

## Supporting Information

### **Amorphous carbon enriched with pyridinic nitrogen as efficient metal-free electrocatalyst for oxygen reduction reaction**

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## Experimental Section

### *Preparation of the N-doped carbon films*

N-doped carbon ( $d_N$ -C) films were deposited on Si(100) and polycrystalline Ti substrates by using radio frequency magnetron sputtering at a constant power of 150 W applied on a pure C target at the room temperature. A mixture of Ar/N<sub>2</sub>/CH<sub>4</sub> (20/25/5 sccm) gases was used for discharging and reactive deposition of  $d_N$ -C films and different negative bias ( $V_b$ ) (floating of -12.3, -50, -100, -150, -200 V) was applied to the substrate during deposition. The as-deposited  $d_N$ -C films were annealed to 700 °C for 5 min under a flowing Ar gas. For convenience, the obtained films were designated as  $d_N$ -C ( $V_b$ ), where  $V_b$  is negative substrate bias. For comparison, when  $V_b$  is -100 V, pure C film was also synthesized under the same condition except that N<sub>2</sub> gas was not used during deposition.

### *Characterization of the $d_N$ -C films*

The structure for the  $d_N$ -C films deposited on Si(100) was characterized by X-ray diffraction (XRD) (D8\_tools) with a Cu K $\alpha$  line at 0.15418 nm as a source. The microstructure of the films deposited on Ti was examined by transmission electron microscopy (TEM) (JEOL TEM-2010) at 150 kV, high resolution TEM (HRTEM) and selected area electron diffraction (SAED) (JEOL TEM-2010) at 200 kV. The composition and chemical bonding state of the films were characterized by X-ray photoelectron spectroscopy (XPS) (ESCALAB-250) with a monochromatic Al K $\alpha$  radiation source. The thermal stability of the films was investigated by thermogravimetric analysis (TGA) (Diamond TG/DTA6300) with a heating rate of 10 °C/min in an argon atmosphere.

The electrocatalytic performance of the film catalysts for oxygen reduction reaction (ORR)

was studied by a rotating disk electrode technique in a conventional three-electrode electrochemical cell equipped with the gas flow systems using a potentiostat (PARSTAT 2273). The film deposited on Ti substrate was adhered to the glassy carbon disk (GCE) with a diameter of 5.0 mm using conductive silver glue. Insulating glue was used to seal the edge of Ti substrate to ensure that the silver glue was not in contact with the electrolyte. The modified GCE, an Ag/AgCl electrode (KCl saturated) and a platinum electrode were employed as working, reference and counter electrodes, respectively. The electrolyte was N<sub>2</sub> or O<sub>2</sub> saturated 0.1 M KOH solution with or without 3 M methanol. Commercial 20 wt% Pt/C (E-TEK) catalyst was purchased and used for comparison. The electron transfer number (*n*) per O<sub>2</sub> molecule in ORR and kinetic current density (*J<sub>k</sub>*) were determined according to the Koutecky-Levich (K-L) equation.

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{0.62nFD^{2/3}\nu^{-1/6}C_{O_2}\omega^{1/2}} \quad (1)$$

where *J* is the measured current density, *F* the Faraday constant (96485 C mol<sup>-1</sup>), *D* the diffusion coefficient of O<sub>2</sub> in electrolyte (1.9×10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>), *ν* the kinetic viscosity of the solution (0.01 cm<sup>2</sup> s<sup>-1</sup>), *C<sub>O2</sub>* the concentration of O<sub>2</sub> in solution (1.2×10<sup>-6</sup> mol cm<sup>-3</sup>), and *ω* the electrode rotation rate.

Anion-exchange membrane fuel cell tests were conducted using a fully automated test station. The Pt loading at anode was 0.3 mg cm<sup>-2</sup>, whereas the catalyst loading at cathode was 3 mg cm<sup>-2</sup> for d<sub>N</sub>-C (-100 V). For comparison, a cathode containing 0.2 mg<sub>Pt</sub> cm<sup>-2</sup> was also fabricated.

