

Electronic Supplementary Information for

# Nitrogen intercalated Pd metallene nanoribbons with optimized electronic structure for oxygen reduction catalysis

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## **Experimental Section**

### **Chemicals and Materials**

Sodium tetrachloropalladate ( $\text{Na}_2\text{PdCl}_4$ ), ethylenediamine (EN), L-ascorbic acid (AA), polyvinylpyrrolidone (PVP,  $M_w = 40000$ ), molybdenum hexacarbonyl ( $\text{Mo}(\text{CO})_6$ ), diiron nonacarbonyl ( $\text{Fe}_2(\text{CO})_9$ ), dicobalt octacarbonyl ( $\text{Co}_2(\text{CO})_8$ ), tungsten hexacarbonyl ( $\text{W}(\text{CO})_6$ ), urea, Nafion (5 wt%) and PVP ( $M_w = 58000$ ) were supplied by Aladdin. Pt/C (20 wt%) was provided by Alfa Aesar.

### **Synthesis of Pd MNRs**

The synthesis of Pd MNRs was based on a previous report with minor modification.<sup>1</sup> First,  $\text{Mo}(\text{CO})_6$  (50 mg), AA (80 mg) and PVP (600 mg,  $M_w = 40000$ ) were dissolved in 2 mL EN by sonication. Subsequently, 0.5 mL  $\text{Na}_2\text{PdCl}_4$  (0.1 M) was dripped in the gained solution and the mixture was held for 8 h at 120 °C in an oil bath. Eventually, Pd MNRs were centrifuged with water, ethanol and acetone.

### **Synthesis of N-Pd MNRs**

The above Pd MNRs (2 mg) were added into a water (6 mL) containing urea (60 mg) and PVP (85 mg,  $M_w = 58000$ ). The resulting mixture was vigorously stirred for 20 min and then transferred to a Teflon-lined stainless-steel autoclave (25 mL). The above mixture was heated for 1 h at 180 °C. At last, the resulting sample was purified by alternating centrifugal washing with water, ethanol and acetone.

### **Materials Characterization**

The microstructure, composition, electronic structure, and crystal information of catalyst were characterized by transmission electron microscopy (TEM, JEOL-2100F) equipped with energy

dispersive X-ray spectroscopy (EDX) system, atomic force microscopy (AFM, Bruker Dimension ICON), X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI), and X-ray diffraction spectrometer (XRD, PANalytical Empyrean). Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed on Agilent ICPOES730.

### **Electrocatalytic Experiments**

During the electrochemical measurements, all potentials were referred to reversible hydrogen electrode (RHE). The ORR properties were tested on CHI 852D electrochemical analyzer with a three-electrode system consisting of counter electrode (Pt wire), working electrode (rotating disk electrode (RDE, a diameter of 3 mm) with catalyst coating) and reference electrode (Ag/AgCl electrode (KCl saturated)). To prepare catalyst ink, different samples (2 mg) were dispersed in 200  $\mu\text{L}$  of ethanol, 750  $\mu\text{L}$  of  $\text{H}_2\text{O}$  and 50  $\mu\text{L}$  of Nafion solution (0.5 wt %) under ultrasonication. The rotating disk electrode was covered with 2.0  $\mu\text{L}$  catalyst ink. Linear sweep voltammetry (LSV) was recorded with a rotating speed of 1600 rpm at a scan rate of 10  $\text{mV s}^{-1}$  in an  $\text{O}_2$ -saturated 0.1 M KOH solution.

The electron transfer number ( $n$ ) could be estimated from the Koutecky-Levich equation as follows:

$$j^{-1} = j_k^{-1} + j_d^{-1}$$

$$j_d = 0.2nFD^{2/3}\nu^{-1/6}\omega^{1/2} C_{\text{O}_2}$$

In which  $j_d$ ,  $j_k$  and  $j$  stand for limiting diffusion current density, kinetic current density and measured current density, respectively,  $F$  is the Faraday constant ( $96485 \text{ C mol}^{-1}$ ),  $\nu$  is the electrolyte viscosity ( $1.13 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ ),  $D$  is  $\text{O}_2$  diffusion coefficient ( $1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ),  $C_{\text{O}_2}$  is dissolved  $\text{O}_2$  concentration in 0.1 M KOH ( $1.2 \times 10^{-3} \text{ mol L}^{-1}$ ), and  $\omega$  is the rotation speed of electrode (rpm).

