

Electronic Supplementary Information for

**Hydrogen-intercalation-induced lattice expansion of mesoporous PtPd
nanocrystals for enhanced alkaline hydrogen evolution**

Ziqiang Wang, Yanhao Mao, Hugang Zhang, Kai Deng, Hongjie Yu, Xin Wang, You Xu,

Hongjing Wang* and Liang Wang*

State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering,

Zhejiang University of Technology, Hangzhou, 310014, P. R. China.

E-mails: hjw@zjut.edu.cn; wangliang@zjut.edu.cn

Experimental Section

Chemicals and Materials: Ascorbic acid (AA) and HCl were purchased from Aladdin (Shanghai, P.R. China). Pluronic F127 (PEO₁₀₀PPO₆₅PEO₁₀₀), H₂PtCl₆·6H₂O and Na₂PdCl₄ were obtained from Sigma-Aldrich. Commercial Pt/C catalyst (20 wt%) was ordered from Alfa Aesar.

Synthesis of PtPd MNCs: Typically, 0.02 M of H₂PtCl₆ (2.4 mL), 0.02 M of Na₂PdCl₄ (0.8 mL), 6 M of HCl (50 μ L), and Pluronic F127 (40 mg) were mixed together in a vial to form a homogeneous solution under sonication. Then 0.1 M of AA (4 mL) was added to the above solution, which was kept at 40 °C in a water bath for 4 h with constant sonication. The product was collected by centrifugation and wash with water for several cycles.

Synthesis of PtPdH MNCs: The pre-prepared PtPd MNCs (2mg) was dispersed in 10 mL DMF, which was kept in an oil bath at 160 °C for 16 h. The obtained product was corrected by centrifugation and wash with ethanol/water solution for several cycles.

Characterizations: The size and morphology of the obtained samples were measured by scanning electron microscopy (SEM, ZEISS SUPRA 55). The 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) spectroscopy were also conducted by JEM-2010 operated at 200 kV. The X-ray diffraction (XRD) patterns were obtained by using a PANalytical X'Pert powder diffractometer with a Cu K α radiation X-ray source (λ = 0.154056 nm) at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) was investigated by using an ESCALAB MK II spectrometer (VG Scientific, UK) by using Al K α X-rays as the light source.

Electrochemical measurements: A conventional three-electrode cell was used to estimate the electrochemical performance of samples by an electrochemical work-station CHI 660E under

ambient conditions, which used Hg/HgO electrode as a reference electrode and graphite rod as the counter electrode. For the preparation of working electrode, PtPdH MNCs powder (2 mg) was dispersed into 1 mL of a mixed solution (700 mL water and 300 mL isopropanol) under ultrasonic treatment for 30 min, then 2.5 μL of as-prepared catalyst ink was coated onto the surface of the polished glassy carbon electrode (GCE, 0.071 cm^2), followed by adding 3 mL of Nafion (0.05 wt%). For comparison, the Pt mass loading of commercial Pt/C in electrode was similar to that of PtPdH MNCs (70.42 $\mu\text{g cm}^{-2}$). Linear sweep voltammetry (LSV) was performed in 1.0 M KOH solution at 5 mV s^{-1} at room temperature. The FE was calculated by comparing the amount of measured hydrogen generated by potentiostatic cathode electrolysis (-0.05 V) with calculated hydrogen (assuming 100% FE). The overpotentials are converted to reversible hydrogen electrodes (RHE) and corrected by ohmic drop using the equation: $E_{(iR\text{-corrected})} = E - iR$, where i is the current and R is the electrolyte ohmic resistance measured by electrochemical impedance spectroscopy. All the electrochemical data were exhibited with iR compensation.

