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Electronic Supplementary Information

Stable and Size-controllable Ultrafine Pt Nanoparticles Derived from the MOF-based Single Metal Ion Trap for Efficient Electrocatalytic Hydrogen Evolution

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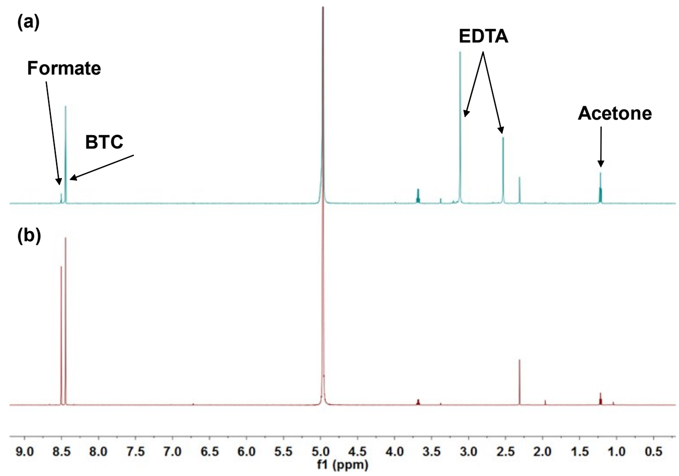

Figure S1. [1]H NMR spectra of alkaline-digested (KOH/D_2O) (a) MOF-808-EDTA and (b) MOF-808.

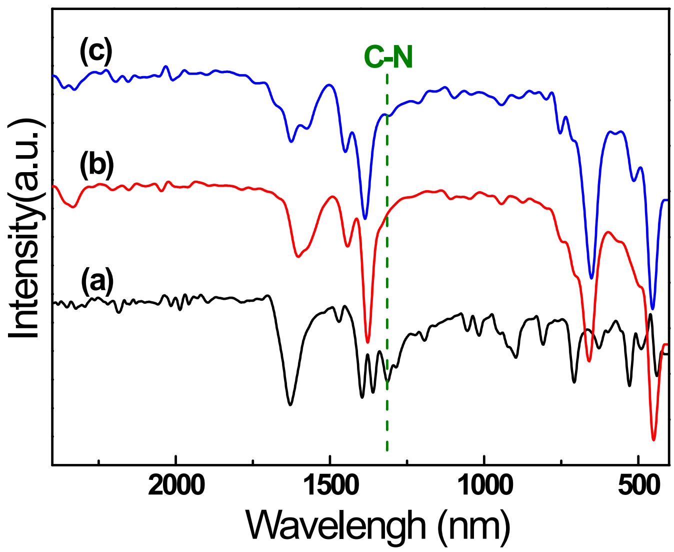

Figure S2. FT-IR spectra of (a) EDTA-2Na, (b) MOF-808, and (c) MOF-808-EDTA.

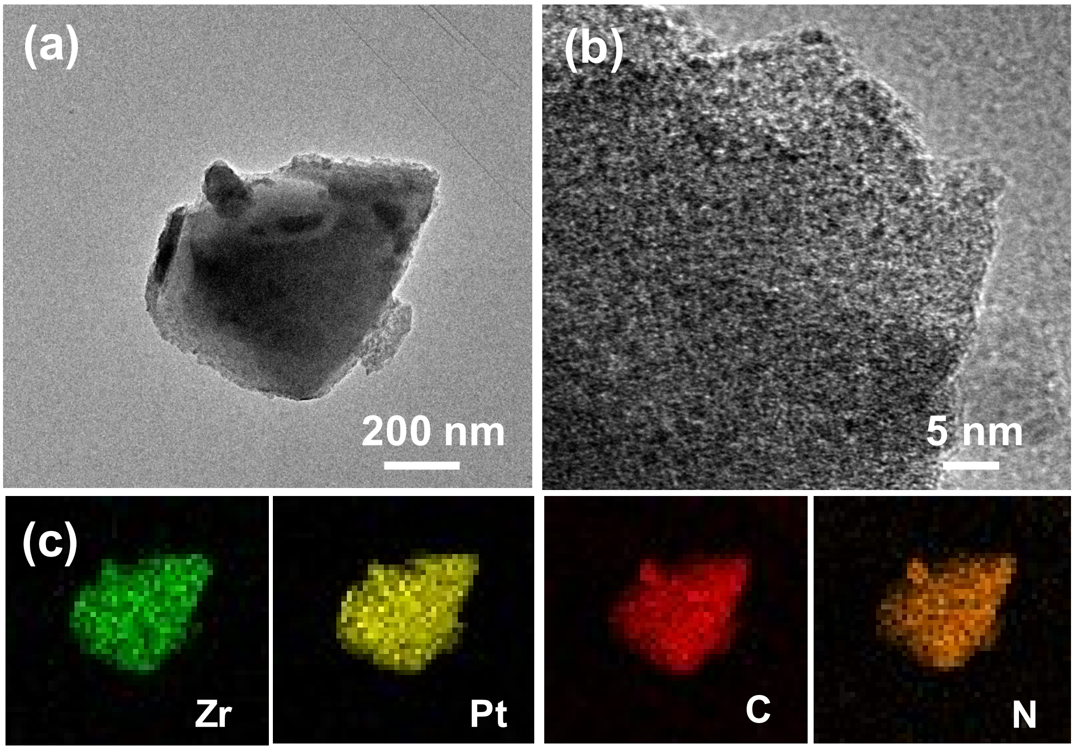

Figure R3. (a) and (b) TEM, and (c) EDS mapping images of fracture surface of 10Pt@MOF-808-EDTA.

