Supporting Information

Sub-5-nm Palladium Nanoparticles *In-situ* Embedded in N-doped Carbon Nanoframes: Facile Synthesis, Excellent Sinter Resistance and Electrocatalytic Properties

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Part I: Experimental

Materials and Reagents: 1-naphthylamine was purchased from Shanghai Macklin Biological Technology CO., Ltd. (Shanghai, China). Palladium chloride (PdCl₂) was supplied by Shanghai Dibo Chemical Technology Co., Ltd. (Shanghai, China). Vulcan XC-72 carbon was acquired from Cabot Company. Nafion (5 *wt*.%) was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. EDTMP, Na₂CO₃ and NaBH₄ were bought from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Distilled deionized water was used throughout this study. All chemicals were of analytical reagent grade and used without further purification.

Synthesis of Pd@N-C NFs: For the synthesis of the Pd@N-C NFs, 0.5 mL of PdCl₂ solution (50 mM) and 360 mg 1-naphthylamine were added into the mixed solvent of 5.0 mL of water and 5.0 mL of ethanol, followed by continuous sonication for 5 min. The obtained complex was separated by the high-speed centrifugation and washed three times with ethanol to remove the excess 1-naphthylamine. Then, the resultant was dried under 40 °C for 10 h, followed by heat treatment in a tube furnace at 600°C under a flowing N₂ atmosphere (ramp rate: 5 °C min⁻¹, hold: 3 h). The synthesis of other Pd@N-C_x nanocatalysts (x represents the feeding ratio of 1-naphthylamine to PdCl₂, i.e. x = 0.5, 1, 5) were similar to that of porous Pd@N-C₁₀ NFs, except for the different mass of 1-naphthylamine, which are 18 mg, 36 mg and 180 mg, respectively.

Synthesis of pure N-C NFs: The N-C NFs were acquired by soaking the Pd@N-C NFs into the concentrated nitric acid for 12 hours to remove the Pd nanoparticles without any influence on the carbon nanoframes.

Synthesis of referential Pd/C: The referential 30 *wt.*% Pd/C was synthesized by reference to previous work of our research group.¹ Detailed synthetic process are as follow: First, 3 mL 0.05 M PdCl₂ and 3 mL 0.05M EDTMP were added to 10mL water. Then, 0.1 M Na₂CO₃ solution was used to adjust the pH of solution to 10.0. After the addition of 37.2 mg Vulcan XC-72 carbon, the mixed solution was sonicated for 30 min. Subsequently, 15 mL 0.1M NaBH₄ solution was added to the suspension and the resulting mixture was sonicated for an additional 60 min. The mixture was centrifuged, washed and then dried under 40 °C for 12 h. The obtained catalyst is noted as referential 30 *wt.*% Pd/C.

Thermal treatment of catalysts: In order to evaluate the sinter-resistance of Pd@N-C NFs and 30 *wt*.% Pd/C in inert atmosphere, we take two catalysts into heat treatment in a tube furnace at different temperature with different time under a flowing N₂ atmosphere (ramp rate: 5 °C min⁻¹).

Characterizations: Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy dispersive X-ray (EDX) elemental mapping measurements were made on a JEOL JEM-2100F transmission electron microscopy operated at an accelerating voltage of 200 kV. The crystallinity of the samples was determined by recording X-ray diffraction (XRD) patterns on a Model D/max-rC X-ray diffractometer using Cu K α radiation source ($\lambda = 1.5406$ Å) and operating at 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo VG Scientific ESCALAB 250 spectrometer with a monochromatic Al K α X-ray source. The binding energy was calibrated by means of the C1s peak energy of 284.6 eV. The chemical composition of samples was investigated by EDX technique and inductively coupled plasma atomic emission

spectroscopy (ICP-AES). Differential scanning calorimetry and thermogravimetric analysis (DSC-TGA) were carried out on a Netzsch STA 449C thermal analyser at a heating rate of 10°C min⁻¹ in O_2 . The Brunauer-Emmett-Teller (BET) specific surface area and pore size distribution was measured at 77 K using a Micromeritics ASAP 2050 system. The mass spectrum of Pd-(C₁₀H₇-NH₂) complex was determined on a GC-MS (Thermo Trace GC Ultra with an ISQ i mass spectrometer) in the *N*,*N*-Dimethylformamide (DMF) solution.

