# *Electronic Supplementary Information*

# New insight into enhanced visible light photocatalytic activity over boron-doped reduced graphene oxide

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## Contents List

## Experimental details

### *Materials*

Graphite powder, sulfuric acid ($H_2SO_4$), potassium persulfate ($K_2S_2O_8$), phosphorus pentoxide ($P_2O_5$), nitric acid ($HNO_3$), potassium permanganate ($KMnO_4$), hydrochloric acid (HCl), hydrogen peroxide, 30% ($H_2O_2$), ethanol ($C_2H_5OH$) and ammonium oxalate ($(NH_4)_2C_2O_4$, AO) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Borane-tetrahydrofuran (THF) adduct was obtained from Aladdin Co., Ltd. All materials were used as received without further purification. Deionized water used in the synthesis was from local sources.

### *Catalyst Preparation*

*(a) Synthesis of Graphene Oxide (GO).* Graphene oxide (GO), the precursor of graphene (GR), was synthesized from natural graphite powder by a modified Hummers' method. Typically, 2 g of graphite powder (supplied from Sinopharm Chemical Reagent Co., Ltd., China) was put into a mixture of 12 mL of concentrated $H_2SO_4$, 2.5 g of $K_2S_2O_8$, and 2.5 g of $P_2O_5$. The solution was heated to 80 $^oC$ in an oil-bath kept stirring for 24 h. The mixture was then carefully diluted with 500 mL of deionized (DI) water, filtered, and washed until the pH of rinse water became neutral. The product was dried under ambient condition overnight. This pre-oxidized graphite was then subjected to oxidation described as follows. In a typical procedure, pre-oxidized graphite powder was added to a mixture of 120 mL of concentrated $H_2SO_4$ and 30 mL $HNO_3$ under vigorous stirring, and the solution was cold to 0 $^oC$. Then, 15 g of $KMnO_4$ was added gradually under stirring and the temperature of the mixture was kept to be below 20 $^oC$ by cooling. Successively, the mixture was stirred at room temperature for 96 h, and then diluted with 1 L of DI water in an ice bath to keep the temperature below 50 $^oC$ for 2 h. Shortly after the further diluted with 1 L of DI water, 20 mL of 30 % $H_2O_2$ was then added to the mixture and a brilliant yellow product was formed along with bubbling. The mixture was filtered and washed with 1:10 HCl aqueous solution to remove metal ions followed by DI water to remove the acid. The filter cake was then dispersed in water by a mechanical agitation. Low-speed centrifugation was done at 1000 rpm for 2 min. The supernatant then underwent two more high-speed centrifugation steps at 8000 rpm for 15 min to remove small GO pieces and water-soluble byproduct. The final sediment was redispersed in water with mechanical agitation or mild sonication using a table-top ultrasonic cleaner, giving a solution of exfoliated GO. *(b) Preparation of B-Doped RGO (B-RGO).* The preparation of B-RGO involves the use of GO and borane-THF adduct as precursors by a simple reflux method as reported previously.[S1] Typically, 500 mg of GO was dispersed into 167 mL of deionized water completely by ultrasonication, and then 1.5 mL of borane-THF adduct was added and this suspension was heated to 373 K in an oil bath with magnetic stirring for 96 h, which allows sufficient reduction of GO to RGO. After that, the products were cooled at room temperature and separated by centrifugation and washed with deionized water, and fully dried at 333 K in oven to get the final B-RGO samples. For comparison purpose, RGO was synthesized via the same procedure as that of B-RGO except for the addition of borane-THF adduct.

### *Characterization*

The crystalline structure of the samples was determined by the powder X-ray diffraction (XRD, Philip X' Pert Pro MPP) using a Cu K$\alpha$ radiation ($\lambda$=1.5418Å) in the $2\theta$ ranging from

