

Supporting Information

Gram-scale synthesis small-sized PtM intermetallics as high-performance catalysts for the hydrogen evolution reaction

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Experimental

Chemicals: Iron(III) chloride (FeCl_3), Cobalt(II) chloride (CoCl_2), nickel(II) chloride (NiCl_2), **Zinc(II) chloride (ZnCl_2)** and manganese(II) chloride (MnCl_2) were purchased from Sigma-Aldrich. Commercial 20% Pt/C was purchased from Johnson Matthey Chemicals Ltd. All reagents and chemicals were used without further purification.

Synthesis of ordered PtM/C-VD: For PtFe/C-VD, FeCl_3 and Pt/C were placed in porcelain boats and placed next to each other in a tube furnace. The porcelain boat with FeCl_3 (500mg) is placed in the front, and the porcelain boat with Pt/C(1g) is placed in the back. **The boats were heated under an Ar atmosphere to 700 °C at a rate of 2 °C min⁻¹, then held there for 2 h for sublimation. Subsequently, the above intermediates were calcined at 700 °C under a flow of 5% H₂/Ar for 12 h and resulted as PtFe/C-VD.** Other PtCo/C-VD, PtNi/C-VD and PtMn/C-VD samples also can be

synthesized through similar vapor deposition-high temperature reduction route. Similarly, only adjusting the mass of MCl_3 ($M=Zn, Mn, Fe$) to 100 mg and 1 g, ordered $Pt_3M/C-VD$ and $PtM_3/C-VD$ can be synthesized, respectively.

Physicochemical characterization: X-ray diffractions (XRD) data were measured by a Rigaku Ultima IV X-ray powder diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at a scan rate of $20^\circ \text{ min}^{-1}$. Thermogravimetric analysis (TGA) of the samples was carried out with a Perkin-Elmer thermal analysis system. Measurements were made by heating from 20 to 800 °C at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under air atmosphere. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were performed with a JEOL 2010F TEM/STEM operated at 300 kV. X-ray photoelectron spectroscopy (XPS) characterization was examined using a K-Alpha. All inductively coupled plasma (ICP) measurements were carried out on an IRIS Intrepid instrument (Thermo Fisher, USA).

Electrochemical measurements in a three-electrode configuration: Electrochemical measurements were carried out with a DH7000 electrochemical analyzer (Jiangsu, Donghua Co.). A standard three-electrode system was used, including a glass carbon electrode or a piece of carbon paper as the working electrodes, a carbon rod as the auxiliary electrode, and a saturated Ag/AgCl electrode (SCE) as the reference electrode. The catalyst ink was prepared by ultrasonically dispersing the mixture of 5 mg of catalyst, 950 mL isopropanol and 50 μL of 5 wt.% Nafion solution. Then the catalyst ink was dripped on a glassy carbon (0.196 cm^2) with a loading amount of 1 mg cm^{-2} . 5 μL of the catalyst ink was spread onto the glass electrode and dried in air at room temperature. The loading of Pt on a glassy carbon electrode was about $28 \text{ }\mu\text{g}_{Pt} \text{ cm}^{-2}$ for PtFe/C and $26 \text{ }\mu\text{g}_{Pt} \text{ cm}^{-2}$ for Pt/C. Before testing, a 0.5 M H_2SO_4 electrolyte was passed with N_2/H_2 through the solution for at least 20 min to saturate the electrolyte with N_2/H_2 . The CV curves of different catalysts were obtained in the N_2 -saturated 0.5 M H_2SO_4 solution by sweeping the potential from 0.05 to 1.20 V (vs RHE) at the scan rate of 50 mV s^{-1} . The electrochemical active

surface areas (ECSAs) were calculated from H_{upd} adsorption/desorption peak areas in CV curves collected. The electrochemical stability of three different catalysts, namely PtFe/C-VD, D-PtFe/C-VD, and Pt/C, was evaluated using the CV test at a scan rate of 50 mVs^{-1} for 5000 cycles. For HER measurement, then the catalyst ink was dripped on a carbon fiber paper ($5\text{mm}\times 5 \text{ mm}$) with a loading amount of 1 mg cm^{-2} . All the electrochemical measurements were performed at room temperature and the electrochemical cell was used in an open environment. The HER polarization curves were mainly collected in H_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$ (between 0.05 and -0.30 V vs. RHE) solution at a scan rate of 5 mV s^{-1} . All the collected LSV curves were corrected with the background current of a blank CFP electrode. Durability test was measured at a constant current density of 100 mA cm^{-2} .

Electrochemical measurement of PEMWE: Before the construction of catalysis coated membrane (CCM), the N115 membrane was successively treated with 5 wt% H_2O_2 , deionized water, and $0.5 \text{ M H}_2\text{SO}_4$ at $80 \text{ }^\circ\text{C}$ for 1 h. Then the treated N115 membrane was rinsed with deionized water. D-PtFe/C-VD or PtFe/C-VD was used as a cathode electrocatalyst and commercial IrO_2 was used as an anode electrocatalyst. In order to prepare the catalyst ink, the catalyst was dispersed into a mixed solution of isopropyl alcohol and distilled water (1:1, w/w). Subsequently, Nafion with an ionomer mass fraction of 10 wt% at the anode or 35 wt% at the cathode was added into the solution. The suspension was ultrasonically treated in an ice water bath for 1 h to obtain the catalyst ink. The anode catalyst ink and cathode catalyst ink were sprayed on polytetrafluoroethylene (PTFE) film respectively. Then the PTFE films supported with catalysts and a N115 membrane were hot pressed under 10 Mpa at $135 \text{ }^\circ\text{C}$ for 10 min. After cooling, the PTFE films were stripped to obtain CCM. The loading of the cathode was $0.5 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ and the loading of the anode was $1 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ for IrO_2 . In order to construct a PEM electrolyzer, a well-defined pore Ti plate (provided by mainz Hydrogen Energy Co., Ltd) coated with Pt was used as the porous transport layer (PTL) of the anode, and a piece of carbon paper was used as the PTL of the cathode. The active area was 4 cm^2 . The PEM electrolyzer was operated at 80

°C and the reactant was deionized water, which was circulated through a peristaltic pump. The stability was tested by chronopotentiometry at 0.25 A cm^{-2} .

