

## 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 ( $\text{FeCl}_3$ ), Cobalt(II) chloride ( $\text{CoCl}_2$ ), nickel(II) chloride ( $\text{NiCl}_2$ ), Zinc(II) chloride ( $\text{ZnCl}_2$ ) and manganese(II) chloride ( $\text{MnCl}_2$ ) 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,  $\text{FeCl}_3$  and Pt/C were placed in porcelain boats and placed next to each other in a tube furnace. The porcelain boat with  $\text{FeCl}_3$  (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  $\text{min}^{-1}$ , then held there for 2 h for sublimation. Subsequently, the above intermediates were calcined at 700 °C under a flow of 5%  $\text{H}_2/\text{Ar}$  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  $800^\circ \text{C}$  at a heating rate of  $10^\circ \text{C min}^{-1}$  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  $\mu\text{L}$  of 5 wt.% Nafion solution. Then the catalyst ink was dripped on a glassy carbon ( $0.196 \text{ cm}^2$ ) with a loading amount of  $1 \text{ mg cm}^{-2}$ . 5  $\mu\text{L}$  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  $28 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  for PtFe/C and  $26 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  for Pt/C. Before testing, a 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte was passed with  $\text{N}_2/\text{H}_2$  through the solution for at least 20 min to saturate the electrolyte with  $\text{N}_2/\text{H}_2$ . The CV curves of different catalysts were obtained in the  $\text{N}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  solution by sweeping the potential from 0.05 to 1.20 V (vs RHE) at the scan rate of  $50 \text{ mV s}^{-1}$ . The electrochemical active

surface areas (ECSAs) were calculated from  $H_{\text{upd}}$  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  $50 \text{ mVs}^{-1}$  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  $1 \text{ mg cm}^{-2}$ . 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  $-0.30 \text{ V vs. RHE}$ ) solution at a scan rate of  $5 \text{ mV s}^{-1}$ . 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  $100 \text{ mA cm}^{-2}$ .

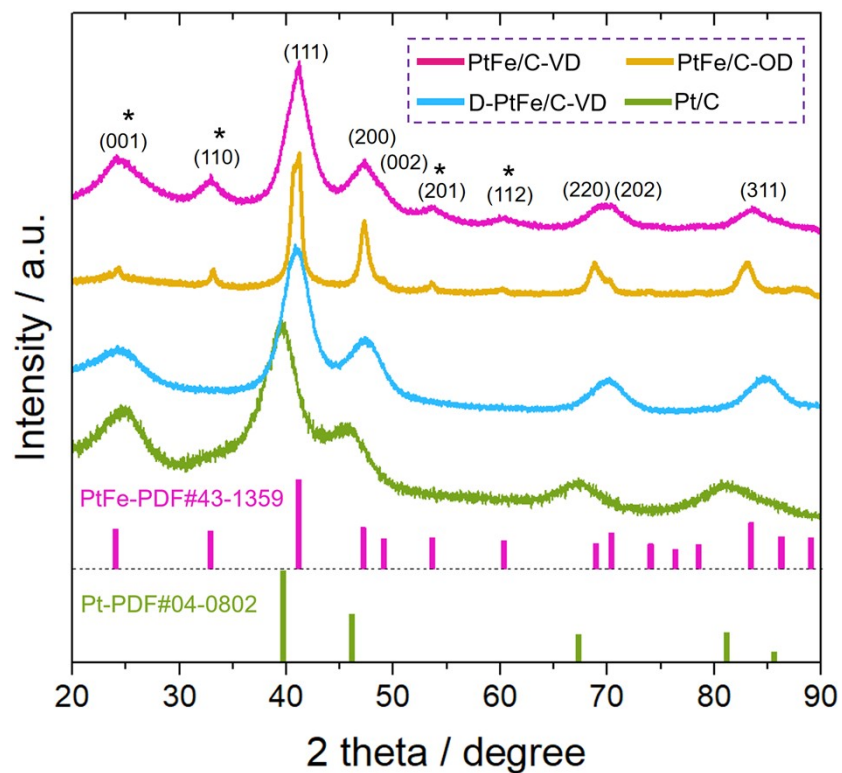
**Electrochemical measurement of PEMWE:** Before the construction of catalysis coated membrane (CCM), the N115 membrane was successively treated with  $5 \text{ wt}\%$   $\text{H}_2\text{O}_2$ , deionized water, and  $0.5 \text{ M H}_2\text{SO}_4$  at  $80 \text{ }^\circ\text{C}$  for  $1 \text{ h}$ . 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  $\text{IrO}_2$  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 ( $1:1, \text{ w/w}$ ). Subsequently, Nafion with an ionomer mass fraction of  $10 \text{ wt}\%$  at the anode or  $35 \text{ wt}\%$  at the cathode was added into the solution. The suspension was ultrasonically treated in an ice water bath for  $1 \text{ h}$  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  $10 \text{ Mpa}$  at  $135 \text{ }^\circ\text{C}$  for  $10 \text{ min}$ . 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  $\text{IrO}_2$ . 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  $4 \text{ cm}^2$ . 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  $0.25 \text{ A cm}^{-2}$ .

