

Electronic Supplementary information for

Polyaniline Nanosheet Derived B/N co-Doped Carbon Nanosheets as Efficient Metal-Free catalysts for Oxygen Reduction Reaction

Yi Zhang,^{†ab} Xiaodong Zhuang, ^{†b} Yuezeng Su,^{*a} Fan Zhang,^{*b} Xinliang Feng^{bc}

^a*School of Aeronautics and Astronautics, Shanghai Jiao Tong University, Shanghai 200240, China*

^b*School of Chemical and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China,*

^c*Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany*

** Corresponding author: E-mail adress:*

†These two authors contributed equally to this work.

Experimental Section

Chemical reagents and Materials:

3-Aminobenzeneboronic acid hemisulfate salt (ABB) and Pt/C were obtained from Sigma-Aldrich. All other reagents were purchased from Aladdin Reagent Inc (Shanghai, China). Unless otherwise stated, all the reagents were of analytical grade and used as received without further purification. Graphene oxide (GO) was synthesized from natural graphite flakes by a modified Hummers method^{s1}.

Preparation of amino modified GO (AGO):

GO sheets (1.0 g) were added to dry DMF (250 mL), and sonicated for a few hours until completely dispersed. Then, N-Hydroxysuccinimide (NHS, 3.42g) and N-(3-(dimethylamino)propyl)-N'-ethylcarbodiimide hydrochloride (EDC•HCl, 5.75g) were added to the dispersion at 0 °C. After stirring for another 2 h, p-phenylenediamine (4.92g) was added, and the mixture was continuously stirred for 2h at room temperature. After filtration and washing by water and ethanol, the product was vacuum dried at 60 °C overnight.

Preparation of graphene oxide based 2D and boronic acid substituted polyaniline (GO-CBP):

AGO sheets (0.1 g) were dispersed in 1M HCl (100 mL) by sonication. Then, aniline (0.22g, 2.36mmol), m-phenylenediamine (0.341g, 3.15mmol), and ABB (0.439g, 2.36mmol) were added to the dispersion at 0 °C and sonicated for 30 min. Ammonium persulfate (2.34g) in 1M HCl (20mL) was added dropwise to the dispersion at 0 °C over 1 h. The mixture was stirred overnight at room temperature. At last, the dispersion was blackish green. The product was collected by filtration and washed by water, ethanol and N-methyl-2-pyrrolidone sequentially. After vacuum drying at 60 °C overnight, GO-CBP was yielded (890 mg, 80.9%). For comparison, The control sample without AGO template (CBP) was synthesized under the same condition.

Thermal treatment of GO-CBP:

GO-CBP was placed in a quartz boat and heated to 1000°C under the heating rate of

5°C min⁻¹ under nitrogen flow, and then held at this temperature for 1 h. After cooling to room temperature, the black powder G-CBP was ground. The control samples with different annealing temperature (600°C and 800°C) were carried out under the same method. For comparison, the pyrolyzed products under 600, 800 and 1000°C were named G-CBP-600, G-CBP-800 and G-CBP-1000, respectively. If not mentioned, G-CBP was typically discussed as G-CBP-1000 in the context.

CO₂ activation of G-CBP:

For the activation by carbon dioxide, G-CBP was heated to 1000°C at a heating rate of 5°C/min⁻¹ in a horizontal furnace under nitrogen gas flow (60 mL/h) and then switched to carbon dioxide gas flow (60 mL/h) for 15 min at the same temperature. After cooling to room temperature, the as-prepared activated B/N co-doped porous carbon nanosheets (G-CBP-a) were obtained (yield: 35 wt%).