Computational details: The spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP) code.¹⁻³ The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional with van der Waals correction was applied to optimize the geometric structures.⁴ The interactions between the ions and valence electrons were described by Projector augmented wave (PAW) potentials.^{5, 6} A Monkhorst-Pack k-point grid of $4 \times 4 \times 1$ was used for the geometric structures optimization and total energy calculations.⁷ The force on each atom was less than 0.01 eV/\AA , and the convergence criteria of the total energy for all the calculations were set as $1 \times 10^{-5} \text{ eV}$. A plane wave cutoff energy of 450 eV was chosen for all of the calculations.



Fig. S1. The photograph of PtFe/C-VD catalyst.

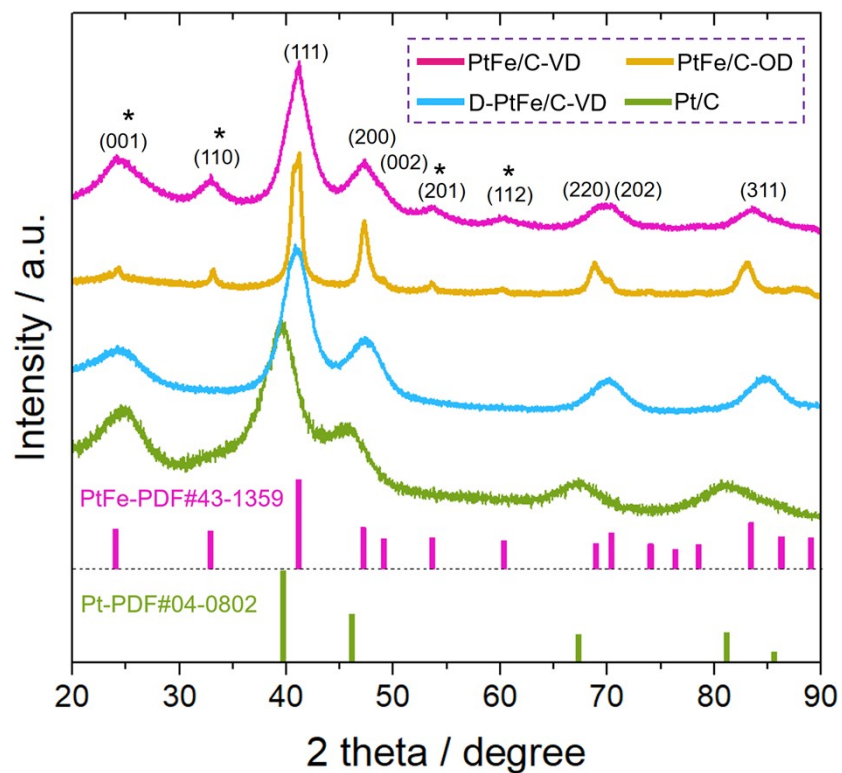


Fig. S2. XRD patterns of PtFe/C-VD, PtFe/C-OD, D-PtFe/C-VD and Pt/C samples.

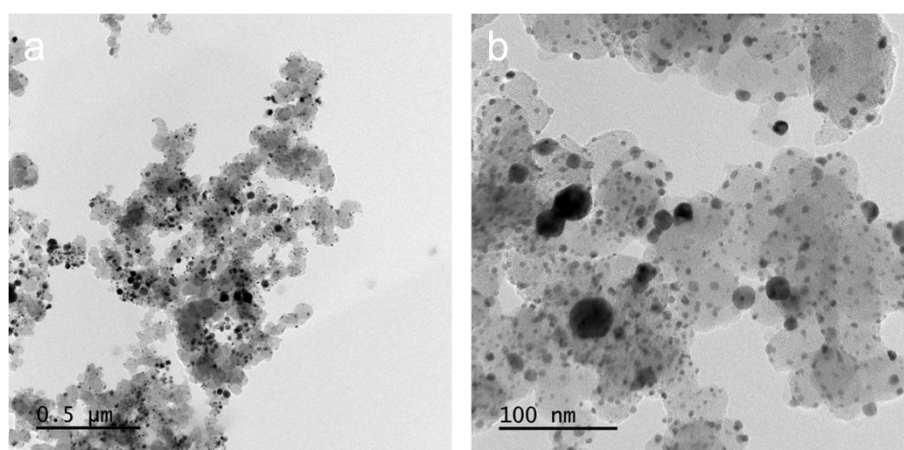


Fig. S3. TEM image of Pt/C annealed for 12 h at 700 °C.

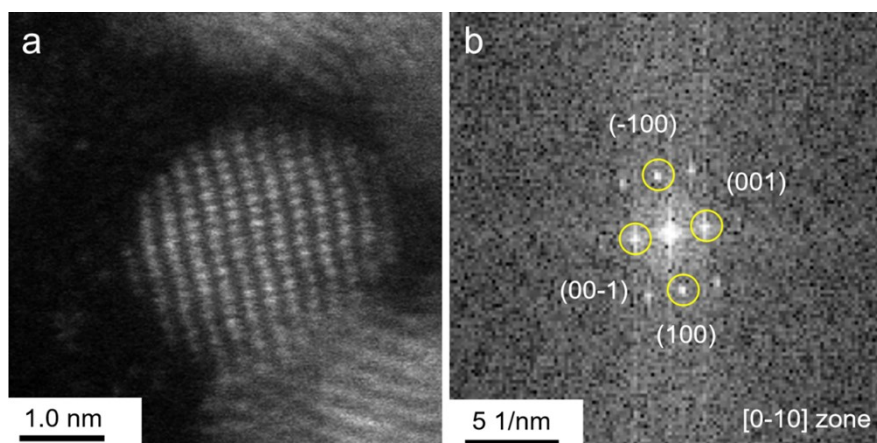


Fig. S4. (a) STEM image and (b) FFT pattern of disordered PtFe nanoparticle in D-PtFe/VD.

