Electronic Supplementary Information

Electrochemical Doping of Three-dimensional Graphene Networks

Used as Efficient Electrocatalysts for Oxygen Reduction Reaction

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Methods

Chemicals. Tetrabutylammonium perchlorate (TBAP, for electrochemical analysis, $\geqslant$99.0%), sodium tetrafluoroborate (NaBF$_4$, for electrochemical analysis, $\geqslant$99.0%), acetonitrile (anhydrous, 99.8%), nafion (5 wt%) and methanol (99.8%) were purchased from Sigma-Aldrich. Potassium hydroxide (pellets for analysis EMSURE) was purchased from Merck. All chemicals were used as received without any further purification. Ultrapure Milli-Q water (Milli-Q System, Millipore, Billerica, MA, USA) was used in all related experiments.

Synthesis of three-dimensional graphene network (3DGN). Briefly, 3DGN was synthesized on Ni foam by the ethanol-CVD method based on our previous reports.[1,2] Then the Ni foam was removed by the mixed FeCl$_3$ and HCl solution. After that, a piece of 3DGN without Ni foam was transferred onto a glass plate and fixed by silicon gel. Last, Ag paint was placed on one side of the 3DGN, which was used to connect the 3DGN with the workstation.

Electrochemical doping of 3DGN. The doping process was carried out on an Auto Lab workstation (PGSTAT302A). The 3DGN, Ag/AgCl (saturated with LiCl in ethanol) and Pt were used as working, reference and counter electrodes, respectively. The TBAP in acetonitrile solution (0.1 M) was used as both electrolyte and N source. Upon the application of cyclic voltammogramic scan within the potential range of ± 2V at scan rate of 5 mV/s, 10 cycles were used to dope the 3DGN. Before the electrochemical doping, the cell was bubbled with pure N$_2$ to remove the oxygen. During the doping process, the whole setup was kept in a desiccator in order to prevent water or oxygen to affect the reaction. After the electrochemical doping, the obtained N-3DGN was immersed into Milli-Q water to remove acetonitrile. Then the N-3DGN film was

mixed with proper volume of Milli-Q water to obtain 1 mg/mL N-3DGN aqueous solution.

The B-3DGN was synthesized by the same procedure except that $NaBF_4$ in acetonitrile solution (0.1 M) was used as B source. The doping conditions, *i.e.,* potential range, scan rate and cycle numbers, are same to those for preparation of N-3DGN. The difference between the aforementioned two processes is the starting potential. For the preparation of N-3DGN, the scan starts from 2 V, while it starts from -2 V for B-3DGN.

The NB-3DGN was synthesized by two-step doping strategy. N and B were incorporated into 3DGN by the aforementioned electrochemical method in sequence. TBAP and $NaBF_4$ in acetonitrile were used as N and B source, respectively. The other doping conditions are same to those for N-3DGN and B-3DGN.

Characterizations. Field emission scanning electron microscopy (FESEM, Model JSM-7600F, JEOL Ltd., Tokyo, Japan) was used to characterize the samples. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XLelectron spectrometer (VG Scientific) using 300 W AlKα radiation. The base pressure was about 10^{-9} mbar. The binding energy was referenced to the C1s line at 284.8 eV from adventitious carbon. Curve fitting of the C 1s, N 1s and B 1s spectra was performed using a Gaussian-Lorentzian peak shape.

Raman spectra were recorded on a WITec CRM200 confocal Raman microscopy system, using an emission wavelength of 532 nm laser with an air cooling charge coupled device (CCD) as detector (WITec Instrument Corp, Germany) under ambient conditions. Before measurement, the instrument was calibrated with silicon wafer.

