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Supporting Information

Oxygenophilic Ionic Liquids Promote the Oxygen Reduction Reaction in Pt-Free Carbon Electrocatalysts

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1. Supplementary Text (Experimental Section)

1.1 Chemicals:

Electrical conductive graphene was offered by Carmery graphene marketing centre, Institute of Coal Chemistry, Chinese Academy of Science. 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ($[C_4C_1im][NTf_2]$) and 1-Ethylimidazolium bis(trifluoromethylsulfonyl) imide ($[C_2im][NTf_2]$) were purchased from IoLiTec. Urea, and $Fe(NO_3)_3{\cdot}9H_2O$ were purchased from Sigma. KOH and $HClO_4$ were bought from VWR. All the chemicals were used as obtained without further treatment. Deionized water was applied for all the experiments. All the chemicals were used as received without any extra-treatment.

1.2 Electrocatalyst preparation:

1.2.1 The synthesis of pristine catalyst materials

The nanocarbon electrocatalyst was synthesized *via* a hydrothermal process, followed by a high temperature carbonization treatment. To be specific, 1 g urea was first dissolved in 20 mL deionized water to form a homogeneous solution, then 100 mg of high conductivity graphene was added into this solution. After magnetically stirring for 30 min at room temperature, the mixture was then sealed into stainless steel autoclaves with a Teflon inlet and heated up to 180 ºC for 5.5 h under self-generated pressures of around 10 bars. After cooling to room temperature, the obtained product was then filtered and washed by deionized water for several times. The sample was then frozen at -20 °C, followed by a freeze-drying process for 72 hours. The as-obtained powder was then annealed at 1000 °C in a flowing N_2 atmosphere for 2.0 h. The hydrothermal process promotes the self-assembly of urea and graphene, while the high temperature pyrolysis further improves the carbon backbone and converts the nitrogen source into a more favourable form of nitrogen-based active sites (pyridinic-N and quaternary-N). The resulting sample was named as GN. The Fe-containing electrocatalyst was synthesized following the same procedure with the addition of $Fe(NO_3)_3$. Specifically, 1 g urea and 505 mg $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in 20 mL deionized water to form a homogeneous solution, followed by the same procedure for GN. The resultant product was named as GNFe.

1.2.2 Surface modification of Electrocatalysts via ionic liquids

8 mg of electrocatalysts (GN, GNFe) was mixed with 1400 μL H_2O and 528 μL ethanol, respectively. Then 1.1 μL of $[C_4C_1im][NTf_2]$ or $[C_2im][NTf_2]$, which was equivalent to 20 wt% of the catalyst, was carefully added into the solution. The mixture was then ultrasonicated for 10 min to homogeneously disperse the ionic liquids (ILs) into slurry. The mixture was then anchored on a shaker to shake for 60 hours to make the ILs fully interacted with the electrocatalysts. GN and GNFe without any addition of ILs was treated with same process for comparison. For morphology and surface chemistry characterization, the obtained slurry was then frozen in liquid nitrogen at -197 °C, followed by a freeze-drying process for 72 hours. The obtained samples were named as GN, GN-IL1, GN-IL2, GNFe, GNFe-IL1, GNFe-IL2, respectively. Herewith IL1 refers to $[C_4C_1im][NTf_2]$, IL2 refers to $[C_2im][NTf_2]$.

1.3 Electrocatalytic performance measurements:

After the modification of ILs in the electrocatalyst slurry, 72 μL of nafion solution (5 % w/w) was added. The mixture was then sonicated for 10 min with probe ultrasonicator to obtain a homogeneous slurry, then 5 μL of the slurry was deposited onto the glassy carbon disk (3.0 mm in diameter) of rotating disk electrode (RDE). All tests were measured using a standard three-electrode cell on electrochemical workstation (Metrohm Autolab PGSTAT204), where an