Calculation of hydrogen content: The amount of H atoms in the PtPd-H is in proportion to the fraction of guest atoms ($X = \text{H}/(\text{Pt}+\text{Pd})$), as expressed by the equation: $a = a_0 + 0.19X$ (\AA), where the a_0 is the lattice constant of the normal PtPd MNs (2.28 \AA). The constant of 0.19 is deduced from the lattice parameter of Pd, PdH_{0.43} and PdH_{0.706} based on the Vegard's law.¹

Calculation of TOF: The TOF is calculated from the following equation:²

$$\text{TOF} = j \times N_A / (n \times F \times \Gamma)$$

where j is the current density, N_A is the Avogadro number, n is the number of electron transferred for the evolution of a single H₂ molecule, F is the Faraday constant, and Γ is the surface concentration.

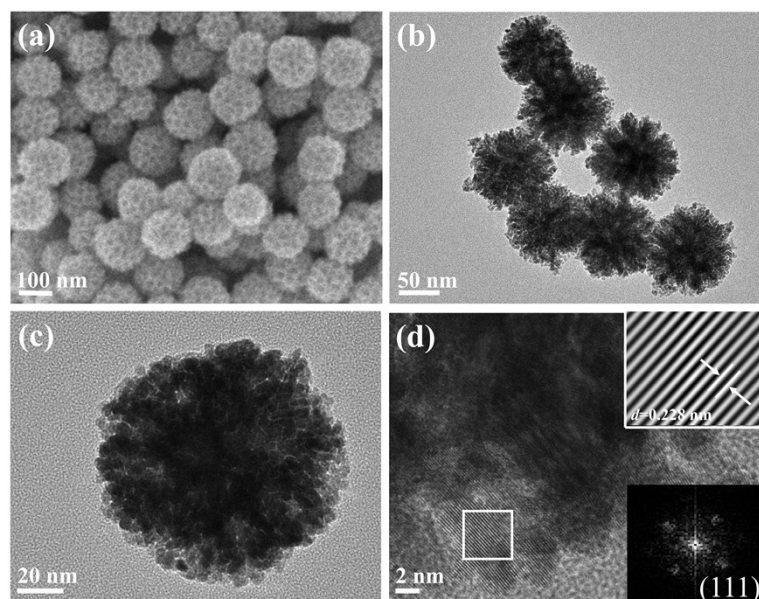


Fig. S1 (a) SEM, (b and c) TEM and (d) HRTEM images of PtPd MNCs. The inset in (d) represents the corresponding Fourier-filtered lattice fringes of the selected area.

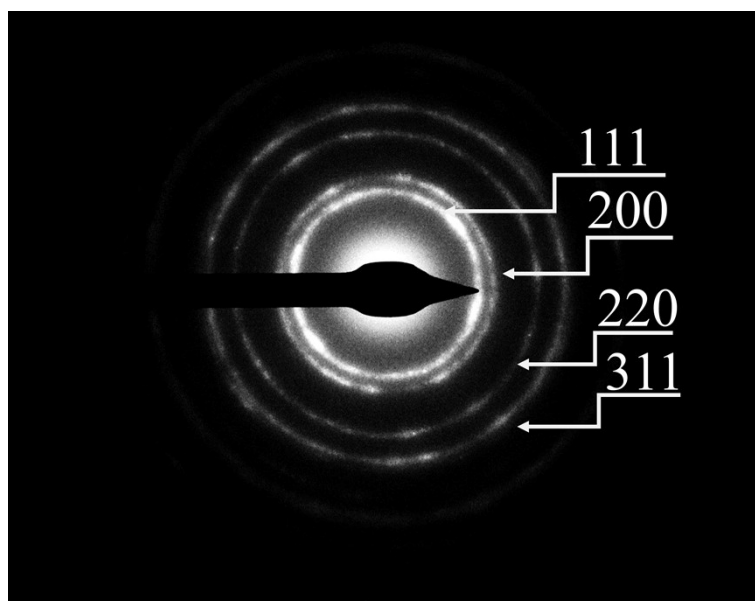


Fig. S2 SAED pattern of PtPdH MNCs.