Electrochemical measurements. The rotating disk electrode (RDE) voltammograms were recorded on an electrode rotator and Auto lab potentiostat (PGSTAT302A). First, 20 μL of N-

3DGN, B-3DGN or NB-3DGN aqueous solution (1 mg/mL) were mixed with 10 μL of 0.5 wt% nafion aqueous solution, respectively. Then, 25 μL of the aforementioned mixed solution was dropped onto glassy carbon electrode (GCE, 5 mm in diameter), giving an approximate catalyst loading of 0.016 mg. Before test, the electrode was dried in air at room temperature. The GCE modified with N-3DGN, B-3DGN and NB-3DGN, referred to as N-3DGN/GCE, B-3DGN/GCE and NB-3DGN/GCE, respectively, were used as working electrode in sequence. Pt and Ag/AgCl (3 M KCl) electrode were used as counter and reference electrodes, respectively. For comparison, a commercially available catalyst of 30 wt% Pt/C (Pt(30%)/C) aqueous suspension (1 mg/mL) was used for preparation of a working electrode in the control experiment. In all ORR experiments, 0.1 M KOH aqueous solution was used as the electrolyte. High-purity N_2 and O_2 were used to purge the solution for at least 30 min to achieve O_2-free or O_2-saturated electrolyte solution, respectively. The rotating rate increased from 400 to 2,000 rpm in an O_2-saturated electrolyte at a scan rate of 5 mV/s.

The number of transferred electrons (n) per O_2 molecule in the ORR and kinetic current density can be calculated from the Koutecky-Levich equation shown as follows,[3]

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

$$B = 0.2nFC_0(D_0)^{2/3}v^{-1/6} \tag{2}$$

where J is the measured current density, J_K and J_L are the kinetic- and diffusion-limiting current densities, respectively, ω is the angular velocity of the disk ($\omega=2\pi N$, N is the linear rotation speed), n is the overall number of electrons transferred in ORR, F is the Farady constant (F=96485 C mol^{-1}), C_0 is the bulk concentration of O_2 (C_0=1.2×10^{-6} mol cm^{-3}), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH (D_0=1.9×10^{-5} cm^2 s^{-1}), and v is the kinematic viscosity of the electrolyte (v=0.01 cm^2 s^{-1}). The constant of 0.2 is adopted when the rotation rate is

expressed in rpm.[3,4]

The cyclic voltammograms, stability and the tolerance to the crossover effect of CH_3OH of N-3DGN, B-3DGN and NB-3DGN at -0.25 V were carried out on an Auto lab potentiostat. The N-3DGN/GCE, B-3DGN/GCE and NB-3DGN/GCE were used as working electrode in sequence. Pt and Ag/AgCl (3 M KCl) electrode were used as counter and reference electrodes, respectively. Noted that the loading of electrocatalysts on GCE in the measurement of stability and cyclic voltammograms is not same in order to separate the signal curves from each other. In other experiments, the loading of N-3DGN, B-3DGN and NB-3DGN on GCE in the electrochemical measurements is kept same.
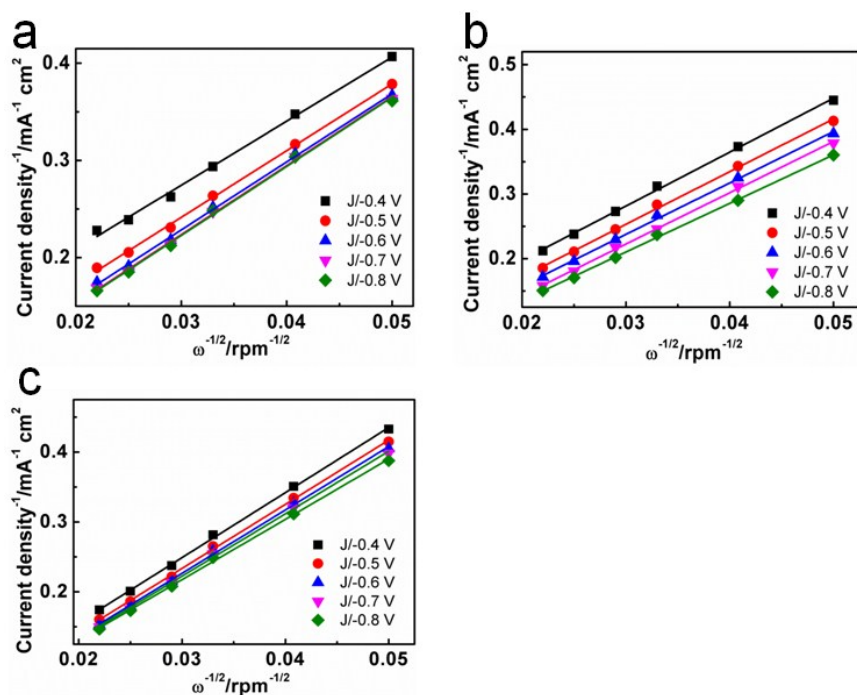

