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Electronic Supplementary Information

Single platinum atoms anchored on N-doped carbon materials composed of bipyridine as efficient hydrogen evolution electrocatalysts

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Calculations

We carried out density functional calculations to calculate the binding energies between Bpy-derived CTF and the three Pt salts ($Pt(NO_3)_2$, $Pt(acac)_2$, K_2PtCl_4) using Gaussian 16 software.[1] All structures were optimized using M06 functional.[2] The 6-31G** basis set was used for C, H, O, N, and Cl atoms, and the SDD basis set was used for Pt atom. The basis set superposition error was considered in the calculations. A building block fragment of CTF was used as the model to represent the CTF. The binding energies were calculated using:

$$E_{bind} = E_{CTF-Pt} - E_{CTF} - E_{Pt}$$

where $E_{CTF\text{-}Pt}$ is the energy of the complex of CTF model and Pt salt. E_{CTF} and E_{Pt} are the energies of the CTF model and Pt salt, respectively.

Reference

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016. Gaussian 16, Revision B.01.

[2] Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements. Theor. Chem. Acc. 2008, 120, 215-241.

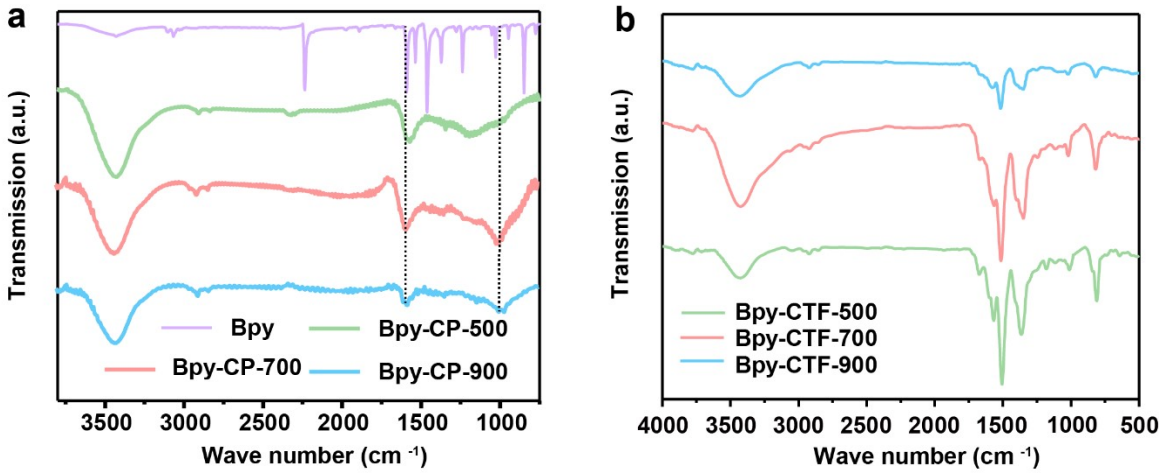

Fig. S1 (a) FT-IR spectra of the monomer Bpy and Bpy-CP-500/700/900. (b) FT-IR spectra of the Bpy-CTF-500/700/900.

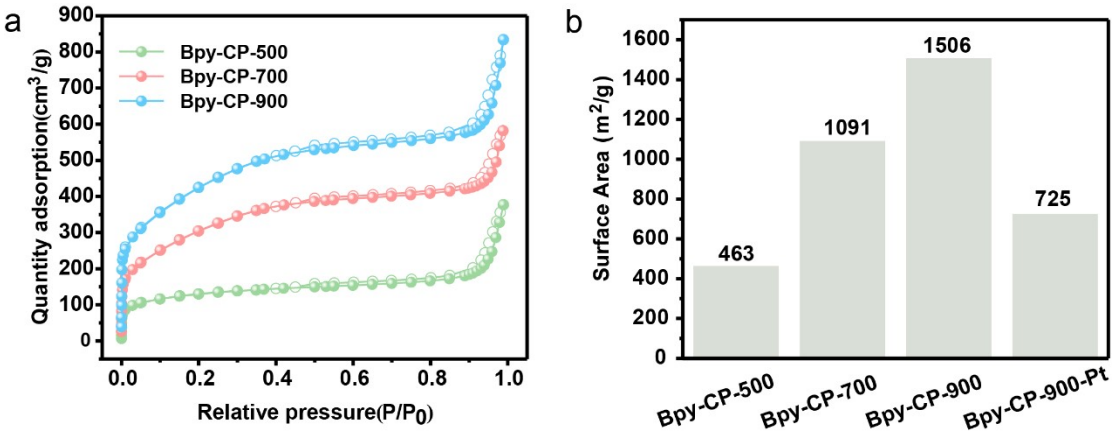

Fig. S2 (a) The N_2 adsorption-desorption isotherms (77 K) of Bpy-CP-500, Bpy-CP-700, and Bpy-CP-900. (b) The BET surface area of Bpy-CP-500/700/900 and Bpy-CP-900-Pt.

