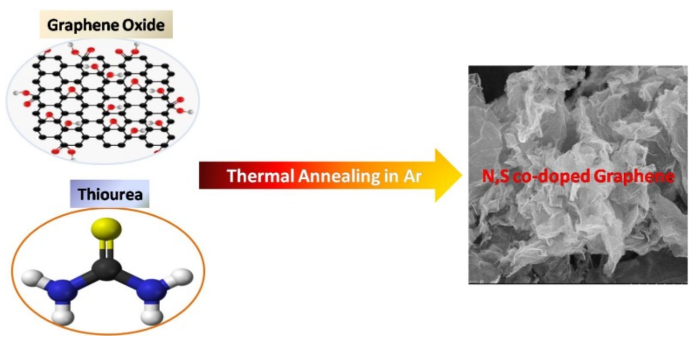
Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Experimental Details

Materials preparation: Graphene oxide (GO) was prepared by modified Hummer's method[12]. GO (200 mg) and thiourea (1600 mg) were first mixed in ethanol with sonication for 90 min to obtain a homogeneous dispersion. Ethanol was removed by the rotary evaporation. The collected solid mixtures were dried in vacuum oven. Finally, the doping process was carried out by annealing graphene oxide at 600 ℃, 700 ℃, 800 ℃, 900 ℃ and 1000 ℃ for 2 h in argon to form N,S co-doped graphene (denoted as NSG600, NSG700, NSG800, NSG900, NSG1000, respectively). The undoped graphene was also prepared under the same condition in the absence of thiourea for comparison.



Scheme S1. The synthetic route of N,S co-doped graphene

Electrochemical testing: All the electrochemical tests including CV and LSV were carried out using an electrochemical workstation (CHI 760E, CH Instrument, USA) with a typical three-electrode. A platinum mesh was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. At first, 5 mg NSG was added into 1 ml ethanol to get a well dispersed suspension (5 mg/ml) under sonication. Then, 50 µl Nafion solution (5 wt%) as a binder was added into the catalyst suspension. To prepare the electrode, 5 µl catalyst suspension was dropped onto the surface of a pre-polished glassy carbon electrode (GCE). After fully dried at room temperature, the catalyst casted GCE was used as the working electrode to measure its ORR activity in 0.1 M KOH solution saturated with O_2. For the measurement of linear sweep voltammetry (LSV), rotating ring-disk electrode (RRDE) was employed at a rotation rate of 1600 rpm in 0.1 M KOH solution saturated with O_2. All the measurements were conducted at room temperature (25±1 °C).

Reference S1 W. S. Hummers Jr and R. E. Offeman, *Journal of the American Chemical Society*, 1958**, 80,** 1339-1339.