Ag/AgCl in 3 M KCl solution was served as the reference electrode, and platinum wire as the counter electrode. The catalyst loading was *ca.* 0.285 mg cm^{-2} (ionic liquid was not included in calculation). Commercial Pt/C (20 wt %, Sigma-Aldrich, 738549) with the same mass loading was prepared for comparison. 0.10 M KOH solution and 0.10 M $HClO_4$ solution were prepared as alkaline and acid electrolytes, respectively. Linear sweep voltammograms (LSV) were obtained at a rotation rate of 1600 rpm and scan rate of 10.0 mV s^{-1}. The current-time chronoamperometric responses were recorded after the first 1000 s activation period for stabilizing the electrodes at the 0.527 V and 0.169 V *vs.* RHE at a rotation rate of 800 rpm in O_2-saturated 0.1 M KOH and 0.1 M $HClO_4$, respectively. Electrochemical impedance spectroscopy (EIS) measurements were conducted in oxygen saturated electrolyte under 1600 rpm and at the potential under which the current density reaches 2.5 mA cm^{-2} in basic electrolyte and 2.3 mA cm^{-2} in acid electrolyte for eachsample.

For the RRDE tests, the scan rate was 10 mV s^{-1} at disk potential, and the ring potential was set at 1.5 V vs RHE in order to oxidize the H_2O_2 produced. The working electrode was 5 mm GC disk with a Pt ring electrode at 375 μm gap. 14 μL5 μL of the slurry was deposited onto the GC disk of RRDE to make same mass loading per unit area as RDE. The following equations were used to calculate n (the apparent number of electron transferred during ORR process) and %H_2O_2 (the percentage of H_2O_2 released during ORR):

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

$$\%H_2O_2 = 100\frac{2I_R/N}{I_D + (I_R/N)}$$

Where N=0.249 refers to the H_2O_2 collection efficiency at the ring, was provided by the manufacturer. I_D is the Faradaic current at the disk, and I_R is the Faradaic current at the ring.

1.4 Characterization:

The morphology and structure of the samples were characterized using a JEM 2010 (JEOL Ltd., Tokyo, Japan) transmission electron microscope (TEM). The N_2 adsorption-desorption isotherm was measured using an NOVA 4200e system (Quantachrome Instruments, USA). The specific surface area was calculated by the multipoint Brunauer–Emmett–Teller (BET) method, and the pore-size distribution was calculated based on Quenched Solid Density Function Theory (QSDFT) using the adsorption branch. X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos Ultra DLD Setup using monochromatic Al K alpha (1486.74 eV) radiation. The contact angle of electrocatalyst in this contribution was determined on Dataphysics OCA20. Thermogravimetric analysis (TGA) was measured with TGA Q500. Fourier transform infrared spectroscopy (FTIR) spectra was measured on Tensor27 (Bruker).

2. Supplementary Figure

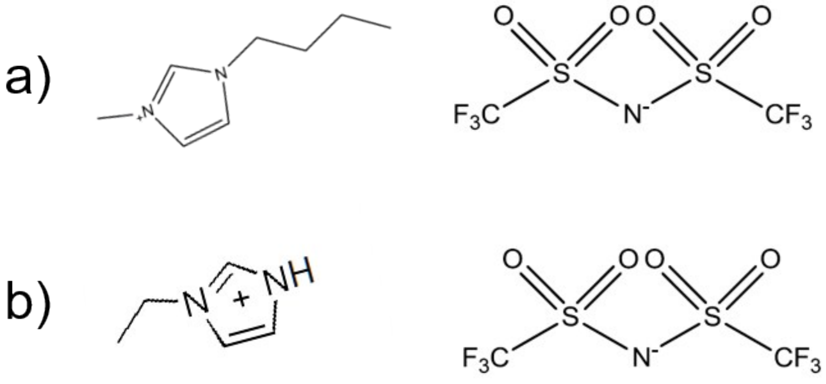

Figure S1. Chemical structure of (a) IL1: 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ($[C_4C_1im][NTf_2]$), and (b) IL2: 1-Ethylimidazolium bis(trifluoromethylsulfonyl) imide ($[C_2im][NTf_2]$).