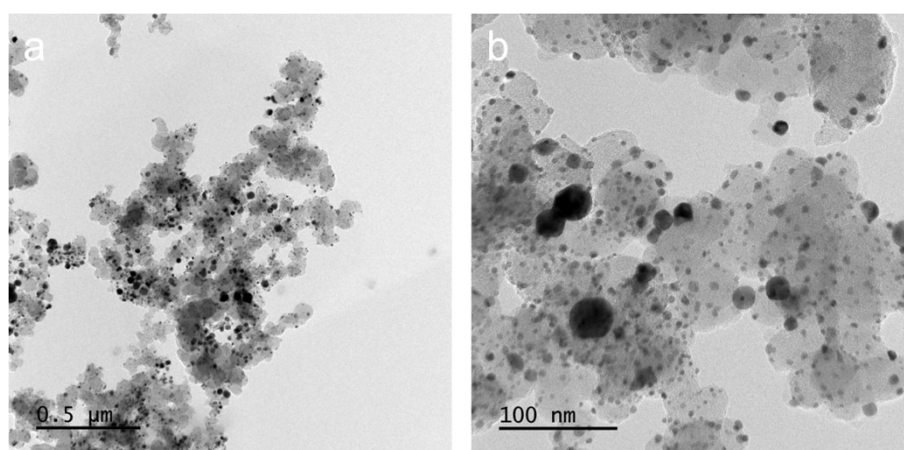
**Computational details:** The spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP) code.<sup>1-3</sup> The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional with van der Waals correction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



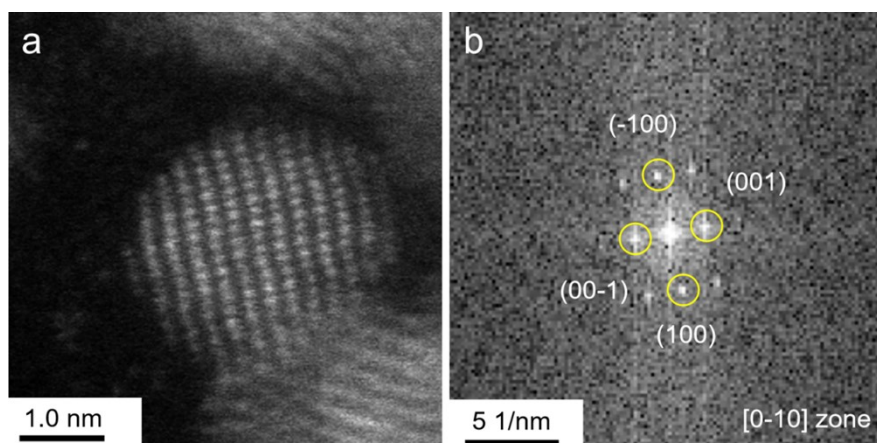
**Fig. S1.** The photograph of PtFe/C-VD catalyst.



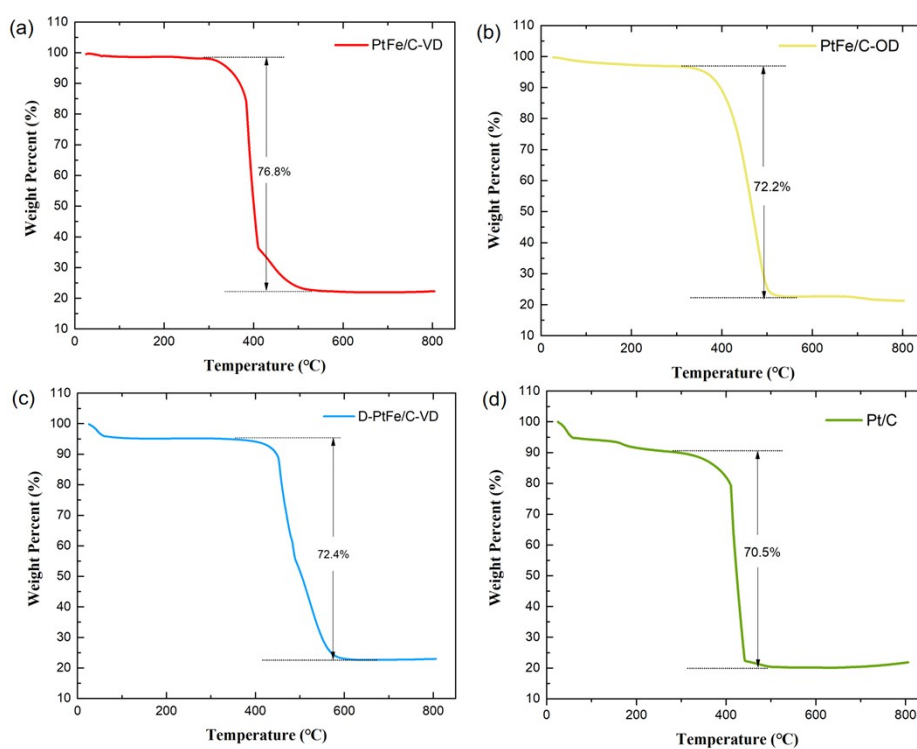
**Fig. S2.** XRD patterns of PtFe/C-VD, PtFe/C-OD, D-PtFe/C-VD and Pt/C samples.