Supplementary Results

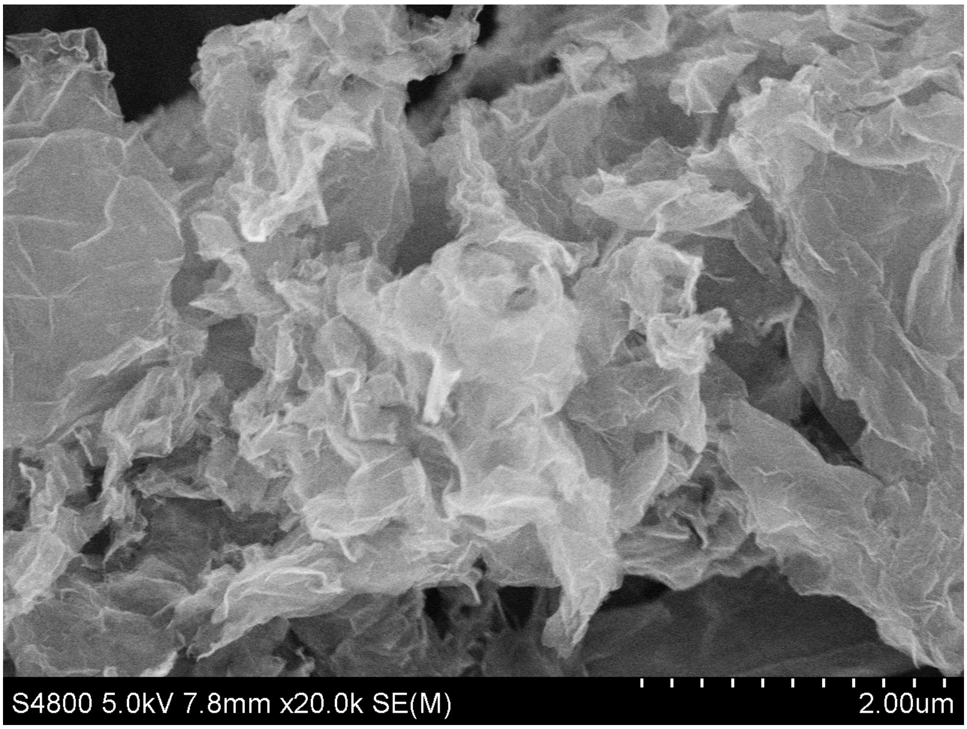


Figure S1. SEM image of NSG700.

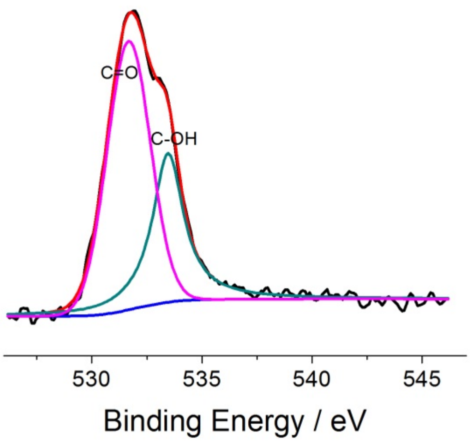


Figure S2. XPS O1s peak of NSG700.

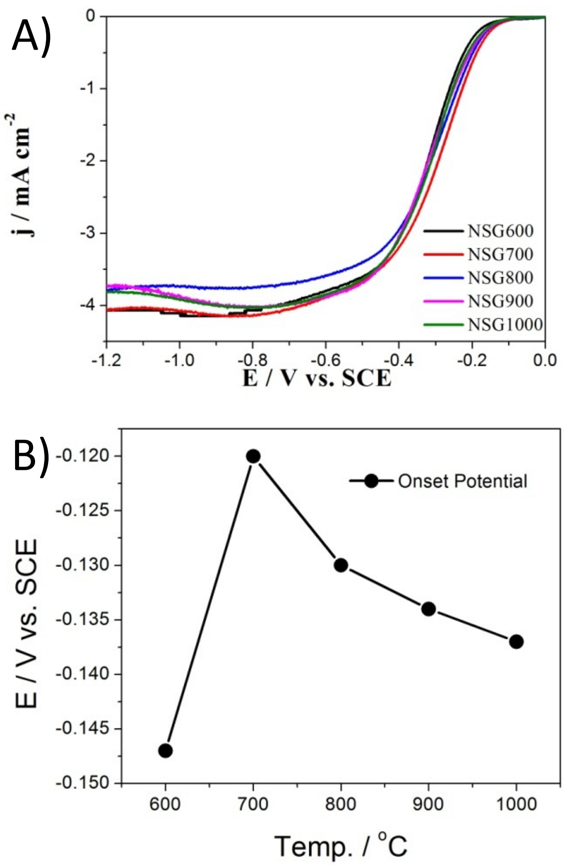


Figure S3. LSV curves of ORR on NSGs with different annealing temperatures (A) and the dependence of the onset potential on the temperature (B).