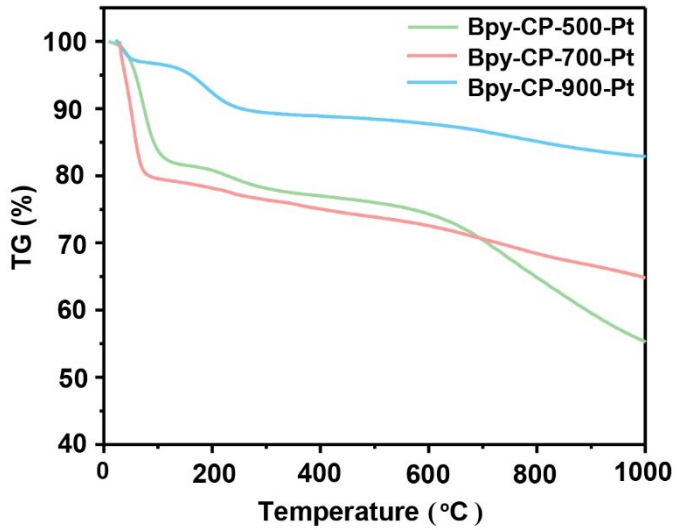

Fig. S3 Thermogravimetric curve for Bpy-CP-500-Pt, Bpy-CP-700-Pt, and Bpy-CP-900-Pt.

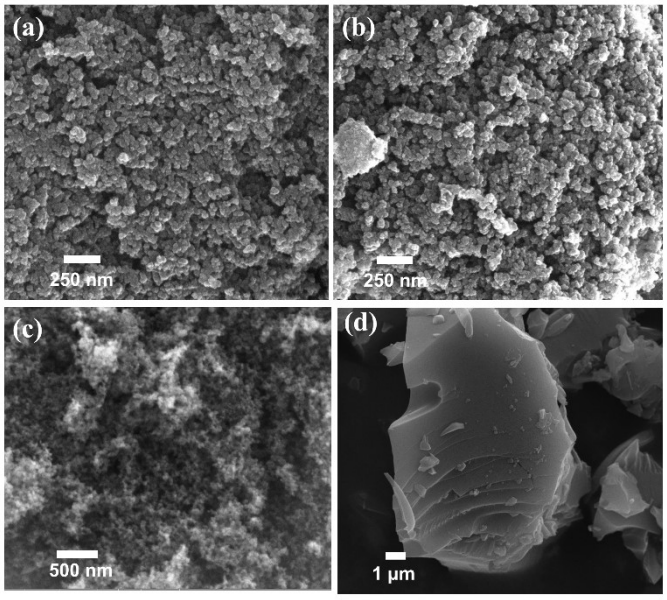

Fig. S4 The Scanning electron microscope (SEM) image of (a) Bpy-CP-500, (b) Bpy-CP-700, (c) CPs, and (d) Bpy-CTF-900