General Characterization:

SEM measurements were performed on a FEI Sirion-200 field emission scanning electron microscope. TEM studies were conducted on a JEOL-2100 electron microscope at an operating voltage of 200 kV. The sample was dissolved in water and the suspension was dropped onto a copper grid covered with carbon film. XRD analysis was performed on a Rigaku D/Max 2500 X-ray diffractometer with Cu K α radiation ($k = 1.54 \text{ \AA}$) at a generator voltage of 40 kV and a generator current of 50 mA with a scanning speed of 5°/min from 10° to 60°. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an AXIS Ultra DLD (Kratos Co., Japan). Infrared spectra were recorded on a Spectrum 100 (Perkin Elmer, Inc., USA) by using pressed KBr pellets. Thermogravimetric analysis were carried out on a Q5000IR (TA Instruments, USA) at a heating rate of 20°C/min under nitrogen flow. Autosorb-iQA3200-4 (Quantatech Co., USA) was used to characterize the specified surface area calculated from the Brunauer-Emmett-Teller (BET) plot of nitrogen adsorption isotherm in the relative pressure range of 0.05-0.3. The pore width distribution was computed from the density functional theory (DFT) according to the nitrogen adsorption isotherm in the relative pressure range of 0.05-0.99.

Electrochemical characterization:

For electrode preparation, 1 mg of G-CBP-a was dispersed in 1 mL solvent mixture of Nafion (5%) and ethanol (V: V ratio = 1:9) for 0.5~1 h under sonication. Then 10 μ L portion of G-CBP-a suspension was slightly dropped on the disk surface of the pre-polished glassy carbon electrode. For comparison, a commercially available catalyst of 20 wt% Pt/C powder was used and 1 mg/mL Pt/C suspension was prepared as the same procedure above. The electrodes were then dried for 15 min at room temperature before measurement. Electrochemical measurements of cyclic voltammetry, rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) were performed by a basic bipotentiostat (Pine Research Instrumentation, USA) with a three-electrode cell system. A rotating glass carbon disk and platinum ring electrode (Pine Research Instrumentation, USA) after loading the electrocatalyst was used as the working electrode, an Ag/AgCl (KCl, 3M) electrode as the reference electrode, and a Pt wire as the counter electrode. The electrochemical experiments were conducted in O₂ saturated 0.1 M KOH electrolyte for the oxygen reduction reaction. The potential range is cyclically scanned between -1.0 and +0 V at a scan rate of 100 mV/s at the room temperature after purging O₂ gas for 30 min. RDE measurements were conducted at different rotating speeds from 225 to 1600 rpm, using a Pine Model.

We performed rotating ring-disk electrode (RRDE) voltammetry. The linear sweep voltammetry (LSV) was carried out at the modified GC disk electrode with a scan rate of 10 mV/s while the Pt ring was polarized at 0.5 V for oxidizing HO₂⁻ intermediate from the LSV on disk electrode. The transferred electron number (*n*) per oxygen molecule in the ORR process was calculated using Eq. (1)^{s2}. *I_D* is the faradic disk current and *I_R* is the faradic ring current. *N* = 0.37 is the collection efficiency.

$$n = 4I_D / (I_D + I_R / N) \quad (1)$$

The transferred electron number (*n*) per oxygen molecule in the ORR process was calculated by the Koutechy–Levich (K–L) equations^{s3, s4}.

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (2)$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (3)$$

$$J_K = nFkC_0 \quad (4)$$

in which *J* is the measured current density, *J_K* and *J_L* are the kinetic- and diffusion-limiting current densities, μ is the angular velocity of the rotating electrode ($\omega=2\pi N$, *N* is the linear rotation speed), *n* is the exchange electron transfer number in ORR, *F* is the Faraday constant (*F* = 96485 C mol⁻¹), *C₀* is the concentration of O₂, *D₀* is the diffusion coefficient of O₂, ν is the kinematic viscosity of the electrolyte, and *k* is the electron transfer rate constant. Since the electrolyte was O₂ saturated 0.1 M KOH in this report, *C₀*, *D₀* and ν were used as 1.2×10^{-3} M, 1.9×10^{-5} cm² s⁻¹, and 0.01 cm² s⁻¹, respectively.

