Electronic Supplementary Material (ESI) for ChemComm.

I. Detailed Experimental Section

Materials and Reagents: Graphite powder (99.9995% purity, 100 mesh, briquetting grade, mesh) was purchased from Alfa Aesar. Other chemicals such as H_2SO_4, $KMnO_4$, and ammonia (25%), bought from Nanjing Chemical Reagent CO. Ltd., were all of analytical grade and used as received. Ultrapure water obtained from a Milli-Q water purifying system was used for preparation of all aqueous solutions.

Preparation of Graphene Oxide (GO) Suspension: GO was synthesized from graphite flakes by the modified Hummers method. The as-synthesized GO was purified by dialysis for one week to remove residual salts and acids. The final GO gel was re-dispersed in water, subjected to ultrasonication for 1 h, resulting in a stable colloidal GO suspension.

Electrochemical Synthesis of Graphene and N-doped Graphene (NG): The preparation of NG in large scale was carried out in a three-electrode system (graphite rod as the working electrode, Pt wire as the counter electrode and Ag/AgCl electrode as the reference) on a CHI 900 Potentiostat (CH Instrument, USA). The electrolyte was an GO suspension (0.25 mg mL^{-1}) containing 0.05 M NH_4Cl-ammonia (NH_4Cl/NH_3H_2O, 1:1 molar ratio). Constant potential deposition was carried out at voltage of -0.8 V, -1.2 V and to -1.6 V for 6 h with continuous stirring. The resulting deposits were then thoroughly washed several times with ethanol, and dried at room temperature under air atmosphere.

As control experiments, graphene was prepared through electrochemical deposition at a constant potential of -1.2 V for 6 h in different electrolytes. NaCl-G was obtained in an aqueous GO suspension (0.25 mg mL^{-1}) containing 0.05 M NaCl. $NaNO_3$-G was deposited in an GO suspension mixed 1:1 with 0.1 M $NaNO_3$. The electrolyte for Urea-G was an 0.25 mg mL^{-1} GO dispersion mixed containing 0.05 M urea and 0.05 M NaCl.

Preparation of Graphene, NG Modified Electrode: The glassy carbon electrodes (GCE, d=3 mm) were polished to a mirror-like surface using 0.05 μm alumina slurry, then rinsed thoroughly with ethanol and water in an ultrasonic bath to remove any alumina residues, and finally dried with blowing N_2 gas. A suspension of NG (5 μL, 0.5 mg mL^{-1}) was casted on GCE and dried at room temperature to obtain the NG modified electrode(NG/GCE). Similarly, a graphene/GCE was prepared.

Characterizations: Morphologies of samples were characterized by a JEM-2100 transmission electron microscopy (TEM, Hitachi Inc., Japan) and S-4800 scanning electron microscopy (SEM, Hitachi Inc., Japan). TEM samples were prepared by drying a droplet of the graphene or NG suspensions on a Cu grid with carbon film. Atomic force microscopy (AFM) images were obtained on a 5500 AFM/SPM system (Agilent Technologies Inc., USA) in tapping mode at room temperature. Raman spectra were recorded using an InVia micro-Raman system with an excitation wavelength of 488 nm (Renishaw Inc., UK). X-ray photoelectron spectra (XPS) were carried out on a K-Alpha spectrometer (Thermo Fisher Scientific Inc., Switzerland) equipped with a monochromatic Al Kα source operated at 150 W.

ORR Measurements: Cyclic voltammograms were carried out in a three electrode system using Ag/AgCl electrode as the reference, a Pt wire as the counter electrode and modified glassy carbon as the working electrode on a CHI 900 potentiostat (CHI Inc., USA). Rotating disk electrode (RDE) experiments were carried out on a HP-1A RRDE system (Jiangfen Electroanalytical Instrument, China). The RDE consists of a 4 mm diameter GC disk. In all of the electrochemical measurements, 0.1 M KOH aqueous solution saturated with O_2 was used as the electrolyte.

