

Supporting Information

Rapid Adsorption Enables Interface Engineering of PdMnCo Alloy/Nitrogen-Doped Carbon as Highly Efficient Electrocatalysts for Hydrogen Evolution Reaction

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1. Supplementary Methods

1.1. Materials synthesis

Chemicals. Manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), polyvinylpyrrolidone (PVP, K-30), methanol, ethanol, palladium chloride (PdCl_2) are purchased from Sinopharm Chemical Reagent Co. Ltd (China). Potassium hexacyanocobaltate (III) ($\text{K}_3[\text{Co}(\text{CN})_6]$) is purchased from J&K Chemical. All chemicals are of analytical grade and used without any further purification.

Synthesis of $\text{Mn}_3[\text{Co}(\text{CN})_6]_2$. $\text{Mn}_3[\text{Co}(\text{CN})_6]_2$ nanocubes are synthesized by a one-step co-precipitation reaction. Solution A: 0.075 mmol of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 0.3 g PVP (K-30) are dissolved in 15 ml $\text{C}_2\text{H}_5\text{OH}$ / 5 ml H_2O system under agitated stirring to get a transparent solution. Solution B: 0.04 mmol $\text{K}_3[\text{Co}(\text{CN})_6]$ is dissolved in 10 ml of distilled water. Solution B is added into solution A slowly and regularly using a syringe. The whole reaction process is kept at room temperature with agitated stirring. After 10 min, the reaction is aged at room temperature for 1 h without any interruption. The resulting white precipitate is centrifuged and washed several times with absolute ethanol and finally dried in an oven at 60 °C.

Synthesis of Substrate. To obtain the $(\text{Mn},\text{Co})_4\text{N}$ nanocrystals embedded in nitrogen-doped carbon layers, $\text{Mn}_3[\text{Co}(\text{CN})_6]_2$ is heated to 750 °C with a heating rate of 5 °C min^{-1} and kept for 4 h in Ar.

Synthesis of PdMnCo/NC . In a typical procedure, 4 mg of as-prepared substrate is dispersed in 410 μl of 5 mmol, 10 mmol, and 15 mmol PdCl_2 methanol solution, respectively, and then forms a uniform suspension through 90 seconds ultrasonication. The resulting black suspension is separated by an external magnetic field and washed several times with methanol.

Then the PdMnCo/NC-1, PdMnCo/NC-2 and PdMnCo/NC-3 can be obtained by drying under vacuum at 45 °C. Usually, the whole synthesis time is 6 hours, which includes the time for synthesis of substrate.

1.2 Physicochemical characterization

The powder X-ray diffraction (XRD) patterns are collected on a Japan Rigaku D/MAX-cA X-ray diffractometer equipped with Cu K α radiation over the 2 θ range of 20–80°. Scanning electron microscopy (SEM) images are performed on a Zeiss Supra 40 field-emission scanning microscopes operating at 5 kV. Transmission electron microscope (TEM) are carried out on a Hitachi H7650 transmission electron microscope operating at 100 kV and high-resolution transmission electron microscopy (HRTEM) images are taken on a JEOL-2010 transmission electron microscope, which is operated at 200 kV. High resolution high angle annular dark-field scanning TEM (HAADF-STEM), energy dispersive spectrometer (EDS), elemental mapping images and line-scan analysis images are obtained on JEM-ARM 200F. Inductively coupled plasma (ICP) data is obtained by using an Optima 7300 DV instrument. Specific surface areas are calculated from the results of N₂ physisorption at 77 K (Micromeritics ASAP 2020) by using the BET (Brunauer–Emmet–Teller) and BJH (Barrett–Joyner–Halenda) methods.

1.3 Electrochemical measurements

All of the electrochemical measurements are performed in a three-electrode system on an electrochemical workstation (CHI 660E) in 0.5 M H₂SO₄ electrolyte. Typically, 4 mg of catalyst and 30 μ L Nafion solution (Sigma Aldrich, 5 wt %) are dispersed in 1 mL ethanol solution by sonicating for 1 h to form a homogeneous ink. Then 5 μ L of the dispersion (containing 20 μ g of catalyst) is loaded onto a glassy carbon electrode with 3 mm diameter (loading 0.285 mg cm⁻²). While an Ag/AgCl (in 3 M KCl solution) electrode and a platinum

foil are served as the reference electrode and counter electrodes, respectively. All of the potentials are calibrated to a reversible hydrogen electrode (RHE). The working electrode is polished with Al_2O_3 powders with size down to 0.05 μm . Commercial Pt/C (E-TEK, Pt: 40 % wt), Pd/C (Sigma-Aldrich, Pd: 30 % wt) and Pd powder (Alfa-Aesar) catalysts are used as a reference to evaluate the electrocatalytic performance of various samples. Hundreds of potential cycles are conducted in 0.5 M H_2SO_4 solution with continuous N_2 gas in the potential region from 0.05 to 1.05 V at a sweep rate of 50 mVs^{-1} , in order to let residue organics and ions release. Linear sweep voltammetry with a scan rate of 2 mV s^{-1} is conducted with a flow of N_2 gas maintained over the electrolyte during the HER experiment to eliminate dissolved oxygen. All potentials in this work are conducted without iR compensation.

1.4 Calculation details:

All the simulations are carried out a spin-polarized density functional theory (DFT) by Vienna ab-initio simulation package (VASP).¹ Projector augmented wave (PAW) method² and Generalized gradient approximation with PBE functional³ are utilized to treat electron-core interactions and exchange-correlation interactions, respectively. For dispersion interaction system as graphene covering on metal surface, VDW-DF with optB88 functional is used.⁴ The computations are stopped when the total energy and force per atom convergence criterion are less than 10^{-5}eV and $-0.01\text{eV}/\text{\AA}$, respectively. The kinetic cutoff energy based on plane wave basis set is set to be 400eV. For the Brillouin zone integrations, a k-point mesh grid of $3\times 3\times 1$ and $7\times 7\times 1$ by Monkhorst-Packing method for optimizations and static computations are used, respectively.⁵

The Gibbs free energy change of adsorbing hydrogen atom is obtained by Eq. (1)

$$\Delta G_{\text{H}^*} = \Delta E_{\text{H}^*} + \Delta \text{ZPE} - T\Delta S \quad (1)$$

Where ΔE_{H^*} , ΔZPE and ΔS are the hydrogen adsorption energy, the difference in zero-point energy (ZPE) and entropy between the adsorbed hydrogen atom and gaseous hydrogen (H_2), respectively.

$$\Delta E_{H^*} = E_{H^*} - E_{surf} - 1/2 H_2 \quad (2)$$

Where E_{H^*} and E_{surf} are the total energy with and without the adsorption of hydrogen, H_2 is the total energy of H_2 in the gas phase. For the adsorption energy of hydrogen, negative and positive number represent exothermic and endothermic, respectively.