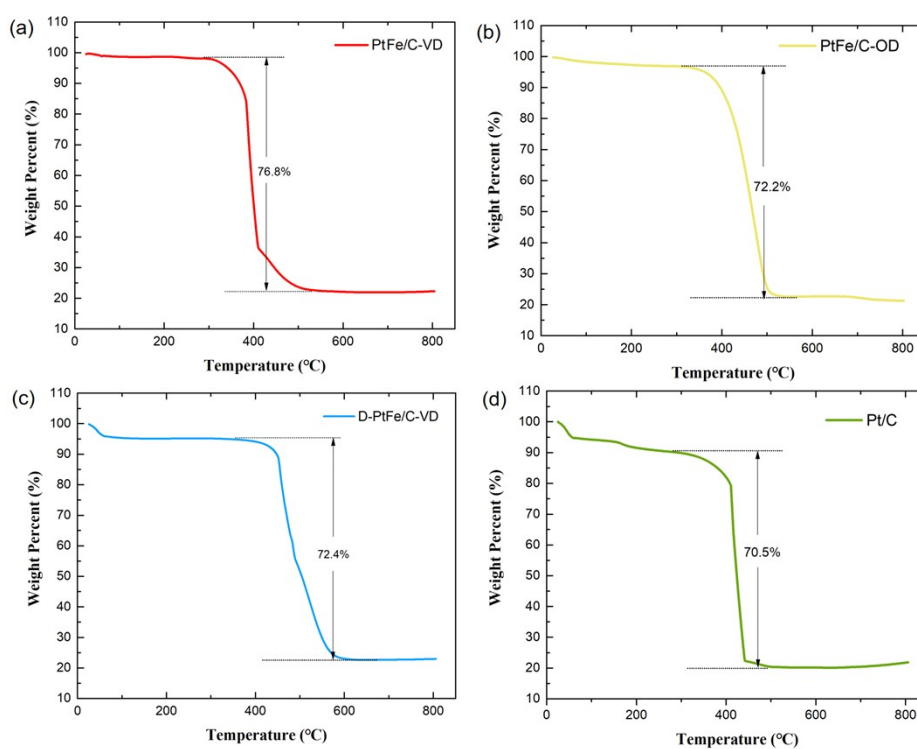


Fig. S5. TGA curves of (a) PtFe/C-VD, (b) PtFe/C-OD, (c) D-PtFe/C-VD and (d) Pt/C samples.

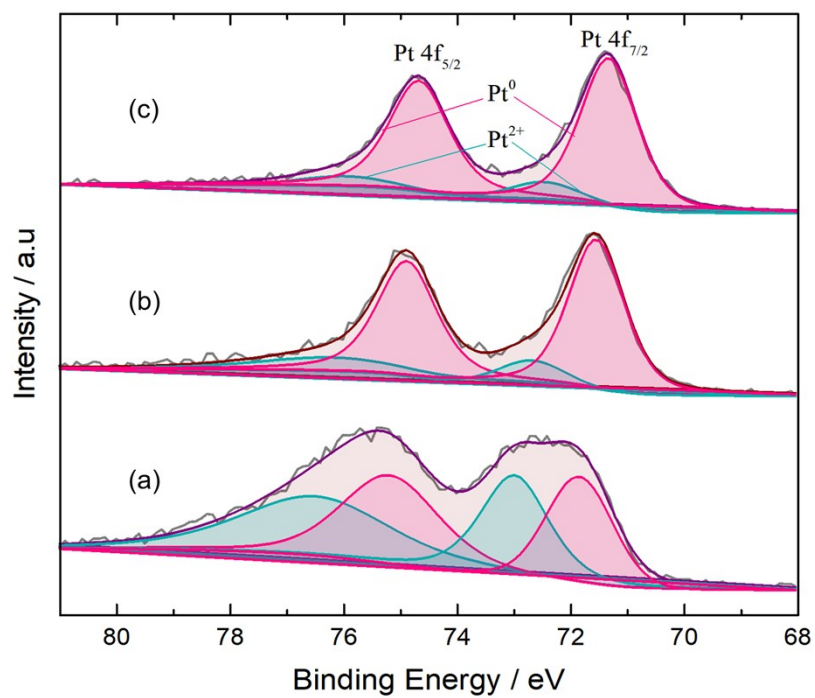


Fig. S6. XPS spectra of Pt 4f in (a) commercial Pt/C, (b) D-PtFe/C-VD and (c) PtFe/C-VD.

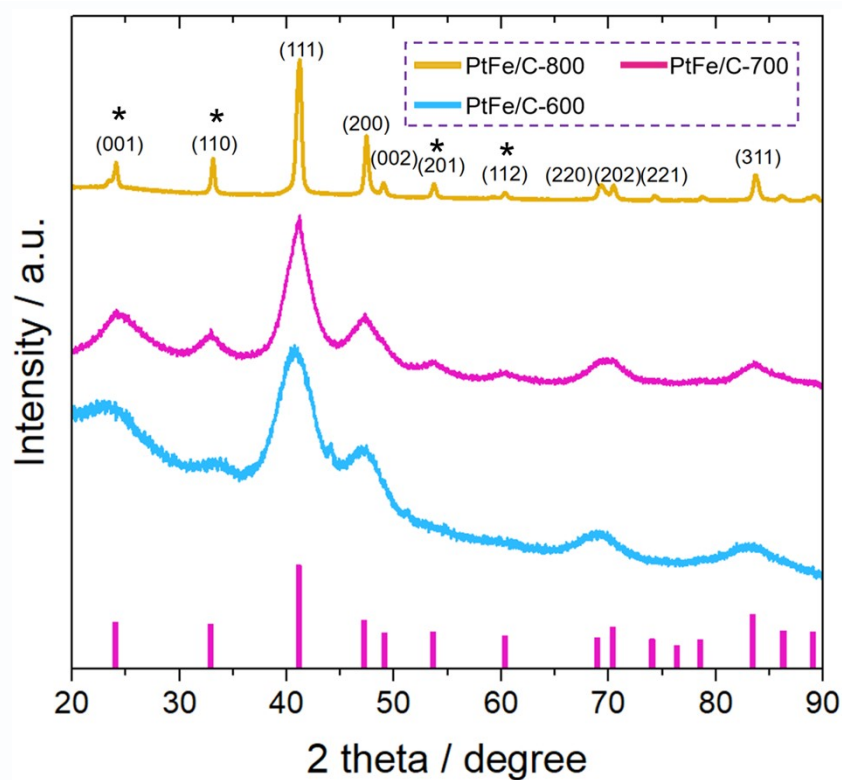


Fig. S7. XRD patterns of PtFe/C samples annealed at different temperature for 12 h.