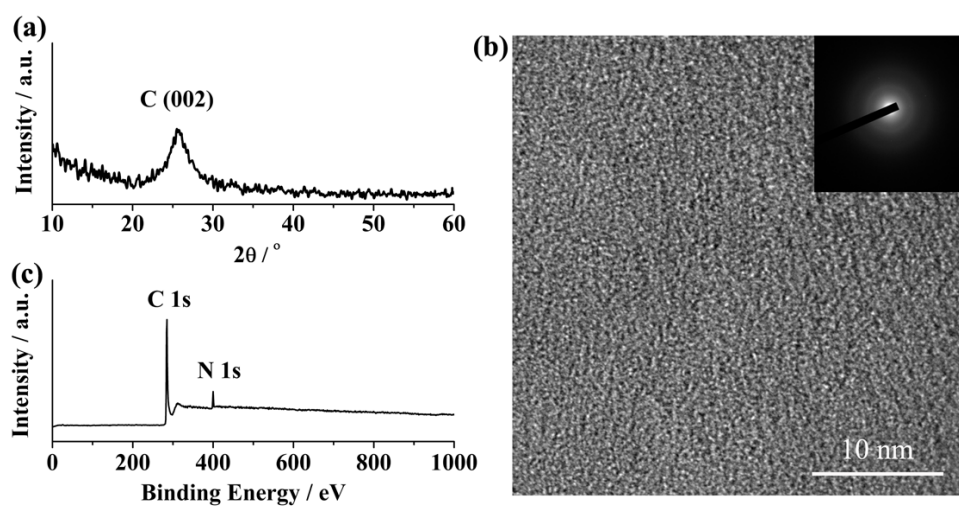


Fig. S1 (a) XRD pattern, (b) HRTEM image, (inset) SAED pattern and (c) overview-scan XPS spectrum for a typical  $d_N$ -C (-100 V).

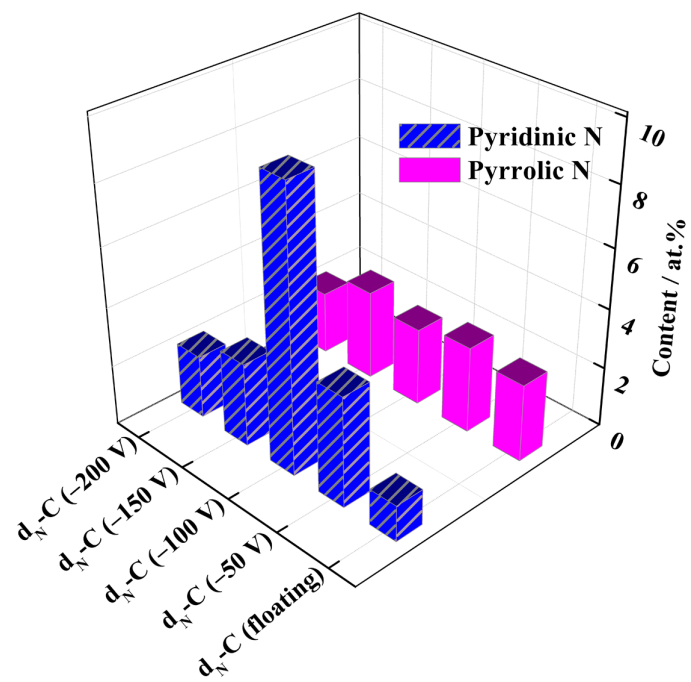


Fig. S2 The pyridinic N and pyrrolic N content on the surface for d<sub>N</sub>-C (V<sub>b</sub>).

Table S1. The total N, pyridinic N and pyrrolic N content on the surface for the d<sub>N</sub>-C (V<sub>b</sub>) and the ORR performance parameters for different catalysts.

Catalysts	Content (at.%)			Onset potential (V)	$J_k$ at -0.6 V (mA cm <sup>-2</sup> )	$n$
	Total N	Pyridinic N	Pyrrolic N			
d <sub>N</sub> -C (floating)	3.8	1.2	2.6	-0.05	11.63	2.47
d <sub>N</sub> -C (-50 V)	6.6	3.7	2.9	-0.03	16.39	3.41
<b>d<sub>N</sub>-C (-100 V)</b>	<b>12.0</b>	<b>9.4</b>	<b>2.6</b>	<b>-0.02</b>	<b>29.63</b>	<b>3.95</b>
d <sub>N</sub> -C (-150 V)	5.8	2.8	3.0	-0.06	14.29	3.12
d <sub>N</sub> -C (-200 V)	4.2	2.1	2.1	-0.10	12.99	2.97
Pure C	–	–	–	-0.16	5.95	2.03
<b>Pt/C</b>	–	–	–	<b>-0.02</b>	<b>30.56</b>	<b>3.99</b>