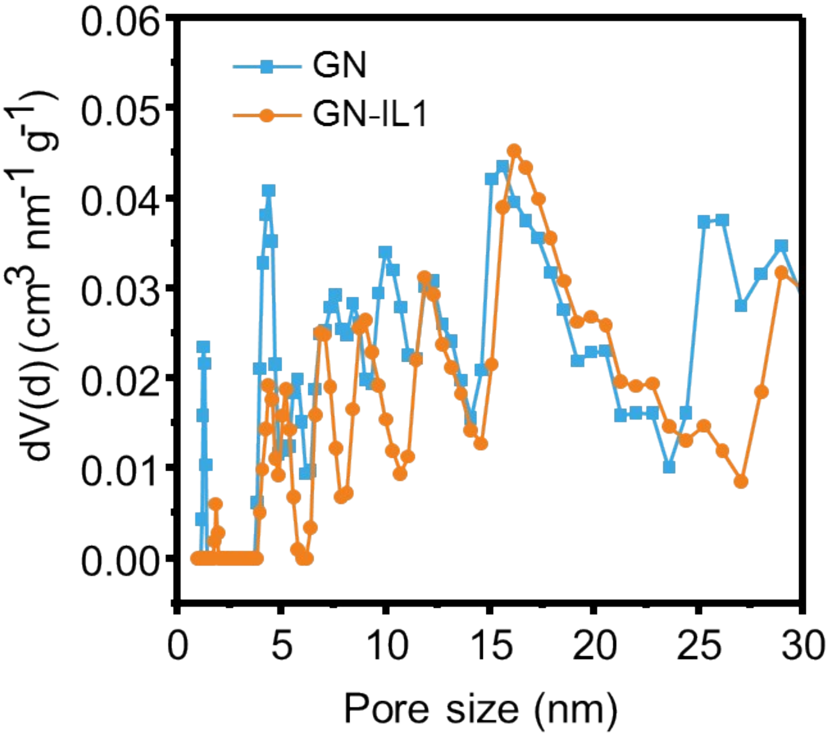

Figure S2. Pore size distribution of GN and GN-IL1.

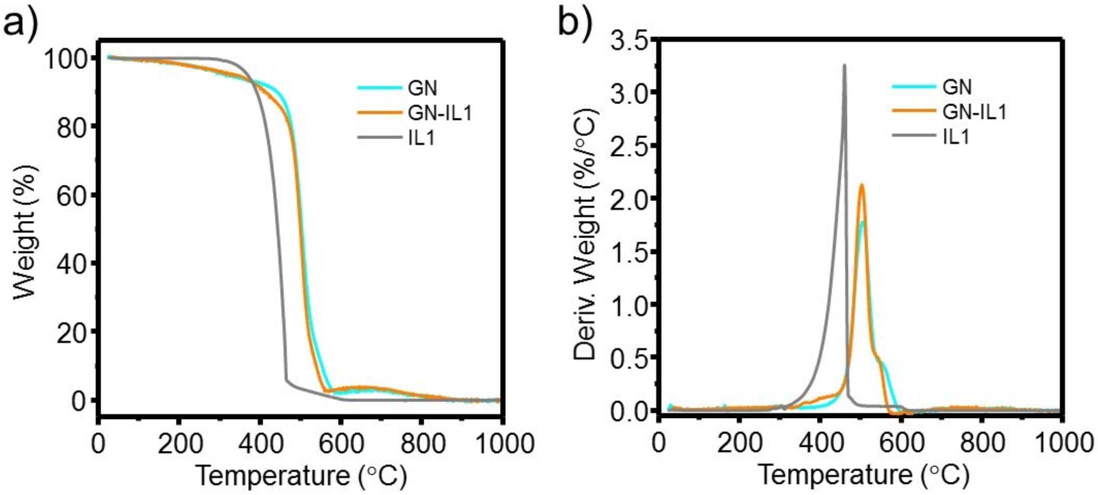

Figure S3. (a)TGA and (b) DSC curves of GN, GN-IL1 and IL1.