Electrochemical active surface area (ECSA) value could be calculated from cyclic voltammetry (CV) curve that was recorded with a sweep speed of 50 mV s<sup>-1</sup> in 0.1 M HClO<sub>4</sub> based on following equation:

$$\text{ECSA} = Q / m \times 420$$

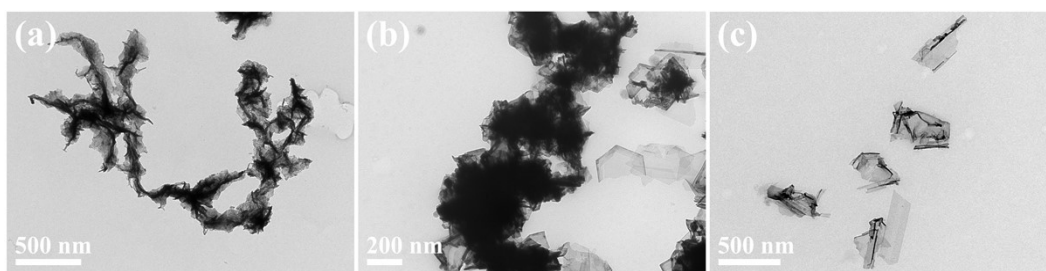
Where  $Q$  is the reduced charge gained by integrating the Pd oxide layer, 420  $\mu\text{C cm}^{-2}$  is the reduced charge of the oxide monolayer on the Pd surface, and  $m$  is the Pd loading on the electrode surface.

The mass activity (MA) and specific activity (SA) in this article are calculated at a potential of 0.9 V. The calculation formulas of MA and SA are as follows:

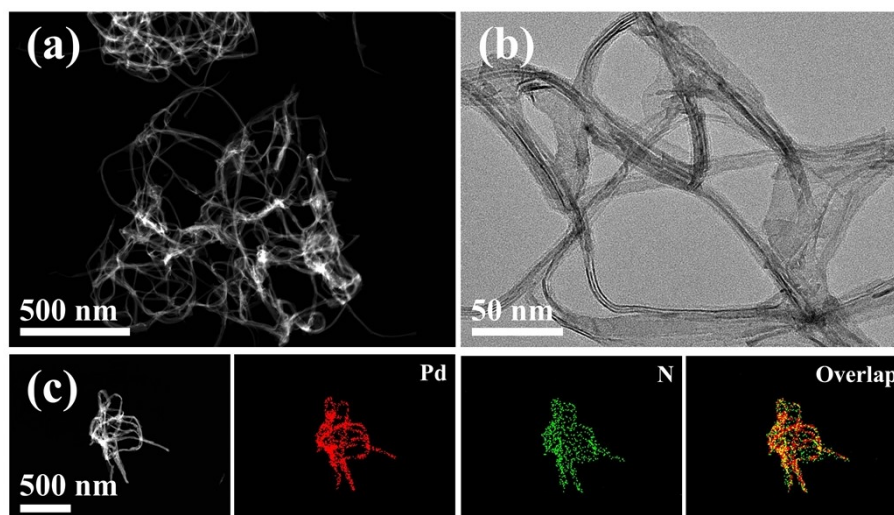
$$\text{MA} = (0.07 \text{ cm}^2 \times j_k) / m_{\text{metal}}$$

$$\text{SA} = (0.07 \text{ cm}^2 \times j_k) / (\text{ECSA} \times m_{\text{metal}})$$

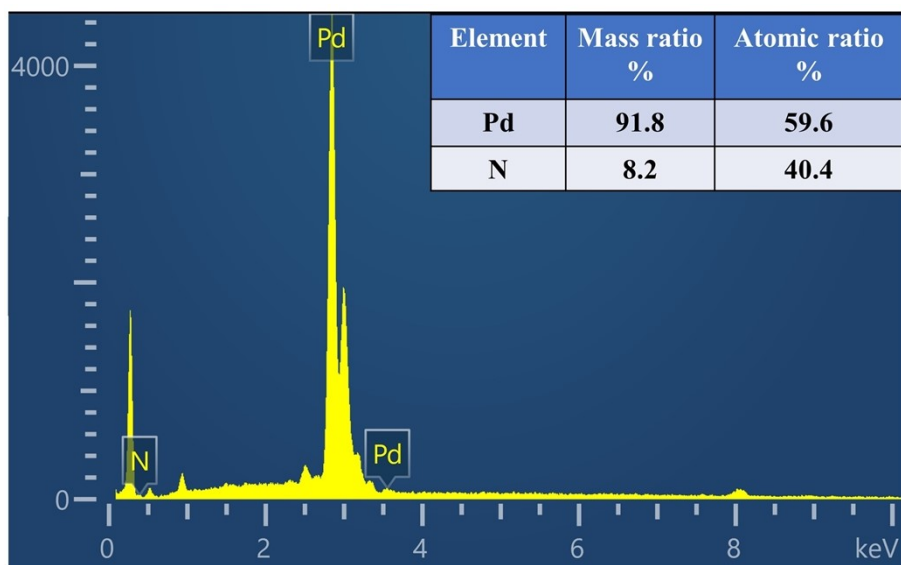
Where  $j_k$  is the kinetic current density at 0.9 V, 0.07 cm<sup>2</sup> is the surface area of the electrode,  $m$  is the metal mass loaded on the glassy carbon electrode.