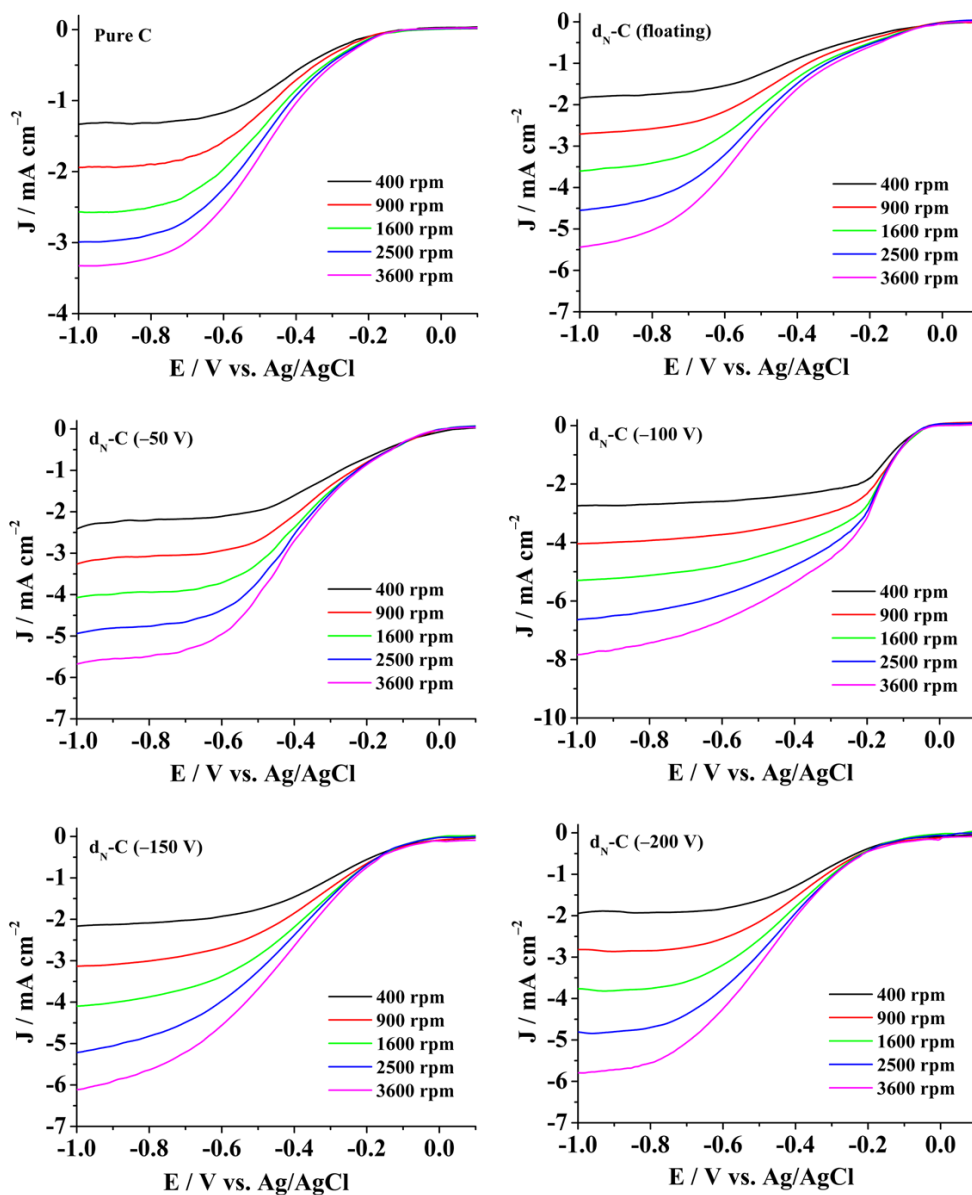


Fig. S3 Linear sweep voltammograms (LSV) for pure C film and d<sub>N</sub>-C (V<sub>b</sub>), and the measurements are performed at a sweep rate of 5 mV s<sup>-1</sup> and different electrode rotation rates in O<sub>2</sub>-saturated 0.1 M KOH solution.

