A graphene-platinum nanoparticles-ionic liquid composite catalyst for methanol-tolerant oxygen reduction reaction

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Materials and Methods

Reagents. Platinum(II) acetylacetonate ($Pt(acac)_2$) was purchased from Alfa Aesar. Carboxylic graphene nanosheets were purchased from XFNano Material Tech Co., Ltd (Nanjing, China). 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) and lithium salt of bis(trifluoromethylsulfonyl)imide (bmsi) were purchased from Sigma Aldrich. All other chemicals were of analytical grade or better quality. Ultrapure water (Millipore, $\geq 18 M\Omega$ cm) was used throughout.

Instrumentation. Electrochemical experiments were conducted on a CHI760D electrochemical workstation (CH Instrument Co., USA). A conventional three-electrode system included a glassy carbon rotating disk electrode (RDE, diameter 5 mm, Pine Research Instrumentation) coated with catalysts, a Pt auxiliary electrode and a saturated calomel reference electrode (SCE). All the potentials are reported with respect to the reversible hydrogen electrode (RHE) and all electrochemical data were obtained at room temperature.

Transmission electron microscopy (TEM) studies were performed on a TECNAI F-30 high-resolution transmission electron microscopy operating at 300 kV. The samples were prepared by dropping ethanol dispersion of samples onto 300-mesh carbon-coated copper grids and immediately evaporating the solvent. X-ray diffraction (XRD) measurements were recorded on a PANalytical X'pert PRO diffractometer using Cu Kα radiation, operating at 40 kV and 30 mA. Thermogravimetric analyze (TGA) of sample was performed on a SDT-Q600 simultaneous TGA/DSC thermogravimetric analyzer (TA Instruments). Sample was heated under nitrogen atmosphere from room temperature to 800 °C at 10 °C min^{-1}.

Synthesis of GN-Pt hybrids. 20 mg Pt(acac)$_2$, 50 mg carboxylic graphene nanosheets were mixed together with 10 mL benzyl alcohol in a glass pressure vessel. The resulting mixture after stirring at room temperature for 5 min was charged with CO to 1 bar and then heated in oil bath which was preheated to 180 °C for 3 h with vigorous stirring. The resulting products were collected by centrifugation, and washed several times with ethanol.

Synthesis of GN-Pt$_3$Ni hybrids. 20 mg Pt(acac)$_2$, 4.3 mg Ni(acac)$_2$, 50 mg carboxylic graphene nanosheets were mixed together with 10 mL benzyl alcohol in a glass pressure vessel. The resulting mixture after stirring at room temperature for 5 min was charged with CO to 1 bar and then heated in oil bath which was preheated to 180 °C for 3 h with vigorous stirring. The resulting products were collected by centrifugation, and washed several times with ethanol.

Synthesis and characterization of [MTBD][bmsi] IL. The [MTBD][bmsi] IL was synthesized by neutralizing a Brønsted base with a Brønsted acid following a reported methodology.[s1] Briefly, equimolar amounts of the precursors 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene [MTBD] and the lithium salt of bis(trifluoromethylsulfonyl)imide [bmsi] (3M) dissolved in water along with 10.6 M HNO$_3$ were cooled in ice to near 0 °C. HNO$_3$ was added dropwise to the [MTBD] until a near neutral pH was reached. After neutralization, the [bmsi] solution was mixed with the [MTBD] and the IL precipitated out as a viscous fluid phase beneath the water phase. The IL was washed several times with ultrapure water and then placed in a vacuum oven at 60 °C for 24 h to remove residual water. The mass spectrum of [MTBD][bmsi] IL was recorded on a Bruker Esquire HCT mass spectrometer equipped with an electrospray ion source (Fig. S8).

Electrochemical studies. 0.2 mg-Pt-containing GN-Pt (based on the inductively coupled plasma-atomic emission spectroscopy measurements) or E-TEK catalyst was dispersed in 1 ml isopropyl alcohol, and then ultrasonicated to form a uniform black ink. The catalysts modified RDE was prepared by applying 15.0 μL well-dispersed catalyst ink onto pre-polished RDE. Therefore, the Pt loadings for all catalysts were 15.3 μg cm^{-2}. After drying at room temperature, 5 μL of 0.1 wt% Nafion solution was applied onto the surface of the catalyst layer to form a layer protecting catalyst particles from detaching. GN-Pt-IL composite catalyst modified electrode was obtained by simply placing a drop of IL on a GN-Pt catalyst modified electrode and rinsing off the unadsorbed IL with a nitrogen stream. Prior to electrochemical experiments, the catalysts modified RDE were subjected to continuous potential cycling (0 to 1.1 V vs. RHE, 50 mV s^{-1}) in 0.5 M aqueous H_2SO_4 until cyclic voltammograms became reproducible. For specific electrochemically active surface area (SEASA) measurements, the electrolyte solutions were purged with high-purity N_2 gas before use for 30 min. The ORR measurements were performed in 0.5 M H_2SO_4 solutions under flow of O_2 using the catalysts modified RDE at a rotation rate of 1,600 rpm and a sweep rate of 10 mV s^{-1}. In the ORR polarization curve, current densities (j) were normalized in reference to the geometric area of the glassy carbon RDE (0.196 cm^2). For the ORR at a RDE, the kinetic current (j_k) was calculated based on the Koutecky-Levich equation,[s2]