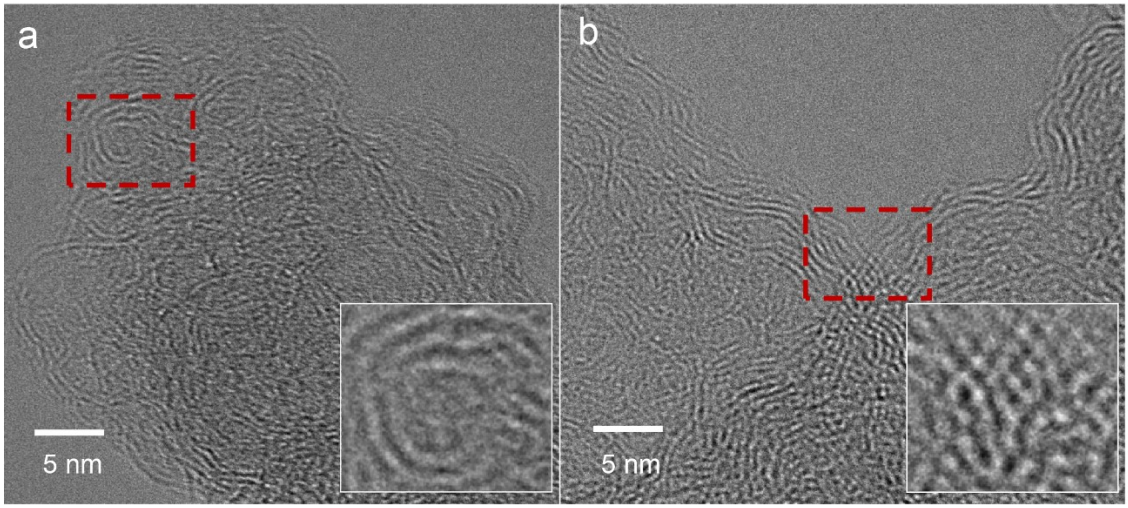

Fig. S5 The HR-TEM images of Bpy-CP-500-Pt (a) and Bpy-CP-700-Pt (b) with 5% theoretical weight loading.

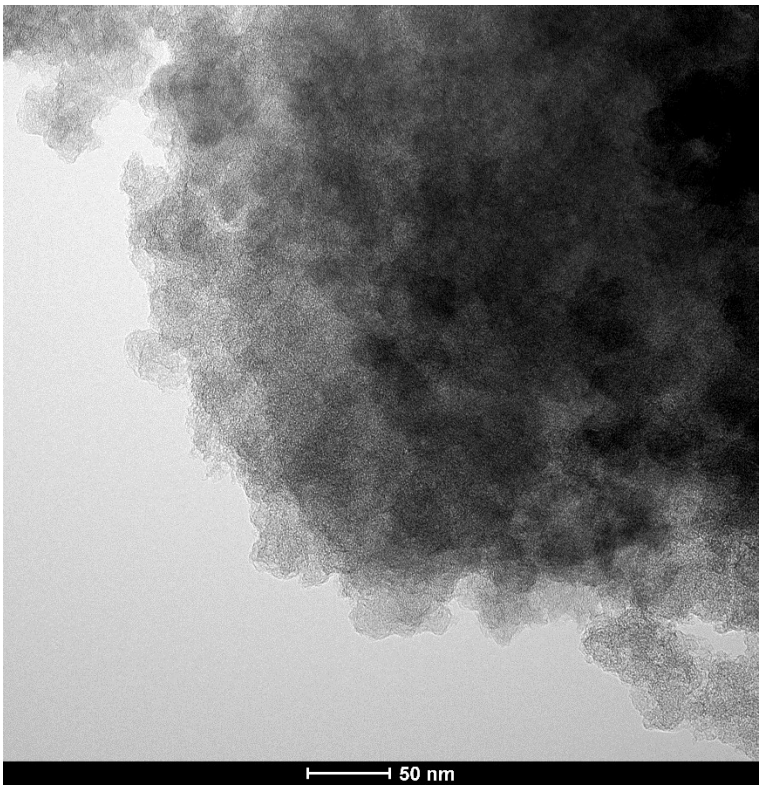

Fig. S6 The HR-TEM image of Bpy-CP-900-Pt (3 wt%).

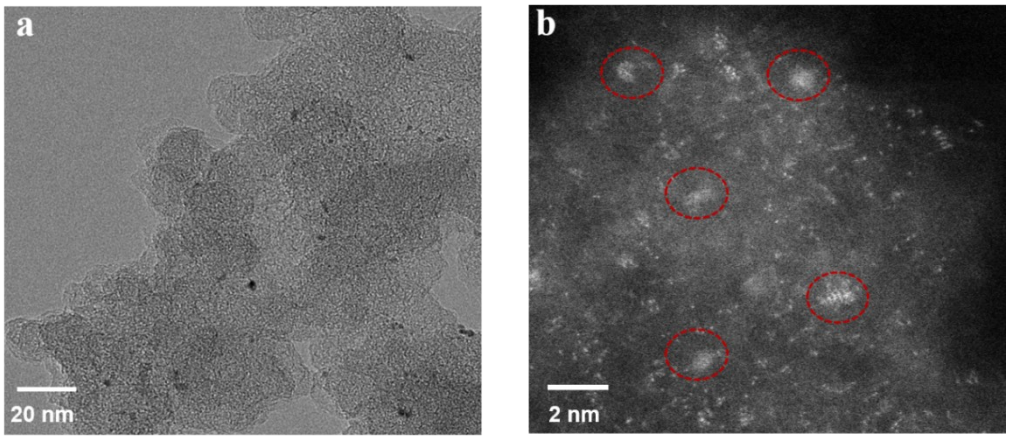

Fig. S7 The HR-TEM (a) and AC-STEM images (b) of Bpy-CP-900-Pt with 10% theoretical weight loading.