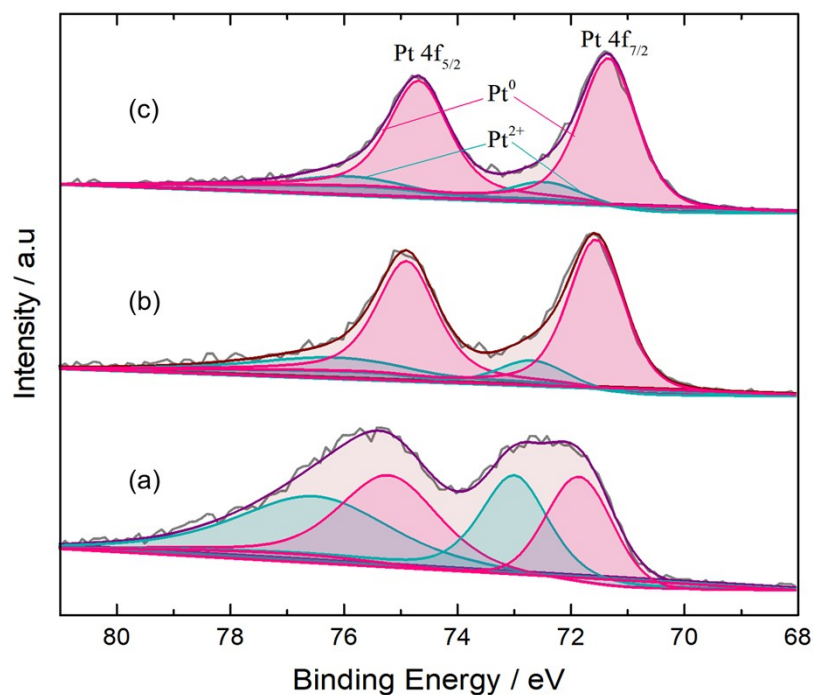
**Fig. S3.** TEM image of Pt/C annealed for 12 h at 700 °C.



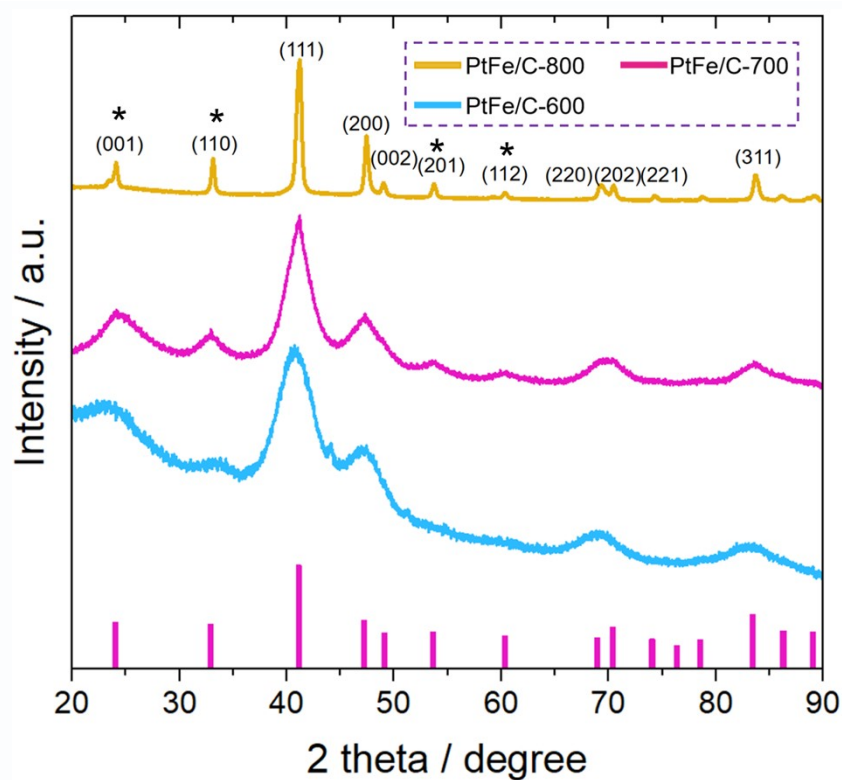
**Fig. S4.** (a) STEM image and (b) FFT pattern of disordered PtFe nanoparticle in D-PtFe/VD.



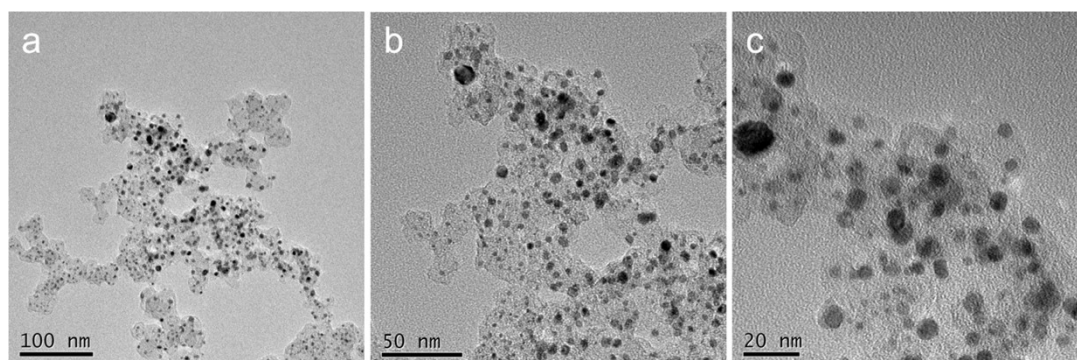
**Fig. S5.** TGA curves of (a) PtFe/C-VD, (b) PtFe/C-OD, (c) D-PtFe/C-VD and (d) Pt/C samples.