$$\frac{1}{j}=\frac{1}{j_k}+\frac{1}{j_\mathrm{d}}$$

where j is the experimentally measured current, j_d is the diffusion-limiting current, and j_k is the kinetic current.

Table S1 Mass activities of various catalysts for ORR at 0.9 V.

Catalyst	Mass activity (A mg^{-1}_{Pt})	Electrolyte	References
GN-Pt-IL	0.135	0.5 M H_2SO_4	This work
GN-Pt	0.0618	0.5 M H_2SO_4	This work
GN-Pt	0.039	0.5 M H_2SO_4	Ref. S3
Pt/C E-TEK	0.031	0.5 M H_2SO_4	Ref. S3
20% Pt/Vulcan carbon	0.04	0.5 M H_2SO_4	Ref. S4
GN-Pt-IL	0.320	0.1 M $HClO_4$	This work
GN-Pt_3Ni-IL	0.870	0.1 M $HClO_4$	This work
Pt/C E-TEK	0.114	0.1 M $HClO_4$	This work
Pt/C E-TEK	0.095 ± 0.008	0.1 M $HClO_4$	Ref. S5
Pd-Pt dendrites	0.241 ± 0.013	0.1 M $HClO_4$	Ref. S5
Pt_3Ni nanoctahedra/ carbon black	~0.3	0.1 M $HClO_4$	Ref. S6
Pt_3Ni truncated nanoctahedra	0.53	0.1 M $HClO_4$	Ref. S7
octahedral Pt_3Ni	0.44	0.1 M $HClO_4$	Ref. S8
Au/Pt_3Ni nanowires	0.479	0.1 M $HClO_4$	Ref. S9
Nanoporous Pt/Ni alloys	0.65	0.1 M $HClO_4$	Ref. S10

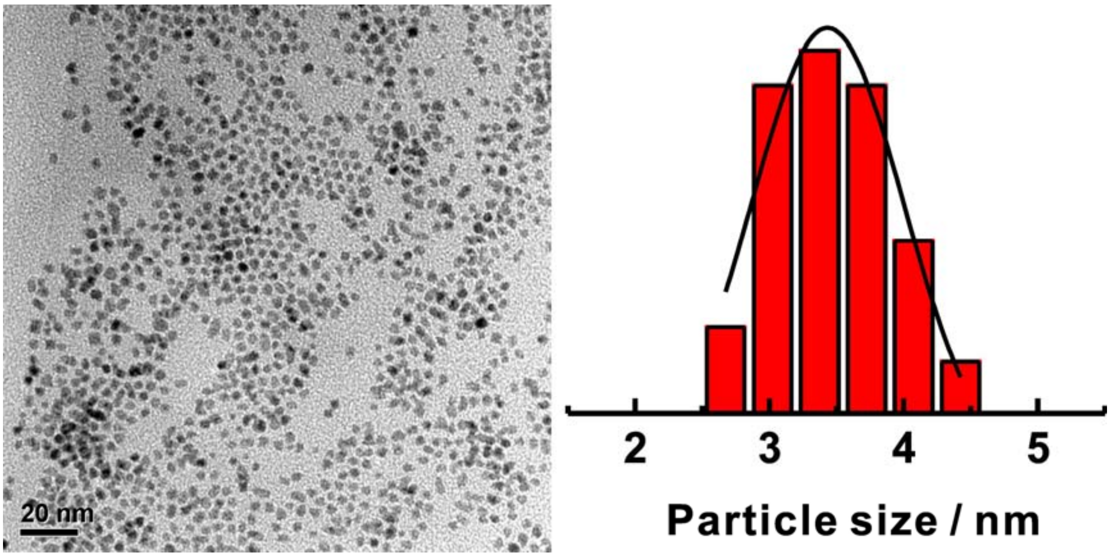

Fig.S1 Pt nanoparticle size distribution of GN-Pt nanohybrids.

