Supplementary Information

Low-loading Pt nanoparticles embedded on Ni, N-doped carbon as a superior electrocatalyst for oxygen reduction

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Experimental Section

1. Materials

All materials used in this work had been listed in the following: pyromellitic dianhydride $(C_{10}H_2O_6, AR)$, urea $(CO(NH_2)_2, >99\%)$, ammonium chloride (NH_4Cl, AR) , ammonium molybdate $((NH_4)_6Mo_7O_{24}\cdot 4H_2O, AR)$, nickel chloride $(NiCl_2\cdot 6H_2O, AR)$ sulphuric acid (H_2SO_4, AR) , chloroplatinic acid $(H_2PtCl_6\cdot 6H_2O, 99.9\%)$, ethylene glycol $(C_2H_6O_2, AR)$, zinc oxide (ZnO, AR), ethylenediaminetetraacetic acid $((HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2, AR)$, carbon black (Vunlcan X-72), 1,10-Phenanthroline hydrochloride $(C_{12}H_8N_2\cdot HCl\cdot H_2O, 99\%)$, Zinc nitrate hexahydrate $(Zn(NO_3)_2 6H_2O, AR)$, melamine $(C_3H_6N_6, AR)$.

2. Preparation of catalysts

2.1 synthesis of Pt@NiNC, Pt@NC, Pt/NiNC and NiNC.

The precursors, polyphthalocyanine (PPc), were synthesized by a facile solid phase synthesis in the muffle furnace. To prepare the NiPPc sample, the ground mixtures of 2.8 g pyromellitic dianhydride, 5.5 g urea, 1.2 g NH₄Cl, 0.025 g (NH₄)₆Mo₇O₂₄·4H₂O, 1.05 g NiCl₂·6H₂O and 1.05 g zinc oxide were transferred to crucible and heated in a muffle furnace for 2 hours. Consequently, the resulting products were washed by ethanol, acetone and deionized water after cooling down to the room temperature. Finally the undissolved substances were dried at 80 °C under vacuum for 12 hours. The Ni@NiNC was synthesized by direct pyrolysis of the NiPPc precursor in Ar atmosphere at 900 °C for 3 hours. The ZnPPc was synthesized with same method as NiPPc, except that 2.30 g zinc oxide was conducted without NiCl₂·6H₂O. sample. In the preparation of Pt@NiNC[EG] (abbreviate into Pt@NiNC), 100 mg Ni@NiNC powders were suspended in mixed system of 40 mL EG by magnetic stirring in a flask. The resulting homogeneous mixture was then heated at 80 °C under flowing in oil bath. Then 5 mL H₂PtCl₆ aqueous solution (0.01 M) was injected into the mixture slowly and stirred for 6 hours. After cooling down to the room temperature, the resulting powders were filtrated and washed three times by ethanol and deionized water, respectively. Similarly, The Pt@NiNC[Aqueous] and Pt@NiNC[Ethanol] were synthesized in water and ethanol, respectively, while other synthetic conditions were unchanged. Pt/NiNC sample was synthesized at 130 °C for 3 hours by conducted 40 mL EG and 100 mg NiNC as the reducing agent and support for Pt, respectively. We replaced NiNC with NC and obtained Pt/NC sample.

2.2 synthesis of Pt@NiNC-2

The NiCl₂ 6H₂O (42 mg), Zn(NO₃)₂ 6H₂O (42 mg) and 1,10-Phenanthroline hydrochloride (300 mg) were dissolved in 500 mL ethanol. Subsequently, 50 mg Vulcan XC-72 was dispersed in above solution and stirred for 12 hours. The resulted suspension solution was dried at 80 °C for 6 hours in order to remove all ethanol. Afterward, the obtained black power was heated under argon gas atmosphere at 900 °C for 3 hours to obtain Ni@NiNC-2. The synthetic process of Pt@NiNC-2 was same with Pt@NiNC in section 2.1, except that Ni@NiNC-2 was conducted instead of Ni@NiNC.

