Supporting Information

Hierarchical Metal-Free Nitrogen-Doped Porous Graphene/Carbon Composites as an Efficient Oxygen Reduction Reaction Catalyst

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1. EXPERIMENTAL SECTION

The Koutecky-Levich plot can be obtained by using the Koutecky-Levich equation, which presents the relation between the inverse of measured current density (j^{-1}) and the inverse of square-root rotation rate ($\omega^{-1/2}$).[1]

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_l} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (1)$$

$$B = 0.62nFD_{O_2}^{2/3}\nu^{-1/6}C_{O_2} \quad (2)$$

Where j is the measured current density; j_k and j_l are the kinetic current density and diffusion-limited current density, respectively; n is the number of electrons transferred per oxygen molecule; F is the Faraday constant (F = 96485 C mol^{-1}); D_{O2} is the diffusion coefficient of O_2 in 0.1 mol L^{-1} KOH ($D_{O2} = 1.9\times10^{-5}$ cm^2 s^{-1}); υ is the kinematic viscosity of 0.1 mol L^{-1} KOH (υ = 1.0×10^{-2} cm^2 s^{-1}); C_{O2} is the bulk concentration of O_2 in the electrolyte ($C_{O2} = 1.2\times10^{-6}$ mol cm^{-3}), and ω is the rotating speed of the electrode. The H_2O_2 yields of as-prepared catalyst can be measured by RRDE measurements and calculated from the ring and disk current by using following equation (3)[2]:

$$H_2O_2(\%) = 200\times\frac{I_R/N}{(I_R/N)+I_D} \quad (3)$$

Moreover, the four-electron selectivity of the catalyst was evaluated based on the H_2O_2 yield. The electron transfer number can be calculated by following equation :

$$n = \frac{4I_D}{(I_R/N)+I_D} \quad (4)$$

where I_R and I_D are the ring and disk current, respectively. N is current collection efficiency of the Pt ring. N is 0.4 obtained from the reduction of $K_3Fe[CN]_6$.

2. RESULTS AND DISCUSSION

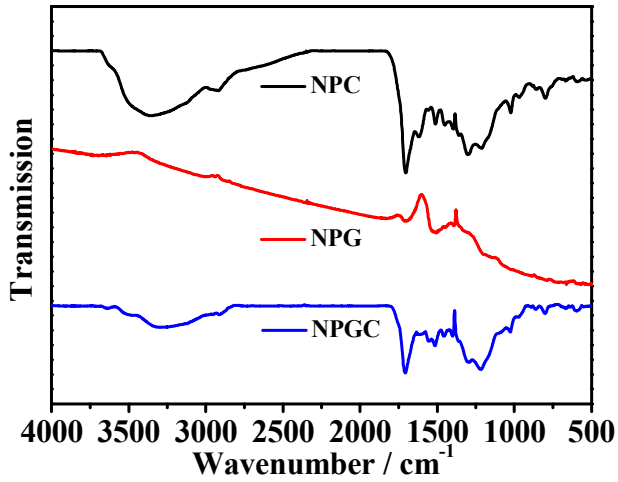

Fig. S1 FTIR spectra of NPC, NPG, and NPGC obtained after hydrothermal reaction.

Fig. S1 shows NPC has two peaks at 1708 and 1619 cm^{-1}, which are attributed to C=O and C=C vibrations, respectively. These results suggest the dehydration and aromatization of glucose have occurred successfully during the hydrothermal process.[3,4] The NPGC has the similar IR spectra to NPC, but different from that of NPG. Combining with the SEM, the result implies reduced graphene oxide (rGO) is coated by the carbon derived from glucose. Meanwhile, the peak around 1290cm^{-1} also proves the existence of C-N bond. It demonstrates the ethylenediamine can react with hydrothermal carbon and GO so that hydrothermal carbon can tightly coat the both surfaces of rGO by the chemical bond. It is noted that the relative peak intensity of -OH (~3360 cm^{-1}) in NPGC becomes weak significantly compared with that of

NPC. The result indicates the higher degree of graphitization of glucose is achieved with addition of GO during hydrothermal carbonization reaction.[4]

Table S1 The mass of GO and graphene/carbon composites before and after hydrothermal reaction.

Reactants	Mass before hydrothermal reaction	Mass after hydrothermal reaction
GO	60 mg	33 mg
glucose + GO	6060 mg	672 mg

Table S2 Summary of specific surface area, pore volume and adsorption average pore size of NPC-950, NPG-950 and NPGC-950.