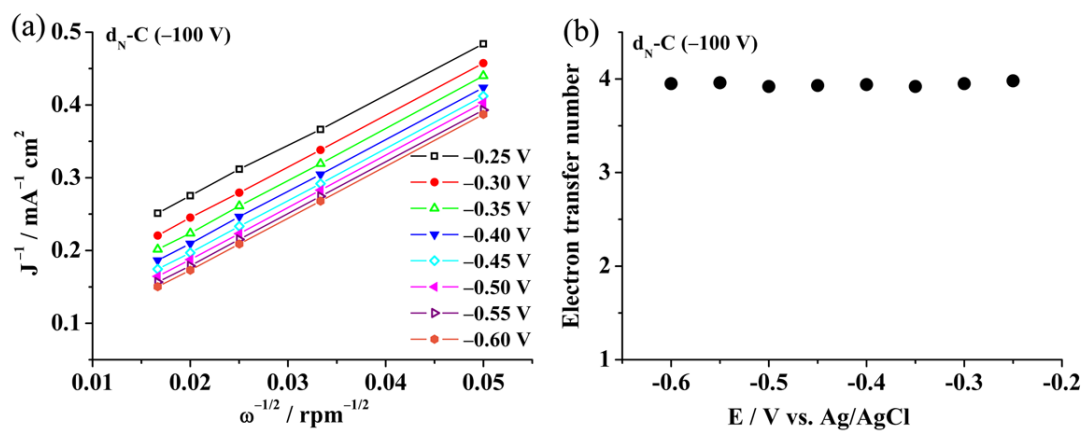


Fig. S4 (a) K-L plots of the d<sub>N</sub>-C (-100 V) for ORR at different electrode potentials and (b) electron transfer number of the d<sub>N</sub>-C (-100 V) for ORR at different electrode potentials.



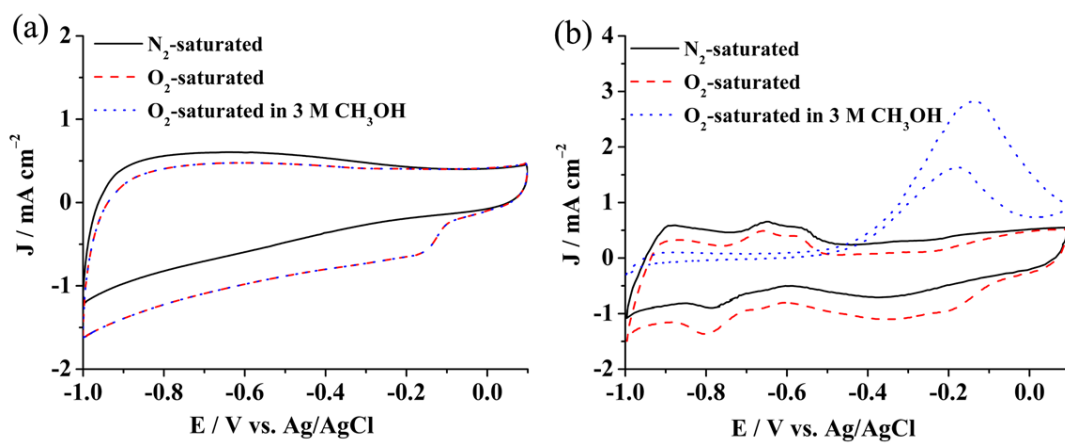


Fig. S5 Cyclic voltammograms of (a)  $\text{d}_\text{N}\text{-C}$  ( $-100$  V) and (b)  $\text{Pt/C}$  catalyst at a sweep rate of  $50 \text{ mV s}^{-1}$  in  $\text{N}_2$ -saturated  $0.1 \text{ M KOH}$ ,  $\text{O}_2$ -saturated  $0.1 \text{ M KOH}$  and  $\text{O}_2$ -saturated  $0.1 \text{ M KOH}$  with  $3 \text{ M CH}_3\text{OH}$  solutions.

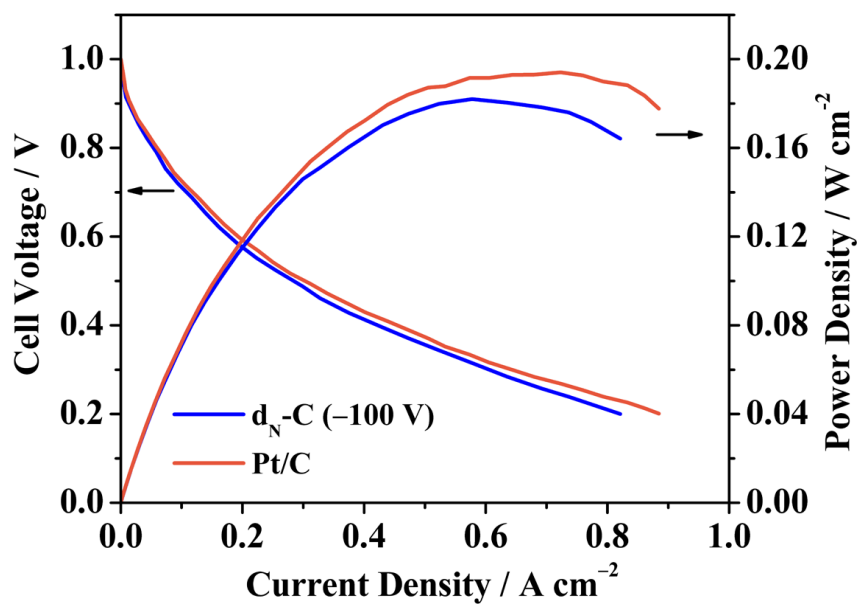


Fig. S6 Anion-exchange membrane fuel cell performances with d<sub>N</sub>-C (-100 V) and Pt/C as cathode catalysts.