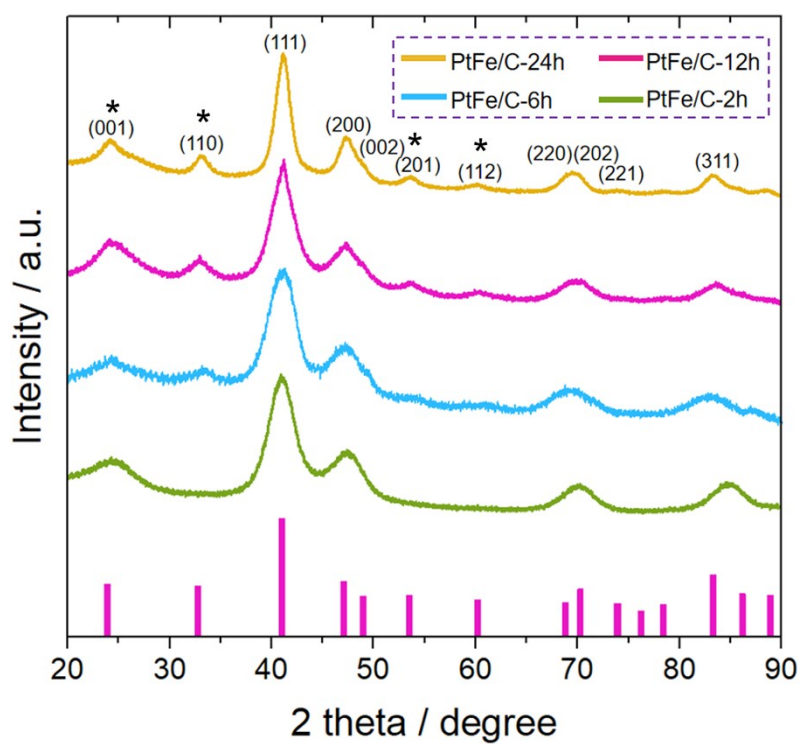
**Fig. S6.** XPS spectra of Pt 4f in (a) commercial Pt/C, (b) D-PtFe/C-VD and (c) PtFe/C-VD.