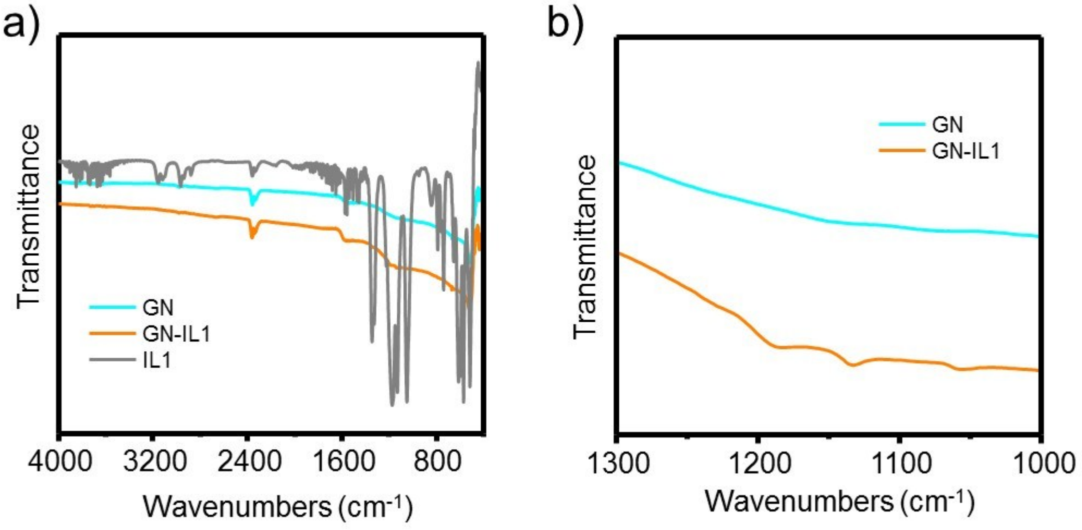

Figure S4. (a) FT-IR spectra of GN, GN-IL1 and IL, and (b) zoomed-in view of FT-IR spectra of GN and GN-IL1

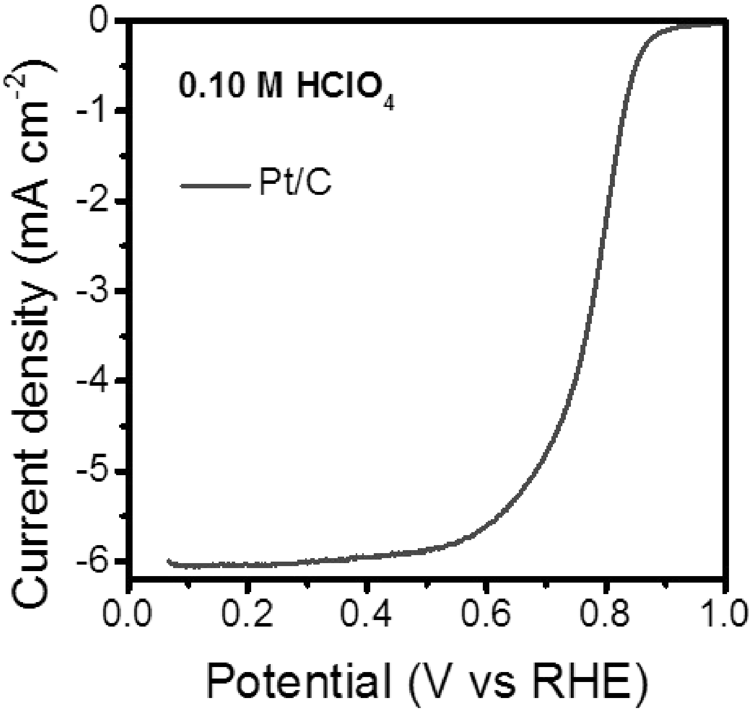

Figure S5. LSV curve of commercial Pt/C catalyst in O_2-saturated 0.10 M KOH solution with a rotating rate of 1600 rpm. The scan rate was 10.0 mV s^{-1}.