2.3 synthesis of Pt@NiNC-3

The NiCl₂ $6H_2O$ (100 mg), $Zn(NO_3)_2$ $6H_2O$ (100 mg) and ethylenediaminetetraacetic acid (400 mg) were dissolved in 500 mL ultrapure water. Subsequently, 50 mg Vulcan XC-72 and 30 mg melamine were dispersed in above solution and stirred for 12 hours at 80°C. The resulted

suspension solution was dried on a heating table with set temperature of 200°C. Afterward, the obtained black power was heated under argon gas atmosphere at 900 °C for 3 hours to obtain Ni@NiNC-3. The synthetic process of Pt@NiNC-3 was same with Pt@NiNC in section 2.1, except that Ni@NiNC-3 was conducted instead of Ni@NiNC.

3. Characterization

The X-ray diffraction (XRD) patterns was acquired on D/Max 2500 VB2+/Pc diffractometer (Rigaku) using X-ray source of Cu K α radiation ($\lambda = 1.54056$ Å). Nitrogen adsorptiondesorption curves were tested on ASAP 2460 (version 2.01) with MicroActive software to analysis surface area and pore size. Transmission electron microscopy (TEM) characterizations were performed on JEM-2100 transmission electron microscopy. Scanning transmission electron microscope (STEM) images and energy dispersive spectroscopy (EDS) mapping images were obtained on the JEOL JEM-ARM200F with EDS detector. X-ray photoelectron spectroscopy (XPS) spectra were measured on Thermo Fisher Scientific ESCALAB 250Xi. XAFS spectra at Pt L_3 -edge and Ni *K*-edge were measured at beamline 1WB1 station of the Beijing Synchrotron Radiation Facility, China. The corresponding EXAFS dates were abstracted by ATHENA software. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted on IRIS Intrepid II (Thermo Fisher).

4. Electrochemical measurements

All electrochemical measurements were performed by conducting a three-electrode system at room temperature and without IR-correction. The glassy-carbon rotating disk electrode, Pt wire and saturated calomel electrode (SCE) were conducted as the working electrode, counter electrode and reference electrode, respectively. For preparing the catalyst-decorated electrode, the 5 mg catalyst and 20 µL Nafion were added into 1 mL ethanol, forming ink by subsequently sonicating for 1 hour. Then 10 µL ink was piped onto the glass carbon electrode (area: 0.1256 cm-2) and dried at room temperature before electrochemical measurements. Cyclic voltammetry (CV) measurements were conducted in N2-staturated 0.5 M H2SO4 aqueous solution at a sweep rate of 50 mV s⁻¹ from 0.031 and 1.08 V (versus reversible hydrogen electrode, vs. RHE, the same below). The ORR polarization curves were performed in O₂staturated 0.5 M H_2SO_4 aqueous solution from 1.18 V to 0.03 V with a sweep rate of 5 mV s⁻¹ and a rotation rate of 1600 rotations per min (rpm). The accelerated durability test (ADT) for ORR was performed in N₂-saturated 0.5 M H₂SO₄ solution by applying cyclic potential sweeps between 0.7 and 1.0 V at a sweep rate of 100 mV s⁻¹ for 5,000 cycles. For CO stripping CV curves, the CO were absorbed on the catalyst layer at a constant potential of -0.43 V in COsaturated 0.5 M H₂SO₄ for 30 min. Then N₂ were bubbled in solution to remove excess CO. Consequently, two CV curves were acquired by CV measurements with potential ranging from 0.031 V to 1.28 V at a sweep rate of 50 mV s⁻¹.

The kinetic current density of electrocatalyst was calculated by conducting mass-transport correction for the rotating disk electrode, and the equation was shown as below:

$$J_K = \frac{J \times J_L}{J_L - J}$$

where J_k is the kinetic current density, J is the current density measured experimentally, and J_L is the measured diffusion-limited current density.

the ECSAs were obtained by two methods in this work:

$$ECSAs_{HUPD} = \frac{Q_H}{0.21 \ (mC \ cm^{-2}) \times V \times M_{Pt}}$$

where $ECSAs_{HUPD}$ is the ECSA obtained by integrating the hydrogen under potential desorption (HUPD) area, Q_H is the integrated area of HUPD area, V is the scanning rate of CV curves, and M_{Pt} is Pt loading on the disk electrode.

$$ECSAs_{CO} = \frac{Q_{CO}}{0.42 (mC \ cm^{-2}) \times V \times M_{Pt}}$$

where $ECSAs_{CO}$ is the ECSA obtained by CO stripping method, Q_{CO} is the integrated area under the CO-stripping peak, V is the scanning rate of CO-stripping CV curves, and M_{Pt} is Pt loading on the disk electrode.