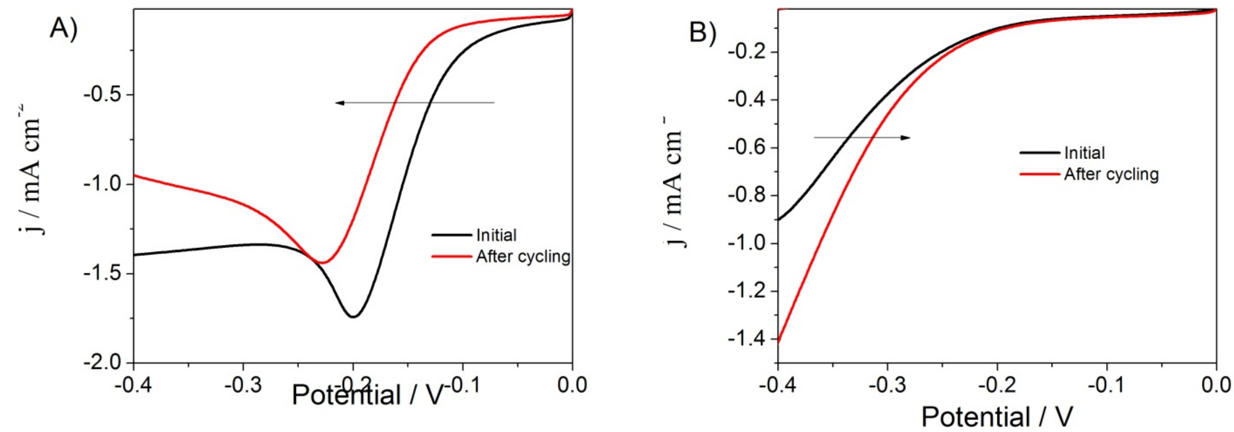


Figure S4. LSV curves of Pt/C (A) and NSG700 (B) at a scan rate of 50 mV s^{-1} before and after the accelerated CV scanning of 2000 cycles from -0.5 V to 0 V at a scan rate of 100 mV s^{-1}.

Table S1. List of the onset potential values of metal-free ORR electrocatalyst.

Samples	Onset potential	Reference
Our work	-0.15V vs. SCE	NA
CVD N-graphene	-0.2V vs. Ag/AgCl	S1
Graphene Carbon Nitride	-0.15V vs. Ag/AgCl	S2
B-doped CNT	-0.15V vs. SCE	S3
BCN graphene	-0.05V vs. SCE	S4
N-doped carbon cage	-0.2V vs. Ag/AgCl	S5
N-graphene melamine	-0.12V vs. Ag/AgCl	S6
3D N-CNT/graphene	-0.22V vs. SCE	S7
P,N co-doped CNT	-0.15V vs. SCE	S8
Iodine doped graphene	-0.15V vs. Ag/AgCl	S9
CNT-graphene complex	0.95V vs. RHE	S10

S1. Qu, Liangti, et al. "Nitrogen-doped graphene as efficient metal-free electrocatalyst for oxygen reduction in fuel cells." *ACS nano* 4.3 (2010): 1321-1326.

S2. Yang, Shubin, et al. "Graphene‐Based Carbon Nitride Nanosheets as Efficient Metal‐Free Electrocatalysts for Oxygen Reduction Reactions." *Angewandte Chemie International Edition* 50.23 (2011): 5339-5343.

S3. Yang, Lijun, et al. "Boron‐Doped Carbon Nanotubes as Metal‐Free Electrocatalysts for the Oxygen Reduction Reaction." *Angewandte Chemie*123.31 (2011): 7270-7273.

S4. Wang, Shuangyin, et al. "BCN Graphene as Efficient Metal‐Free Electrocatalyst for the Oxygen Reduction Reaction." *Angewandte Chemie International Edition* 51.17 (2012): 4209-4212.

S5. Chen, Sheng, et al. "Nitrogen‐Doped Carbon Nanocages as Efficient Metal‐Free Electrocatalysts for Oxygen Reduction Reaction." *Advanced Materials*24.41 (2012): 5593-5597.

S6. Lin, Ziyin, et al. "Facile preparation of nitrogen-doped graphene as a metal-free catalyst for oxygen reduction reaction." *Physical Chemistry Chemical Physics*14.10 (2012): 3381-3387.

S7. Ma, Yanwen, et al. "Three-dimensional nitrogen-doped carbon nanotubes/graphene structure used as a metal-free electrocatalyst for the oxygen reduction reaction." *The Journal of Physical Chemistry C* 115.50 (2011): 24592-24597.

S8. Yu, Dingshan, Yuhua Xue, and Liming Dai. "Vertically aligned carbon nanotube arrays co-doped with phosphorus and nitrogen as efficient metal-free electrocatalysts for oxygen reduction." *The Journal of Physical Chemistry Letters* 3.19 (2012): 2863-2870.

S9. Yao, Zhen, et al. "Catalyst-free synthesis of iodine-doped graphene via a facile thermal annealing process and its use for electrocatalytic oxygen reduction in an alkaline medium." *Chemical Communications* 48.7 (2012): 1027-1029.

S10. Li, Yanguang, et al. "An oxygen reduction electrocatalyst based on carbon nanotube-graphene complexes." *Nature nanotechnology* 7.6 (2012): 394-400.