide***

Graphite oxide (GO) was prepared via a modified Hummers method.[1, 2] Firstly, 5 g graphite powder (325 mesh) and 2.5 g sodium nitrate (Analytical grade, Sinopharm Chemical Reagent Co., Ltd) were mixed with 130 ml sulfuric acid (98%, Beijing Chemical Works) in an ice bath under vigorous stirring for 2 h. Then, 15 g potassium permanganate (Analytical grade, Zhengzhou Third Chemical Reagent Factory) was slowly added into the system while the temperature was kept below 0 °C. The temperature of the mixture was subsequently increased to and kept at 35 °C for 1 h, followed by adding 230 ml water by dropwise. After that, the mixture was further heated to 98 °C for 30 min. 500 ml deionized water and 5 ml hydrogen peroxide (30 wt%, Sinopharm Chemical Reagent Co., Ltd) were added into the mixture. After centrifugation and washing to remove residual salt, the wet GO was freeze-dried for 48 h.

2. ***Synthesis of boron-doped graphene (BG)***

B_2O_3 and GO with a mass ratio (1:5, 1:2, and 2:1) were mixed and ground in an agate mortar. Then, the mixture was transferred into tube furnace and flushed with argon to completely remove the air. After that, the furnace was heated to 1200 °C at a ramping rate of 5 °C min^{-1}, then kept at 1200 °C for 1 h before cooling down to room temperature naturally. The annealed sample was then refluxed in 3 M NaOH solution to remove the unreacted B_2O_3. The treated sample was washed to neutrality by ionized water, and dried overnight, yielding a series of BG with a B content of 0.09, 1.13, and 2.36 at.%, respectively.

3. Fabrication of DSSCs

Counter electrode preparation: 30 mg sample and 0.5 ml binder containing ethyl cellulose, ethanol, and terpineol in a mass ratio of 1:9:8 were ground for 30 min, yielding the counter electrode paste. The obtained paste was coated on the FTO glass, and then heated in a tube furnace at 500 °C in N_2 atmosphere for 30 min. Pt electrode was purchased from Dalian Heptachroma SolarTech Co., Ltd., China.

Device fabrication: The dye-coated TiO_2 photoanodes were prepared by immersing TiO_2 film (Ti-Nanoxide D, Solaronix SA, Aubonne, Switzerland) in a 0.5 mM N719 dye (Solaronix) ethanol solution for 20 h, and then assembled with the G, BG or Pt counter electrodes. The electrodes were separated by a 45 μm thick hot melt ring (Surlyn, Yingkou OPV Tech New Energy Co., Ltd, China) and sealed up by heating. The cell internal space was filled with OPV-AN-I type electrolytes (Yingkou OPV Tech New Energy Co.,Ltd., China).

4. Characterization

The samples were examined by field emission scanning electron microscopy (FESEM, FEI, NOVA NanoSEM 450), and transmission electron microscopy (TEM, FEI, TF30). The Raman spectra were recorded on a DXR Raman Microscope (Thermo Scientific) with an excitation wavelength of 532 nm. The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max2400 diffractometer. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on ESCALAB MK II X-ray photoelectron spectrometer.

5. Electrochemical testing

The cyclic voltammograms (CVs) were carried out in a conventional three-electrode electrochemical cell by using BG as the working electrode, Pt as a counter electrode and Ag/Ag^+ as a reference electrode in an acetonitrile solution containing 0.1 M $LiClO_4$, 10 mM LiI, and 1 mM I_2 at a scan rate of 10 mV s^{-1} using an electrochemical analyzer (CHI660D, Chenhua, Shanghai). The electrochemical impedance spectroscopic (EIS) experiments were conducted in the dark with dummy cells using a computer-controlled potentiostat (Zenium Zahner, Kronach, Germany). The measured frequency ranged from 100 mHz to 1 MHz, and the amplitude of the alternating current was set at 10 mV. Tafel-polarization measurements were carried out with an electrochemical workstation system at a scan rate of 10 mV s^{-1} (CHI660D, Chenhua, Shanghai) in a symmetrical dummy cell. Photocurrent-voltage performance of the DSSCs was conducted in simulated AM 1.5 illumination (I= 100 mW cm^{-2}, PEC-L15, Peccell, Yokohama, Japan) with a Keithley digital source meter (Keithley 2601, Cleveland, OH).