Electrochemical measurements: All electrochemical measurements are conducted with a conventional three-electrode system, Pt wire serves as the auxiliary electrode and a saturated calomel electrode (SCE) works as reference electrode. All catalytic experiments were carried out on CHI 760D electrochemical analyzer (Shanghai, Chenhua Co.) at 30 °C. Cyclic voltammetry and CO-stripping curves of two catalysts are acquired in N₂-saturated 0.5 M H₂SO₄ solution with a scan rate of 50 mV s⁻¹. Electrooxidation of formic acid and corresponding Nyquist plots of catalysts were performed in N₂-saturated 0.5 M H₂SO₄ + 1.0 M HCOOH solution. The working electrode is 3 mm glassy carbon electrode modified with catalysts. The oxygen reduction reaction was conducted in O₂-saturated 0.5 M H₂SO₄ solution with a scan rate of 5 mV s⁻¹ and a rotation rate of 1600 rpm, the working electrode of which is a rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE). The scan rate in the electrochemical stability test of FAO CVs and accelerated durability test (ADT) CVs are both 100 mV s⁻¹. Prior to electrochemical experiments, the working electrodes were preclean by cycling the potential between 0 and 1.2 V vs. RHE for 50 cycles in N₂-saturated 0.5 M H₂SO₄ electrolyte to remove the surface contaminants on electrocatalysts. All electrode potentials were quoted versus reversible hydrogen electrode (RHE). Electrochemical surface area (ECSA) of the catalysts was acquired from CV curves in H_2SO_4 solution, where we assume a value of 0.424 mC cm⁻² for the oxidation of a monolayer of CO. The specific formula is as follows:²

$$ECSA = Q/(0.424 \times Pd_m) (1)$$

in which Q on behalf of the integrated the CO oxidation charge in CO_{ad} stripping voltammograms while the Pd_m represents the Pd loading on the electrode.

Based on the ORR polarization curves, the kinetic current density ($i_{\rm K}$) was calculated by using the Koutecky-Levich equation [Eq. (2)], in which $i_{\rm L}$ and i are the limited diffusion current density and the measured current density, respectively.³

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_L}$$

The number of transferred electrons per oxygen molecule involved in the ORR at the Pd@N-C NFs was determined by the Koutecky-Levich equation [Eq. (2)], with $i_{\rm L}$ expressed by Equation (3),⁴ in which *n* is number of electrons transferred for per oxygen molecule, *F* is the Faraday constant (96485 C mol⁻¹), $D_{\rm O2}$ is the diffusion coefficient of O₂ (1.93×10⁻⁵ cm² s⁻¹), *n* is the kinetic viscosity of the solution (1.009×10² cm² s⁻¹), C_{O2} is the concentration of dissolved O₂ in solution (1.26×10³ mol L⁻¹), and ω is the electrode rotation rate. According to the equation, the number of electrons transferred in the reaction could be determined from the plot of the measured overall current density (*i*) against the square root of the angular velocity ($\omega^{1/2}$).

$$i_L = 0.62nFD_{0_2}^{2/3}v^{-1/6}C_{0_2}\omega^{1/2}$$
(3)

For the RRDE measurements, catalyst inks and electrodes were prepared by the same method as for RDE. The disk electrode was scanned at a rate of 5 mV s⁻¹, and the ring

potential was constant at 1.3 V *vs*. RHE. The yield of H_2O_2 and the electron transfer number (*n*) are calculated by referring to the following equation:⁵

$$y_{H_2 O_2} = \frac{200i_r}{Ni_d + i_r} \qquad n = \frac{4Ni_d}{Ni_d + i_r}$$

in which i_d and i_r indicate the disk current and the ring current, N stands for current collection efficiency of the RRDE (N=0.37).

Part II: Figures and Tables



Fig. S1 Schematic diagram of the synthetic procedure of Pd@N-C NFs.



Fig. S2 (a) XRD pattern and (b) mass spectrum of the $Pd-(C_{10}H_7-NH_2)$ complex square nanoplates.



Fig. S3 (a and b) SEM images of the Pd-($C_{10}H_7$ -NH₂) complex square nanoplates under different magnifications.



Fig. S4 (a and b) TEM images of the $Pd-(C_{10}H_7-NH_2)$ complex square nanoplates under different magnifications.



Fig. S5 (a and b) Large-area SEM images of Pd@N-C NFs.



Fig. S6 (a and b) Magnified SEM images of Pd@N-C NFs.



Fig. S7 The pore-size distribution curve of Pd@N-C NFs.



Fig. S8 (a and b) TEM images of Pd@N-C NFs with different magnifications.



Fig. S9 (a) STEM image of Pd@N-C NFs and (c and d) EDX element mappings.



Fig. S10 (a and b) TEM images of commercial Pd/C with different magnifications; (c) Size distribution of Pd nanoparticles recorded from the panel (b); (d) HRTEM image of commercial Pd/C.



Fig. S11 The TGA curve of Pd@N-C NFs.



Fig. S12 TEM images of the Pd@N-C_N nanocatalysts at different feeding ratios of 1-naphthylamine to Pd^{II} precursor: (a) 0.5: 1 and (b) 1: 1.



Fig. S13 TEM images of the Pd@N-C_N nanocatalysts at different feeding ratios of 1-naphthylamine to Pd^{II} precursor: (a) 40: 1 and (b) 80: 1.