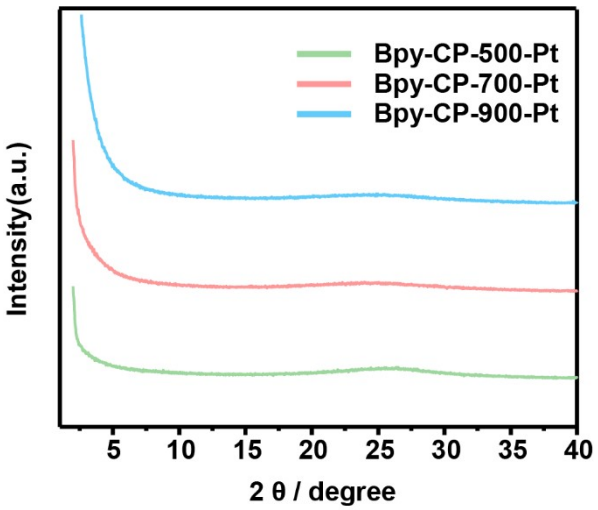

Fig. S8 XRD pattern of Bpy-CP-500-Pt, Bpy-CP-700-Pt, and Bpy-CP-900-Pt.

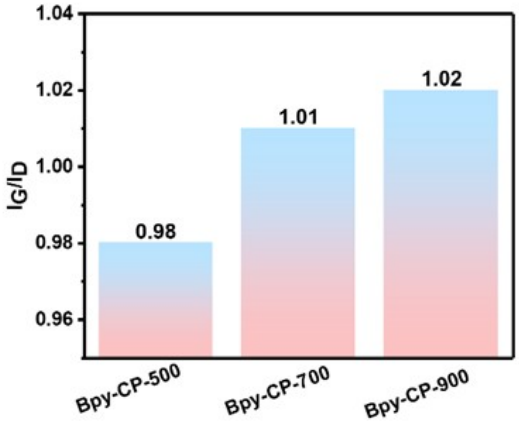

Fig. S9 The I_G/I_D ratios of the Bpy-CP-500, Bpy-CP-500, and Bpy-CP-900.

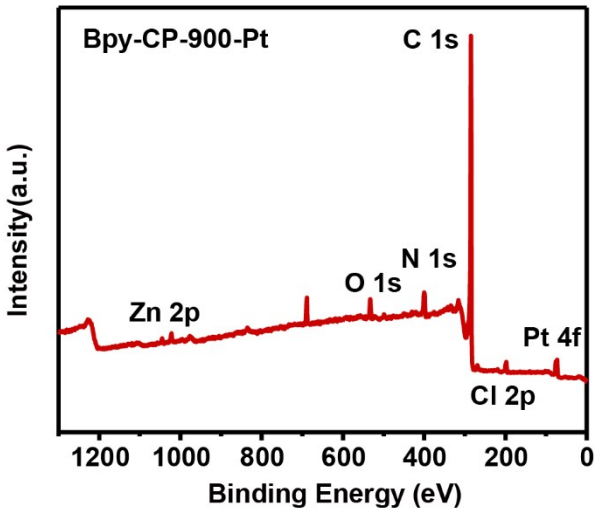

Fig. S10 The full XPS spectrum of Bpy-CP-900-Pt.

