Supporting Information

Single-atom Palladium anchored N-doped carbon towards oxygen electrocatalysis for rechargeable Zn-air battery

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Experiment

Chemicals

Glucose (Glu), Dicyandiamide (DCDA) (99 wt%), Ammonium tetrachloropalladate ($H_8Cl_4N_2Pd$), All the chemicals were procured from Aladdin (China). The aqueous solutions were prepared using deionized (DI) water (18.2 MΩ cm^{-1}). Nafion solution (5.0 wt%), carbon paper, high-purity argon (99.99%) gas was supplied by the Xiangyu

company in Shanxi. All chemicals used in the synthesis of electrocatalysts were of analytical grade (AR) and used without further purification.

Fabrication of electrocatalysts

A simple freeze-drying method was used to prepare a Pd_1/N-C electrocatalyst. Generally, 1 g of Glu and 4 g of DCDA are first dissolved in 60 ml deionized water, and heated in an 80 °C Oil bath under constant stirring until the aqueous solution becomes transparent. Next, 1 mL of 10 mmol L^{-1} $(NH_4)_2PdCl_4$ was dropped into the solution, stirred for 3 h until it was completely dissolved, and then freeze-dried. During the freeze-drying process, a support material with a three-dimensional ordered needle-like structure is formed. The obtained needle-like material was placed into the center of a quartz tube furnace, and the temperature was raised to 800 °C at a heating rate of 5 °C min^{-1} under an Ar flow and calcined for 2 h. The obtained sample was expressed as Pd_1/N-C. As a control, Pd-NPs/N-C (adding 1 mL of 100 mmol L^{-1} $(NH_4)_2PdCl_4$) and N-C electrocatalyst also synthesized use the same method.

Characterization

Scanning electron microscopy (SEM) was performed by a Field emission JSM-7900F and Transmission electron microscopy (TEM) images were performed on a Ticnai G2 F20 S-Twin instrument. Atomic high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) characterization and corresponding energy-dispersive spectroscopy (EDS) were conducted on EM-ARM300F. Bruker D8 Advance (Germany) was used to probe powder X-ray diffraction (XRD). The X-ray

photoelectron spectrum (XPS) were collected on an Axis Ultra DLD spectrometer equipped with an Al Kα excitation and with C as internal standard (C 1*s* = 284.6 eV). N_2 adsorption-desorption experiments were conducted on a BELS ORP physical adsorption apparatus, and the specific surface area testing was performed by the Brunauer-Emmett-Teller (BET), and the pore size was calculated by Barrett-Joyner-Halenda (BJH). Raman spectrum was recorded on an Alpha 300 R spectrometer. The actual Pd loadings were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Aglient 5110). Fourier Transform infrared spectroscopy (FT-IR) was collected on a Bruker Tensor-27 analyzer using the pressed KBr pellets. Thermogravimetric analysis (TGA) was conducted with a Thermogravimetric (TGA Q 50) with a heating rate of 5 °C min^{-1} from 20 ℃ to 800 ℃ under Ar atmosphere.

Results and discussion

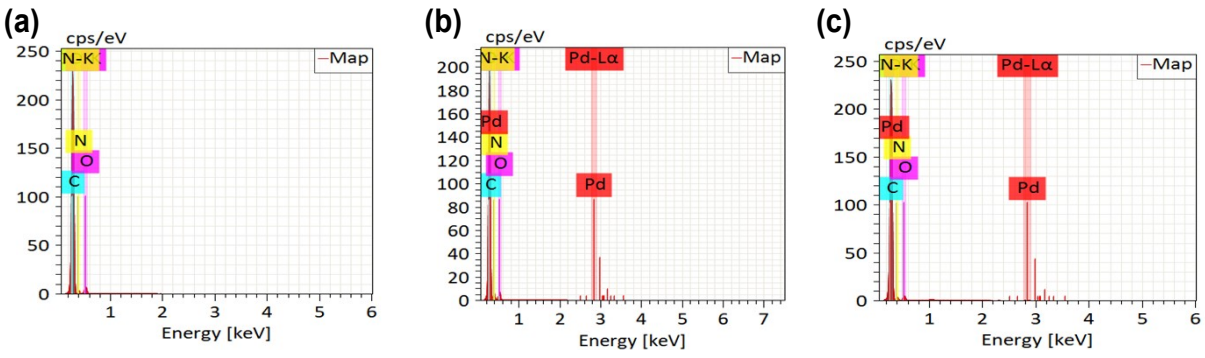

Fig. S1 EDS spectra of (a) N-C, (b) Pd_1/N-C and (c) Pd-NPs/N-C samples.