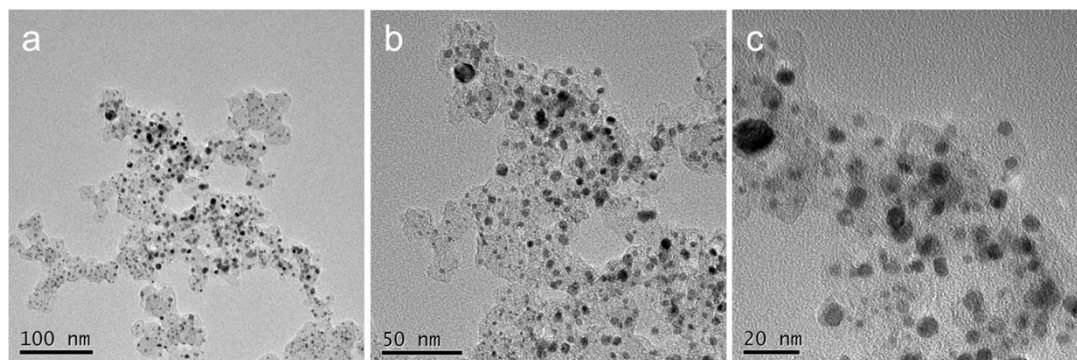


Fig. S8. TEM image of PtFe/C-VD annealed for 12 h at 800 °C.

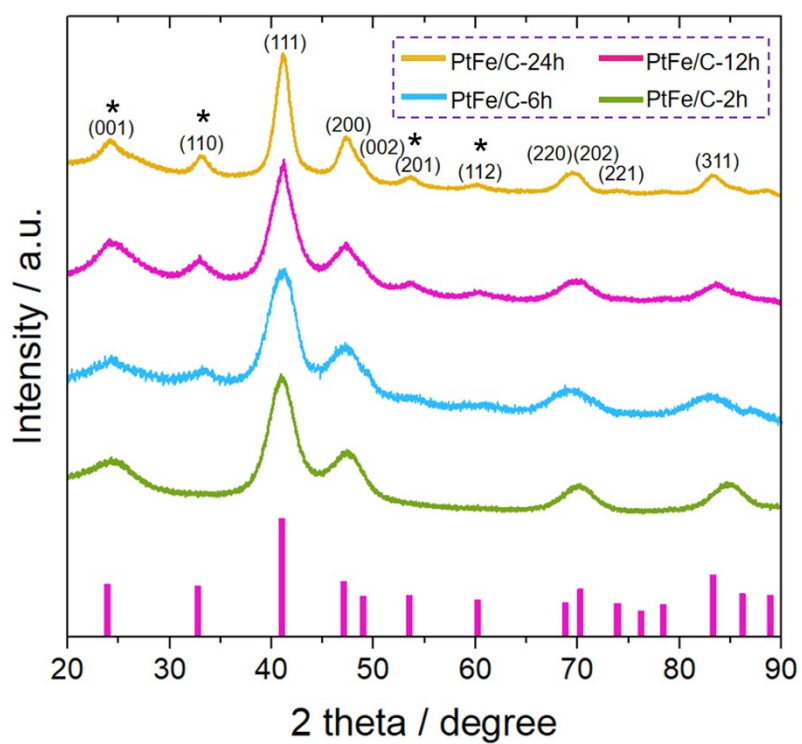


Fig. S9. XRD patterns of PtFe/C samples annealed at different annealing time at 700 °C.

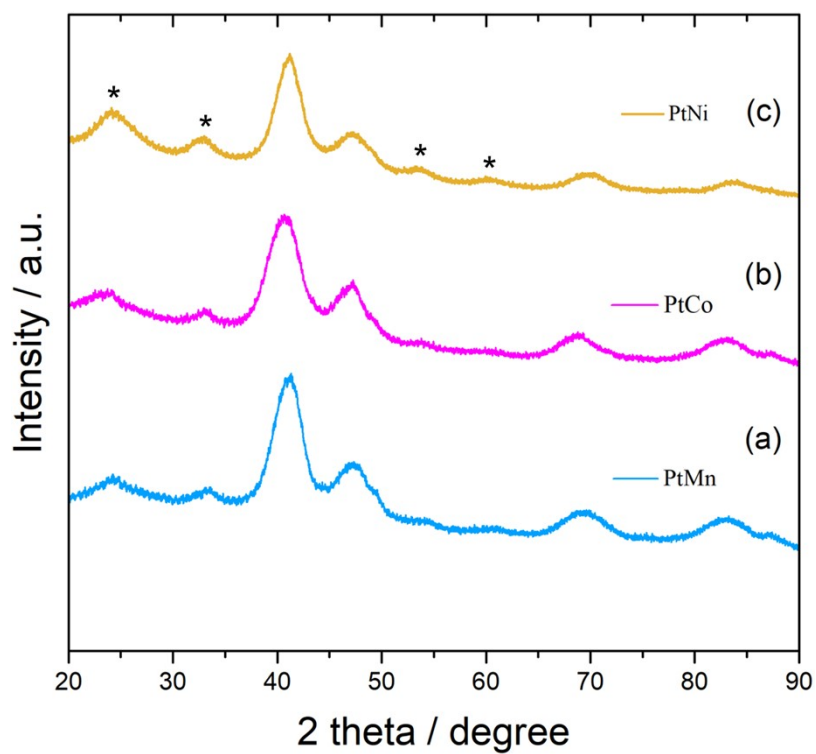


Fig. S10. XRD patterns of ordered PtCo/C-VD, PtNi/C-VD and PtMn/C-VD samples.