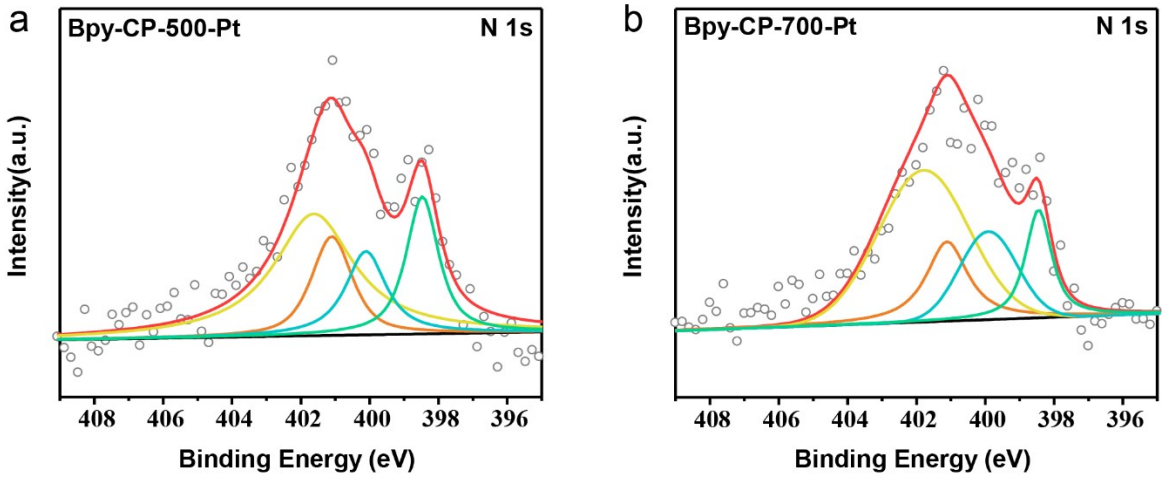

Fig. S11 The N 1s of XPS spectrum of Bpy-CP-500-Pt (a) and Bpy-CP-700-Pt (b).

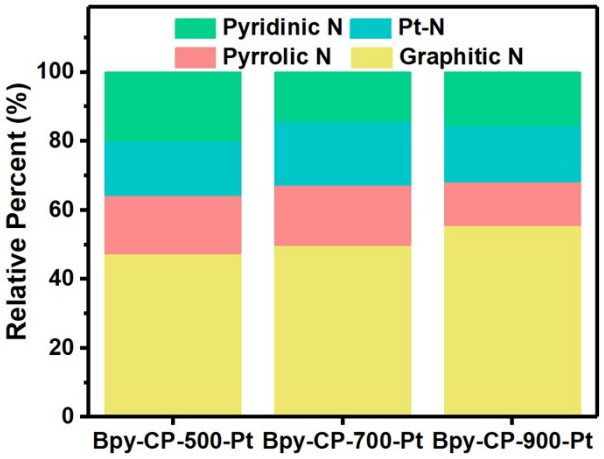

Fig. S12 Relative percentage of four N species in catalysts.

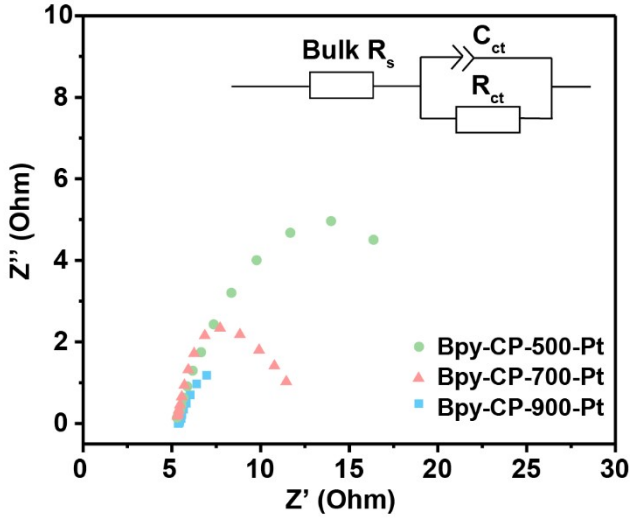

Fig. S13 The Nyquist plots of the Bpy-CTF-500-Pt, Bpy-CTF-700-Pt, and Bpy-CTF-900-Pt.

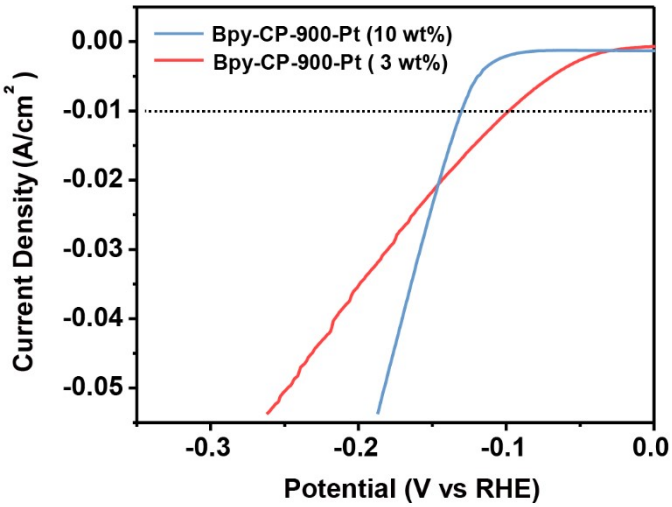

Fig. S14 The polarization curves of Bpy-CP-900-Pt (10 wt%) and Bpy-CP-900-Pt (3 wt%)