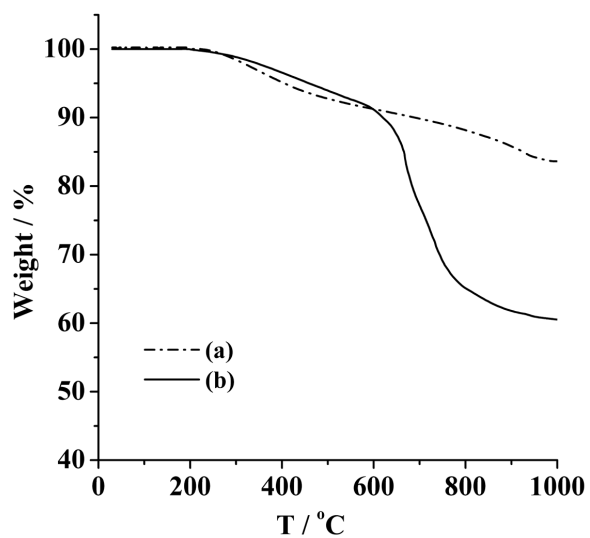


Fig. S7 TGA curves for the as-deposited (a) pure C and (b)  $d_N$ -C film grown at  $V_b$  of  $-100$  V.

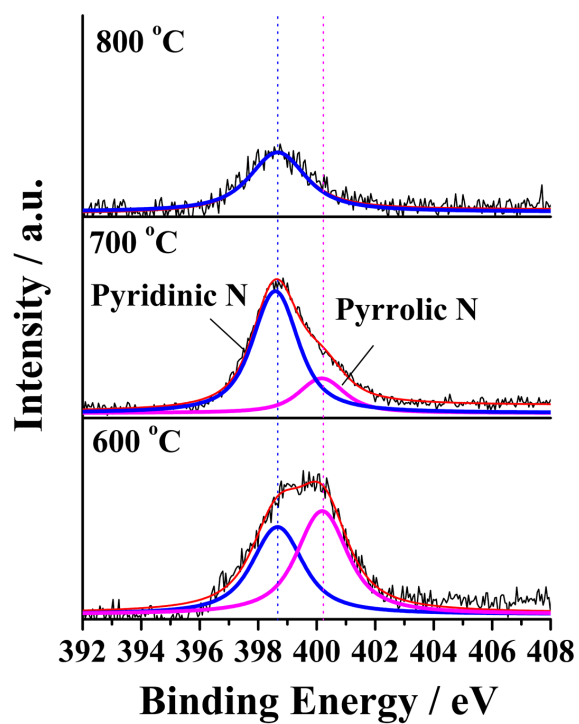


Fig. S8 XPS N 1s spectra for the d<sub>N</sub>-C films grown at V<sub>b</sub> of -100 V and then annealed at different temperatures.

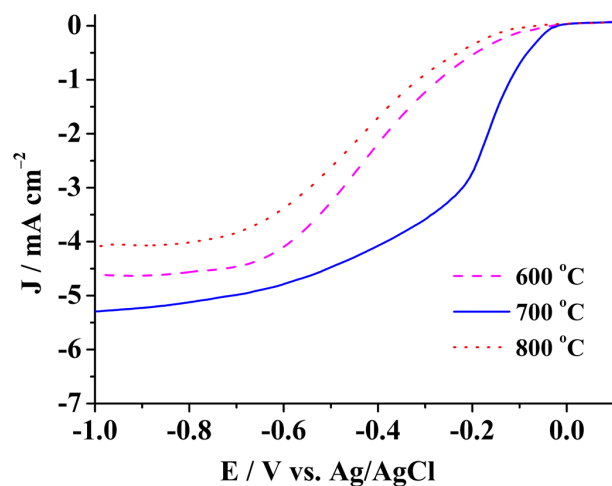


Fig. S9 LSVs of the  $d_N$ -C film grown at  $V_b$  of  $-100$  V and then annealed at different temperatures at a sweep rate of  $5 \text{ mV s}^{-1}$  and an electrode rotation rate of  $1600 \text{ rpm}$  in  $\text{O}_2$ -saturated  $0.1 \text{ M KOH}$  solution.