II. Supplementary Results:

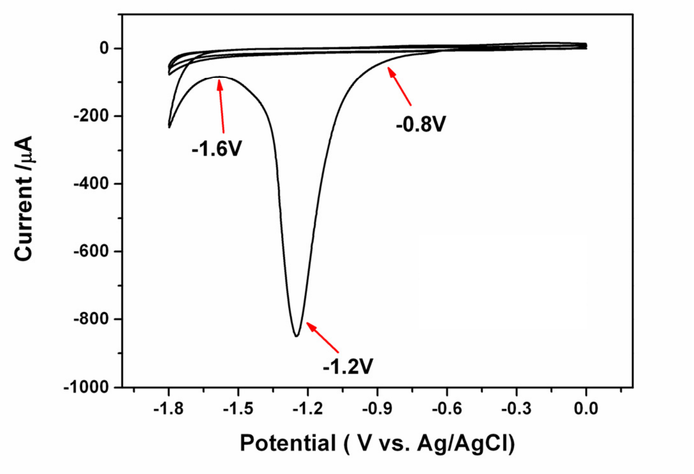

Figure S1. Continuous cyclic voltammograms of GO modified GC electrode in 0.1 M KCl at a scan rate of 50 mV s^{-1}. The oxygen containing species are almost removed in the first potential scan since there is no obvious reduction peak in the second and following potential scans.

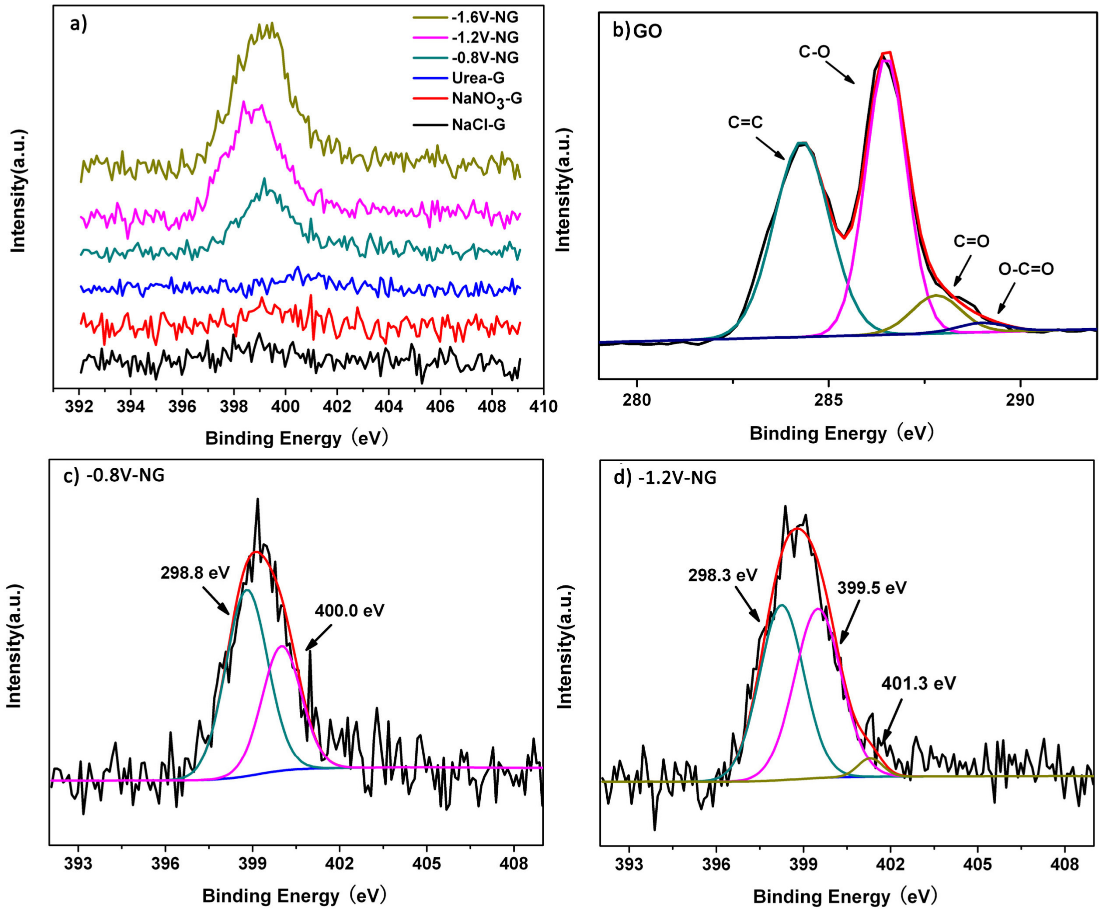

Figure S2. (a) High-resolution C 1s XPS spectra of NaCl-G, NaNO$_3$-G, Urea-G, -0.8 V-NG, -1.2 V-NG and -1.6 V-NG. (b) High-resolution C 1s spectra of GO. (c, d) The deconvolution of N 1s spectra of -0.8 V-NG and -1.2 V-NG.