As for the previous work,⁶ $\Delta ZPE - T\Delta S$ is equal to 0.24eV. Therefore, we may also utilize $\Delta G_{H^*} = \Delta E_{H^*} + 0.24 \text{ eV}$ in this similar work. From the Gibbs free energy diagram, the Gibbs free energy change of hydrogen adsorption is much more prone to zero, the better HER activity.

For graphene (G) covering on the metal substrates, such as Pd, $\sqrt{7} \times \sqrt{7}$ Pd(111) unit cell with the lattice of 7.38 Å matches to 3×3 graphene unitcell with 7.45 Å as referring to previous work,⁷ the match measure is less than 1%. For the Pd (111) surface, four atom layers are selected, the bottom two layers are fixed in their respective bulk positions while the remains are allowed to relax, among the vacuum spacing is about 15Å to avoid interactions between the interlayer. About the ternary alloy PdMnCo, the ratio of Pd: Mn: Co is 25: 2: 1, it is expected with the effective ratio of PdMnCo from the experiment. Five possible configurations and corresponding energy of ternary alloy PdMnCo are tested in Figure S15 and Table S3, respectively. The fifth structure with Pd exposing to the outmost and Mn, Co atoms laying the subsurface in Figure S15 (e) has the lowest energy. It is consistent with previous work,⁸ the heavier atom for the alloy, much easier to expose to the surface. Therefore, the latter simulations refer to this structure.

2. Supplementary Figures

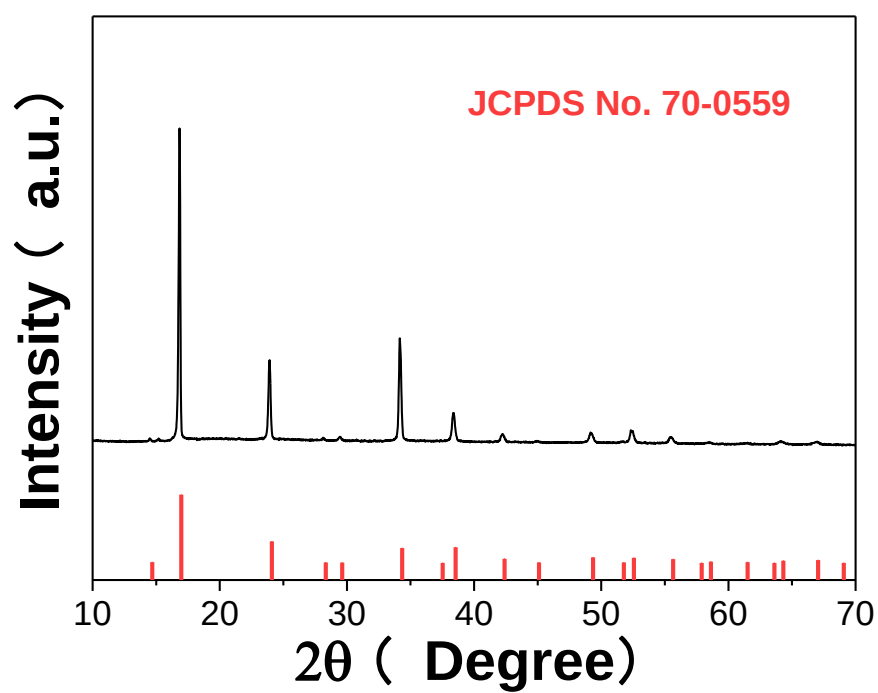


Figure S1. XRD pattern of $\text{Mn}_3[\text{Co}(\text{CN})_6]_2$ nanocubes.

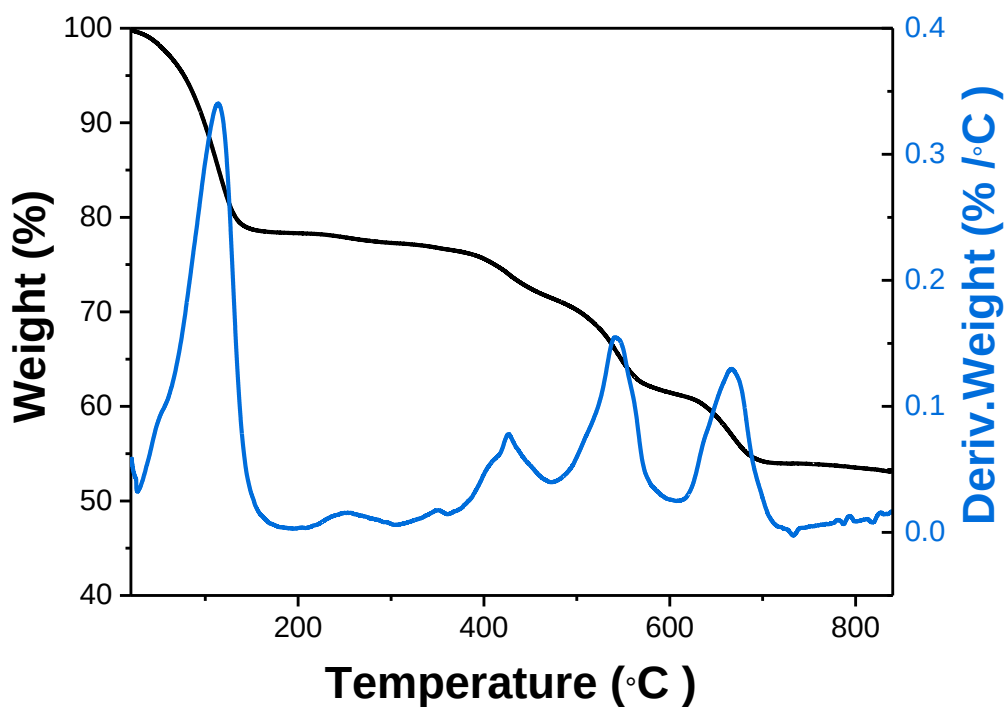


Figure S2. Thermogravimetric analysis (TGA) curves of $\text{Mn}_3[\text{Co}(\text{CN})_6]_2$. As indicated by thermogravimetric analysis (Figure S1), it undergoes the first significant weight loss around 150 °C, illustrating the loss of H_2O molecules from the porous framework structure. When the degradation temperature is further increased to 700 °C, a second weight loss stage is observed between 400 °C and 700 °C due to MOF decomposition.