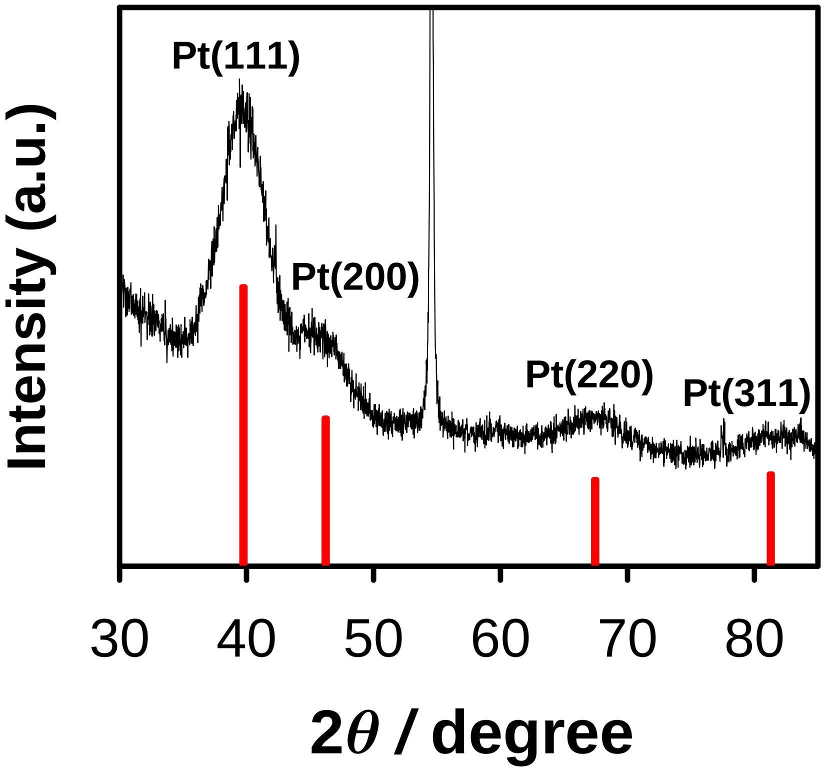

Fig. S2 XRD pattern of GN-Pt nanohybrids.

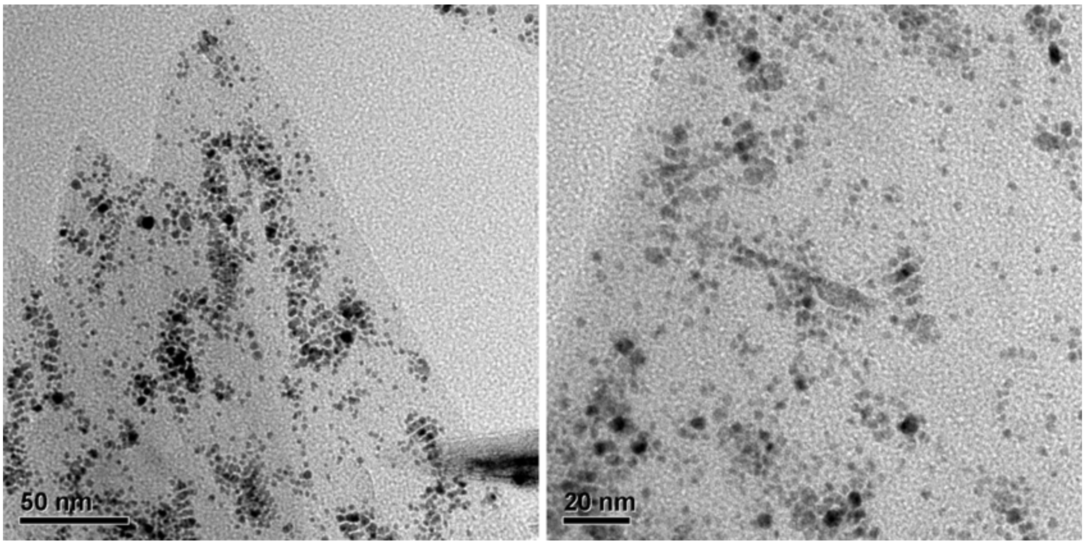

Fig. S3 GN-Pt nanohybrids synthesized in the absence of CO.