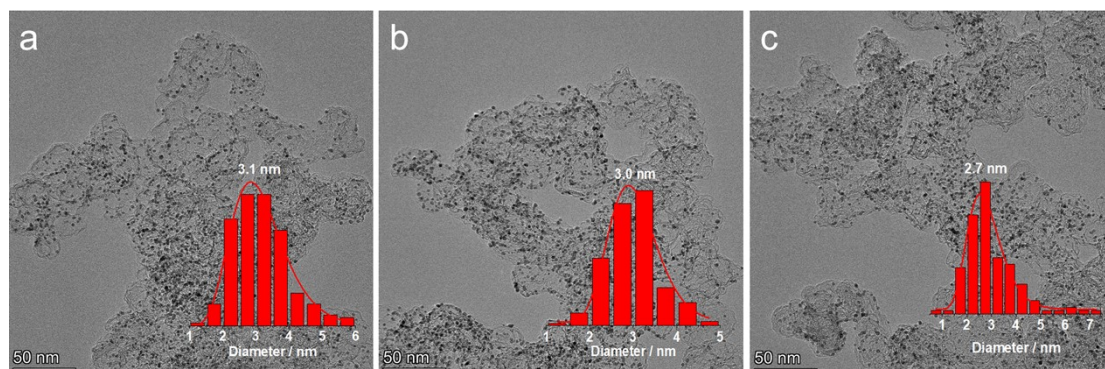


Fig. S11. TEM images of (a) PtCo/C-VD, (b) PtNi/C-VD and (c) PtMn/C-VD catalysts.

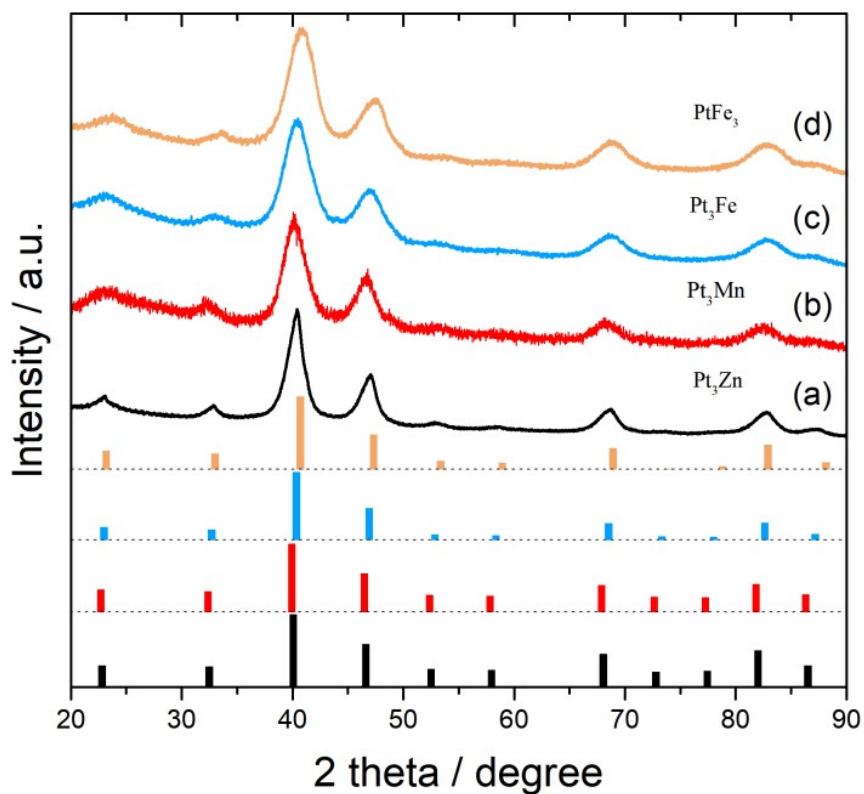


Fig. S12. XRD pattern of ordered Pt₃Zn/C-VD, Pt₃Mn/C-VD, Pt₃Fe/C-VD and PtFe₃/C-VD catalysts.

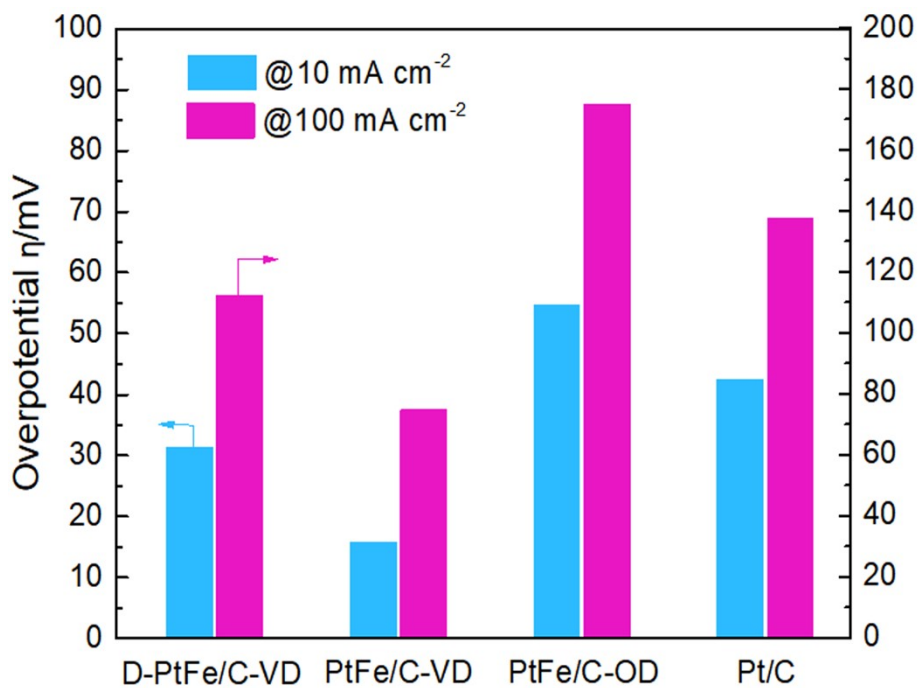


Fig. S13. Comparison of overpotentials at 10 mA cm⁻² and 100 mA cm⁻², respectively.