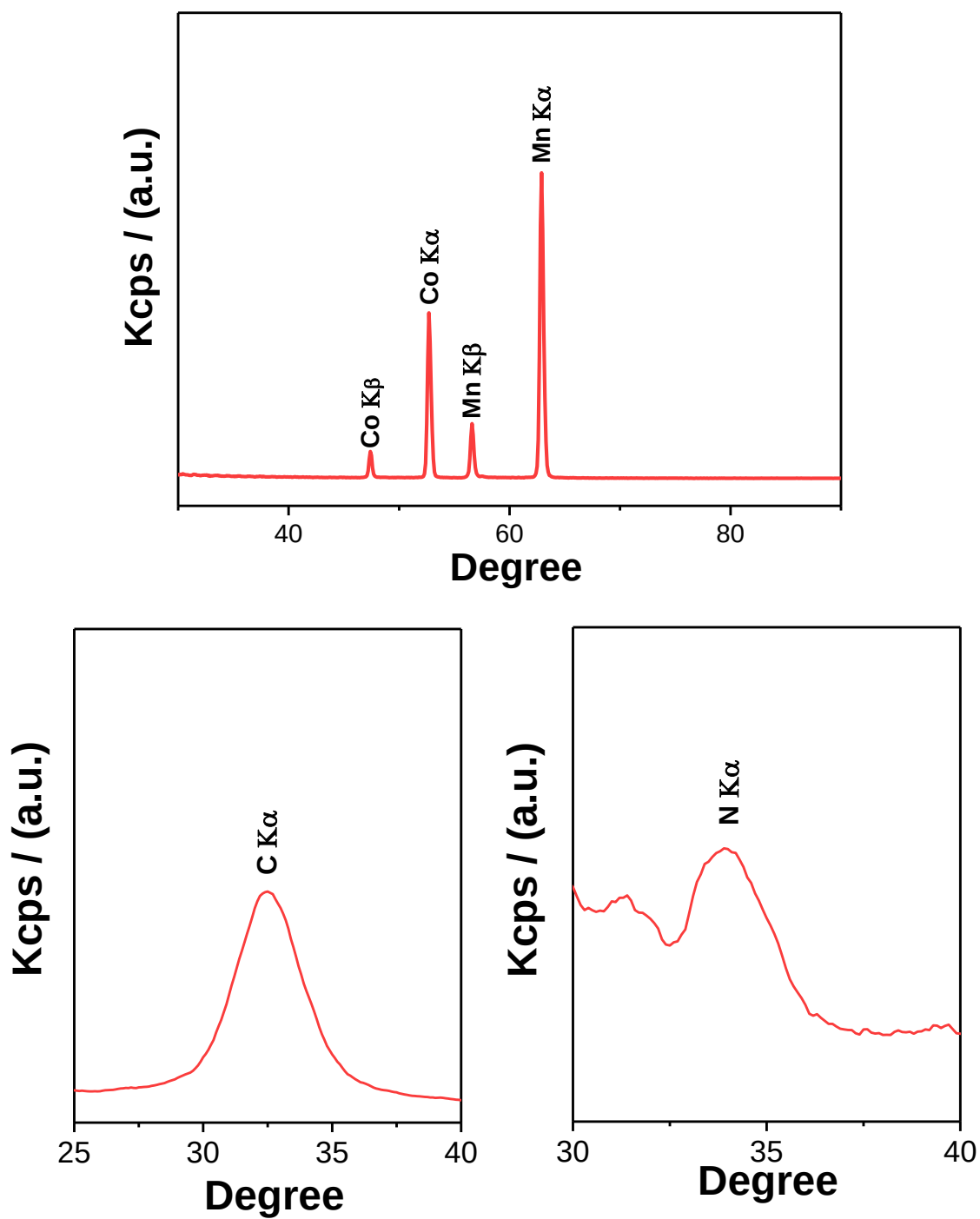


Figure S3. The XRF spectra for the substrate. Spectra of XRF shown in Figure S5 confirm the presence of Co, Mn, C, and N. The Mn, Co content of the substrate is determined to be 36 wt% and 34.31 wt%, respectively.

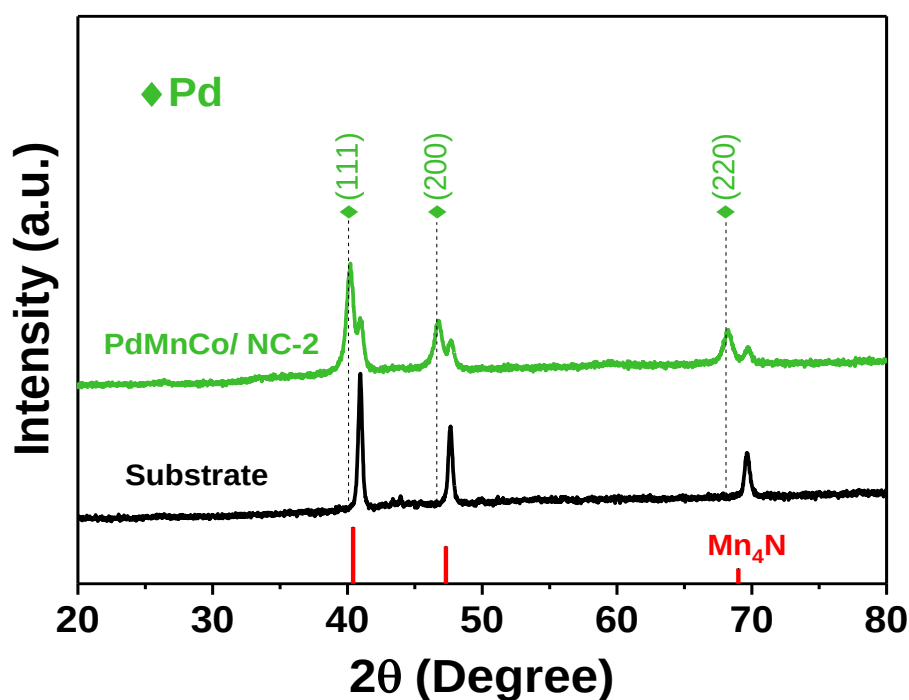


Figure S4. XRD patterns of substrate and as-prepared PdMnCo/NC-2. Typical XRD patterns of substrate and PdMnCo /NC-2 are shown in Figure S4. The red vertical lines demonstrate the diffraction angles of the Mn_4N lattice referred to JCPDS No.01–1202: 40.4° for (1 1 1), 47.3° for (2 0 0), and 68.9° for (2 2 0). Peaks of substrate (40.9° , 47.6° , and 69.6°) are similar to those of the Mn_4N , except for slight shifts to higher angles. Moreover, spectra of XRF shown in Figure S2 reveal that the Mn, Co content of the substrate is 36 % and 34.31%, respectively. Since no Co-based peaks are detected in the XRD pattern, the shifts of angle can be attributed to the replacing of Mn atoms by Co atoms in Mn_4N lattice. Thus, it is determined to be $(\text{Mn},\text{Co})_4\text{N}$.