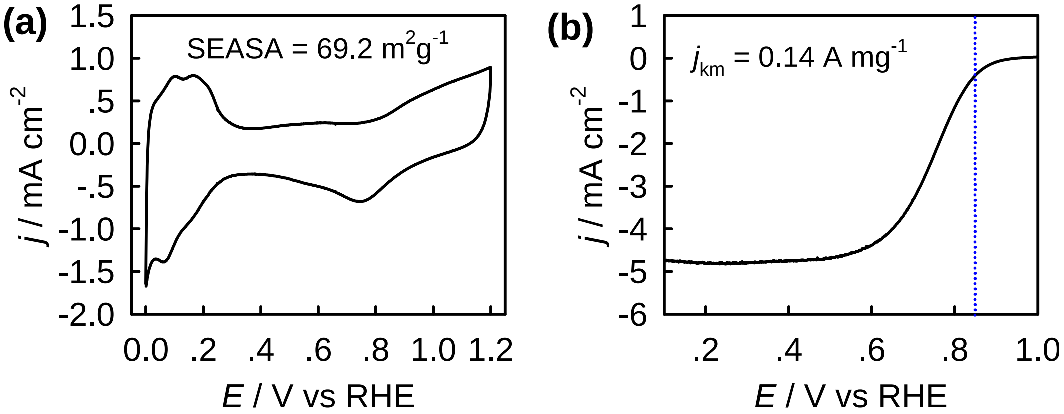

Fig. S4 (a) Cyclic voltammograms for commercial Pt/C catalyst in 0.5 M H_2SO_4 aqueous solution at 50 mV s^{-1}. (b) ORR polarization curves for commercial Pt/C catalyst recorded at room temperature in an O_2-saturated 0.5 M H_2SO_4 aqueous solution at a sweep rate of 10 mV s^{-1} and a rotation rate of 1,600 rpm.

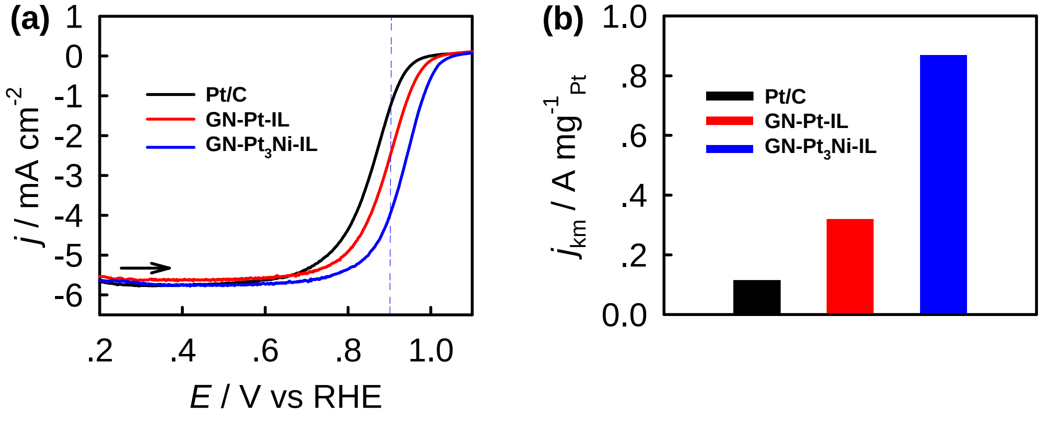

Fig. S5 (a) ORR polarization curves for Pt/C, GN-Pt-IL, and GN-Pt$_3$Ni-IL catalysts in 0.1 M O_2-saturated $HClO_4$ solution at a sweep rate of 10 mV s^{-1} and a rotation rate of 1,600 rpm. (b) Mass activity (j_{km}) at 0.9 V for these three catalysts, which is given as kinetic current densities (j_k) normalized to the Pt mass. the Pt loadings for all catalysts were 15.3 μg cm^{-2}.