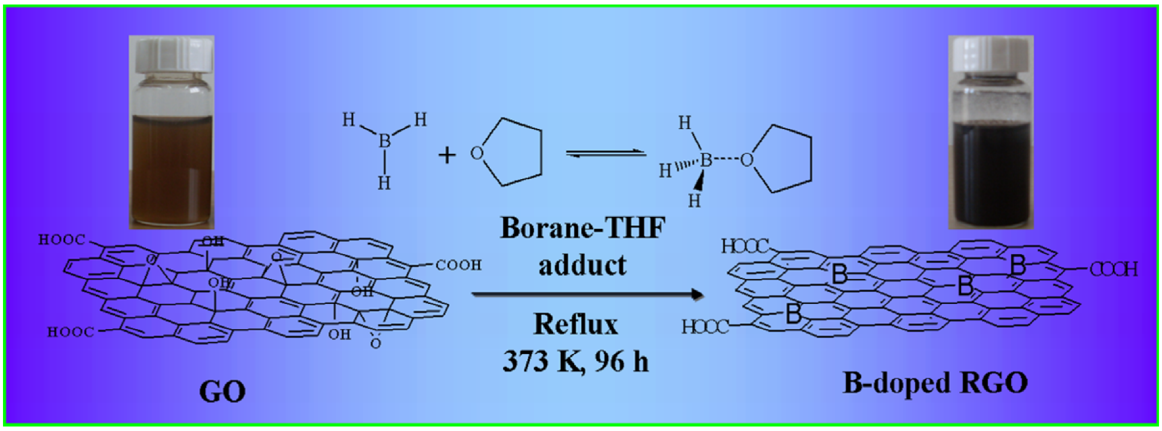
5° to 80° with a scan rate of 0.08° per second. Raman spectroscopic measurements were performed on a Renishaw inVia Raman System 1000 with a 532 nm Nd:YAG excitation source at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific ESCA Lab250 spectrometer which consists of a monochromatic Al K$\alpha$ as the X-ray source, a hemispherical analyzer and sample stage with multi-axial adjustability to obtain the composition on the surface of samples. All of the binding energies were calibrated by the C 1s peak at 284.6 eV. Field-emission scanning electron microscopy (FE-SEM) was used to characterize the morphology of the samples on a FEI Nova NANOSEM230 spectrophotometer.

Fluorescence lifetimes were measured on an Edinburgh Analytical Instrument PLS920 system by the time-correlated single-photon counting method and the solution contained 4 mL of $H_2O$, 0.5 mg of catalyst powder and 0.1 mL of 10 ppm RhB. The exciting and receiving wavelengths were set at 483 and 576 nm, respectively.

The electrochemical analysis was carried out in a conventional three-electrode cell using a Pt plate and an Ag/AgCl electrode as the counter electrode and reference electrodes, respectively. The working electrode was prepared on fluoride-tin oxide (FTO) glass that was cleaned by sonication in ethanol for 30 min and dried at 353 K. The sample powder (5 mg) was ultrasonicated in 0.5 mL anhydrous ethanol to disperse it evenly to get slurry. The slurry was spreading onto FTO glass whose side part was previously protected using Scotch tape. The working electrode was dried overnight under ambient conditions. A copper wire was connected to the side part of the working electrode using a conductive tape. Uncoated parts of the electrode were isolated with epoxy resin. The exposed area of the working electrode was 0.25 $cm^2$. The electrochemical impedance spectroscopy (EIS) measurements were measured by applying an AC voltage with 5 mV amplitude in a frequency range from 1 Hz to 100 kHz under open circuit potential conditions with a CHI-660D electrochemical workstation (CH instruments, USA) and the electrolyte contained 10 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ and 0.5 M KCl.

### *Photocatalytic activity measurement*

The photocatalytic activities of the samples were evaluated by the degradation of Rhodamine B (RhB) in an aqueous solution under the irradiation of visible light. Typically, a 10 mg portion of catalyst was suspended in 60 mL of 10 ppm RhB solution. Before irradiation, the suspensions were stirred in the dark for 2 h to ensure the establishment of adsorption-desorption equilibrium. Under ambient conditions and stirring, the quartz tube was exposed to the visible light irradiation produced by a 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfectlight Co. Ltd.) with a UV−CUT filter to cut off light of wavelength $\lambda < 420$ nm. A 3 mL sample solution was taken at a certain time interval during the experiment and centrifuged to remove the catalyst completely. The solution was analyzed on a Varian UV-vis spectrophotometer (Cary-50, Varian Co. Ltd). The percentage of degradation of RhB, is reported as $C/C_0$. Here, $C$ is the concentration of RhB solution at each irradiated time interval, while $C_0$ is the initial concentration of RhB solution after the adsorption-desorption equilibrium is reached. Controlled photoactivity experiments using $K_2S_2O_8$ as electron scavenger and ammonium oxalate (AO) as hole scavenger for was performed similar to the above photocatalytic experiments except that the radical scavengers (60 mg) were added to the reaction system.