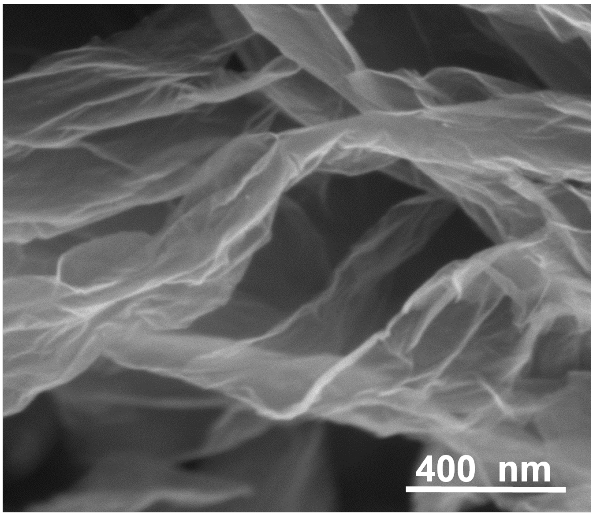

Fig. S1 SEM image of as-prepared graphene.

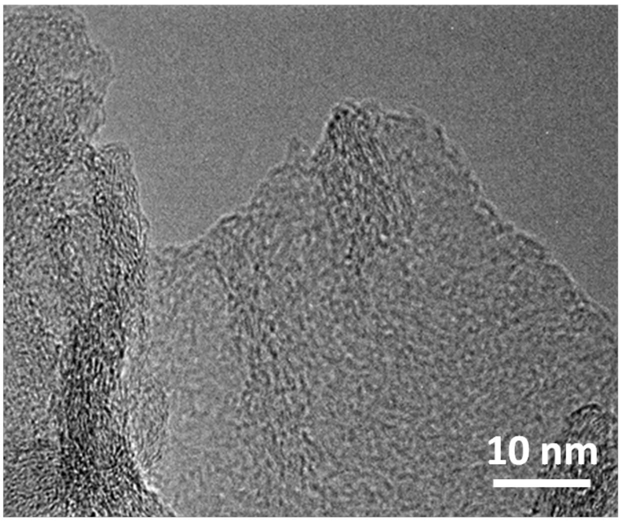

Fig. S2 HRTEM image of BG

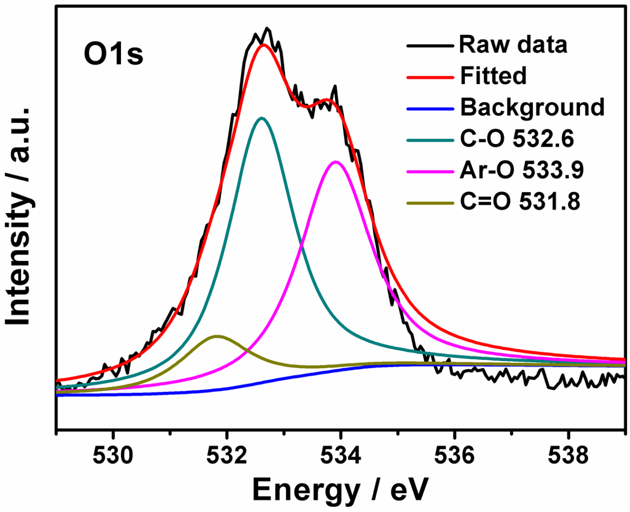

Fig. S3 O1s XPS spectrum of BG.

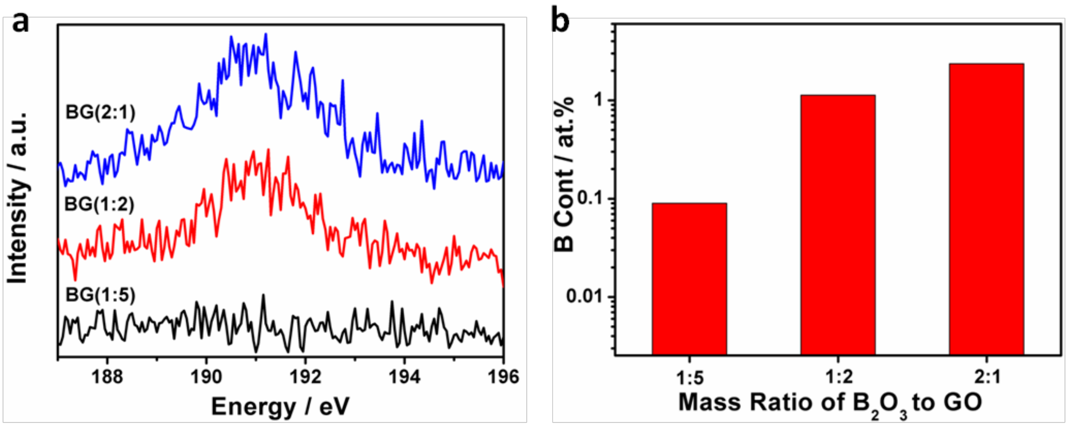

Fig. S4 (a) B1s XPS spectra of BG obtained at different mass ratios of B_2O_3 to GO, (b) the B content vs the mass ratio of B_2O_3 to GO.