Samples	$S_{BET}/m^2\ g^{-1}$	Pore volume/$cm^3\ g^{-1}$	Adsorption average pore size/nm
NPC-950	1033.85	0.61	2.34
NPG-950	397.37	0.41	4.12
NPGC-950	1510.83	0.82	2.16

Table S3 Summary of the contents of C, N, and O in NPGC-750, NPGC-850, NPGC-950 and NPGC-1000.

Samples	Content of C (atomic %)	Content of O (atomic %)	Content of N (atomic %)			
			Pyridinic N	Pyrrolic N	Graphitic N	Total N
NPGC-750	77.74	18.59	1.62	1.69	0.36	3.67
NPGC-850	78.93	18.01	1.59	1.11	0.35	3.05
NPGC-950	81.02	17.90	0.26	0.13	0.69	1.08
NPGC-1000	81.71	17.36	0.14	0.12	0.67	0.93

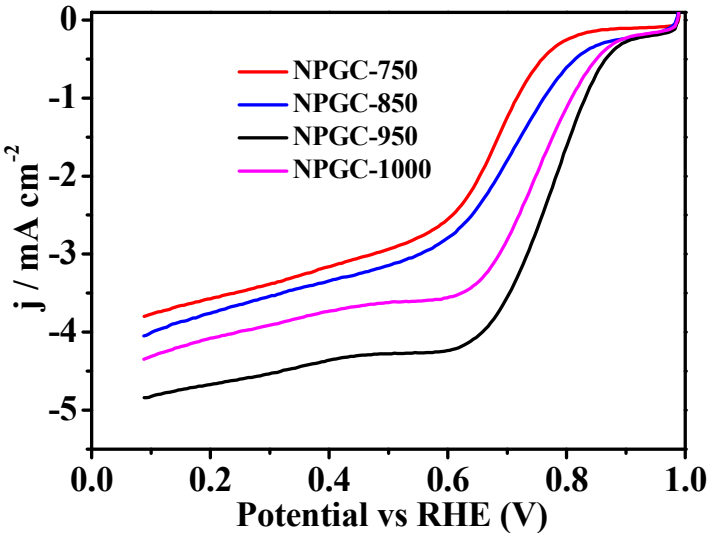

Fig. S2 LSV curves of as-prepared samples at different temperature in O2-saturated 0.1 mol L-1 KOH at the rotating speed of 1600 rpm.

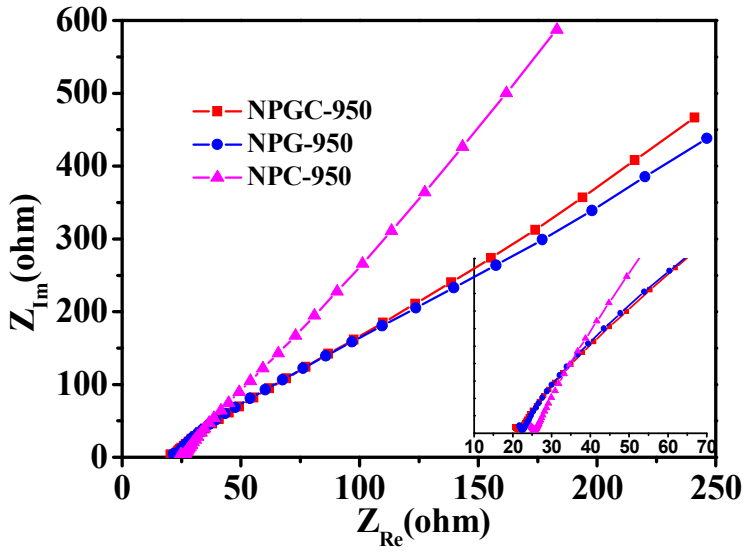

Fig. S3 Nyquist plots of NPC-950, NPG-950, and NPGC-950.

Electrochemical impedance spectroscope (EIS) tests were analyzed by Nyquist plots of as-prepared catalysts in Fig. S2. The arc diameter in Nyquist plots at low frequency region is on behalf of the charge transfer resistance (R_{ct}).[5,6] According to the Nyquist plots, it is clearly observed that the diameter of the arc of NPGC-950 is much smaller than NPC-950, very close to that of NPG-950. This result proves the introduction of reduced graphene oxide significantly enhances conductivity of NPG-950.

References

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