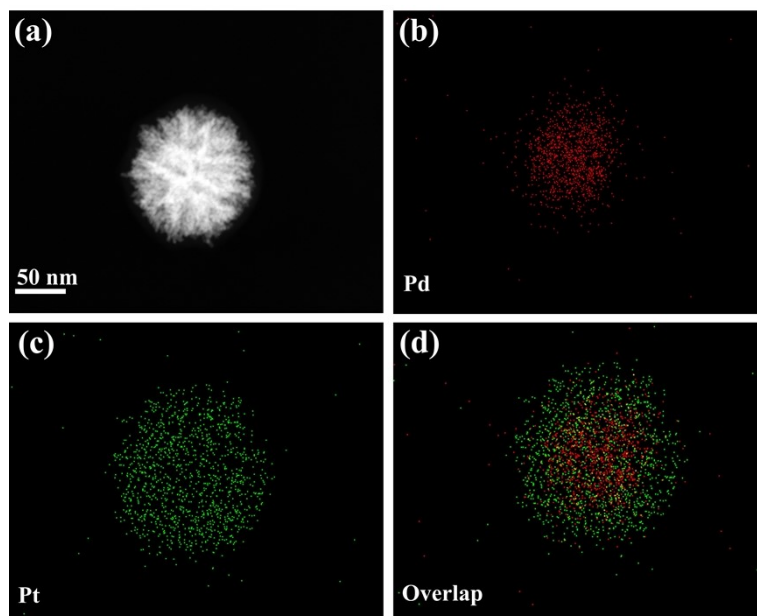


Fig. S3 (a) HAADF-STEM image of a PtPdH MNCs and (b-d) corresponding EDX element mapping images of PtPdH MNCs.

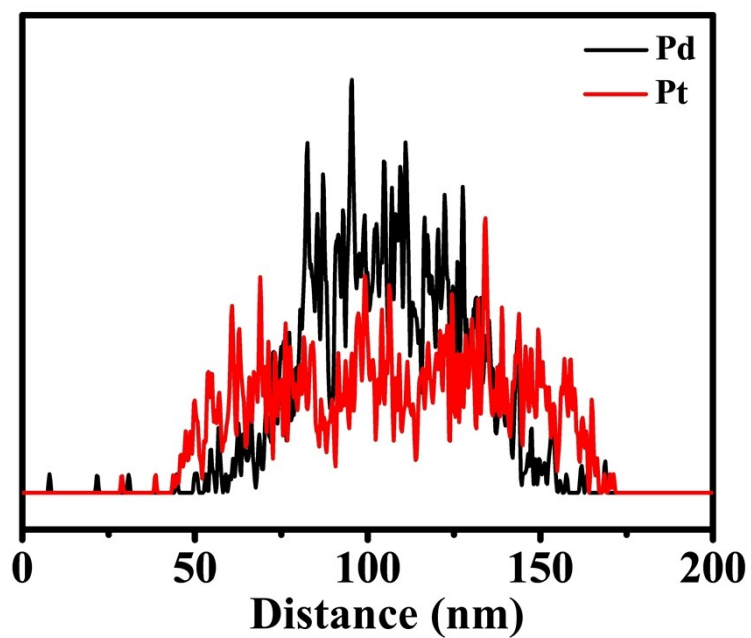


Fig. S4 Elemental distribution line profiles of PtPdH MNCs.