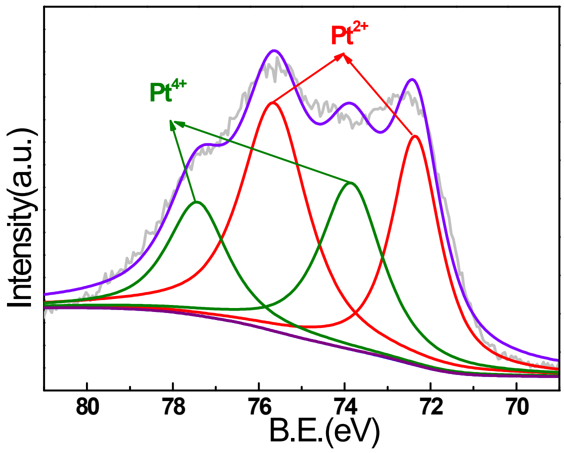

Figure S4. XPS spectra Pt 4f in 20Pt@MOF-808-EDTA.

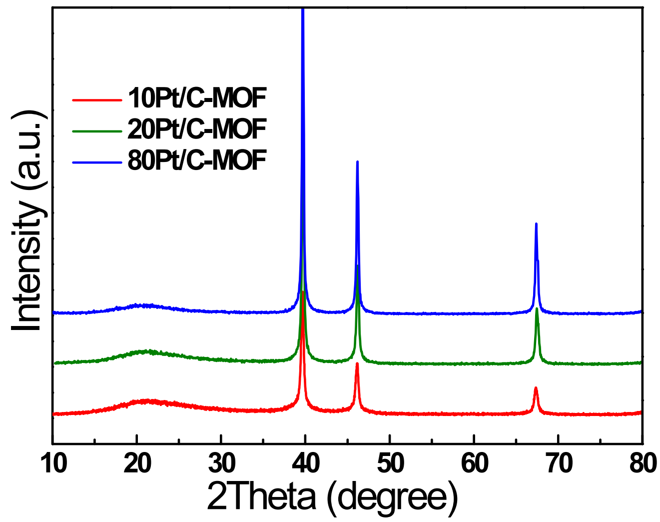

Figure S5. The XRD patterns of *x*Pt/C-MOF.

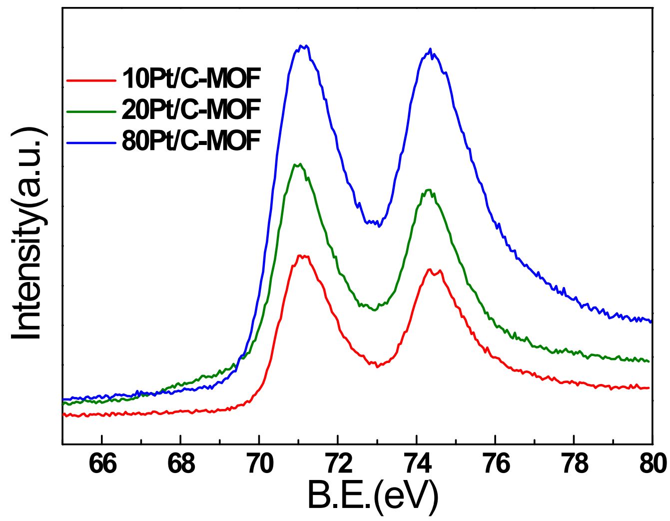

Figure S6. The Pt 4f XPS spectra of *x*Pt/C-MOF.

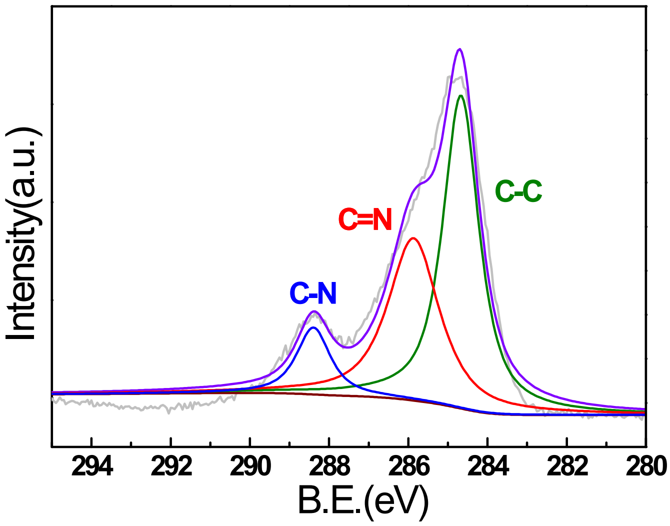

Figure S7. The C 1s XPS spectra of 80Pt/C-MOF.