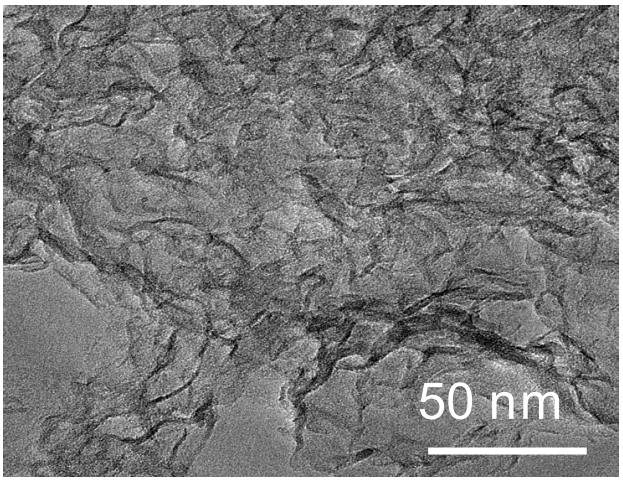

Fig. S2 TEM image of N-C.

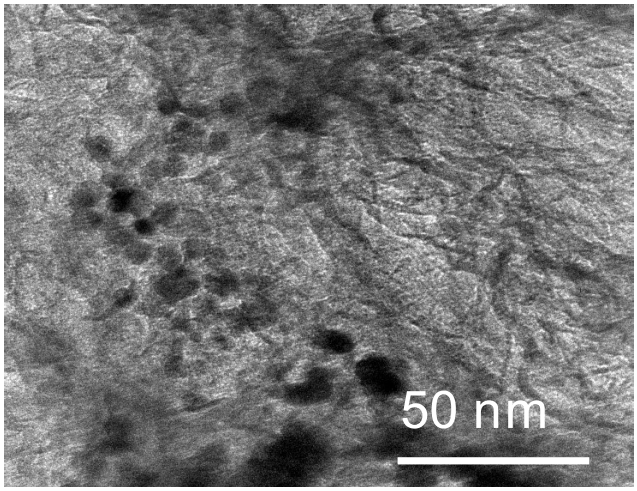

Fig. S3 TEM image of Pd-NPs/N-C.

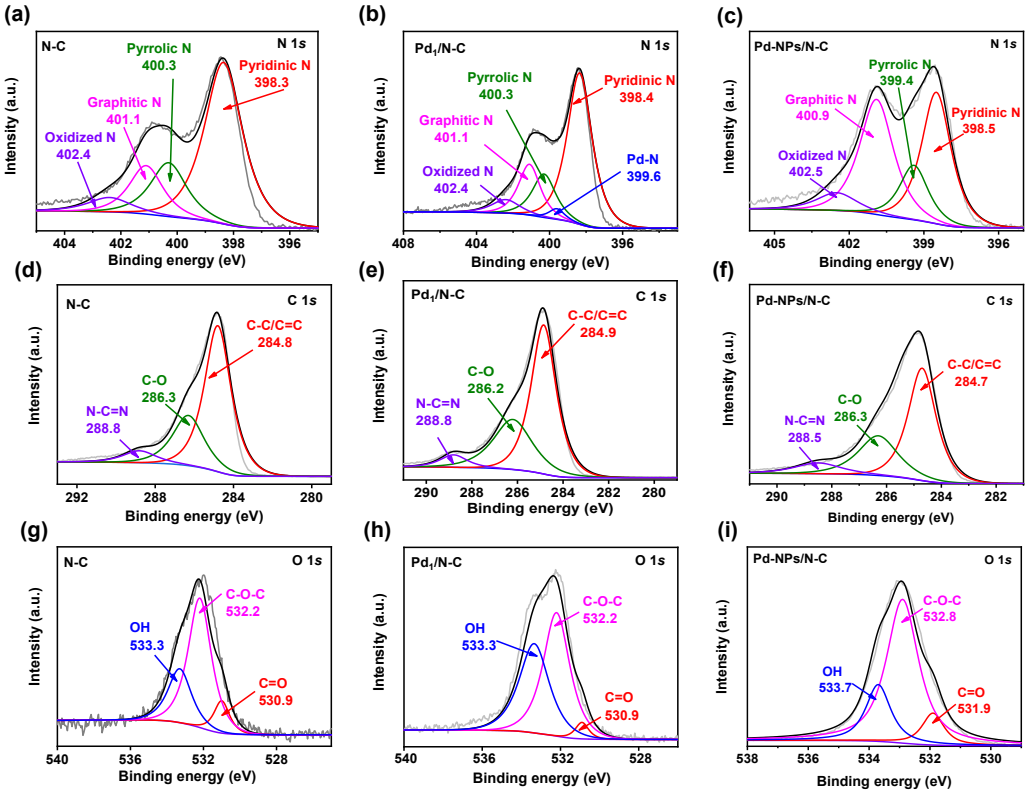

Fig. S4 High-resolution XPS spectra of (a-c) N 1*s*, (d-f) C 1*s*, (g-i) O 1*s* for N-C, Pd_1/N-C and Pd-NPs/N-C.