The MA and SA were calculated by the following equations, respectively:

$$MA = \frac{J_K \times A}{M_{Pt}}$$
$$SA = \frac{MA}{ESCAs}$$

where J_k is kinetic current density, A is area of disk electrode and M_{Pt} is Pt loading on the disk electrode.

Supporting Tables

sample	Pt (wt.%)	sample	Pt (wt.%)
Pt@NiNC[EG]	8.0	Pt/NiNC	9.0
Pt@NiNC[Ethanol]	8.0	Pt/NC	9.1
Pt@NiNC[Aqueous]	8.0		

Table S1. Pt content of samples in this work measured by ICP.

Table S2. ORR performance of commercial Pt/C, Pt@NiNC[EG], Pt@NiNC[Ethanol] and

Pt@NiNC[Aqueous].

sample	$\frac{\text{ECSAs}_{\text{HUPD}}}{(\text{m}^2 \text{ g}_{\text{Pt}}^{-1})}$	$\frac{\text{ECSAs}_{\text{CO}}}{(\text{m}^2 \text{ g}_{\text{Pt}}^{-1})}$	E _{1/2} (V)	Mass activity@0.9 V (mA mg _{Pt} ⁻¹)
Pt/C	66.8	66.2	0.82	4.3
Pt@NiNC [EG]	102.9	109.8	0.85	28.0
Pt@NiNC [Ethanol]	9	32.3	0.77	3.5
Pt@NiNC [Aqueous]	0	1.7	0.64	0.7

ECSAs_{HUPD}: ECSA obtained by integrating the hydrogen under potential desorption (HUPD) area.

ECSAs_{CO}: ECSA obtained by CO stripping method.

E_{1/2}: half-wave potential of ORR polarization curve.

 Table S3. Pore structure dates of polyphthalocyanine, Ni@NiNC and Pt@NiNC from BET

 surface area measurement.

sample	BET	microspore	mesopore	total	microspore	mesopore
	surface	surface	surface	pore	pore	pore
	area	area	area	volume	volume	volume
	$(m^2 g^{-1})$	$(m^2 g^{-1})$	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	$(cm^3 g^{-1})$	$(cm^3 g^{-1})$
polyphthal- ocyanine	14.90	5.80	9.10	0.0261	0.041	0.0220
Ni@NiNC	239.96	30.02	209.93	0.3015	0.0055	0.2960
Pt@NiNC	192.51	12.37	180.14	0.2989	0.0019	0.2970

sample	<i>E</i> _{1/2} (V)	$J_{\rm k}@0.9 \text{ V}$ (mA cm ⁻²)	$\frac{\text{ECSAs}}{(\text{m}^2 \text{ g}_{\text{Pt}}^{-1})}$	Mass activity @0.9 V (mA mg _{Pt} ⁻¹)	Specific activity @0.9 V (A m ⁻²)
Pt/C	0.82	0.34	66.8	4.3	0.064
Pt@NiNC	0.85	0.87	102.9	28.0	0.272
Pt/NiNC	0.81	0.38	73.4	10.8	0.147
Pt/NC	0.78	0.12	68.4	3.2	0.047

Table S4. ORR performance of Pt/C, Pt@NiNC, Pt/NiNC and Pt/NC.

 J_k : kinetic current density.

E_{1/2}: half-wave potential of ORR polarization curve.

ECSAs: electrochemically active surface area obtained by integrating the hydrogen under potential desorption (HUPD) area.

	Mass activity (mA mg _{Pt} ⁻¹)						
sample	Before ADT			After ADT			
	0.95 V	0.9 V	0.85 V	0.95 V	0.9 V	0.85 V	
Pt/C	0.8	4.3	25.3	0.3	1.6	8.7	
Pt@NiNC	4.1	28.0	156.0	2.8	21.9	131.0	
	Specific activity (A m ⁻²)						
sample	Before ADT			After ADT			
	0.95 V	0.9 V	0.85 V	0.95 V	0.9 V	0.85 V	
Pt/C	0.012	0.064	0.379	0.007	0.035	0.189	
Pt@NiNC	0.040	0.272	1.516	0.029	0.224	1.340	

Table S5. ORR mass activity and specific activity of Pt/C, Pt@NiNC before and after ADT.