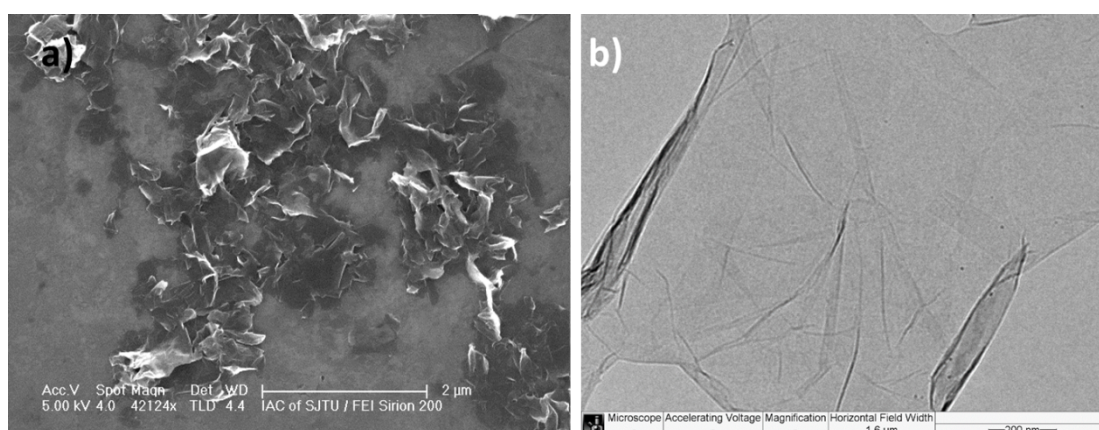


Fig. S1 Representative SEM (a) and TEM (b) images of AGO.

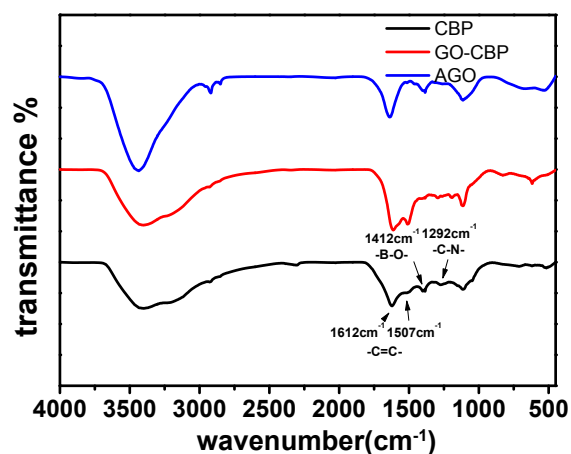


Figure S2 FT-IR spectra of CBP, GO-CBP, AGO.

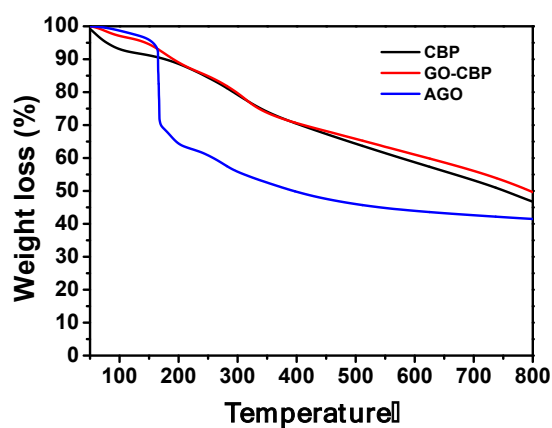


Fig. S3 TGA curves of CBP, GO-CBP, AGO (heating rate =20°C/min under a nitrogen atmosphere).

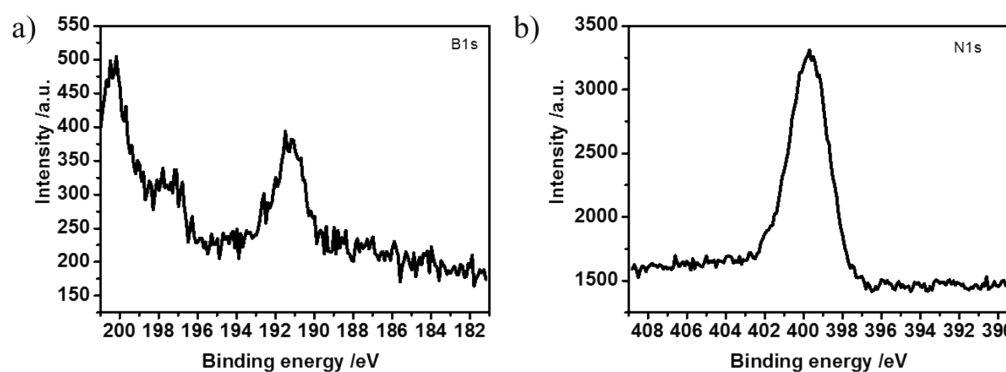


Fig. S4 XPS spectra of B 1s (a) and N 1s (b) of GO-CBP

The XPS spectra illustrate the present of boron and nitrogen elements. The peak at about 197 eV present in the B1s spectra is most probably due to chlorine contaminations on the surface the films.