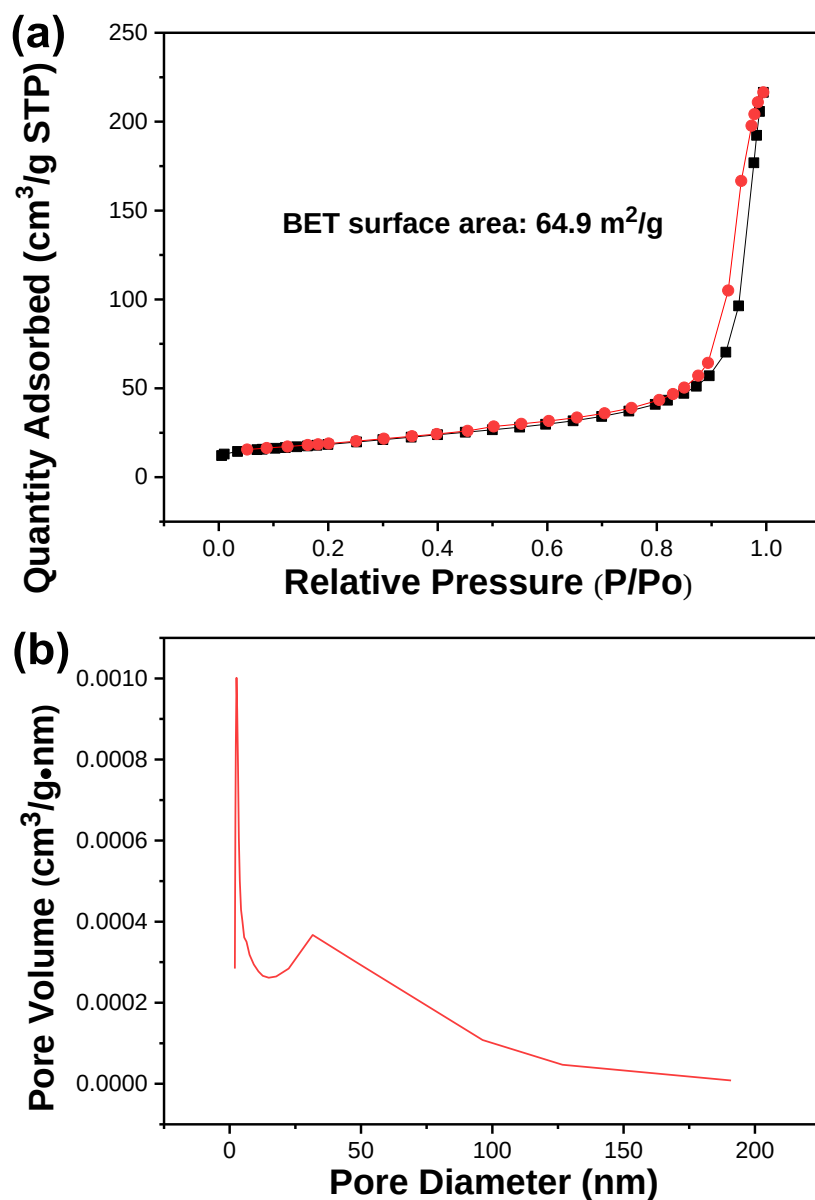


Figure S5. (a) Nitrogen adsorption isotherm at 77 K. (b) Pore size distribution calculated using the BJH equation from N₂ adsorption. The substrate obtained at 750°C showed a moderate Brunauer–Emmett–Teller (BET) specific surface area of 64.9 m²g⁻¹ and the pore size distribution results demonstrate a strong and narrow peak at 2.7 nm, which can be formed during the thermal transformation process, inheriting the high porosity of its precursor, while the wide size distribution can be attributed to the connection of several small pores.

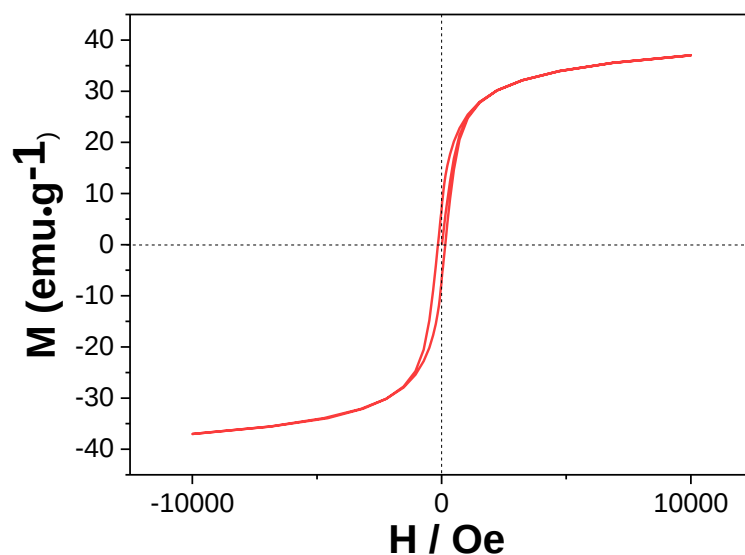


Figure S6. Room temperature M–H curves for the substrate. The saturation magnetization value M_s for the product is 37 emu g^{-1} and the coercivity value H_c is 124 Oe.