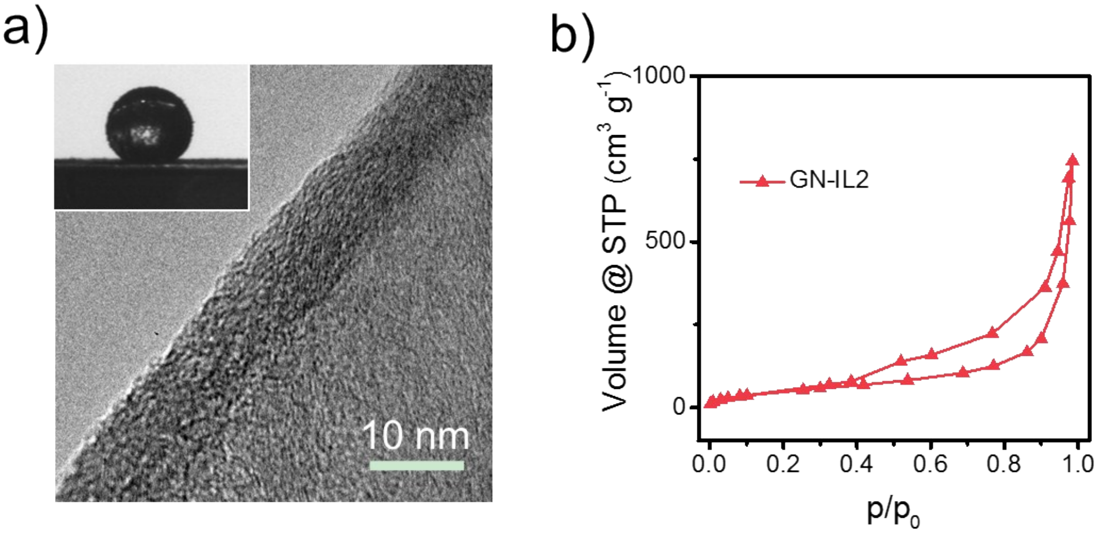

Figure S6. (a) TEM image of GN-IL2 and the static water contact angle measurement (inset). (b) N_2 sorption isotherm of GN-IL2.