**Scheme S1.** Illustration for preparation of B-RGO by a simple reflux method.[S1]

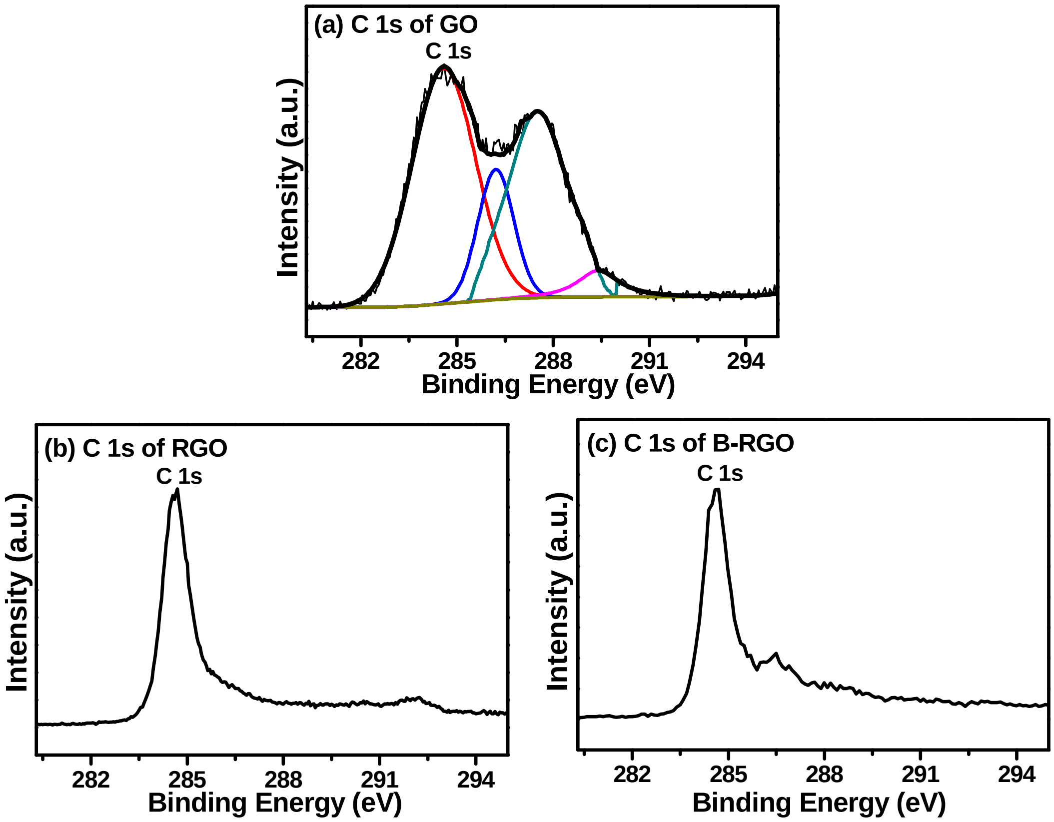


**Fig. S1** C 1s XPS spectra of (a) GO, (b) RGO and (c) B-RGO.

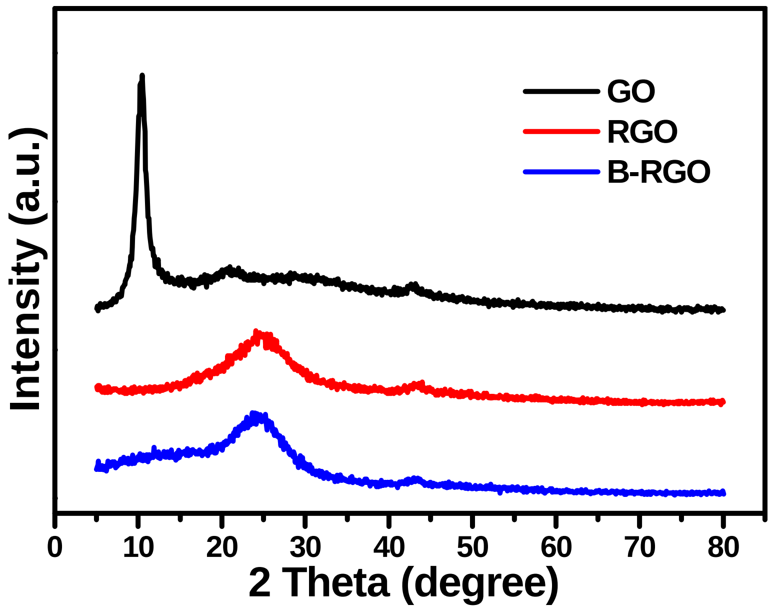


**Fig. S2** The XRD patterns of GO, RGO and B-RGO.

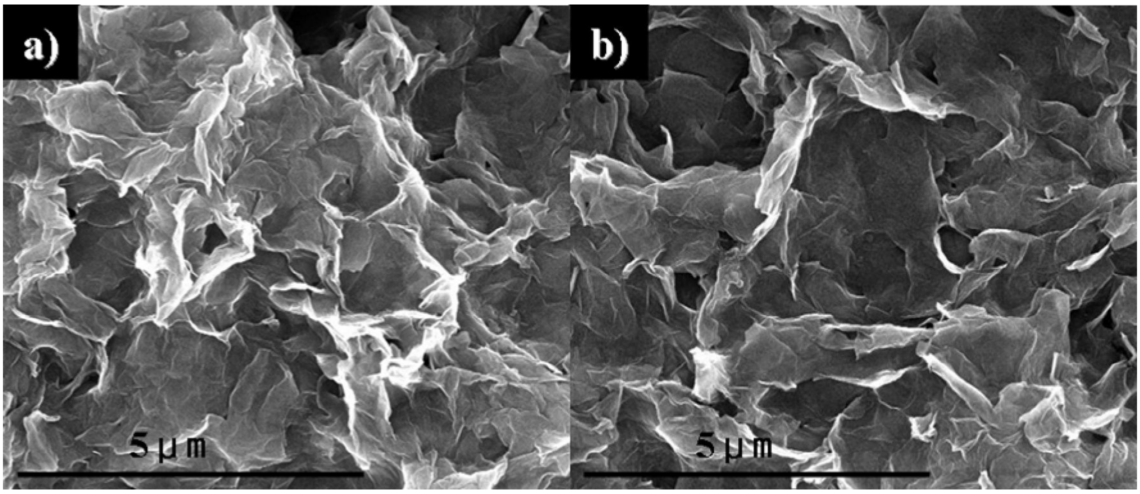