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

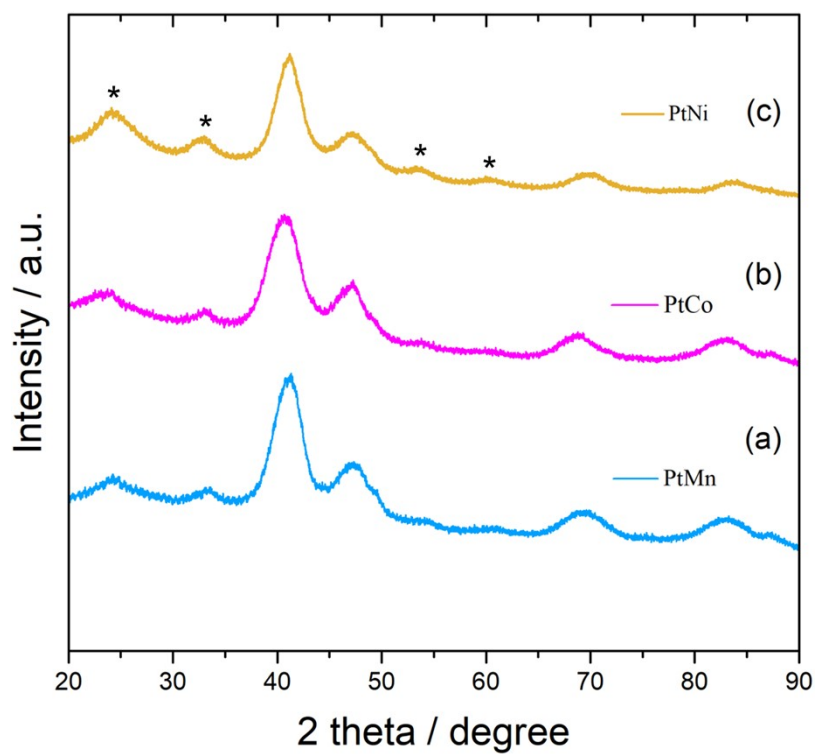


**Fig. S8.** TEM image of PtFe/C-VD annealed for 12 h at 800 °C.

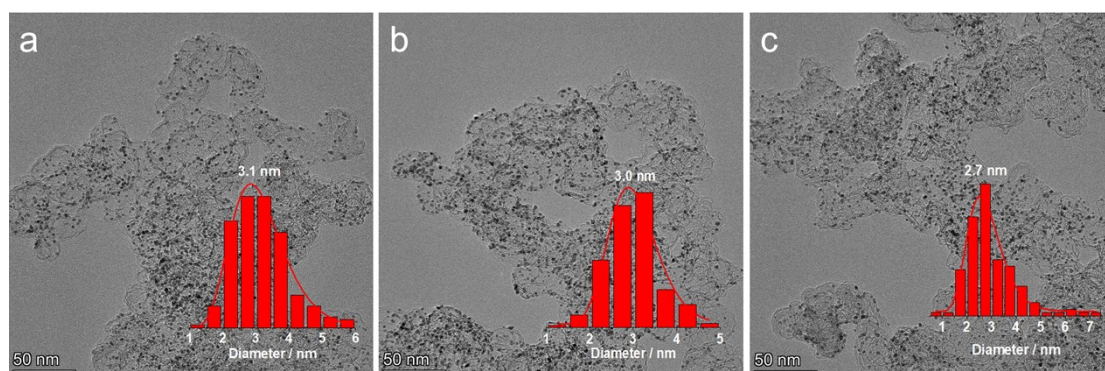


**Fig. S9.** XRD patterns of PtFe/C samples annealed at different annealing time at 700 °C.

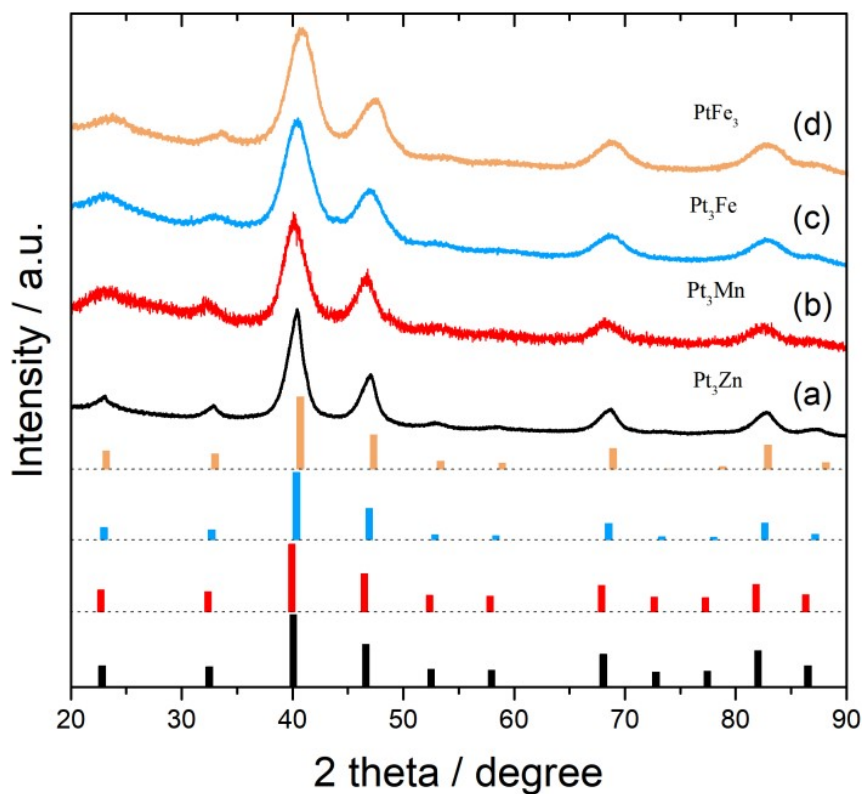




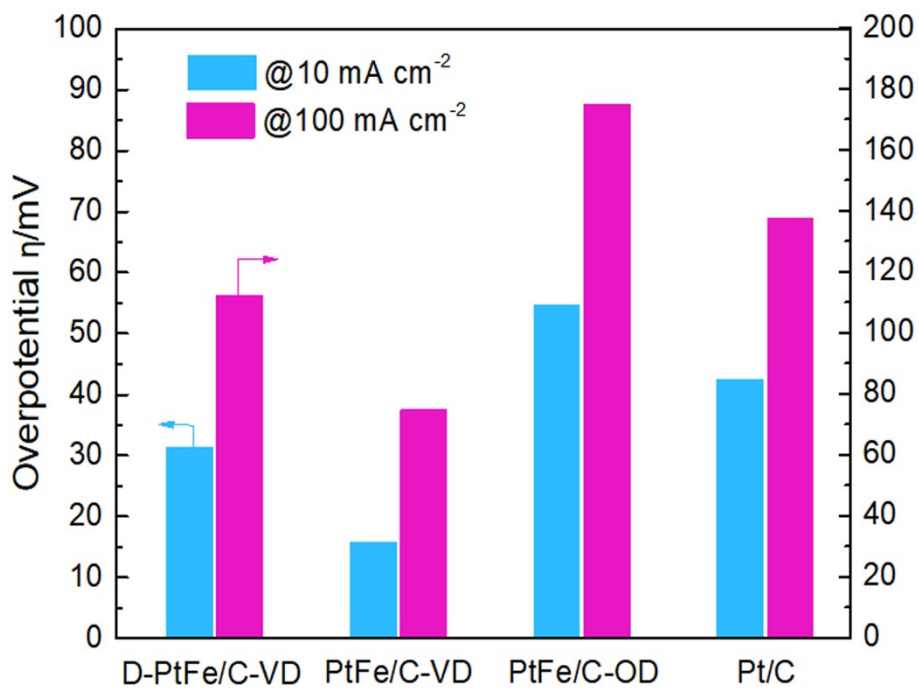
**Fig. S10.** XRD patterns of ordered PtCo/C-VD, PtNi/C-VD and PtMn/C-VD samples.



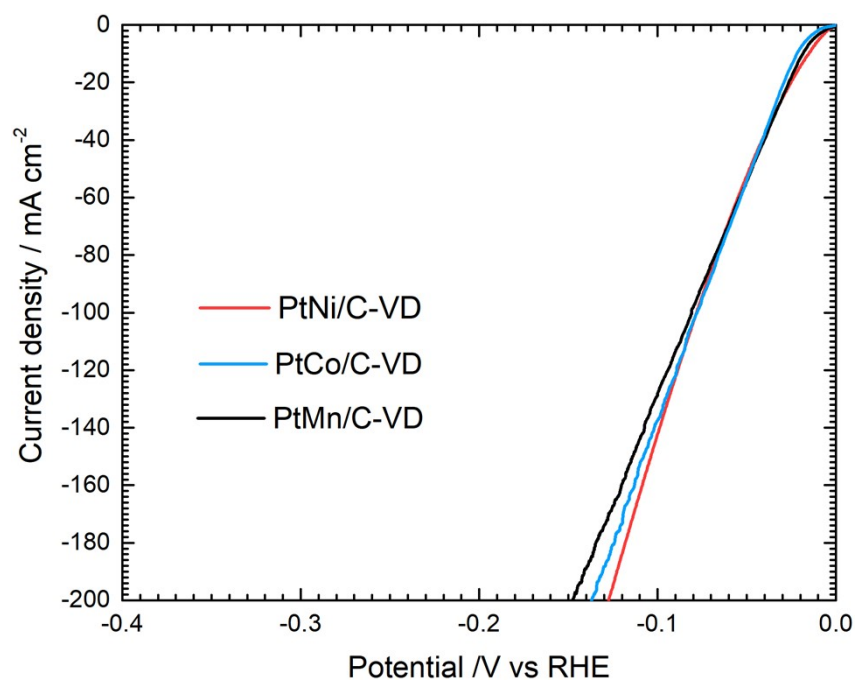
**Fig. S11.** TEM images of (a) PtCo/C-VD, (b) PtNi/C-VD and (c) PtMn/C-VD catalysts.