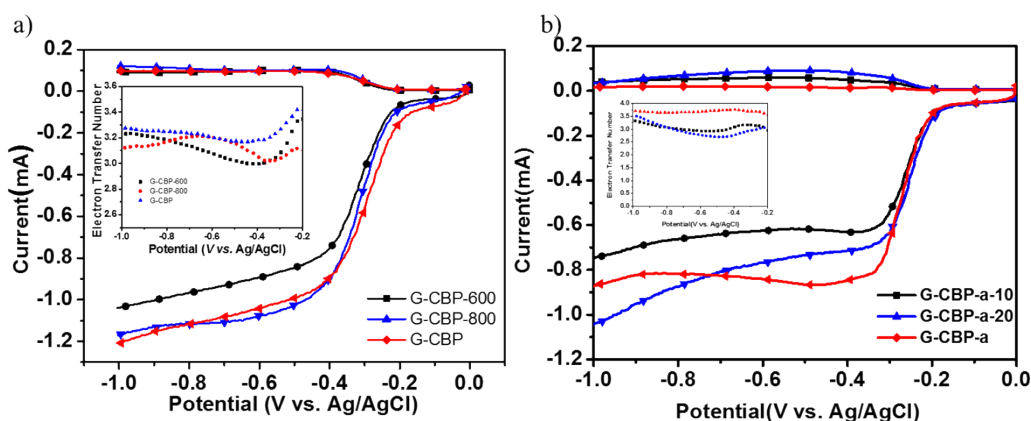


Fig. S5 (a) RRDE voltammograms of G-CBP series pyrolysis at 600°C (G-CBP-600), 800°C (G-CBP-800) and 1000°C (G-CBP) in 0.1 M KOH solution saturated with O₂. The ring-disk electrode rotation rate was 1600 rpm, and the Pt ring electrode was held at 0.5 V. (Inset: electron transfer number calculated from RRDE curve) (b) RRDE voltammograms of G-CBP-a with different active time for 10min (G-CBP-a10), 20min (G-CBP-a20) and 30min (G-CBP-a) in 0.1 M KOH solution saturated with O₂. The ring-disk electrode rotation rate was 1600 rpm, and the Pt ring electrode was held at 0.5 V. (Inset: electron transfer number calculated from RRDE curve).

To optimize the property, G-CBP had activation with different time, and was labeled as G-CBP-a10 (10min), G-CBP-a (15min) and G-CBP-a20 (20min). It can be observed that the G-CBP-a has the best electrocatalytic property.

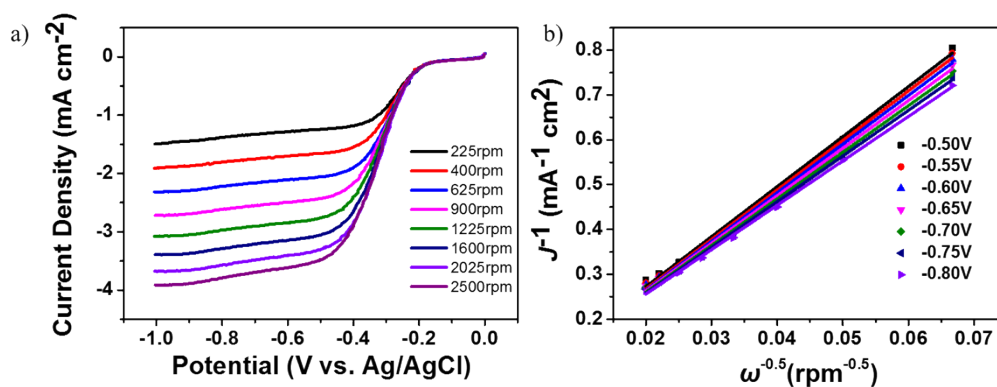


Fig. S6 (a) RDE voltammograms of G-CBP in 0.1 M KOH solution saturated with O₂.