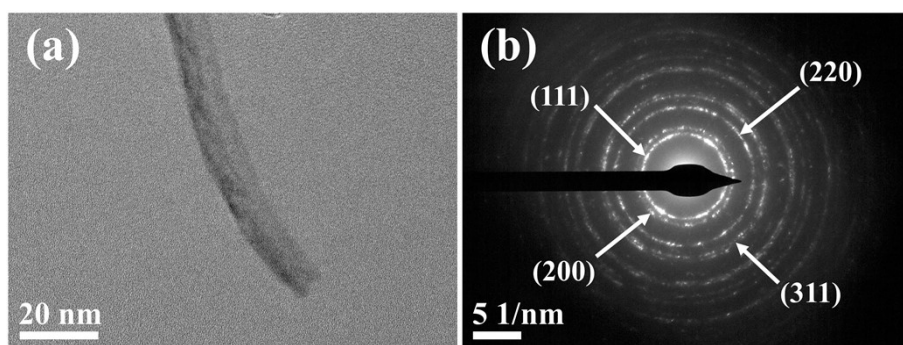
**Fig. S1** TEM images of the samples prepared by replacing  $\text{Mo}(\text{CO})_6$  with (a)  $\text{Fe}_2(\text{CO})_9$ , (b)  $\text{Co}_2(\text{CO})_8$  and (c)  $\text{W}(\text{CO})_6$ , respectively, under the same synthetic conditions.



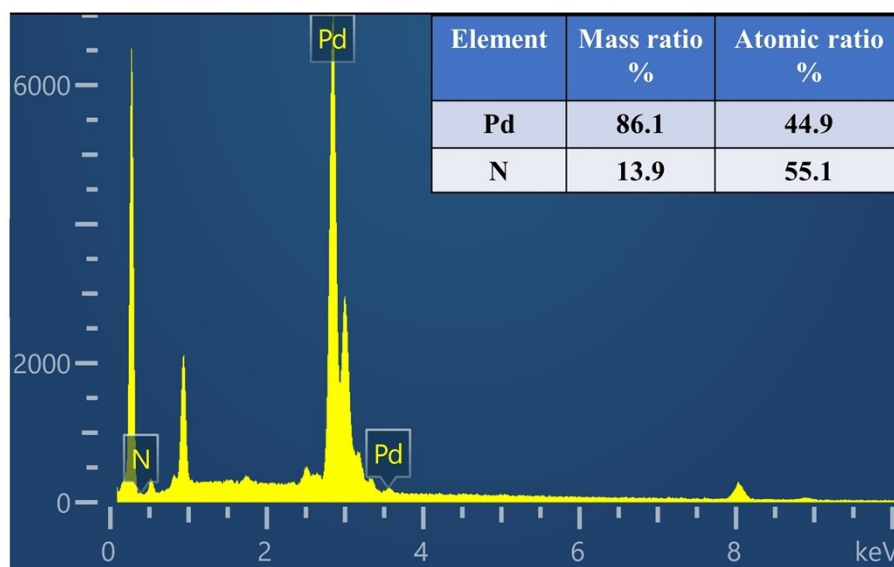
**Fig. S2** (a) HAADF-STEM and (b) TEM images of Pd MNRs. (c) HAADF-STEM image and relevant EDX mapping images of Pd MNRs.



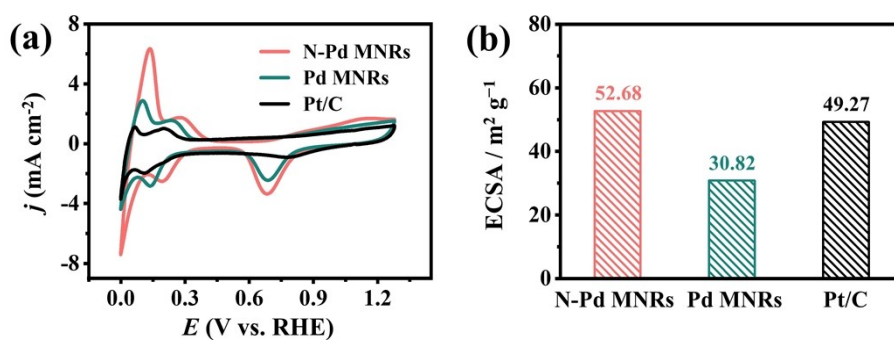
**Fig. S3** EDX spectrum of Pd MNRs.