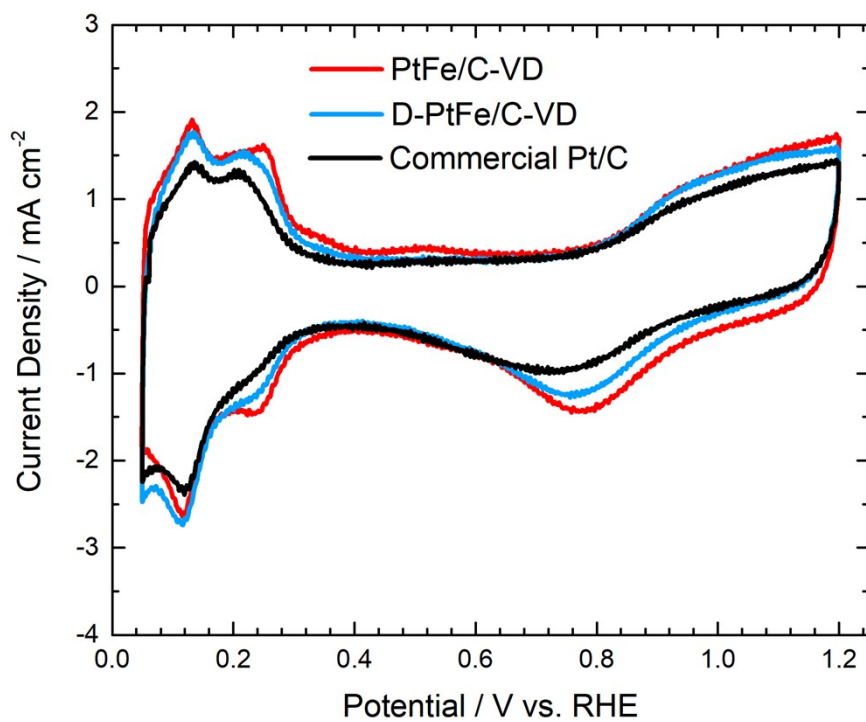
**Fig. S12.** XRD pattern of ordered Pt<sub>3</sub>Zn/C-VD, Pt<sub>3</sub>Mn/C-VD, Pt<sub>3</sub>Fe/C-VD and PtFe<sub>3</sub>/C-VD catalysts.



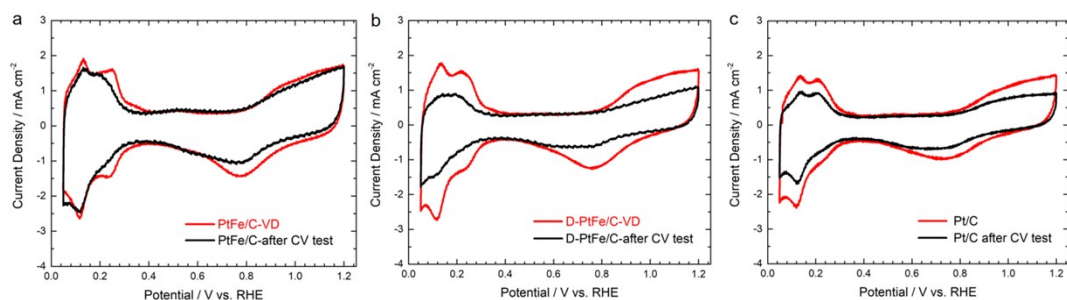
**Fig. S13.** Comparison of overpotentials at 10 mA cm<sup>-2</sup> and 100 mA cm<sup>-2</sup>, respectively.



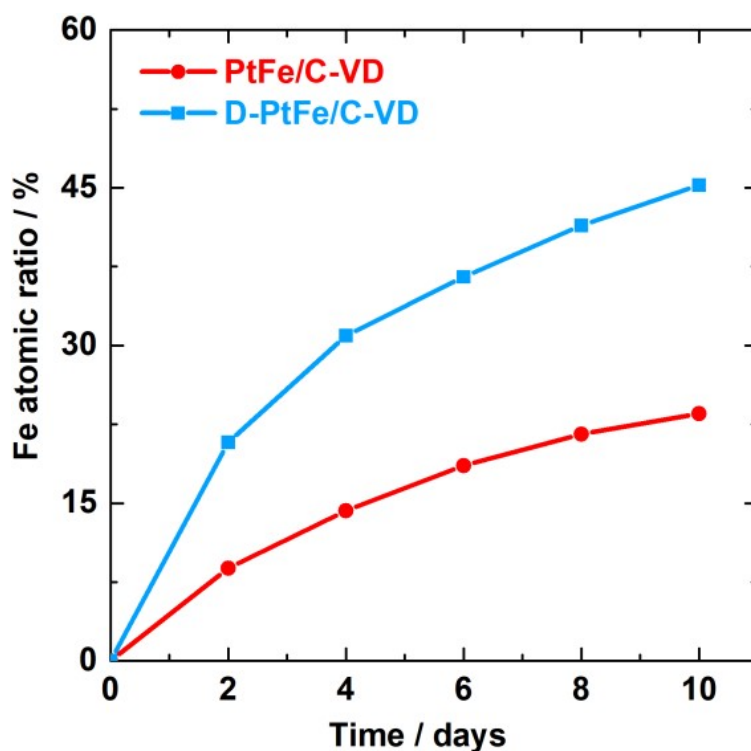
**Fig. S14.** HER polarization curves of (a) PtCo/C-VD, (b) PtNi/C-VD and (c) PtMn/C-VD in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.