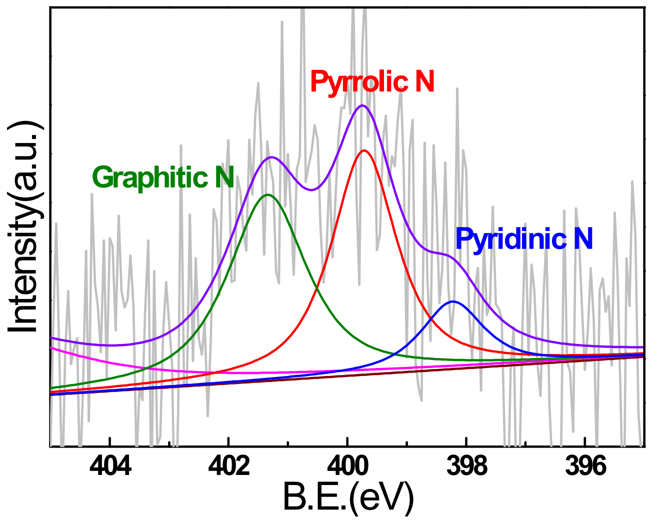

Figure S8. The N 1s XPS spectra of 80Pt/C-MOF.

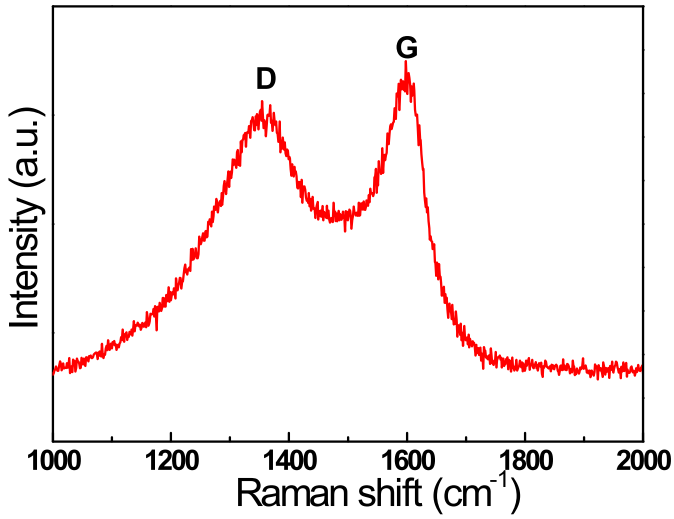

Figure S9. The Raman spectrum of 80Pt/C-MOF.

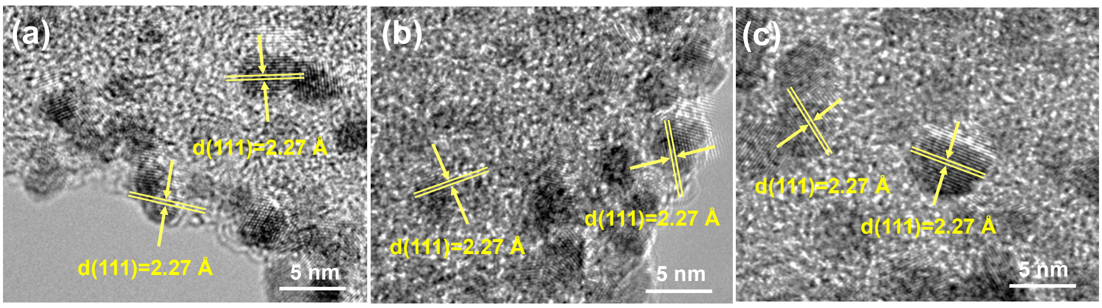

Figure S10. HRTEM images of (a) 10Pt/C-MOF, (b) 20Pt/C-MOF, and (c) 80Pt/C-MOF.