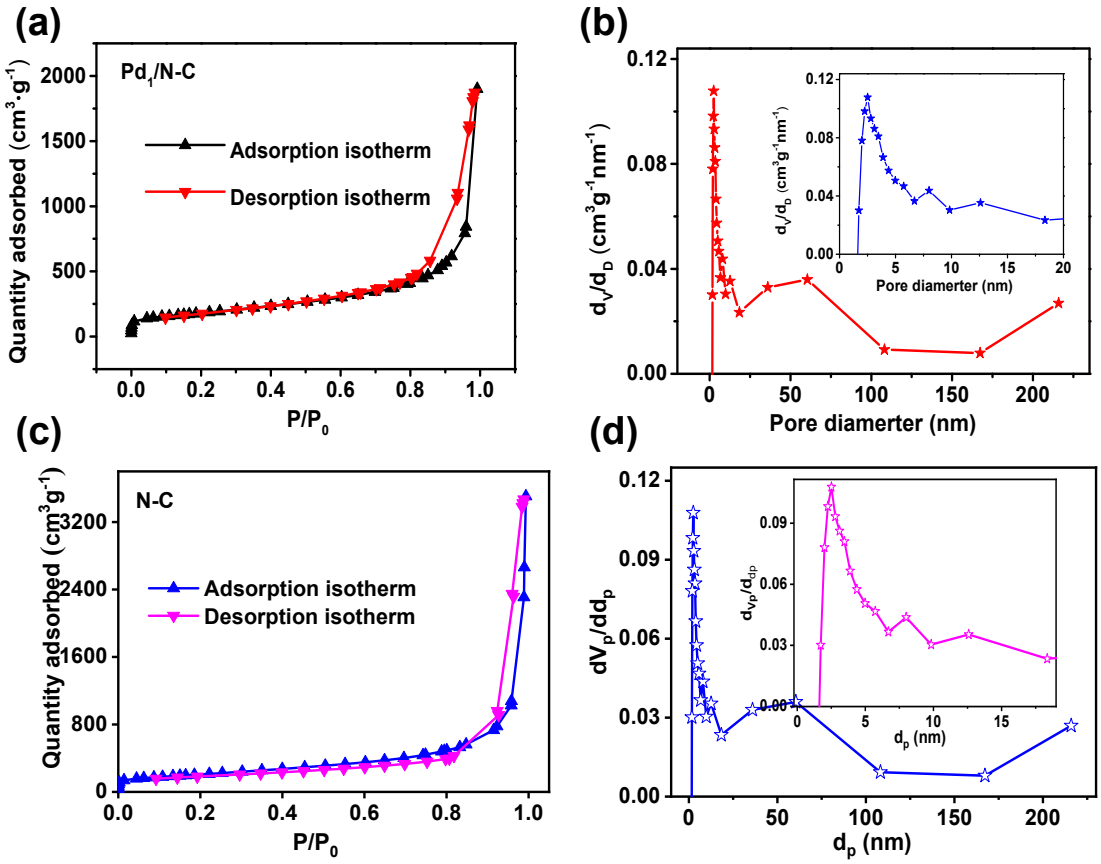

Fig. S5 (a) N_2 sorption isotherms, (b) and (inset) pore size distribution curves of Pd_1/N-C, (c) N_2 adsorption-desorption isotherms of N-C, (d) and (inset) the pore size distribution curve.