Supporting Figures



Scheme S1. Illustration for the preparation of the Pt@NiNC electrocatalyst derived from polyphthalocyanine.



Fig. S1. a) TEM image of Pt@NiNC[Ethanol] and the corresponding histogram of particle diameter distribution (inset). b) TEM image of Pt@NiNC[Aqueous].



Fig. S2. XRD patterns of the Ni@NiNC, Pt@NiNC[EG], Pt@NiNC[Ethanol] and Pt@NiNC[Aqueous].



Fig. S3. CV curves in N₂-saturated 0.5 M H₂SO₄ solution and CO stripping CV curves of a) Pt@NiNC[Aqueous], b) Pt@NiNC[Ethanol], c) Pt@NiNC[EG]. d) LSV curves of the Pt/C, Pt@NiNC[EG], Pt@NiNC[Ethanol] and Pt@NiNC[Aqueous] for ORR at a sweep rate of 5 mV s⁻¹ with 1600 rpm.

As shown in Fig. S1a and Fig. S5, the Pt@NiNC[Aqueous] and Pt@NiNC[EG] exhibited the Pt NPs with obviously different sizes of *ca*. 4.0 nm and 2.4 nm, respectively. The Pt@NiNC[Aqueous] showed the Pt NPs with large size of around 100 nm, and a small amount of Pt NPs were observed in Fig. S1b. Meanwhile, the XRD patterns in Fig. S2 showed the relative sharp peaks in the following order: Pt@NiNC[Aqueous] > Pt@NiNC[Ethanol] > Pt@NiNC[EG]. The relative broad diffraction peaks of Pt demonstrated the small particle size and low crystallinity of the formed Pt NPs with the numerous Pt exposure with highly active sites, which were also confirmed in TEM images. In addition, to assess the ORR performance, we used CV measurements to evaluate the electrochemically active surface areas (ECSAs) by calculating the CO-stripping area and hydrogen under potential desorption (HUPD) area and LSV measurements to observe the ORR catalytic activity (Fig. S3). The Pt@NiNC[EG] showed the largest ECSAs and best ORR catalytic activity with most positive half-wave potential and largest mass activity among these catalysts. The enhanced activity of Pt@NiNC[EG] could be contributed to the smallest size of Pt NPs and largest ECSAs which exposed most active sites for ORR. And we inferred that the physical property (viscosity and polarity) of solvent could have a vital impact on the nucleation and growth behavior of Pt NPs during the galvanic reaction, which showed evident effects on structure of Pt NPs and corresponding catalytic performance.



Fig. S4. a) TEM image and b) corresponding lattice fringes, c) SAED patterns of Ni@NiNC.



Fig. S5. TEM image of Pt@NiNC and the corresponding histogram of particle diameter distribution (inset) for Pt@NiNC.



Fig. S6. a) Pt 4*f* spectra and the b) corresponding Pt(0) content, Pt(0) and Pt(II) $4f_{7/2}$ peak binding energy of Pt@NiNC, Pt@NC and Pt/NiNC. c) Ni 2*p* XPS spectra of Pt@NiNC, NiNC, and Pt/NiNC. d) Ni-N 2*p* peak binding energy. e) N 1s XPS spectra and f)TM-N/ pyrrolic content of Pt@NiNC, NiNC, and Pt/NiNC.