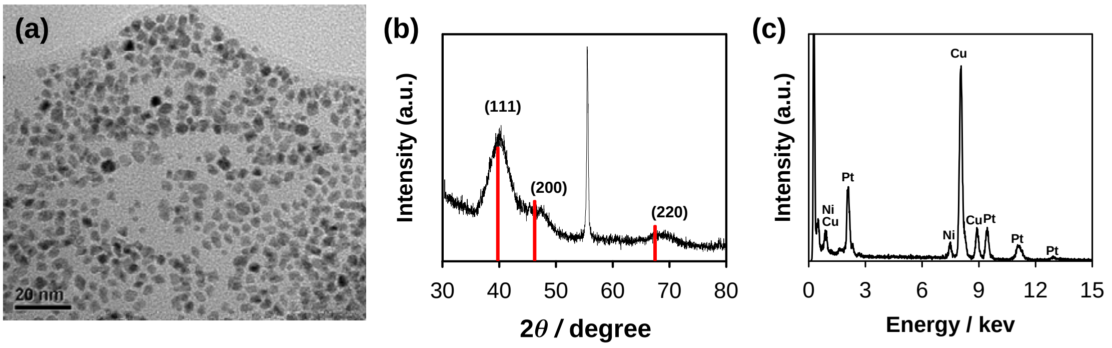

Fig. S6 TEM image (a), XRD pattern (b), and EDX spectrum (c) of GN-Pt$_3$Ni hybrids. Monodisperse nanoparticles grown on GN can be observed (Fig. S6a). The diffraction peaks slightly shift to higher angles compared with those for pure Pt (Fig. S6b), indicating the formation of Pt-Ni alloy. The energy-dispersive X-ray (EDX) analysis suggests that the average molar ratio between Pt and Ni is 3:1. These results clearly indicate the formation of GN-Pt$_3$Ni hybrids.

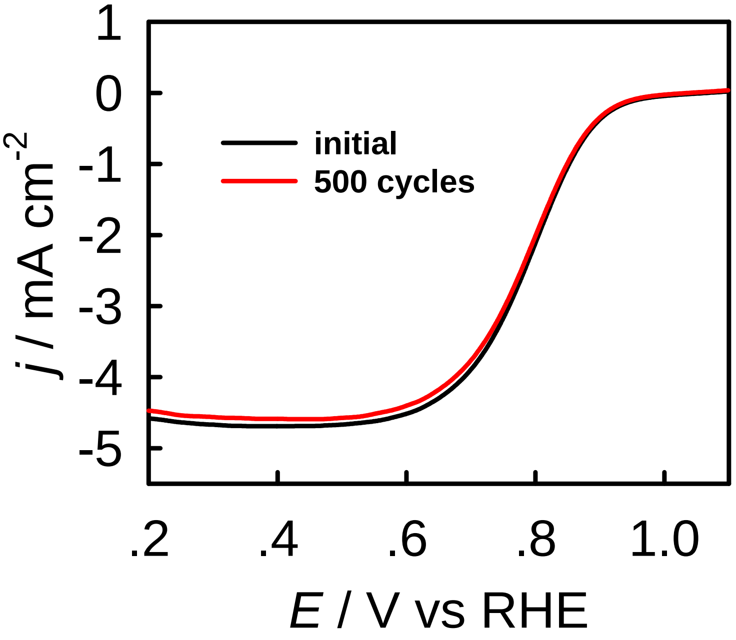

Fig. S7 ORR polarization curves for GN-Pt-IL catalyst in 0.5 M O_2-saturated H_2SO_4 solution at a sweep rate of 10 mV s^{-1} and a rotation rate of 1,600 rpm before and after 500 potential cycles. The potential cycles were from 0.5 to 1.0 V in 0.5 M O_2-saturated H_2SO_4 solution at room temperature at a sweep rate of 10 mV s^{-1} and a rotation rate of 1,600 rpm.

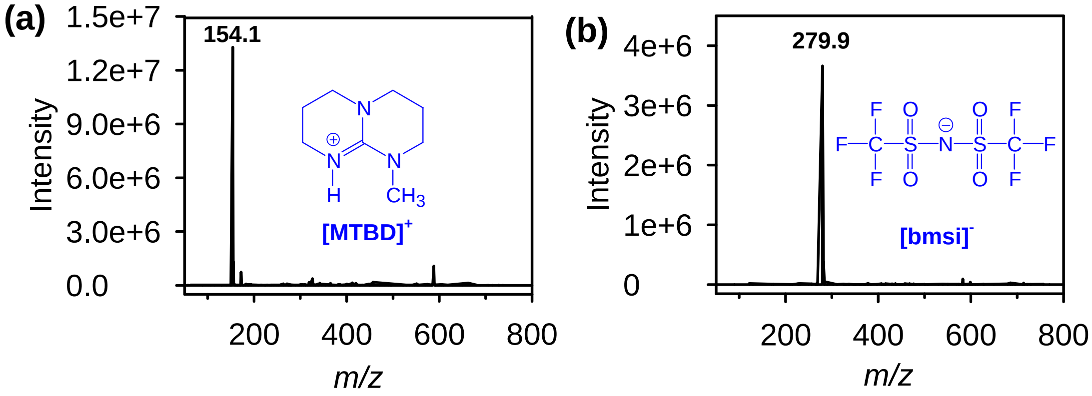

Fig. S8 Mass spectrum of [MTBD][bmsi] IL recorded in positive ion mode (a) and negative ion mode (b).

References

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