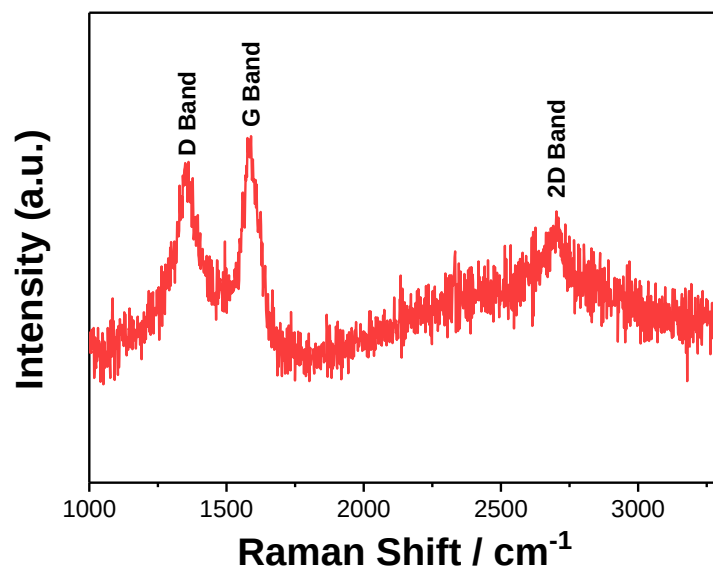


Figure S7. The Raman spectrum of the annealed products of $\text{Mn}_3[\text{Co}(\text{CN})_6]_2$. Two distinct peaks at 1358 cm^{-1} and 1586 cm^{-1} are typically assigned to the D and G bands of carbon and the broad and weak second-order band appeared at around 2700 cm^{-1} is the representative character of few-layered graphene.^{9, 10}

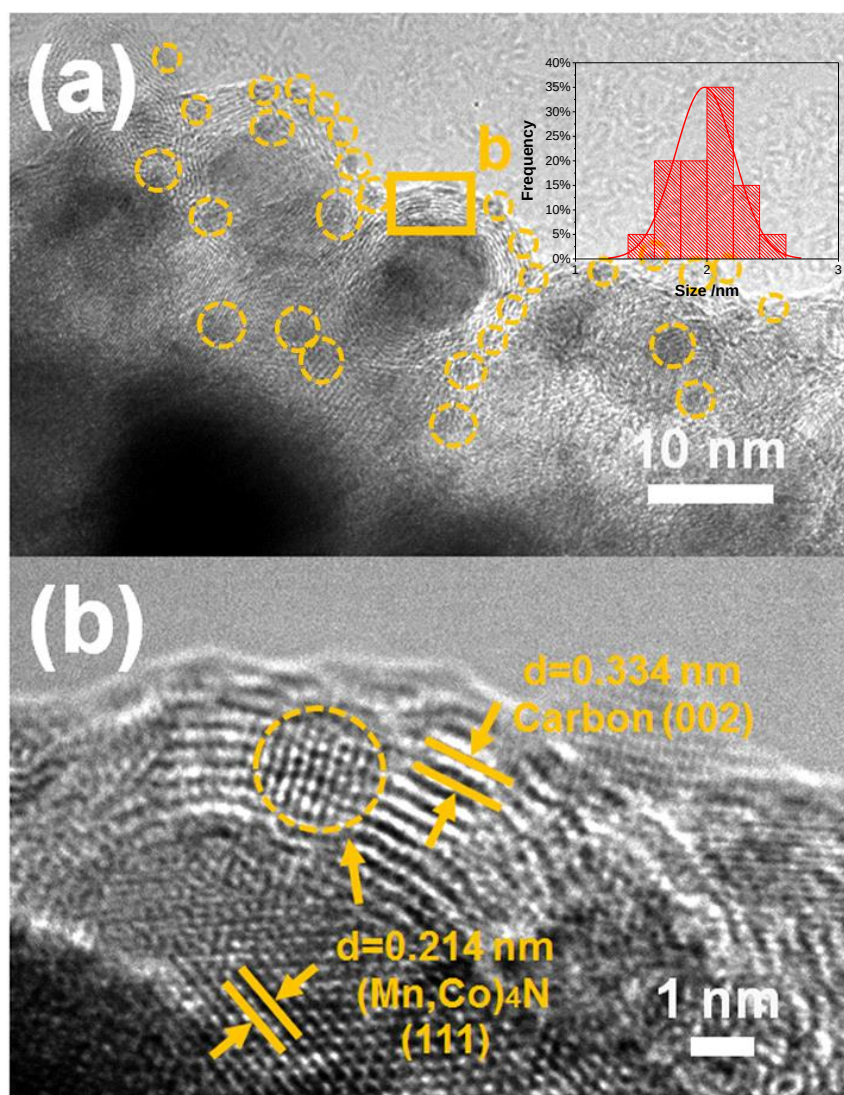


Figure S8. HRTEM image of the substrate at (a) low magnification (b) high magnification. Figure S8a illustrates that the substrate is consist of carbon wrapped core and outer carbon surface embedded indistinct ultrasmall NPs. At higher magnification, Figure S8b clearly shows that the carbon layer fringes do not wrap up the fringes of surface embedded NPs, further confirming the existence of carbon surface supported NPs model, rather than only inner core-shell structure. Besides, the supported NPs show the same fringe space with the carbon wrapped inner core, which can be related to the (111) plane of (Mn, Co)₄N.

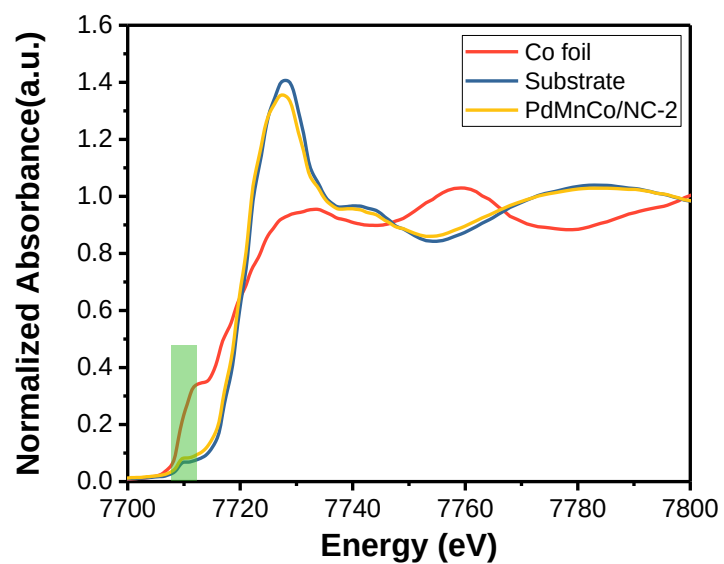


Figure S9. XANES spectra at the Co K-edge for the Co foil, substrate and PdMnCo/NC-2.