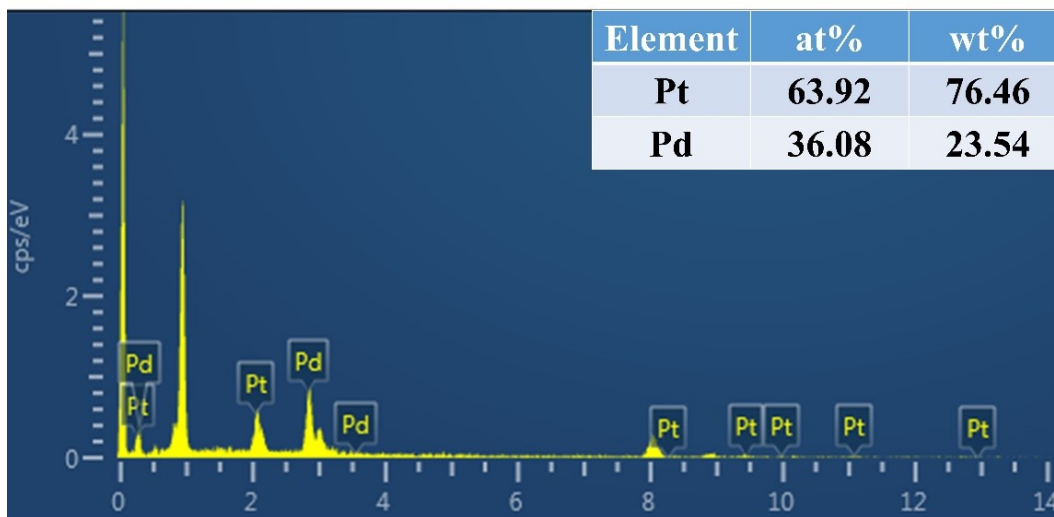


Fig. S5 EDX spectrum of PtPdH MNCs and corresponding mass and atomic ratios of Pt/Pd.

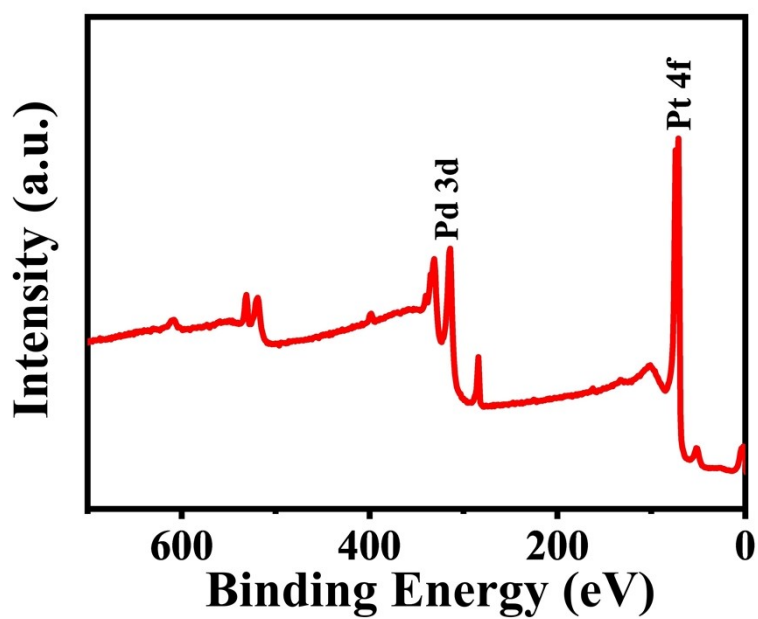


Fig. S6 The XPS survey spectrum of the PtPdH MNCs.

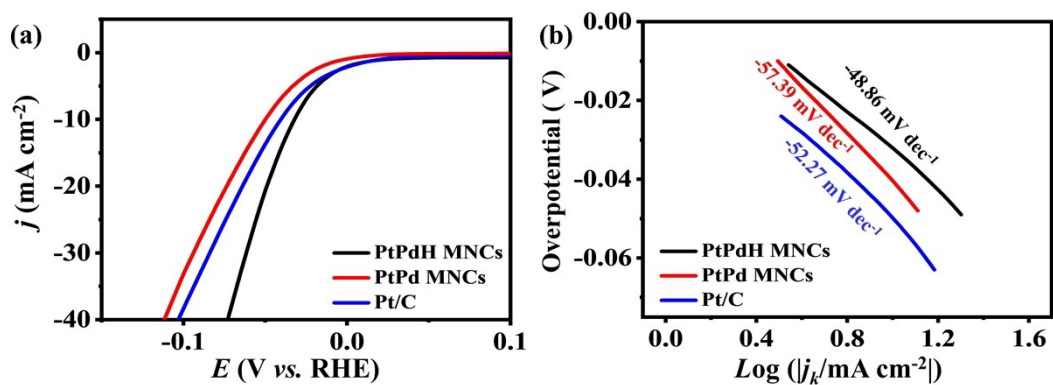


Fig. S7 (a) LSV curves for various catalysts in 0.5 M H_2SO_4 electrolyte and (b) corresponding Tafel plots.