As shown in the XPS spectra (Fig. S6a-b), the Pt@NiNC showed the higher relative content of Pt(0) (65%) than Pt@NC (46%) and Pt/NiNC (60%). Additionally, the 4f7/2 peak of Pt(0) and Pt(II) for Pt@NiNC clearly shifted to a lower binding energy at 71.37 and 72.40 eV, respectively, compared with Pt@NC (71.48 and 72.55 eV) and Pt/NiNC (71.73 and 72.65 eV). The increased Pt(0) content and more low-binding-energy shifts demonstrated that the Pt could obtain more electrons from the adjacent Ni-N-C complexes. Moreover, we also collected the Ni 2p XPS spectra of Pt@NiNC, Pt/NiNC and NiNC supports. As shown in Fig. S6c-d, the Ni-N peak in Pt@NiNC was located at 855.70 eV, which was higher than those in Pt/NiNC (855.30 eV) and NiNC (854.95 eV). It was reconfirmed the electrons transfer between Ni-N-C and Pt. The electron transfer enhanced the Pt–Ni bonding at the Pt NPs/ Ni–N–C interface, and hence strengthened the metal-support interaction. In addition, considering the Pt-N interaction, we also deconvoluted the N 1s XPS into four species and summarize the TM-N/ pyrrolic content (Fig. S6f). The TM-N/ pyrrolic content of Pt@NiNC was little larger that of NiNC, due to smaller proportion of Pt NPs bonding with N species. Notably, Pt/NiNC showed larger increasement of TM-N/ pyrrolic content compared with NiNC, implying that some Pt-N bonds existed in Pt/NiNC. However, the N species always attracted electrons from Pt NPs, causing that Pt NPs in Pt/NiNC obtained less electrons from NiNC supports.



Fig. S7. TEM images of a) Pt/NiNC and b) Pt/NC. The insert of a) and b) showed their corresponding histograms of particle diameter distribution.



Fig. S8. XRD patterns of the Ni@NiNC, Pt@NiNC, NiNC, Pt/NiNC and Pt/NC.



Fig. S9. a) Tafel curves and b) CV curves of Pt/C, Pt@NiNC, Pt/NiNC, Pt/NC and NiNC at a sweep rate of 50 mV s⁻¹.



Fig. S10. CO-stripping CV curves of Pt/C and Pt@NiNC in 0.5 M H_2SO_4 solution at scan rate of 50 mV s⁻¹.



Fig. S11. The original TEM images of a) Pt@NiNC and c) commercial Pt/C. The TEM images of b) Pt@NiNC and d) commercial Pt/C after 5,000 potential cycles. The inserted pictures in a-d) were the corresponding histograms of particle diameter distribution.



Fig. S12. TEM images of a) Pt@NiNC[Phen], and b) Pt@NiNC[EDTA]. c) XRD patterns of Ni@NiNC, Pt@NiNC, Ni@NiNC[Phen], Pt@NiNC[Phen], Ni@NiNC[EDTA] and Pt@NiNC[EDTA]. d) CV curves, e) LSV curves, f) the mass activity and specific activity of Pt/C, Pt@NiNC, Pt@NiNC[Phen] and Pt@NiNC[EDTA].

To confirm the method in this work was scalable, we prepared Ni@NiNC[Phen] (the pyrolyzed products of NiCl₂, Vulcan and phenanthroline (Phen)) and Ni@NiNC[EDTA] (the pyrolyzed products of NiCl₂, Vulcan and ethylene diamine tetraacetic acid (EDTA)) as supports, and further conducted the same galvanic-replacement method to synthesized the Pt@NiNC[Phen] and Pt@NiNC[EDTA], respectively. As shown in Fig. S12, Pt@NiNC[Phen] and Pt@NiNC[EDTA] showed similar Pt particle sizes and Pt crystalline structure with Pt@NiNC. Moreover, Pt@NiNC, Pt@NiNC[Phen] and Pt@NiNC[EDTA] showed similar Pt particle sizes and Pt crystalline structure with Pt@NiNC. Moreover, Pt@NiNC, Pt@NiNC[Phen] and Pt@NiNC[EDTA] showed similar ECSA (102.9 m² g_{Pt}⁻¹, 99.0 m² g_{Pt}⁻¹ and 98.0 m² g_{Pt}⁻¹), MA (28.0 mA mg_{Pt}⁻¹, 26.1 mA mg_{Pt}⁻¹ and 25.6 mA mg_{Pt}⁻¹) and SA (0.272 A m⁻², 0.263 A m⁻² and 0.262 A m⁻²). Therefore, our synthetic method in this work was scalable.



Fig. S13. a) LSV and b) CV curves of Pt/C, Pt@NiNC, Pt/NiNC, Pt@NC and NiNC in O_2 -saturated 0.1 M HClO₄ solution. c) The calculated mass activity and specific activity of Pt/C, Pt@NiNC, Pt/NiNC and Pt@NC.