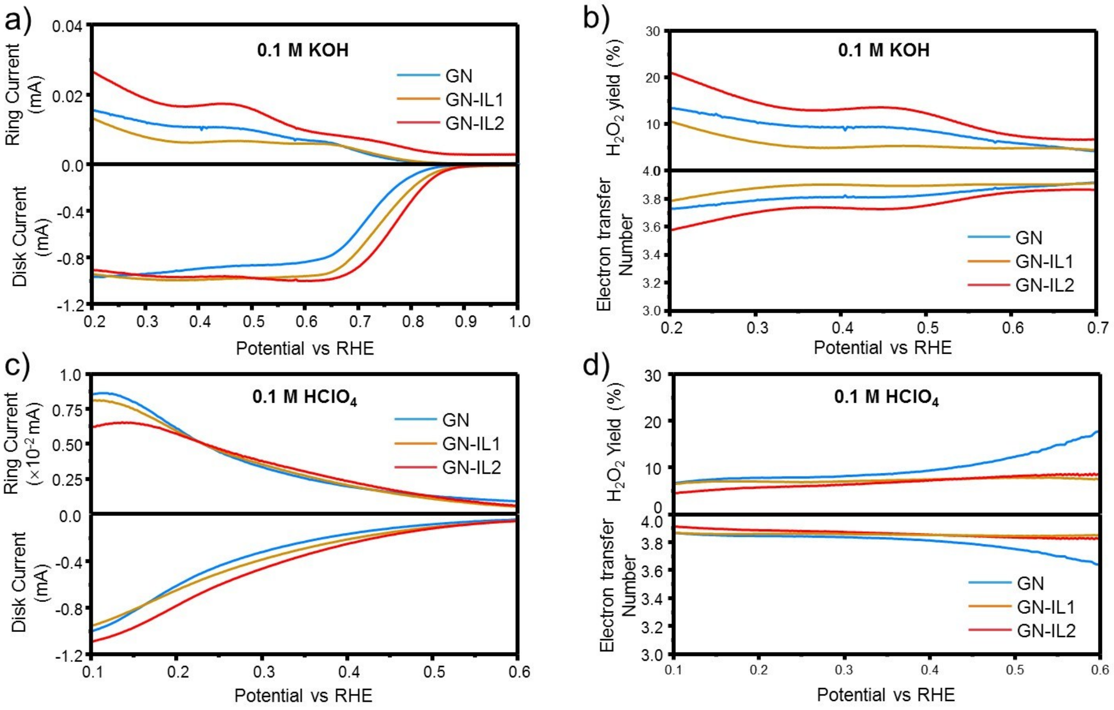

Figure S7. (a)RRDE measurement results and (b) peroxide yields and electron transfer numbers of the catalysts calculated from the RRDE measurement results in 0.1 M KOH at a rotation rate of 1600 rpm. (c)RRDE measurement results and (d) peroxide yields and electron transfer numbers of the catalysts calculated from the RRDE measurement results in 0.1 M $HClO_4$ at a rotation rate of 1600 rpm.

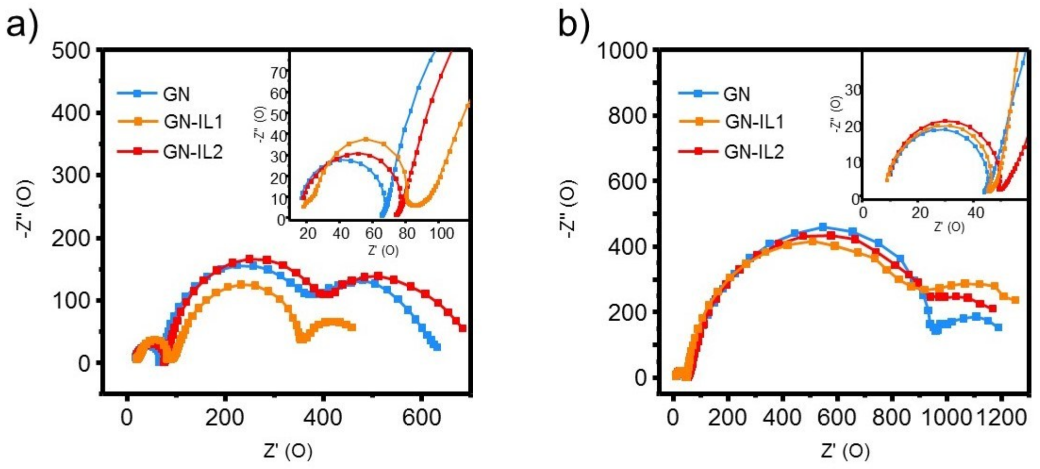

Figure S8. EIS recorded with samples GN, GN-IL1 and GN-IL2 in oxygen-saturated of a) 0,1M KOH and b) 0.1M $HClO_4$ at 1600rpm.