**Fig. S3** Typical SEM images of (a) B-RGO and (b) RGO.

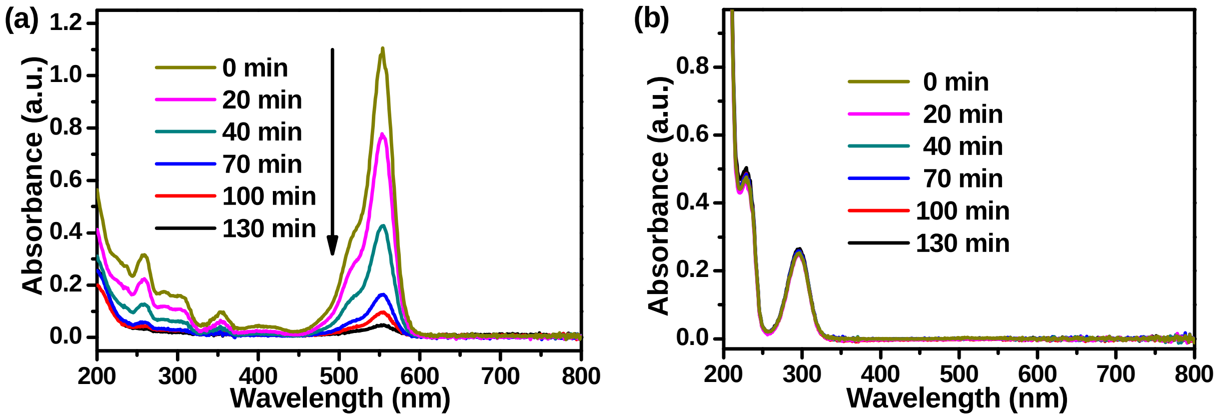


**Fig. S4** UV-vis absorption spectra for the photocatalytic degradation of (a) RhB and (b) salicylic acid over B-RGO under visible light irradiation (λ > 420 nm).

**Reference:**

[S1] J. Han, L. L. Zhang, S. Lee, J. Oh, K.-S. Lee, J. R. Potts, J. Ji, X. Zhao, R. S. Ruoff and S. Park, *ACS Nano*, 2013, **7**, 19-26.