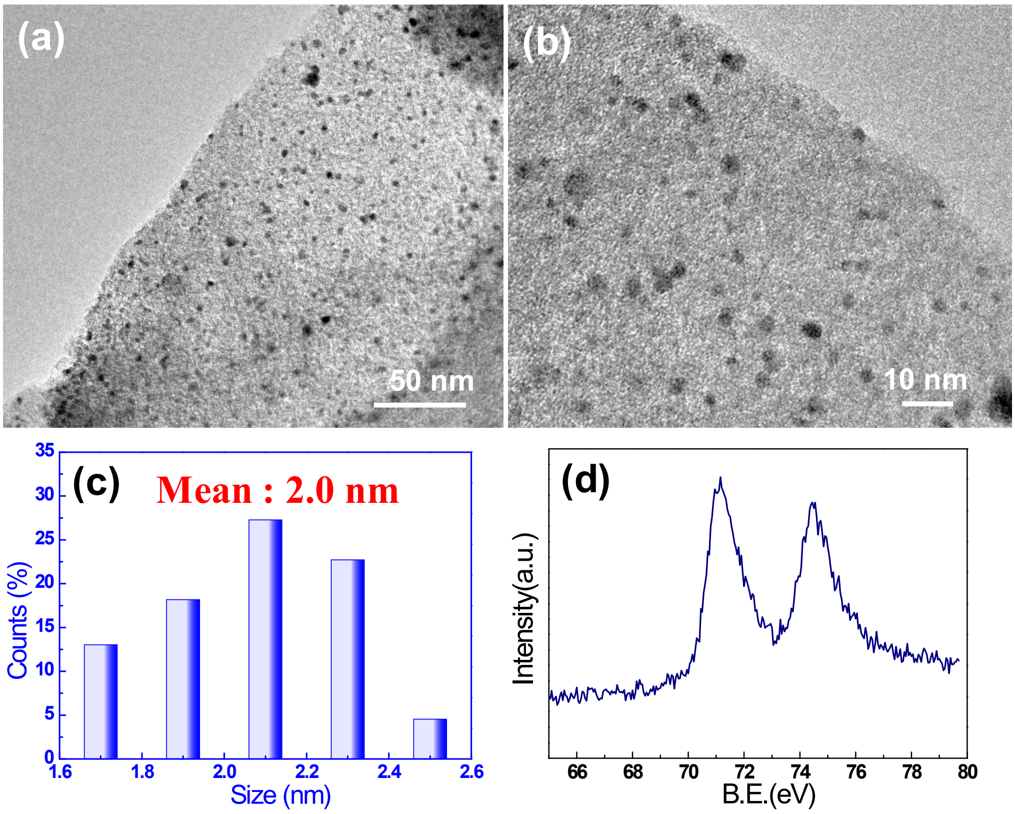

Figure S11. (a, b) TEM images, (c) the size distribution, and (d) XRD pattern of 2Pt/C-MOF.

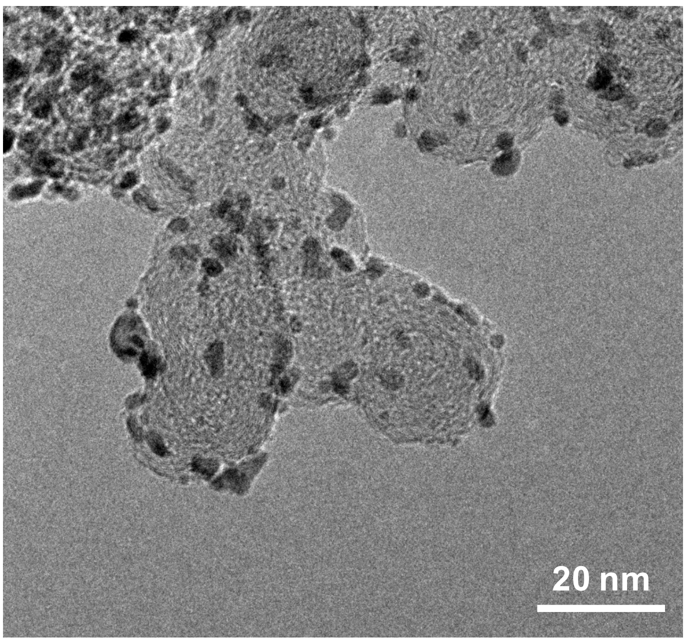

Figure S12. TEM images of commercial Pt/C.

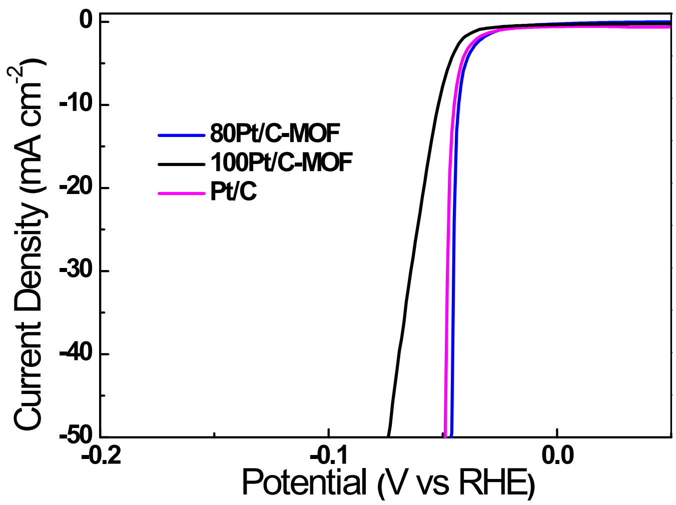

Figure S13. LSV curves of 80Pt/C-MOF, 100Pt/C-MOF, and Pt/C.