Fig. S14 TEM images of the Pd@N-C_N nanocatalysts at different feeding ratios of 1-naphthylamine to Pd^{II} precursor: (a) 5: 1 and (b) 10: 1.



Fig. S15 TEM images of Pd/C sample obtained through directly heating carbon adsorbed Pd^{II} precursor without 1-naphthylamine.



Fig. S16 HRTEM images of Pd@N-C NFs.



Fig. S17 TEM images of Pd@N-C products synthesized at 800 °C.



Fig. S18 The CV curves of Pd@N-C NFs and pure N-C nanoframes for the FAO.



Fig. S19 FAOR curves before and after continuous multi-circle scan of (a) Pd@N-C NFs and (b) commercial Pd/C.



Fig. S20 (a) RRDE test of the Pd@N-C NFs in 0.5 M H_2SO_4 solution, (b) H_2O_2 yield and electron transferred number of ORR by calculating the current of ring-disk electrode.



Fig. S21 (a) CV curves and (b) ORR polarization curves of commercial Pd/C in 0.5 M H_2SO_4 solution before and after the ADT.



Fig. S22 (a-c) TEM images under different magnifications and (d) size distribution of Pd particles of the Pd@N-C NFs after the ADT (1000 cycles).



Fig. S23 TEM images of the commercial Pd/C: (a) before and (b) after the ADT.



Fig. S24 (a) The CV curves of N-doped Pd/C and Pd/C for the FAO; (b) The polarization curves of N-doped Pd/C and Pd/C for the ORR.



Fig. S25 TEM images of (a) Pd/C and (b) N-doped Pd/C; (c) XRD patterns of Pd/C and N-doped Pd/C; (d) N 1s XPS spectra of N-doped Pd/C and Pd/C.

No.	Catalysts	T/°C	<i>t</i> / h	Atmosphere	<i>d</i> / nm	Ref.
1	Pd@N-C NFs	600	3	N ₂	~4.6	This work
2	Pd/N-MCN	350-750	5	N ₂	4-14	6
2	Carbon-supported Pd-Co	600	2	$H_2 + N_2$	9.6	7
5	Pd-P-C framework	400	3	N_2	8.7	8
6	Fe ₃ O ₄ @CPd	450	3	-	5-10	9
7	H-PtPd/C	900	2	N_2	27.1	10
8	Pd-Co-Au/C	000	2	10 % H ₂ +90 % Ar	12-15	11
9	Pd-Ti/C	200			24-33	
10	Pd ₃ Fe/C	500	2.5	H ₂	9.7	12

Table S1. Comparations of the particle sizes of reported Pd-based catalysts prepared under different temperatures and Pd@N-C NFs in this work.

Table S2. Comparison of the thermostability of the reported Pd-based catalysts and Pd@N-C NFs in this work.

No.	Catalysts	T∕°C	t	Atmograhara	Particle	Particle	Ref.
				Aunosphere	size _{before} /nm	size _{after} /nm	
1	Pd@N-C NFs	500	1 h	N ₂	~4.6	9.3	This work
		600	1 h	N ₂		12.5	
2	Pt/C-JM	500	-	N ₂	3~5	15~40	13
3	Pt/C	500	40 min	7% H ₂ +93%N ₂	7.5	23.4	14
4	Pt NCs@CNTs	600	1 h	20%H ₂ +80%Ar	6.2	20.8	15
5	Pd-Fe/C	500	3 h	10% H ₂ +90% Ar	10.64	25.3	16

Catalysts	Mass Activity (mA mg ⁻¹)	Electrolyte	Ref.
Pd@N-C NFs	844.8	$0.5 \text{ M H}_2\text{SO}_4 + 1.0 \text{ M HCOOH}$	this work
Pt _{2.85} Cu HCLT	710	$0.5 \text{ M H}_2\text{SO}_4 + 0.25 \text{ M HCOOH}$	17
Pd ₃ Fe/C	696.4	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M HCOOH}$	18
Pt ₃ Sn Nanocube	630	0.1M HClO ₄ + 1.0M HCOOH	19
Pd ₆ Co/3DG	430.8	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M HCOOH}$	20
PdNiCu/C	792	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M HCOOH}$	21
Pd@Graphene	89.5	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M HCOOH}$	22
CuPd@Pd tetrahedra	501.8	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	23
Pd-Mo ₂ N/rGO	532.7	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M HCOOH}$	24
PtCu@PdRh	773	$0.5 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M HCOOH}$	25
Pt _{3.32} Cu HTBNFs	780	$0.5 \text{ M H}_2\text{SO}_4 + 0.25 \text{ M HCOOH}$	26
PtAu/C	~200	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M HCOOH}$	27
Pd ₃ Pt half-shells	318	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M HCOOH}$	28

 Table S3. Comparison of the FAOR activity of the as-prepared Pd@N-C NFs with other Pd-based catalysts reported before.

Part III: References

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