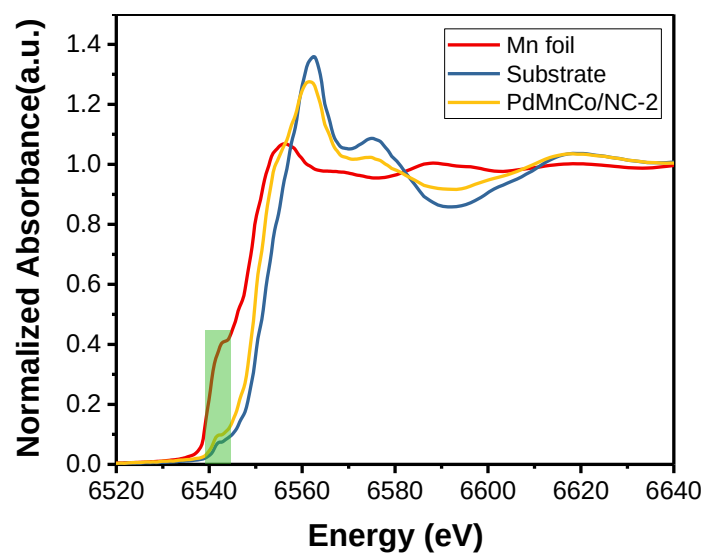


Figure S10. XANES spectra at the Mn K-edge for the Mn foil, substrate and PdMnCo/NC-2.

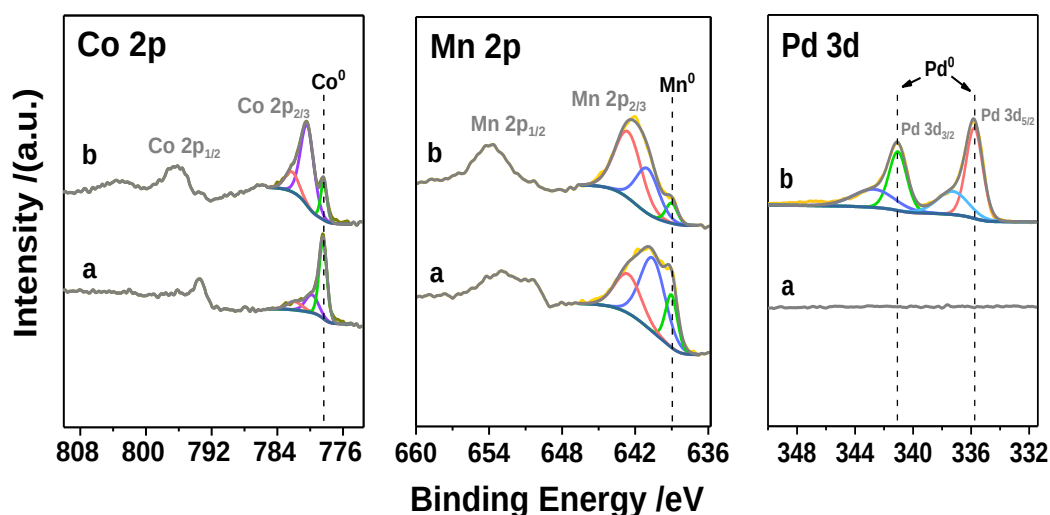


Figure S11. XPS spectra of Co 2p Mn 2p and Pd 3d of the (a) substrate (b) PdMnCo/NC-2.

Peak deconvolution of the spectra is conducted and the results are shown in Figure S8. Two peaks of Mn 2p and Co 2p located at the binding energy of 778.3 eV and 639 eV, respectively, which are close to, but a little higher than that of metallic Co (777.8 eV) and Mn (638.6 eV).^{11, 12} This shift in binding energy can be attributed to the interaction between Mn, Co and N, and the results also imply that it may possess the similarity reduction potential of metallic Mn and Co at a galvanic replacement reaction. Additionally, the binding energy of 780.4 eV and 782.2 eV correspond to Co^{2+} specie,¹³ and the peaks locate at 640.6 eV and 642.6 eV are typically assigned to Mn^{2+} and Mn^{4+} , respectively.^{14, 15} The summary of the Mn 2p, Co 2p, Pd 3d peak-fitting results are shown in Table S2.

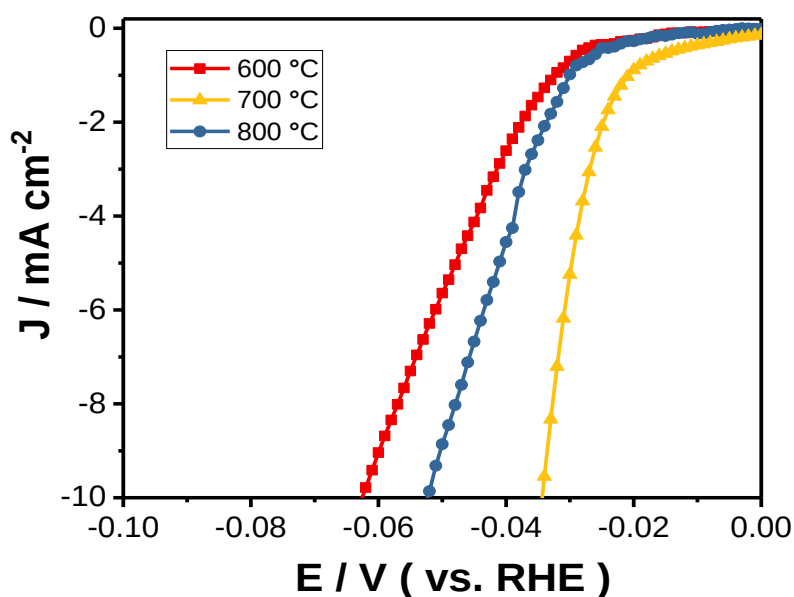


Figure S12. HER performance of PdMnCo/NC comparison with substrate that annealed at 600 °C, 700°C, and 800 °C, respectively.

The electrochemically active surface area (ECSA) of sample was usually estimated using a simple cyclic voltammetry method.^{16, 17} The ECSA of a catalyst sample is calculated from the double layer capacitance according to following formula:

$$ECSA = C_{dl} / C_s$$

However, the exact surface area of our material is difficult to obtain due to the unknown capacitive behavior (C_s) of the electrode of PdMnCo alloy with nitrogen doped carbon. Thus, we can estimate the relative surface areas of three samples, since the double layer capacitance (C_{dl}) is expected to be linearly proportional to effective active surface area for samples with similar composition and this method was employed in our previous study. The double layer capacitance is estimated by plotting the ΔJ at 0.4 V vs RHE against the scan rate, where the slope is twice of C_{dl} . The data showed that C_{dl} of PdMnCo/NC-1, PdMnCo/NC-2 and PdMnCo/NC-3 are 1.65, 11.69 and 5.46 mF/cm², respectively, which is in accordance with the results of the polarization curves.