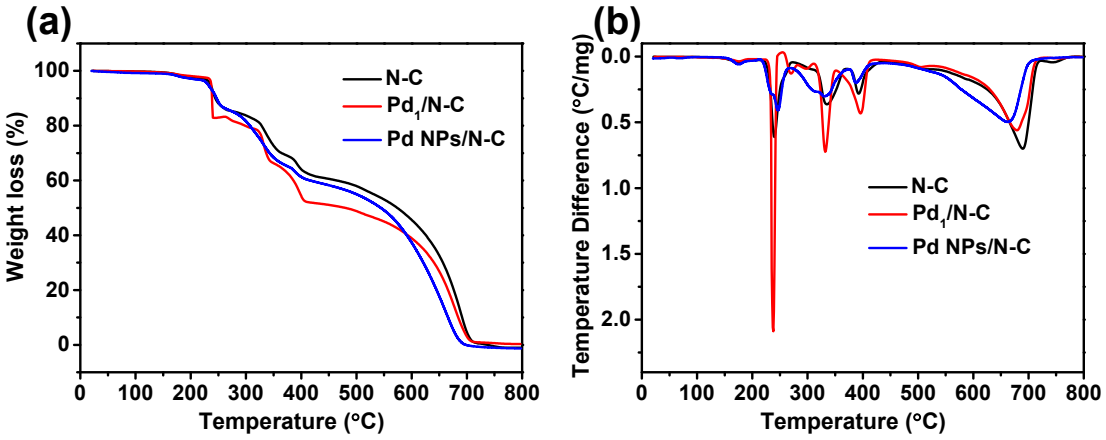

Fig. S6 TGA of N-C, Pd_1/N-C and Pd-NPs/N-C.

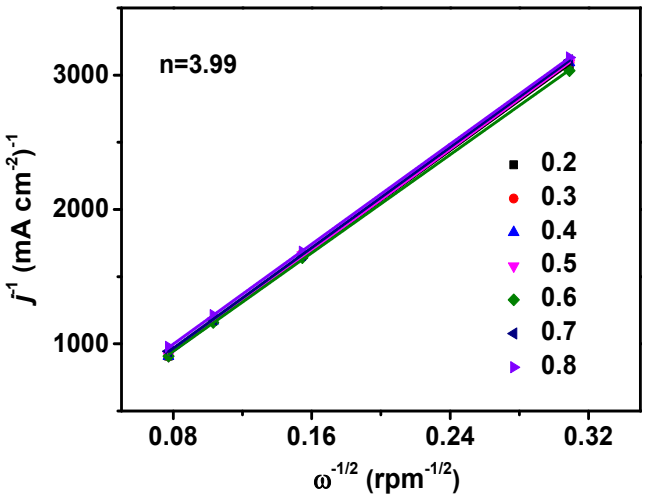

Fig. S7 Koutecky-Levich plots of Pd_1/N-C at diverse potentials (0.2~0.8 V).

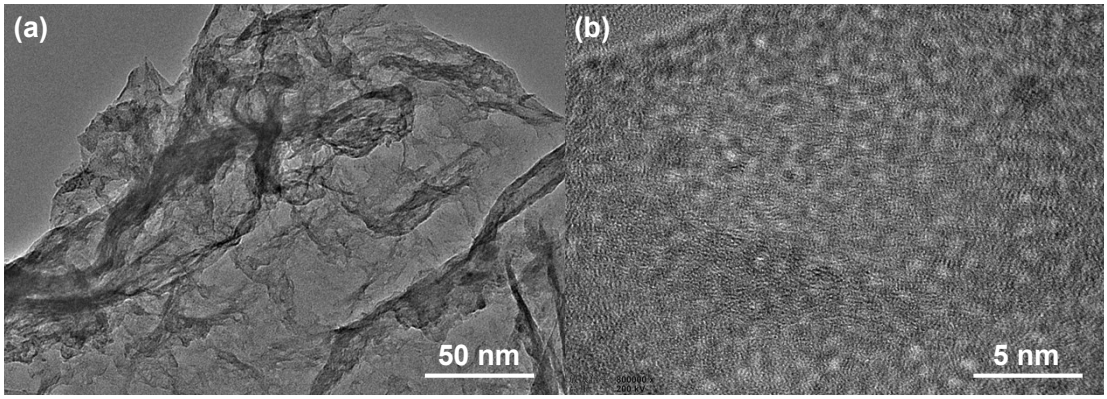

Fig. S8 TEM images of Pd_1/N-C after stability tests.