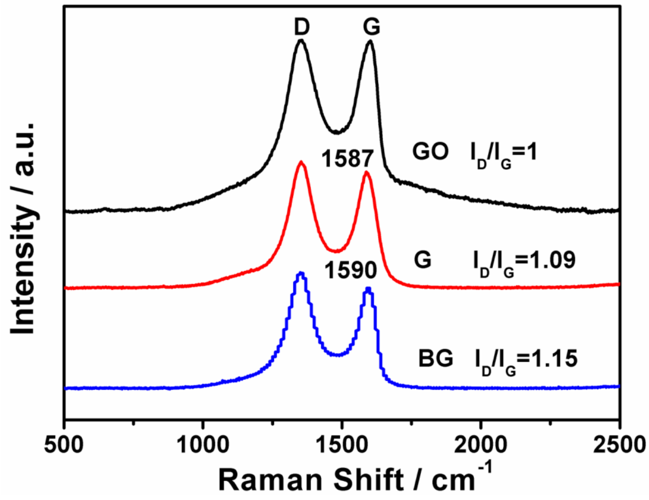

Fig. S5 Raman spectra of GO, G, and BG.

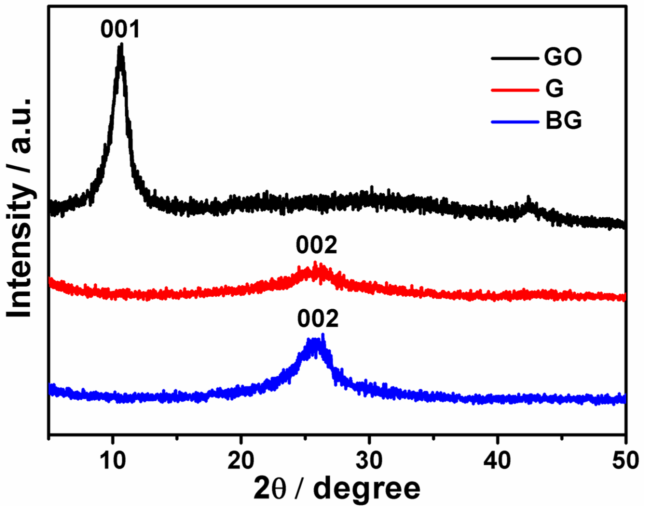

Fig. S6 XRD patterns of GO, G, and BG.

Table S1 The redox peaks of Pt, G, and BG from CVs

	Redox peaks			
	Redox peaks at low potential /mA cm^{-2}		Redox peaks at high potential /mA cm^{-2}	
Pt	0.91	-0.53	1.33	0.13
G	0.12	-0.94	1.06	-0.30
BG	0.50	-0.49	1.81	0.09

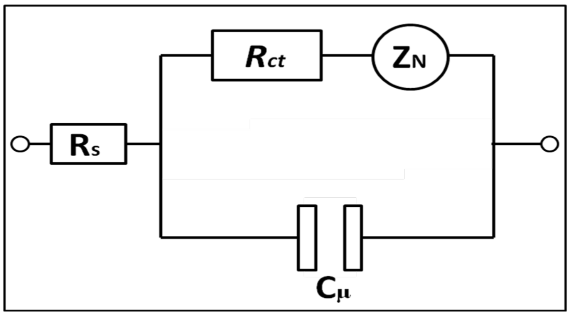

Fig. S7 The equivalent circuit of the cell.

Table S2 Summary of EIS characteristics of Pt, G, and BG.

Counter electrodes	R_s/Ω	R_{ct}/Ω	$C_\mu/\mu F$	Z_N/Ω
Pt	28.30	8.40	6.96	70.40
G	22.66	18.55	7.51	21.41
BG	17.77	1.37	2.41	27.70

Table S3 Characteristics of the J-V curves for BG CEs based on different mass ratios of B_2O_3 to GO.

Counter electrodes	V_{oc}/ V	J_{sc}/ mA cm^{-2}	FF	η/ %
BG(0.09*)	0.65	13.83	0.47	4.16
BG(1.13*)	0.73	13.93	0.66	6.73
BG(2.36*)	0.72	12.99	0.66	6.16

*Atomic percentage (at. %).

References:

1. H. L. Guo, X. F. Wang, Q. Y. Qian, F. B. Wang and X. H. Xia, *ACS Nano*, 2009, **3**, 2653.

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