(b) Koutecky-Levich plots calculated from the RDE result

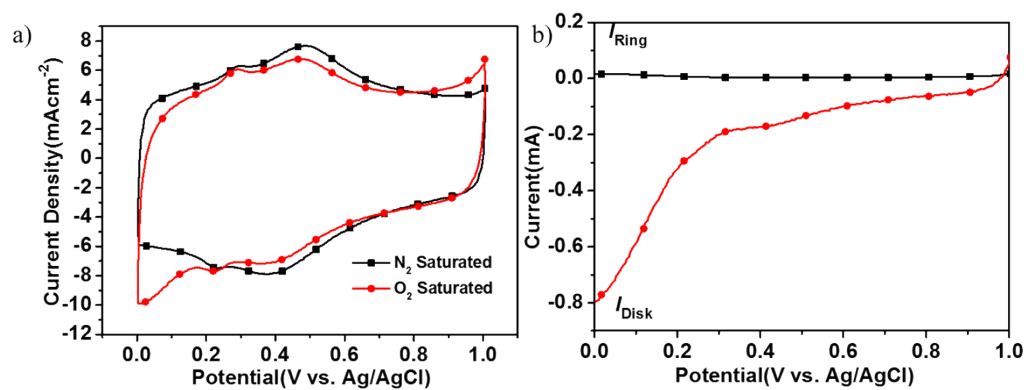


Fig. S7 (a) Typical cyclic voltammograms of G-CBP-a at a scan rate of 100 mV s⁻¹ in

O₂ and N₂-saturated 0.5 M H₂SO₄ solution. (b) RRDE voltammograms of G-CBP-a in

0.5 M H₂SO₄ solution saturated with O₂. The ring-disk electrode rotation rate was

1600 rpm, and the Pt ring electrode was held at 1.0 V.

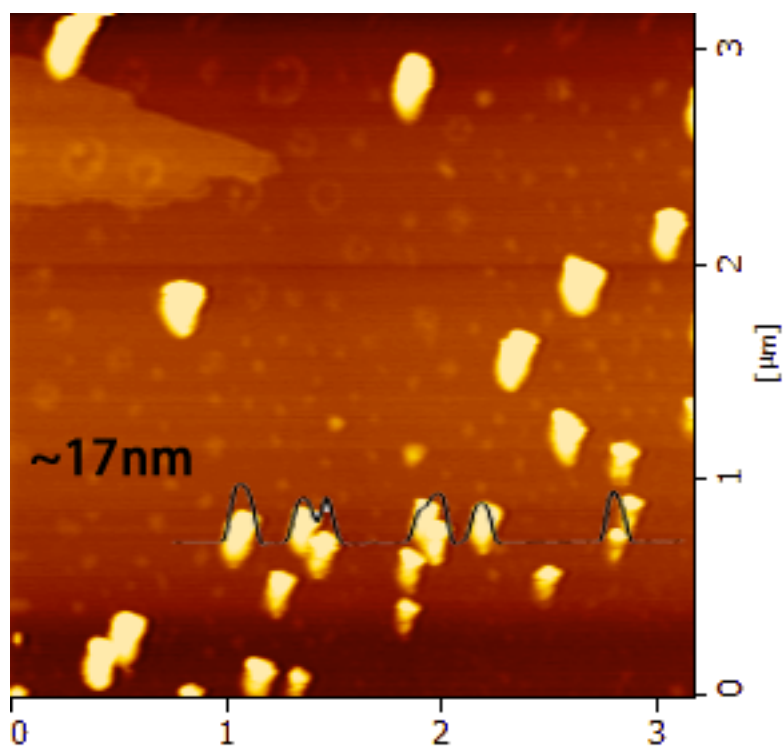


Fig. S8 AFM image of G-CBP-a

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- s3. R. Liu, D. Wu, X. Feng and K. Müllen, *Angew. Chem. Int. Ed.*, 2010, **49**, 2565-2569.
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