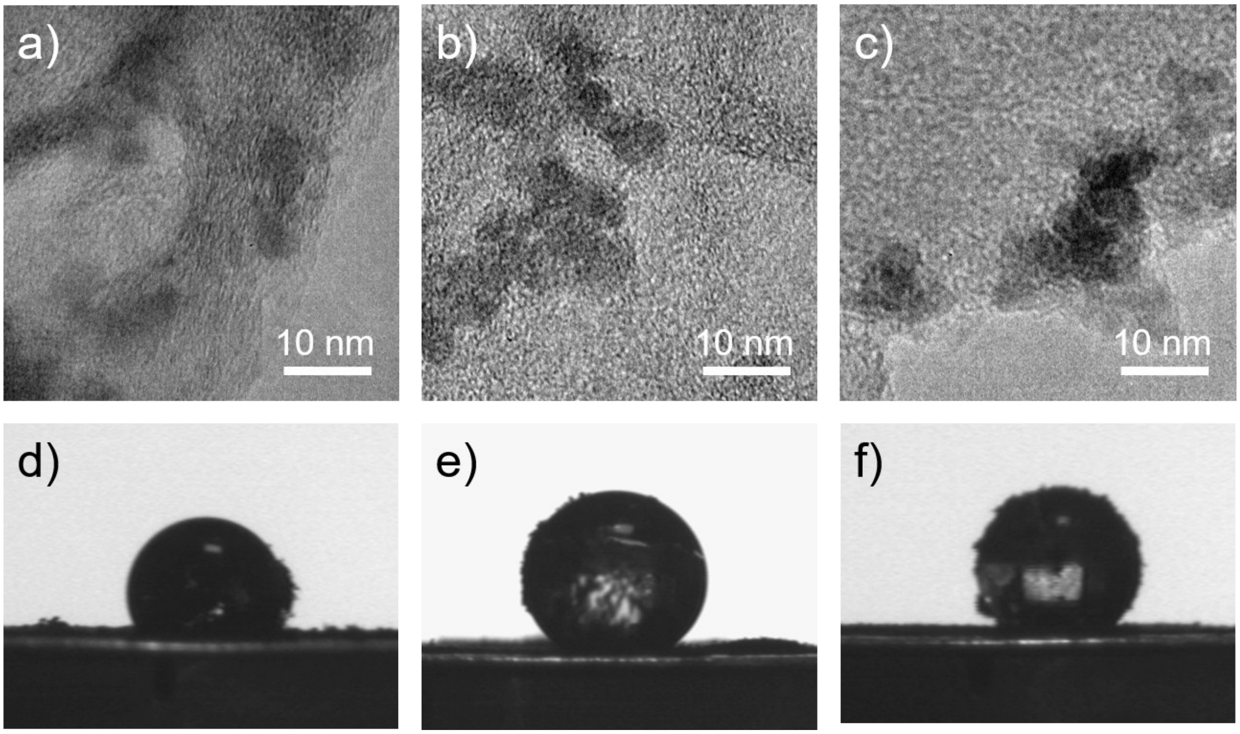

Figure S9. TEM images of (a) GNFe, (b) GNFe-IL1, and (c) GNFe-IL2. The static water contact angle measurements of (d) GNFe, (e) GNFe-IL1, and (f) GNFe-IL2.

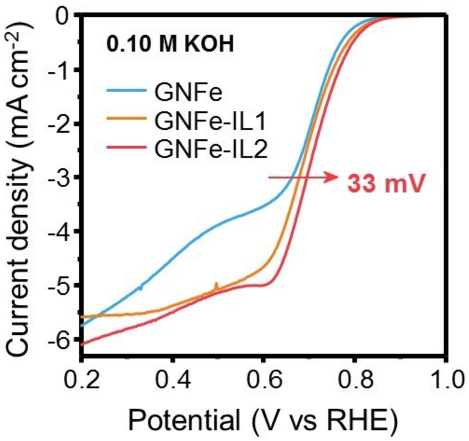

Figure S10. ORR LSV curves obtained in O_2-saturated 0.10 M KOH solution for metal-containing samples. The rotating rate was 1600 rpm, with a scan rate of 10.0 mV s^{-1}. The catalyst loading for all tests was ca. 0.285 mg cm^{-2} (IL was not included).

3. Supplementary Tables

Table S1. XPS results of GN, GN-C_4C_1, and GN-C_2.

Sample	**Atom Species (at. %)**			
	N	N1 (Pyridinic-N)	N2 (Quaternary-N)	N3 (Oxidized-N)
GN	0.6	398.55 eV	400.43 eV	401.7 eV
		42	24	34
GN-IL1	1.2	398.15 eV	399.29 eV	402 eV
		12	26	62
GN-IL2	0.9	398.83 eV	400.17 eV	401.62 eV
		46	12	42

Table S2. Specific surface area and total pore volume of different samples.

Sample	**GN**	**GN-IL1**	**GN-IL2**
SSA (m^2 g^{-1})	258	175	159
Pore volume (cm^3 g^{-1})	0.797	0.675	0.671