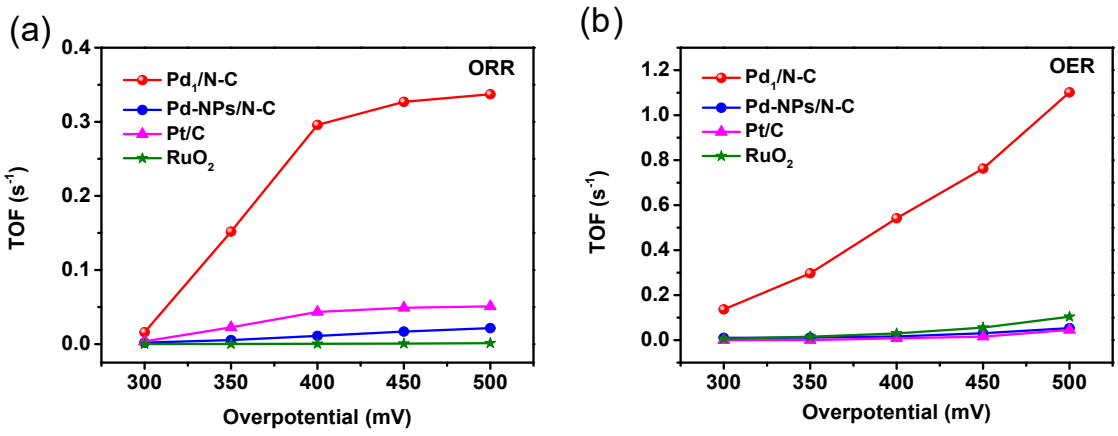

Fig. S9 TOF as a function of overpotential during (a) ORR and (b) OER.

Table S1 The surface contents of various N species determined by XPS for the N-C, Pd_1/N-C and Pd-NPs/N-C.

Entry	catalysts	Atomic ratio of different N species (%)				
		Pd-N Moiety(%)	**Pyridinic N (%)**	**Pyrrolic N (%)**	**Graphitic N (%)**	**Oxidized N (%)**
1	N-C	0	39.1	22.4	21.2	17.3
2	Pd_1/N-C	13.8	33.8	18.5	19	14.9
3	Pd-NPs/N-C	0	30.02	21.52	30.02	18.45

Table S2 Nitrogen adsorption-desorption measurements at 77 k for Pd_1/N-C and N-C.

Catalysts	**S_{BET} (m^2 g^{-1})**	**V_{micro} (cm^3 g^{-1})**	**D_{micro} (nm)**
Pd_1/N-C	641.29	2.8503	17.778
N-C	747.36	4.2167	22.259

Table S3 Performance of recently reported electrocatalyst in Zn-air batteries.

Sample	OCV (V)	PD_{max} (mW cm^{-2})	Stability	VE%	Ref
NFPC	1.6		200	57.9@10 mA cm^{-2}	[1]
sCu-ONPC	1.42	88.5@140 mA cm^{-2}	15	59.5@5 mA cm^{-2}	[2]
NiCo/CNF@NC	1.45	85.8@110 mA cm^{-2}	95	56.2@5 mA cm^{-2}	[3]
Ni SAsPd@NC	1.44	134.2@170 mA cm^{-2}	700	55.6@10 mA cm^{-2}	[4]
Pd/MnO_2–CNT	1.35	297.7@190 mA cm^{-2}	600	61.0@10 mA cm^{-2}	[5]
N-Mo-holey G	1.37	83@120 mA cm^{-2}	500	60.0@2 mA cm^{-2}	[6]
Pd/$Co(OH)_2$	1.40		500	57.0@5 mA cm^{-2}	[7]
Pd_1/N-C	1.38	113.7@175 mA cm^{-2}	495	64.0@5 mA cm^{-2}	This work

Reference

[1] M. G. Wu, Y. Q. Wang, Z. X. Wei, L. Wang, M. Zhuo, J. T. Zhang, X. P. Han and J. M. Ma, *J. Mater. Chem. A*, 2019, **6**, 10918-10925.

[2] Y. F. Wang, M. Jin, X. Zhang, C. J. Zhao, H. J. Wang, S. H. Li and Z. Y. Liu, *ACS Appl. Energy Mater*., 2019, **2**, 8659-8666.

[3] T. T. Gebremariam, F. Y. Chen, Y. C. Jin, Q. Wang, J. L. Wang and J. P. Wang, *Catal. Sci. Technol*., 2019, **9**, 2532-2542.

[4] S. Z. Wang, Z. N. Lin, M. M. Li, Z. H. Yu, M. J. Zhang, M. X. Gong, Y. W. Tang and X. Y. Qiu, *J. Mater. Chem. A*, 2022, **10**, 6086-6095.

[5] W. K. Xiang, Y. H. Zhao, Z. Jiang, X. P. Li, H. Zhang, Y. Sun, Z. J. Ning, F.P. Du, P. Gao, J. Qian, K. Kato, M. Yamauchi and Y. H. Sun, *J. Mater. Chem. A*, 2018, **6**, 23366-23377.

[6] P. Du, K. L. Hu, J. Lyu, H. L. Li, X. Lin, G. Q. Xie, X. J. Liu, Y. Ito and H. J. Qiu, *Appl. Catal. B-Environ*., 2021, **276**, 119172.

[7] S. Hyun, A. Saejio and S. Shanmugam, *Nanoscale*, 2020, **12**, 17858-17869.