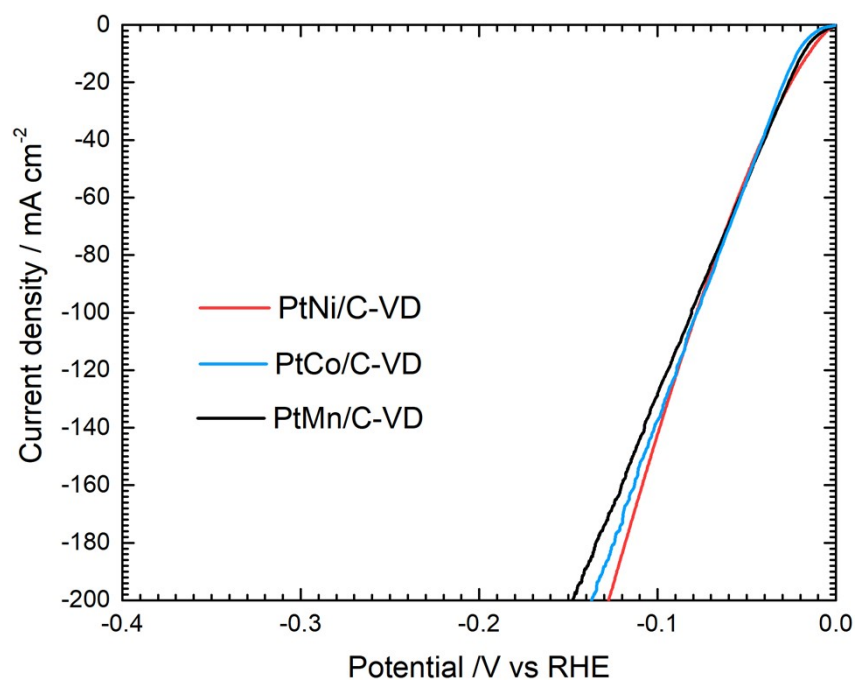


Fig. S14. HER polarization curves of (a) PtCo/C-VD, (b) PtNi/C-VD and (c) PtMn/C-VD in N₂-saturated 0.5 M H₂SO₄ solution.

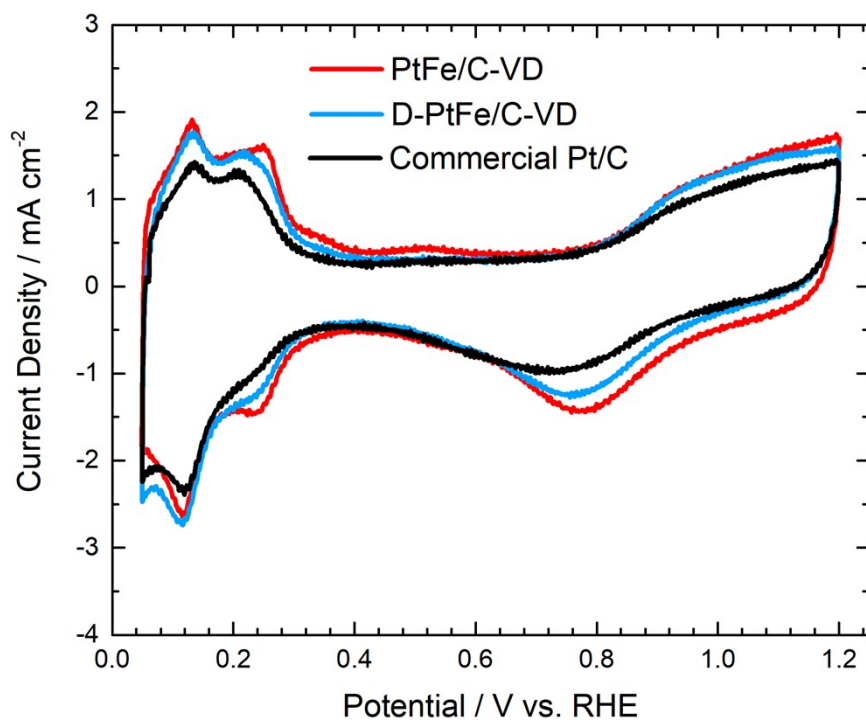


Fig. S15. CV curves recorded at room temperature in a N₂-purged 0.5 M H₂SO₄ solution with a sweep rate of 50 mV s⁻¹.

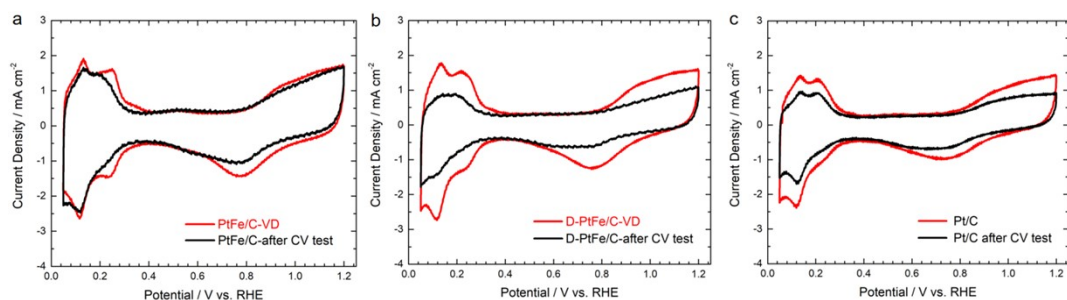


Fig. S16. The Comparison of CV curves in N₂-saturated 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹ before and after CV tests for (a) PtFe/C-VD , (b) D-PtFe/C-VD, and (c) Pt/C, respectively.

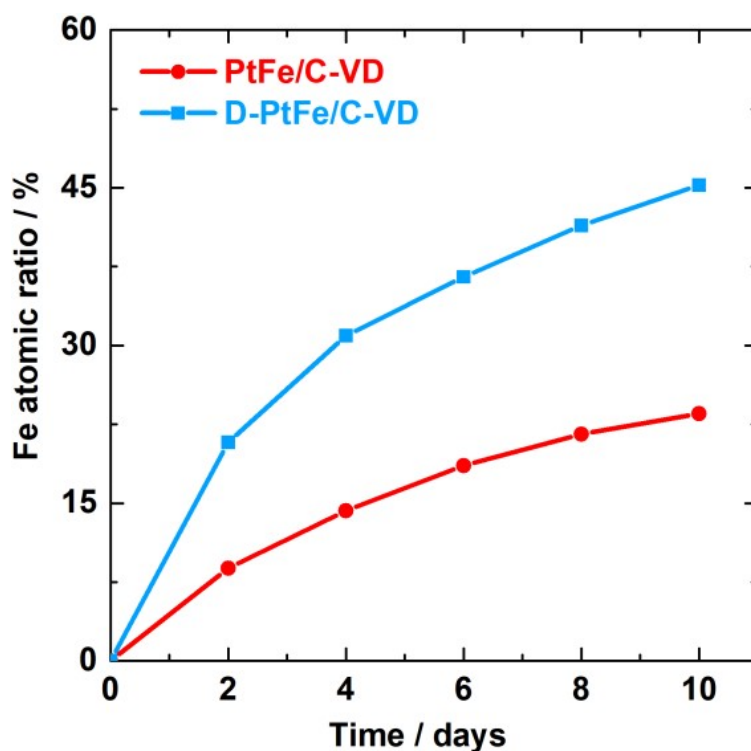


Fig. S17. The atomic ratios of Mn leaching test at 25 °C in 0.5 M H₂SO₄ solution.