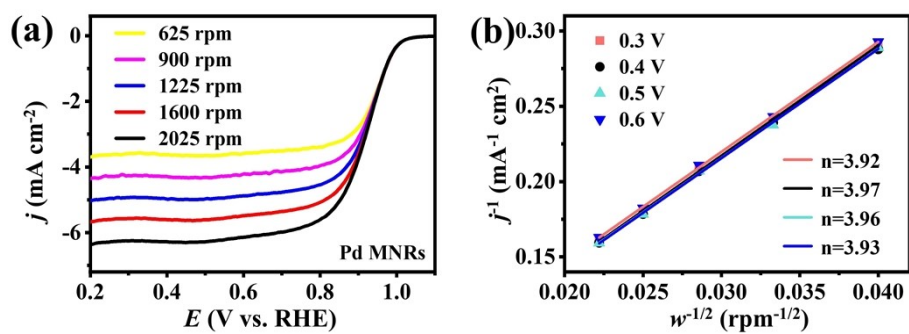
**Fig. S4** (a) TEM image of N-Pd MNRs and (b) corresponding SAED pattern.



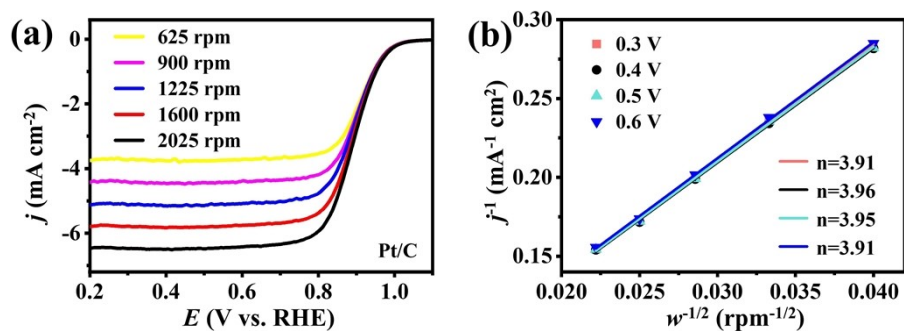
**Fig. S5** EDX spectrum of N-Pd MNRs.



**Fig. S6** (a) CV curves in 0.1 M HClO<sub>4</sub> solution and the corresponding ECSAs (b) of different catalysts.

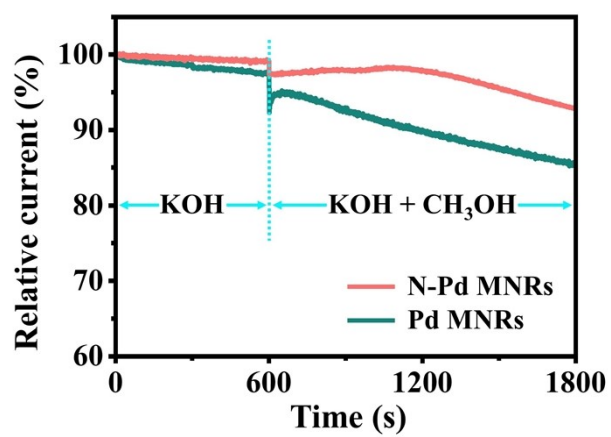


**Fig. S7** (a) ORR polarization curves at different rotating speeds, and (b) electron transfer numbers at different potentials of Pd MNRs.



**Fig. S8** (a) ORR polarization curves at different rotating speeds, and (b) electron transfer numbers at different potentials of Pt/C.





**Fig. S9** Chronoamperometric curves in an O<sub>2</sub>-saturated 0.1 M KOH electrolyte with 3 M CH<sub>3</sub>OH added at around 600 s.

**Table S1** The comparisons of the ORR performance of N-Pd MNRs with some recently reported Pd-based catalysts.

Catalyst	SA (mA cm <sup>-2</sup> )	MA (mA μg <sup>-1</sup> metal)	Ref.
<b>N-Pd MNRs</b>	<b>1.29</b>	<b>0.68</b>	<b>This work</b>
Pd <sub>6</sub> Ni icosahedra	0.66	0.22	2
Pd <sub>3</sub> Pb UPINs/C	1.18	0.59	3
Fe-Pd UPM	0.225	0.736	4
Pd <sub>9</sub> Pt <sub>1</sub> Ni <sub>1</sub> NSs	1.22	0.29	5
Pd <sub>3</sub> Pb nanoplates	/	0.78	6
Pd@PdFe NPs	1.56	0.31	7
Au-NWs@Pd@PEI	/	0.29	8
Pt <sub>2</sub> Pd <sub>1</sub>	1.14	0.44	9
Pd <sub>3</sub> Pb/Pd NSs/C	1.31	0.57	10
PtPdSP mNCs	1.10	0.56	11

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