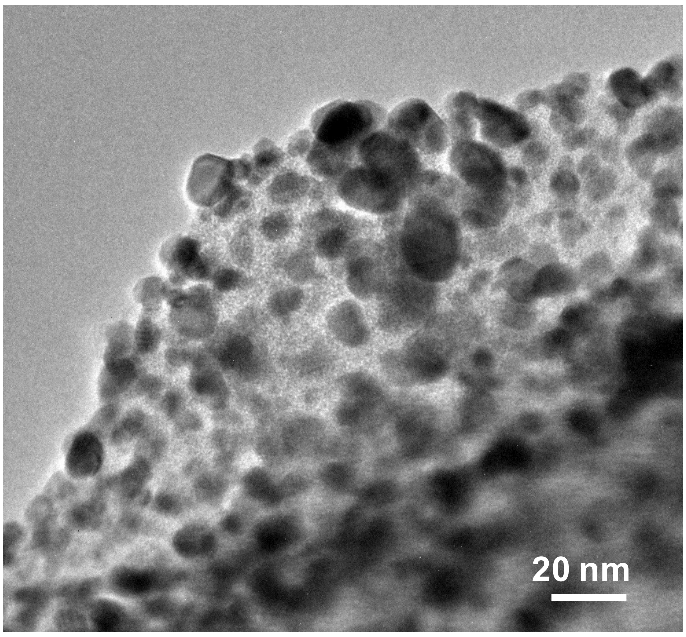

Figure S14. TEM images of commercial Pt/C.

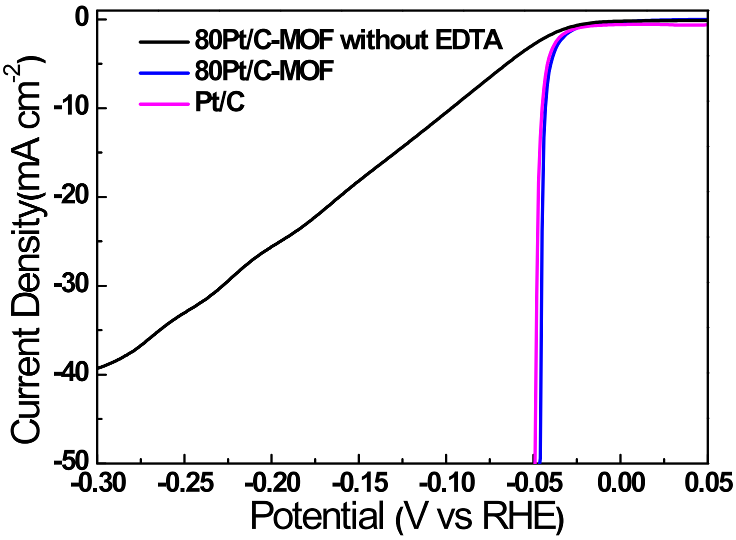

Figure R15. LSV curves of 80Pt/C-MOF without EDTA, 100Pt/C-MOF, and Pt/C.

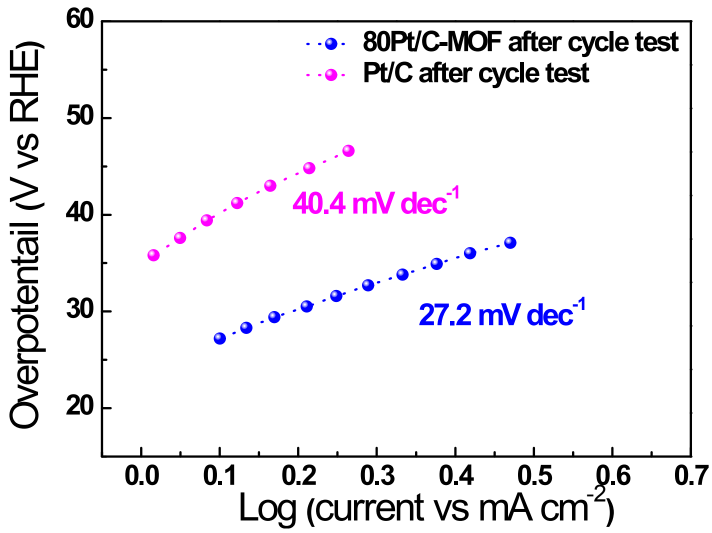

Figure S16. Tafel plots of 80Pt/C-MOF and Pt/C before and after 3000 CV cycles.

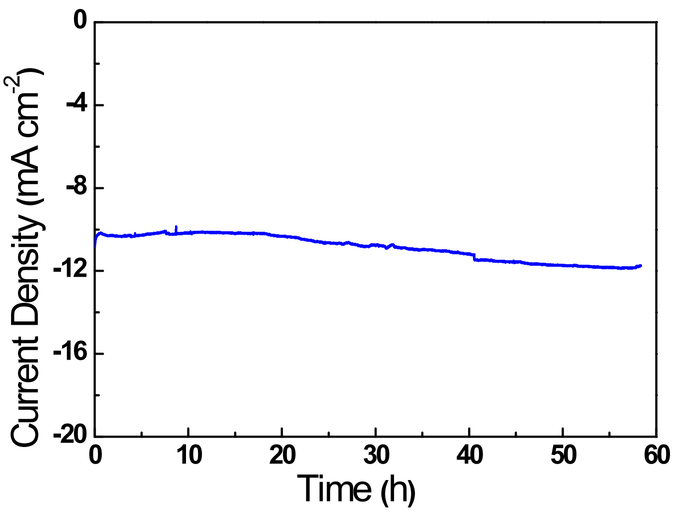

Figure S17. The long term stability of the 80Pt/C-MOF.