**Fig. S15.** CV curves recorded at room temperature in a N<sub>2</sub>-purged 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with a sweep rate of 50 mV s<sup>-1</sup>.

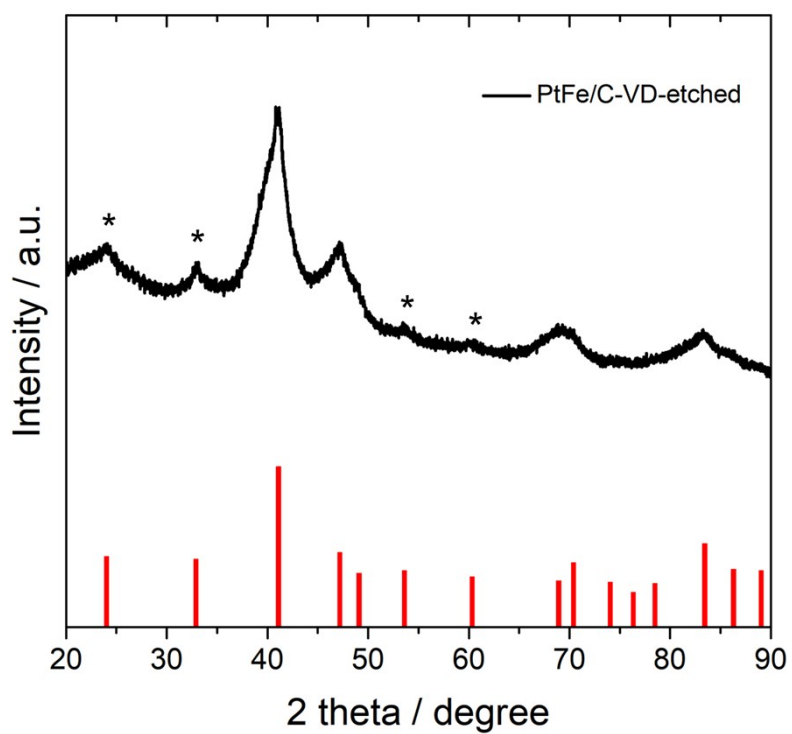


**Fig. S16.** The Comparison of CV curves in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 50 mV s<sup>-1</sup> before and after CV tests for (a) PtFe/C-VD , (b) D-PtFe/C-VD, and (c) Pt/C, respectively.

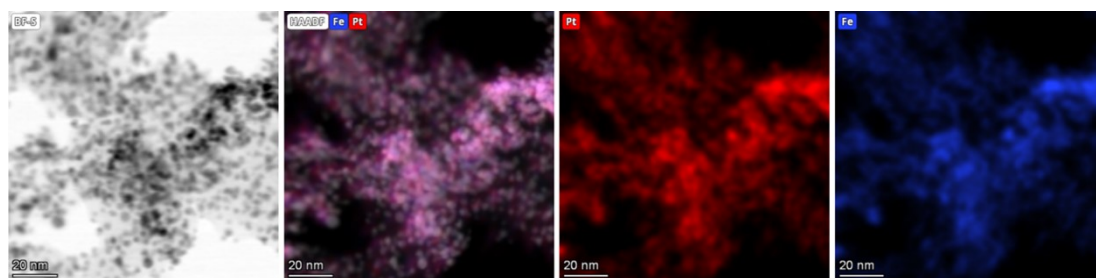


**Fig. S17.** The atomic ratios of Mn leaching test at 25 °C in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

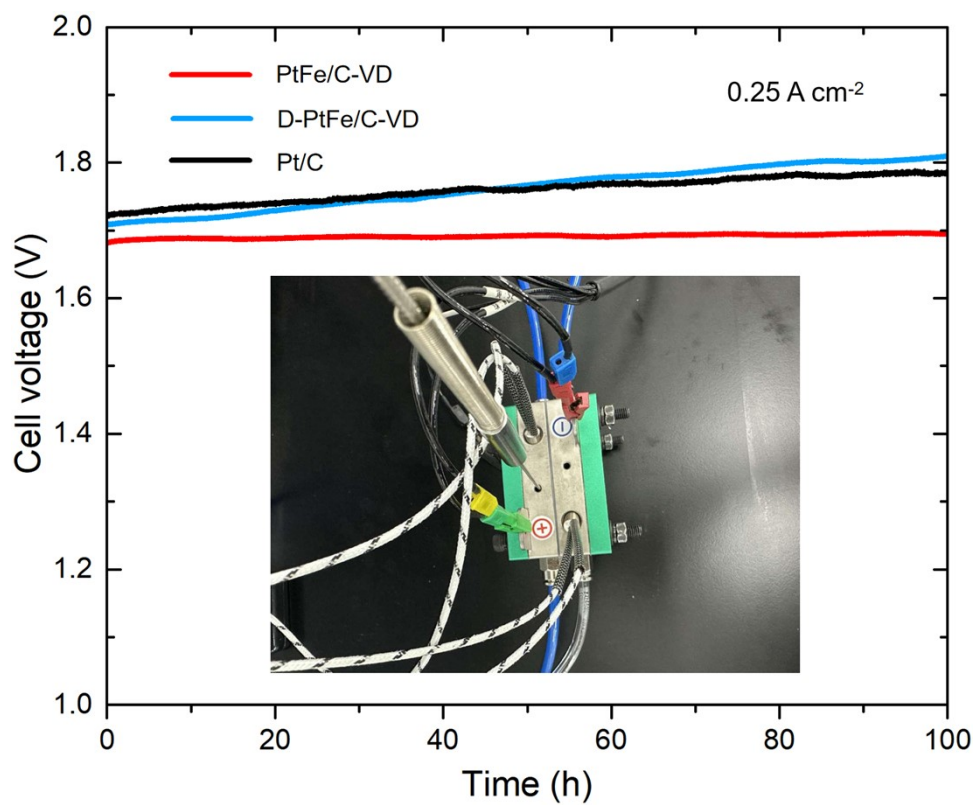
The amount of Fe leaching into the acid electrolyte is determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). After ten days, the Fe leaching loss for the D-PtFe/C-VD catalyst is 23.5%, much lower than that of the D-PtFe/C-VD catalyst (45.3%).