Table S1. Elemental compositions of GO and GO reduced under different electrochemical conditions.

	C at.%	N at.%	O at.%	Cl at.%	N/C %
-0.8 V-NG	82.41	2.49	14.84	0.27	3.02
-1.2 V-NG	85.34	3.07	11.31	0.28	3.60
-1.6 V-NG	85.41	3.37	10.92	0.29	3.95
NaCl-G	88.89	0.34	10.54	0.23	--
NaNO$_3$-G	86.39	0.26	13.35	--	--
Urea-G	87.62	0.33	12.05	--	--
GO	68.89	0.24	30.87	--	--

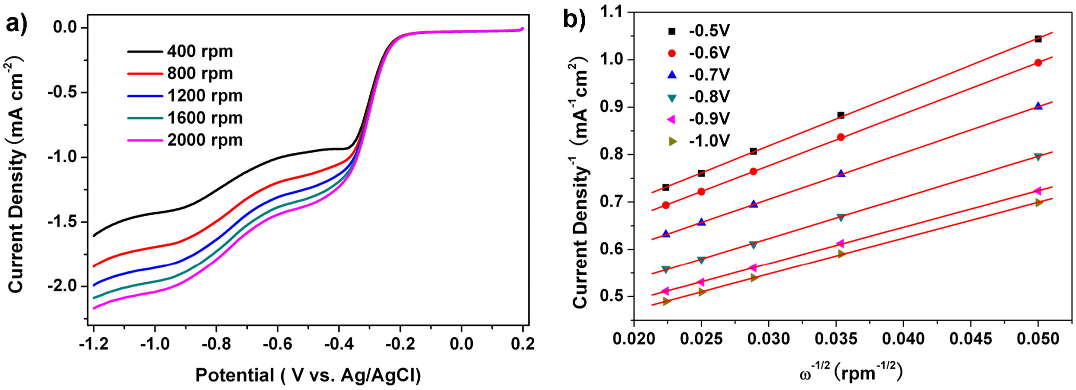

Figure S3. a) RDE measurements of graphene in 0.1 M O_2-saturated KOH at a scan rate of 100 mV s^{-1}. b) Koutecky–Levich plots of graphene/GCE at different potentials.

Table S2. The transferred electron number (*n*) of ORR on graphene/GCE and -1.6 V-NG/GCE at different potentials.

	-0.5 V	-0.6 V	-0.7 V	-0.8 V	-0.9 V	-1.0 V
n/NG	4.00	4.03	4.05	3.95	3.90	3.91
/Graphene	2.48	2.59	2.88	3.25	3.65	3.71

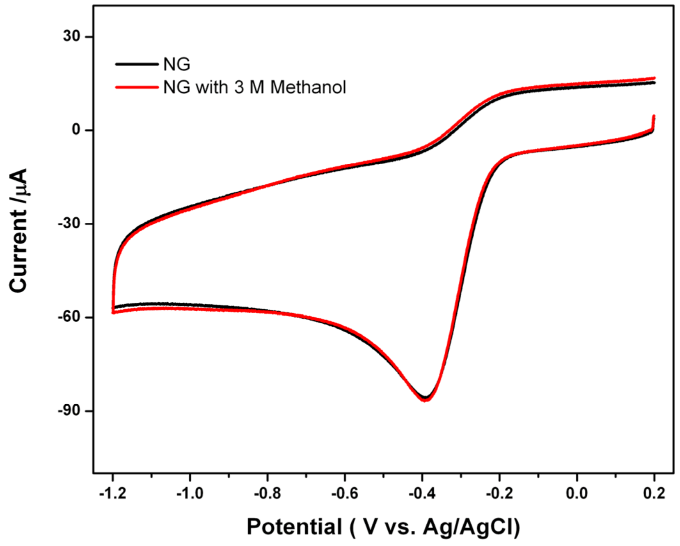

Figure S4. CVs of -1.6 V-NG with and without 3.0 M methanol (in O_2-saturated 0.1 M KOH at a scan rate of 100 mV s^{-1}).