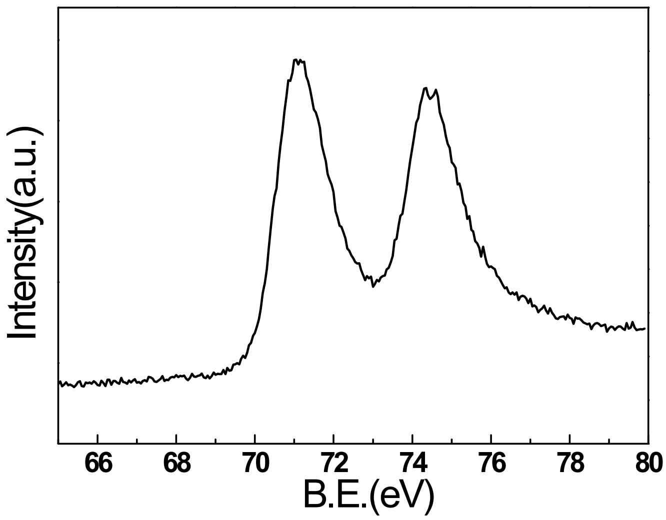

Figure R18. Pt 4f XPS spectra of the 80Pt/C-MOF catalyst after the stability test.

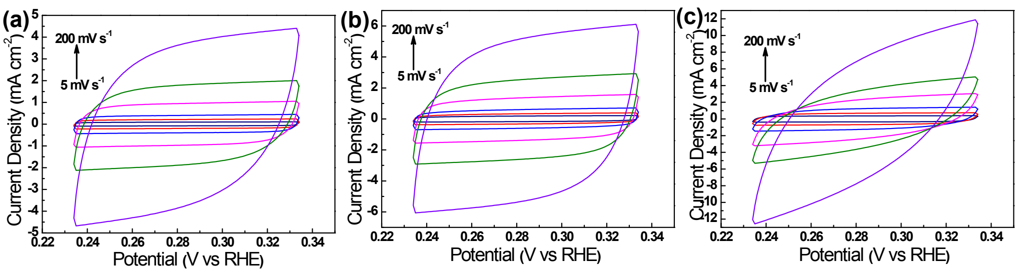

Figure S19. CVs curves of (a) 10Pt/C-MOF, (b) 20Pt/C-MOF, and (c) 80Pt/C-MOF at 5 – 200 mV S^{-1}.

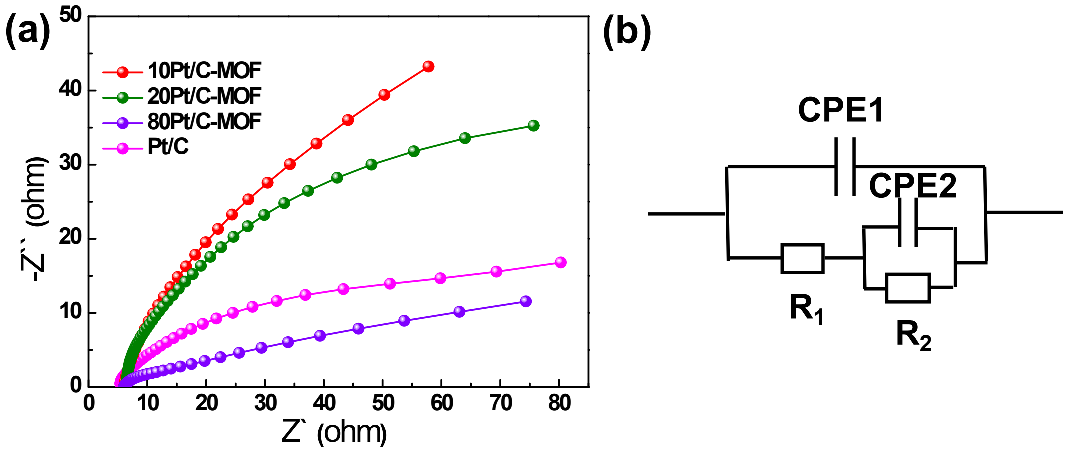

Figure S20. (a) EIS measurements of xPt/C-MOF and Pt/C with (b) the equivalent electrical circuit.

Table S1. Table S1. Comparison of the HER performance for the 80Pt/C-MOF catalyst with state-of-art Pt-based HER electrocatalysts in the literatures in 0.5 M H_2SO_4.