Figure S1. Koutecky-Levich plots of N-3DGN (a), B-3DGN (b) and NB-3DGN (c) at different electrode potentials.
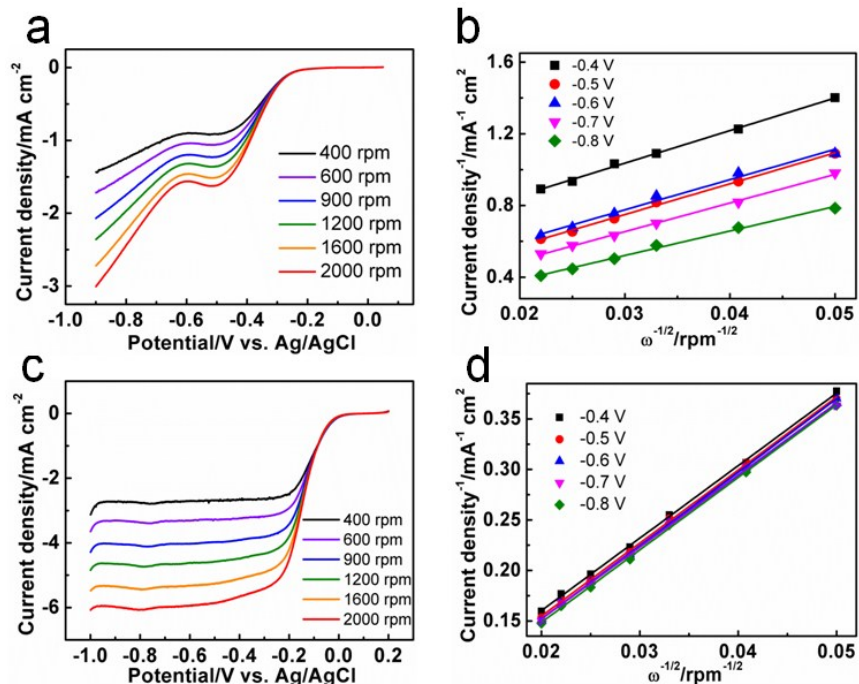
Figure S2. (a) Rotating disk electrode (RDE) linear sweep voltammograms of 3DGN in O_2-saturated 0.1 M KOH with various rotation rates at a scan rate of 5 mV/s. (b) Koutecky-Levich plots of 3DGN at different electrode potentials. (c) RDE linear sweep voltammograms of Pt(30%)/C in O_2-saturated 0.1 M KOH with various rotation rates at a scan rate of 5 mV/s. (d) Koutecky-Levich plots of Pt(30%)/C at different electrode potentials.
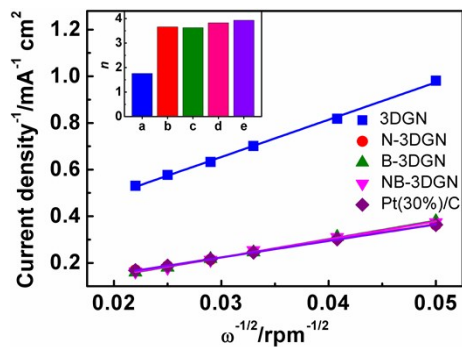

Figure S3. Koutecky-Levich plots of 3DGN, N-3DGN, B-3DGN, NB-3DGN and Pt(30%)/C at -0.7 V. Inset: the transferred electron number of 3DGN, N-3DGN, B-3DGN, NB-3DGN and Pt(30%)/C.

References

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