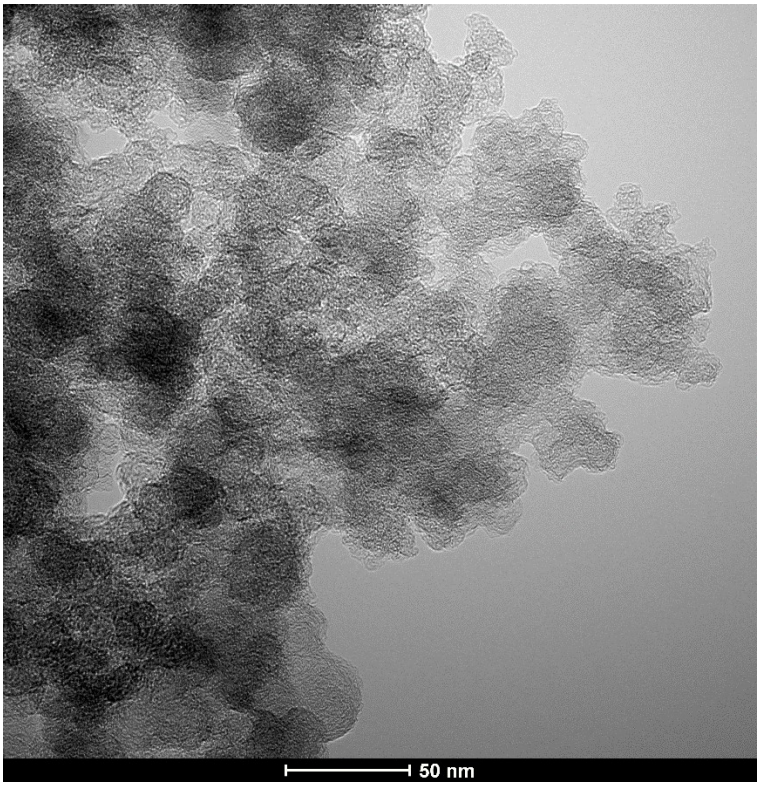

Fig. S15 The HR-TEM image of Bpy-CP-900-Pt after a long-time stability test.

Table S1 Element analyst of Bpy-CP-500-Pt, Bpy-CP-700-Pt, and Bpy-CP-900-Pt.

Catalyst	Content of C (%)	Content of N(%)	Content of H (%)
Bpy-CP-500-Pt	49.27	15.21	3.09
Bpy-CP-700-Pt	71.35	5.11	2.25
Bpy-CP-900-Pt	76.75	3.04	1.71

Table S2 The HER activity of recently reported Pt-based single-atom catalysts.

Catalyst	Overpotential of 10 mA/cm^2 (mV)	Tafel slope (mV/dec)	Reference
Pt-SAs/WSe_2	118	41	*Nat. commun*. 2021, 12, 3021
Pt-SAs/MoS_2	59	31	
Pt@PCM	105	65.3	*Sci. Adv*. 2018, 4, 6657
Pt_1@Fe-N-C	60	42	*Adv. Energy Mater*. 2018, 8, 1701345
Pt_1/OLC	38	36	*Nat. Energy* 2019, 4, 512
Pt_{SA}/N-C	130	67	*Small*. 2021, 17, 2005713
Pt SA/m-WO_{3-x}	38	45	*Angew. Chem. Int. Ed.* 2019, 58, 16038-16042
Pt-MoS_2	60	96	*Energy Environ. Sci.* 2015, 8, 1594-1601
Pt/TiO_2-OVs	60	34	*Mater. Today Energy*. 2021, 20, 100653
Pt/VS_2/CP	77	39.46	*ACS Nano*. 2020, 14, 5600-5608
Pt/f-MWCNT	43.9	30	*Nano Energy* 2019, 63, 103849
Pt1-Mo_2C-C	155	64	*J. Energy Chem*. 2021, 57, 371-377
Bpy-CP-900-Pt	54	29	This work