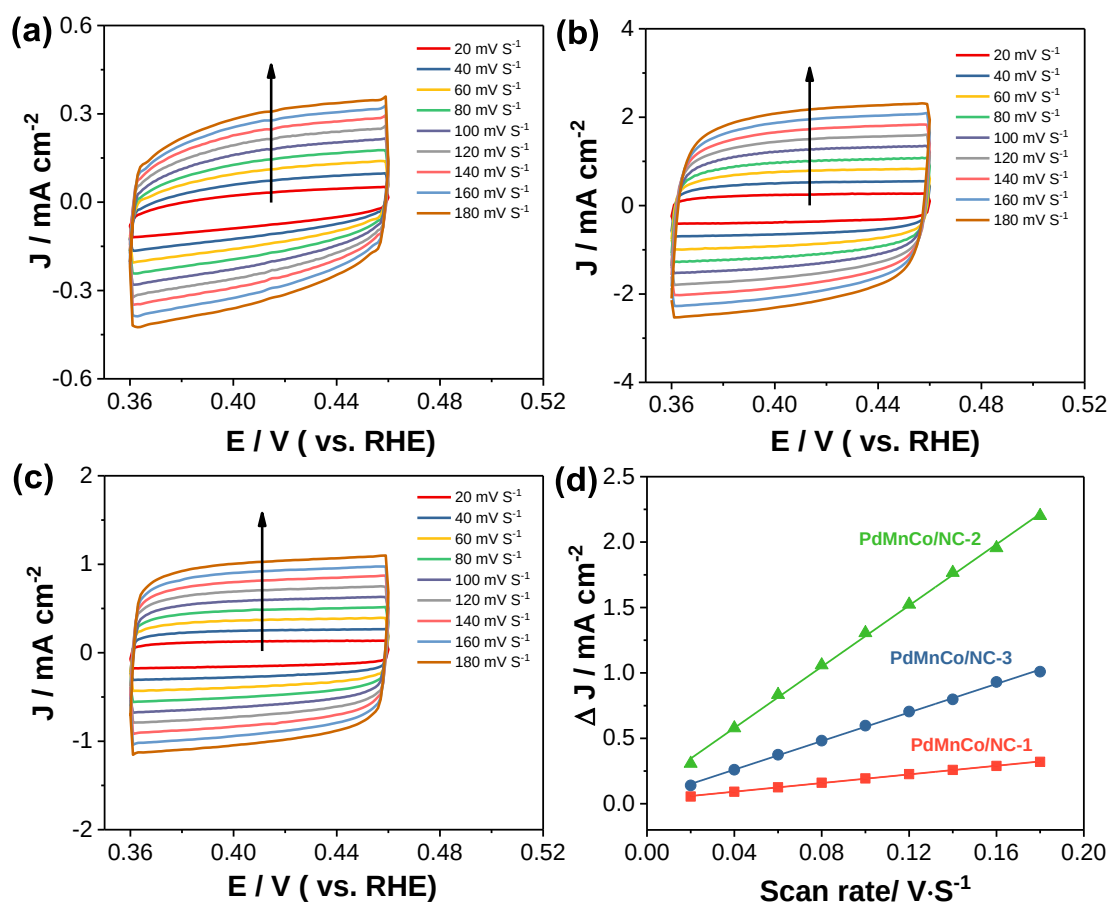


Figure S13. Cyclic voltammograms of PdMnCo/NC-1 (a), PdMnCo/NC-2 (b) and PdMnCo/NC-3 (c) within the range of 0.35 to 0.45 V vs RHE with scan rate from 20 mV/s to

180 mV/s. (d) Variation of double-layer charging currents at 0.4 V vs RHE with potential scan rate.

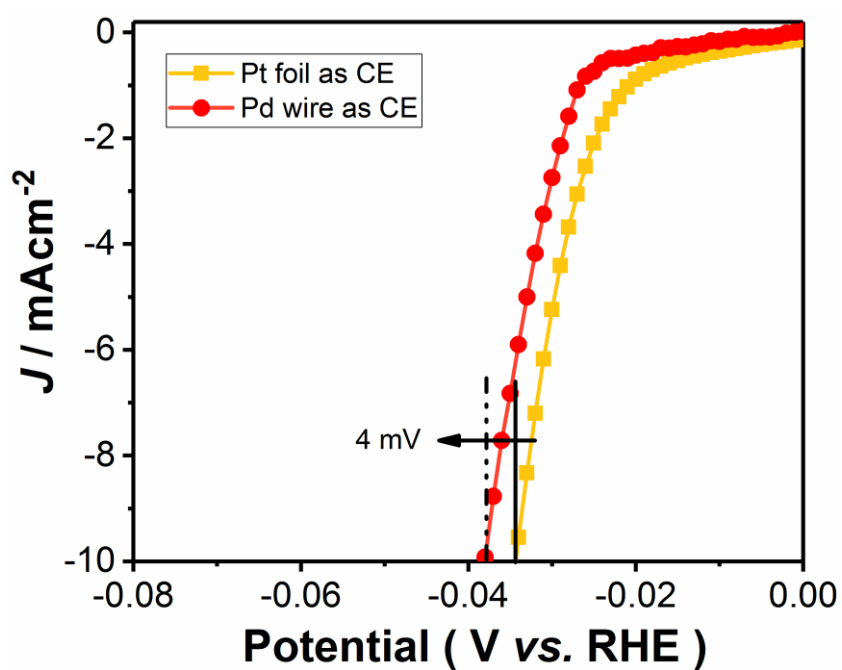


Figure S14. HER performance of PdMnCo/NC-2 comparison with Pt foil and Pd wire as counter electrode (CE), respectively.