Number	Materials	η_{10} (mV)	Tafel plots (mV dec^{-1})	References
1	80Pt/C-MOF	42.1	24.45	This work
	Commercial Pt/C	45.1	28.7	
2	Pt-$Mo_2TiC_2T_x$	30	30	Nature Catalysis, 2018, 1(12): 985.
	Commercial Pt/C	32	32	
3	WC@C@Pt	30	26	Energy Storage Materials, 2018, 10: 268-274.
	Commercial Pt/C	40	29	
4	Pt–GT-1	18	24	Nature Energy, 2018, 3(9): 773.

	Commercial Pt/C	25	30	
5	PtCoFe@CN	45	32	ACS applied materials & interfaces, 2017, 9(4): 3596-3601.
	Commercial Pt/C	55	30	
6	ALDPt/NGNs	40	30	Nature communications, 2016, 7: 13638.
	Commercial Pt/C	51	35	
7	Pt–Cu HTBNFs	43	29.5	Chemical Communications, 2017, 53(51): 6922-6925.
	Commercial Pt/C	45	31	
8	CuPdPt/C	60	25	Journal of Materials Chemistry A, 2016, 4(40): 15309-15315.
	Commercial Pt/C	63	30	
9	$Pt_{3.21}Ni@Ti_3C_2$	20	13.3	Small, 2019: 1805474.
	Commercial Pt/C	37	30.0	
10	PdMnCo/NC-2	34	31	ACS applied materials & interfaces, 2017, 9(44): 38419-38427.
	Commercial Pt/C	58	33	
11	Pt/TiO_2	121	40	Energy & Environmental Science, 2017, 10(11): 2450-2458.
	Commercial Pt/C	59	31	
12	Pt@PCM	105	65.3	Science advances, 2018, 4(1): eaao6657.
	Commercial Pt/C	48	31.1	
13	PtRu@RFCS-6h	19.7	29.9	Energy & Environmental Science, 2018, 11(5): 1232-1239.
	Commercial Pt/C	19.5	27.2	
14	$Pt\text{-}SnS_2$	117	69	ACS applied materials & interfaces, 2017, 9(43): 37750-37759.

	Commercial Pt/C	51	46	
15	AuPt@Pt	50	33	Electrochimica Acta, 2016, 219: 321-329.
	Commercial Pt/C	45	31	
16	AgPt HANS	55	40	International Journal of Hydrogen Energy, 2017, 42(39): 24767-24775.
	Commercial Pt/C	45	33	
17	$Pt_{76}Co_{24}$ NM	31	32	J. Mater. Chem. A, 2017, 5, 10554
	Commercial Pt/C	34	31	
18	$Pt_{53}Ru_{39}Ni_8$	48	34	Journal of colloid and interface science, 2017, 505: 14-22.
	Commercial Pt/C	39	31	
19	β-$Ni_2P_2O_7$/Pt	28	32	ACS applied materials & interfaces, 2019, 11(5): 4969-4982.
	Commercial Pt/C	16	30	
20	Pt@N-HCNs	30	33	Applied Surface Science, 2018, 459: 453-458.
	Commercial Pt/C	29	31	
21	10Pt@HN-BC	60	35	International Journal of Hydrogen Energy, 2018, 43(12): 6167-6176.
	Commercial Pt/C	50	31	
22	PtAg NFs/rGO	55	31	Journal of colloid and interface science, 2018, 513: 455-463.
	Commercial Pt/C	45	31	
23	PtCoNi FNs	47	37	International Journal of Hydrogen Energy, 2017, 42(40): 25277-25284.
	Commercial Pt/C	41	29	
24	Pt-Cu/CNFs-1:2	71	68	Advanced Materials Interfaces, 2017, 4(12): 1700005.
	Commercial Pt/C	50	27	
25	Pt NPs/CNFs	175	50	Electrochimica Acta, 2015, 167: 48-54.
	Commercial Pt/C	65	24	

26	Pt/BCF	55	32	Catalysis Today, 2016, 262: 141-145.
	Commercial Pt/C	19	24	
27	PtAg NCs	38	40	Journal of colloid and interface science, 2017, 494: 15-21.
	Commercial Pt/C	36	31	
28	Pd@PdPt NCs	39	38	Journal of Materials Chemistry A, 2016, 4(42): 16690-16697.
	Commercial Pt/C	35	33	
29	GCE-Ni/Pt	36	43	ACS applied materials & interfaces, 2015, 7(47): 26101-26107.
	Commercial Pt/C	36	31	
30	ECD Pt NIs@f-MWCNT	157	30	International Journal of Hydrogen Energy, 2017, 42(15): 9881-9891.
	Commercial Pt/C	87	21	