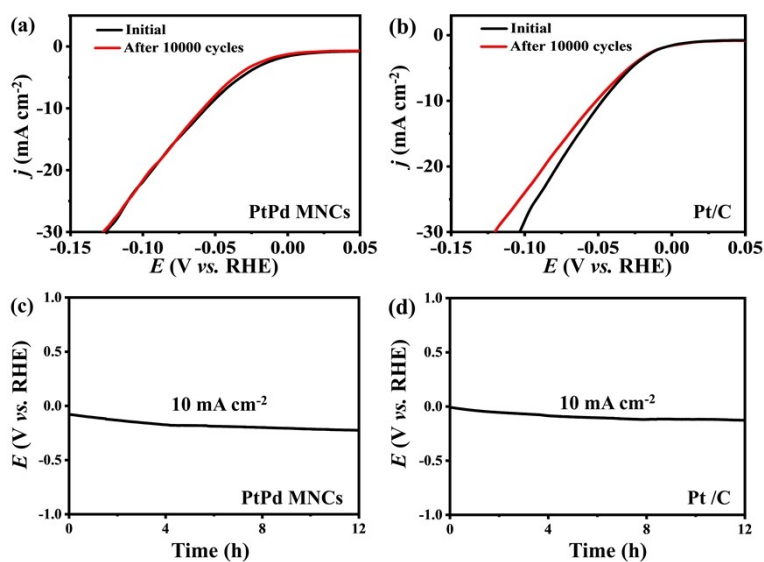


Fig. S7 LSV curves of the PtPd MNCs (a) and Pt/C (b), and $V-t$ curves of the PtPd MNCs (c) and Pt/C (d).

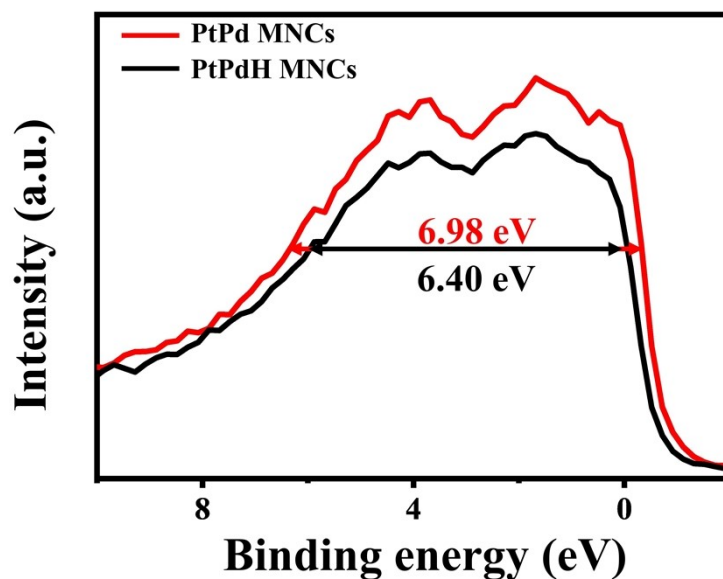


Fig. S9 XPS valence band spectra of PtPdH MNPs and PtPd MNCs.