The amount of Fe leaching into the acid electrolyte is determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). After ten days, the Fe leaching loss for the D-PtFe/C-VD catalyst is 23.5%, much lower than that of the D-PtFe/C-VD catalyst (45.3%).

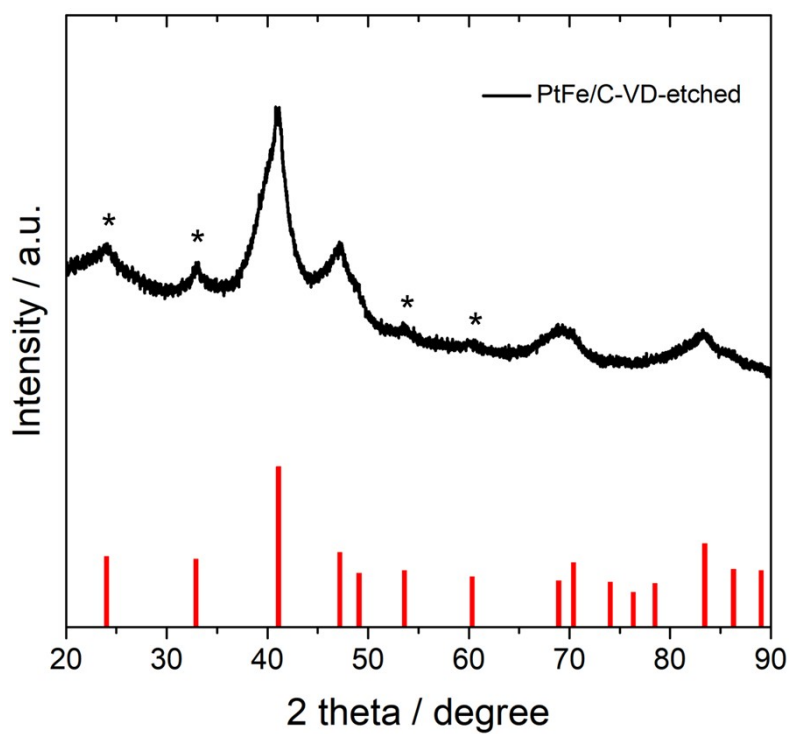


Fig. S18. XRD pattern of PtFe/C-VD after leaching test.

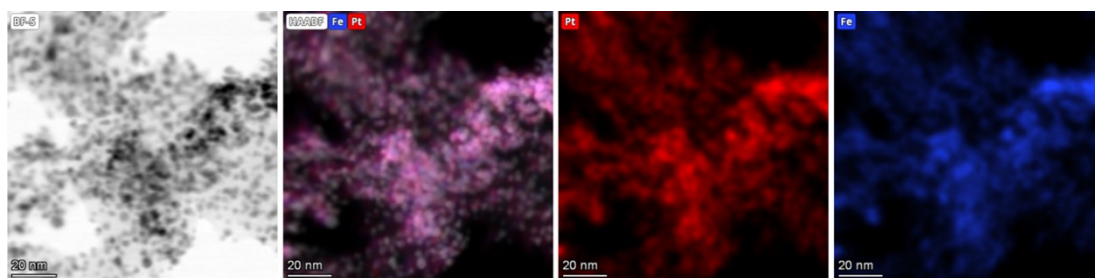


Fig. S19. The elemental mapping distribution of PtFe/C-VD sample after the Fe leaching test.

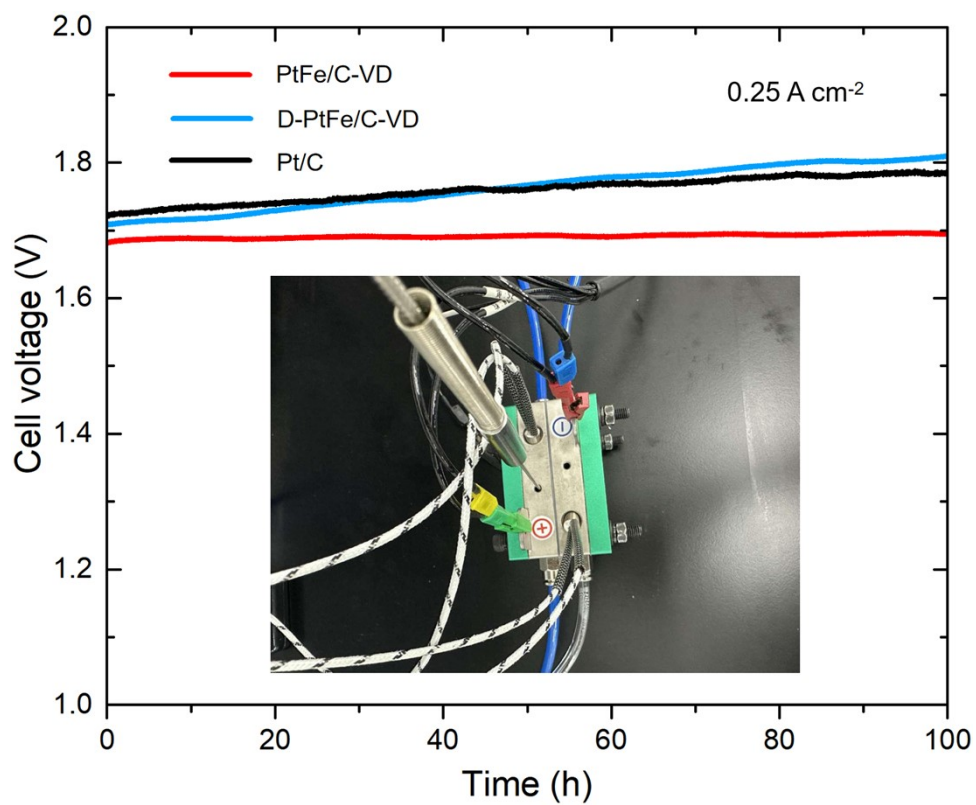


Fig. S20. The chronopotentiometry curves of PtFe/C-VD, D-PtFe/C-VD and Pt/C as PEMWE cathode catalysts at 0.25 A cm⁻².