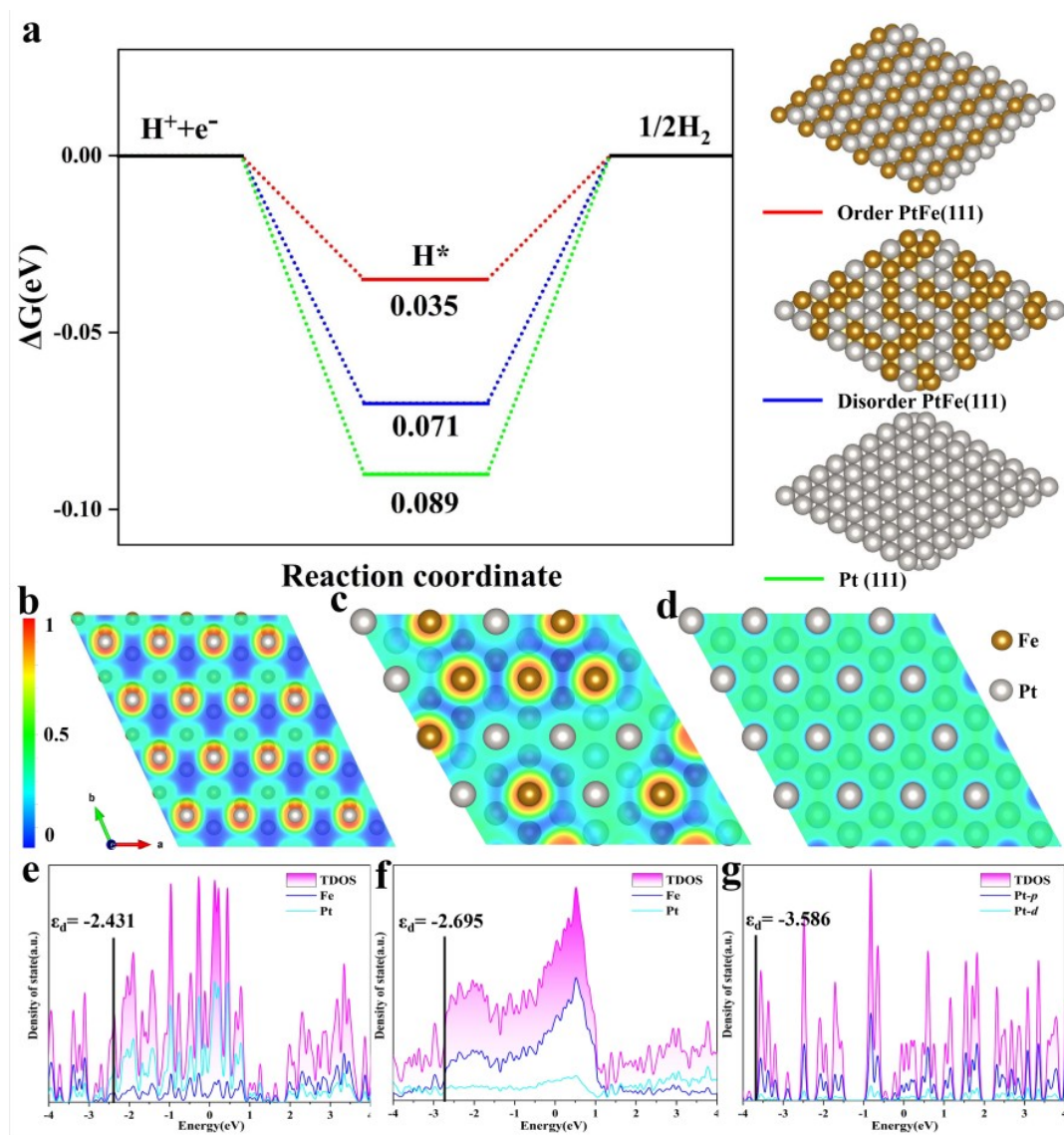
**Fig. S18.** XRD pattern of PtFe/C-VD after leaching test.



**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<sup>-2</sup>.



**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	$8.8 \pm 0.5$ nm	Nano Lett. 2015, 15, 2468–2473.
Ordered	12 nm	Chem. Mater. 2008, 20, 7242–7245.
Ordered Pt <sub>3</sub> Y/C	5~20 nm	J. Am. Chem. Soc. 2017, 139, 5672–5675
Ordered Pt <sub>3</sub> Fe	8.6 nm	J. Am. Chem. Soc., 2015, 137, 6263–6269
Ordered Pt <sub>3</sub> Cr/C	7.2 nm	Nanoscale, 2014, 6, 10686–10692
Ordered Pt <sub>3</sub> 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 <sub>3</sub> Co-700/C	7.2 nm	Nat. Mater., 2013, 12, 81
Ordered PtCo	6.0	J. Mater. Chem., 2004, 14, 1454-1460
Ordered Pt <sub>3</sub> Mn	5 nm	J. Am. Chem. Soc. 2012, 134, 18455
Ordered Pt <sub>3</sub> 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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