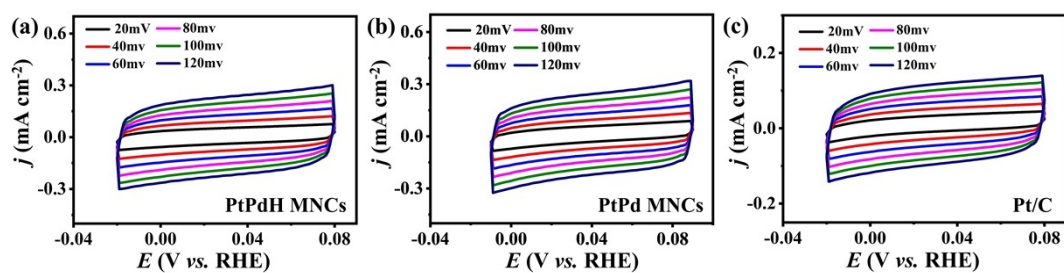


Fig. S10 CV curves for (a) PtPdH MNCs, (b) PtPd MNCs and (c) Pt/C at different scan rates.

Table 1 Summary of HER performance of PtPdH MNCs and reported high-performance noble metal based catalysts in recent literatures under 1 M KOH.

Catalyst	Electrolyte	Overpotential at -10 mA cm⁻² (mV)	Ref.
PtPdH MNCs	0.1 M KOH	-32	This work
Pt-Ni alloy	0.1 M KOH	-65	3
Pt/h-BN	0.1 M KOH	-75	4
PtNi-O nanostructure	0.1 M KOH	-40	5
PtNiP MNs/C	0.1 M KOH	-54	6
Pt-Ni nanowires	0.1 M KOH	-40	7
RhPdH Nanosheets	0.1 M KOH	-40	8
N-Pd/A-Co(II)	0.1 M KOH	-58	9
PdS nanosheets	0.1 M KOH	-49	10
Pd_{0.1}TaS₂	0.1 M KOH	-77	11

References

1. J. Fan, J. Wu, X. Cui, L. Gu, Q. Zhang, F. Meng, B. H. Lei, D. J. Singh and W. Zheng, *J. Am. Chem. Soc.*, 2020, **142**, 3645-3651.
2. S. Anantharaj and S. Kundu, *ACS Energy Lett.*, 2019, **4**, 1260-1264.
3. Z. Cao, Q. Chen, J. Zhang, H. Li, Y. Jiang, S. Shen, G. Fu, B.-a. Lu, Z. Xie and L. Zheng, *Nat. Commun.*, 2017, **8**, 15131.
4. A. Guha, T. Veetil Vineesh, A. Sekar, S. Narayanaru, M. Sahoo, S. Nayak, S. Chakraborty and T. N. Narayanan, *ACS Catal.*, 2018, **8**, 6636-6644.
5. Z. Zhao, H. Liu, W. Gao, W. Xue, Z. Liu, J. Huang, X. Pan and Y. Huang, *J. Am. Chem. Soc.*, 2018, **140**, 9046-9050.
6. L. Ai, J. Su, M. Wang and J. Jiang, *ACS Sustainable Chem. Eng.*, 2018, **6**, 9912-9920.
7. P. Wang, K. Jiang, G. Wang, J. Yao and X. Huang, *Angew. Chem., Int. Ed.*, 2016, **55**, 12859-12863.
8. J. Fan, J. Wu, X. Cui, L. Gu, Q. Zhang, F. Meng, B. H. Lei, D. J. Singh and W. Zheng, *J. Am. Chem. Soc.*, 2020, **142**, 3645-3651.
9. L. Li, Y. Ji, X. Luo, S. Geng, M. Fang, Y. Pi, Y. Li, X. Huang and Q. Shao, *Small*, 2021, **17**, 2103798
10. Y. Wang, K. Xu, Z. Zhu, W. Guo, T. Yu, M. He, W. Wei and T. Yang, *Chem. Commun.*, 2021, **57**, 1368-1371.
11. D. Wang, X. Wang, Y. Lu, C. Song, J. Pan, C. Li, M. Sui, W. Zhao and F. Huang, *J. Mater. Chem. A*, 2017, **5**, 22618-22624.