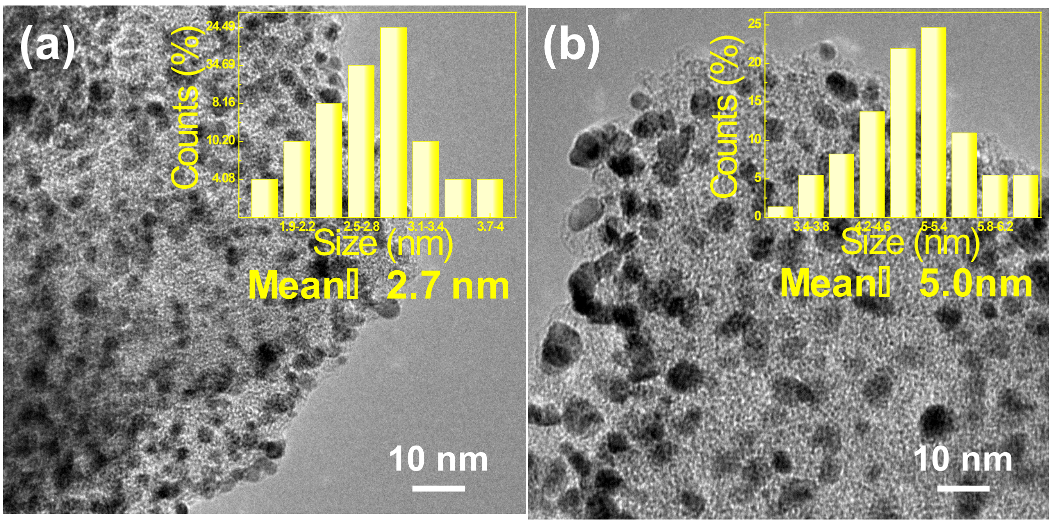

Figure S21. HRTEM images of (a) 10Pd/C-MOF and (b) 80Pd/C-MOF.

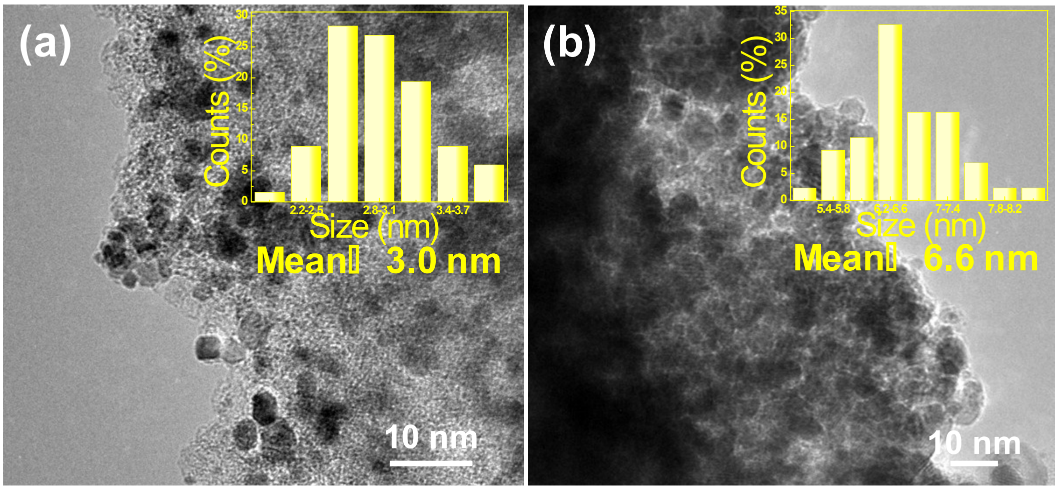

Figure S22. HRTEM images of (a) 10Ru/C-MOF and (b) 80Ru/C-MOF.

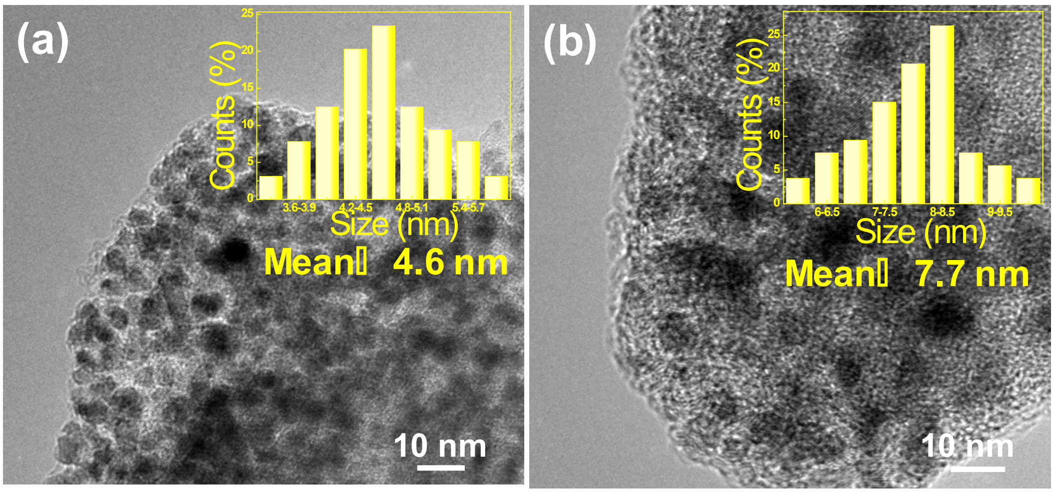

Figure S23. HRTEM images of (a) 10Rh/C-MOF and (b) 80Rh/C-MOF.