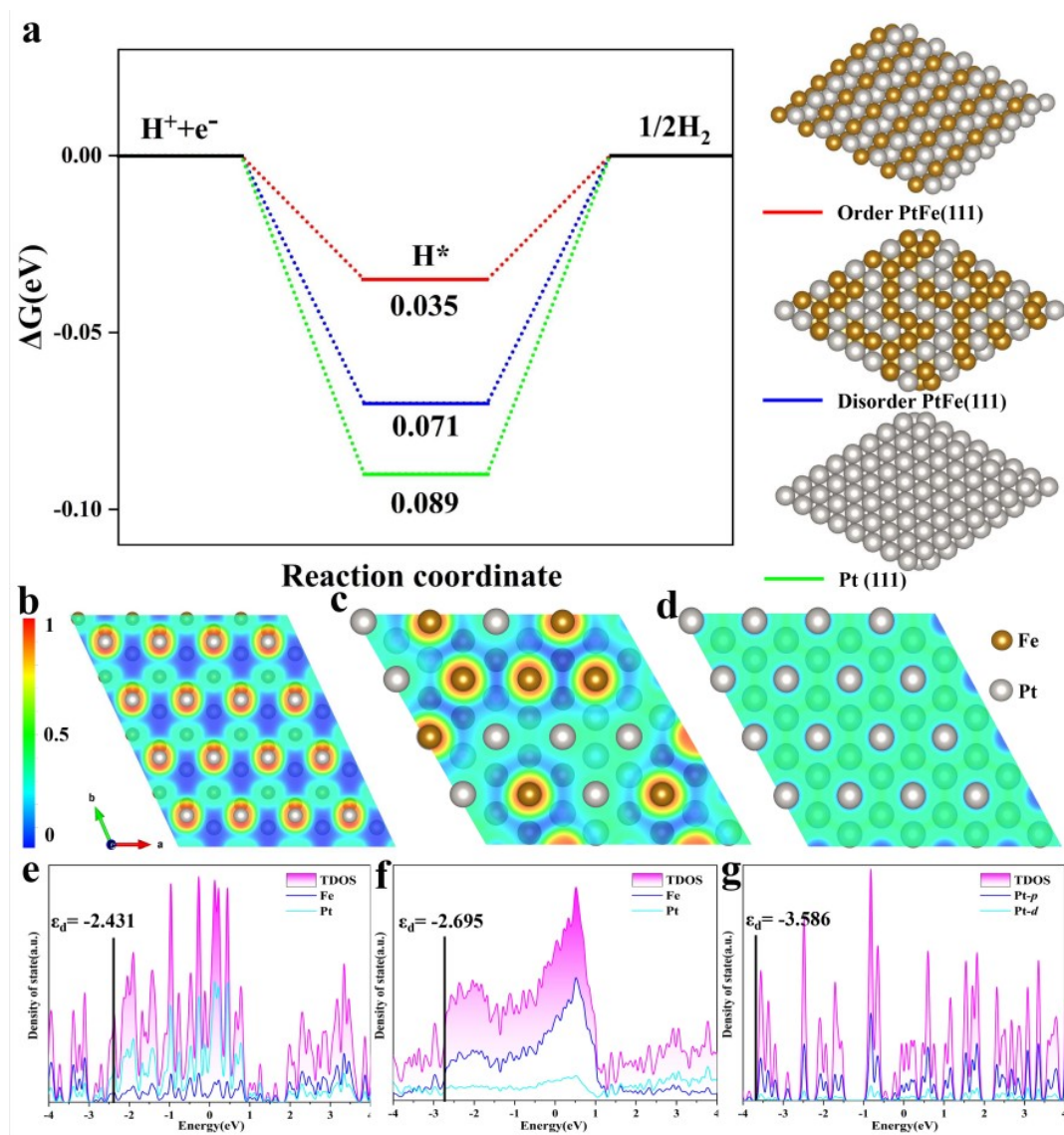


Fig. S21. (a) Gibbs free energy diagram of the HER on ordered PtFe(111), disordered PtFe(111) and Pt(111), respectively. (b-d) The charge local function diagram of the HER on ordered PtFe(111), disordered PtFe(111) and Pt(111). (e-f) TDOS of ordered PtFe(111), disordered PtFe(111) and Pt(111).

Table S1. Comparison of particle-size of ordered PtFe nanoparticles with recently reported ordered Pt-based nanoparticles.

Samples	Particle-size	Reference
Ordered PtFe	8.8 ± 0.5 nm	Nano Lett. 2015, 15, 2468–2473.
Ordered	12 nm	Chem. Mater. 2008, 20, 7242–7245.
Ordered Pt ₃ Y/C	5~20 nm	J. Am. Chem. Soc. 2017, 139, 5672–5675
Ordered Pt ₃ Fe	8.6 nm	J. Am. Chem. Soc., 2015, 137, 6263–6269
Ordered Pt ₃ Cr/C	7.2 nm	Nanoscale, 2014, 6, 10686–10692
Ordered Pt ₃ V/C	6.2 nm	J. Am. Chem. Soc. 2014, 136, 10206–10209
Ordered PtCu/C-700	6.0 nm	Chem. Mater. 2018, 30, 5987–5995
Pt ₃ Co-700/C	7.2 nm	Nat. Mater., 2013, 12, 81
Ordered PtCo	6.0	J. Mater. Chem., 2004, 14, 1454-1460
Ordered Pt ₃ Mn	5 nm	J. Am. Chem. Soc. 2012, 134, 18455
Ordered Pt ₃ Ti/C	6.5 nm	J. Am. Chem. Soc. 2014, 136, 10206–10209
Ordered PtSn/C	6.3 nm	J. Am. Chem. Soc., 2015, 137, 6263–6269
PtFe/C-VD	2.9 nm	This work
PtCo/C-VD	<3.0 nm	This work
PtNi/C-VD	<3.0 nm	This work
PtMn/C-VD	<3.0 nm	This work

References

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