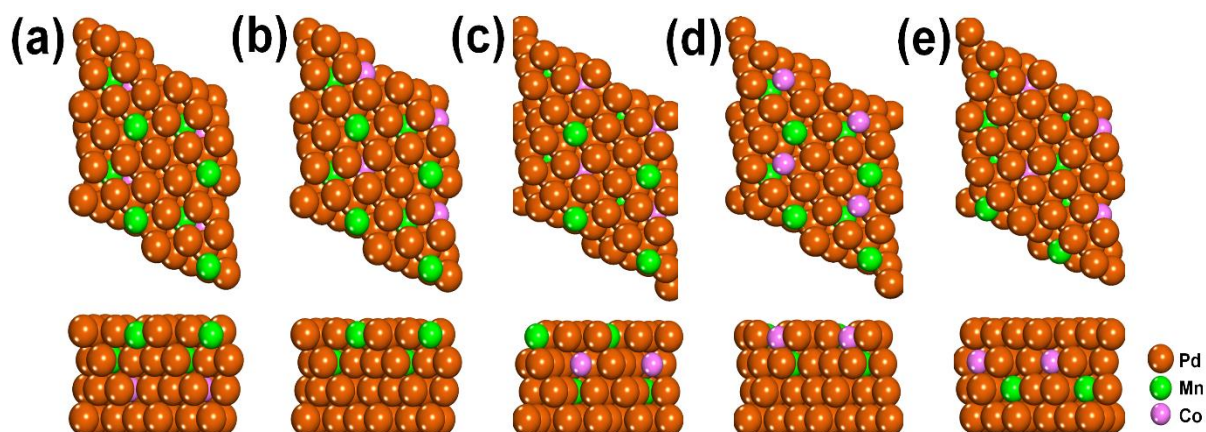


Figure S15. The top (up) and side (down) view of possible structure of ternary alloy PdMnCo (a, b, c, d, e), and the corresponding atom model is on the right.

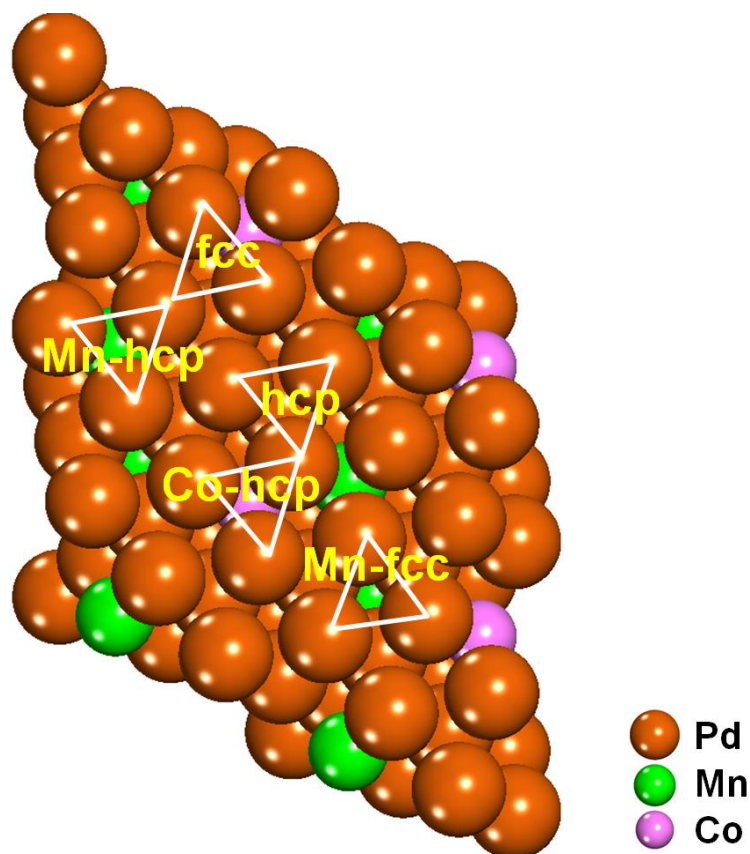


Figure S16. The possible adsorption site of hydrogen atom on the metal surface and metal/carbon interface, where the metal represents Pd(111), Pt(111), PdMnCo(111); the metal/carbon indicates PdMnCo/C, PdMnCo/NGC, PdMnCo/2NGC and PdMnCo/NPC; the hollow site is the stable adsorption site of hydrogen, five hollow sites are considered: Co(Mn, Pd)-hcp (hydrogen atom on the top of Co(Mn, Pd) atom in the second layer), Mn(Pd)-fcc(hydrogen on the top of Mn(Pd) atom in the third layer); the triangular lattice stands for the hollow site. In addition, the judgement of stable configuration of PdMnCo/NGC also utilizes this method.

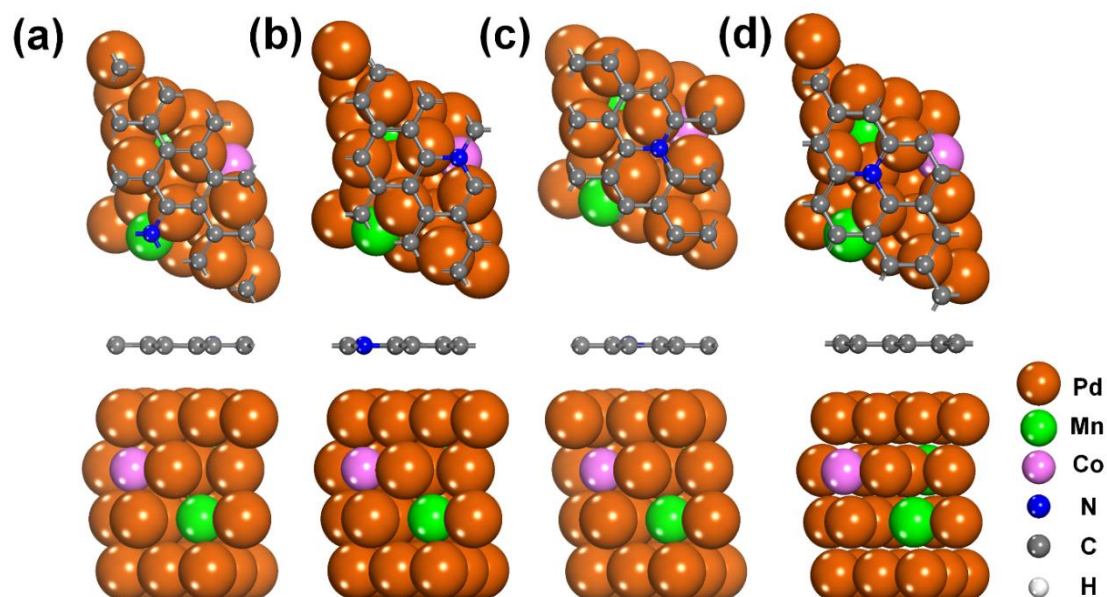


Figure S17. The four possible configurations of PdMnCo/NC: (a) Mn-fcc, (b) Co-hcp, (c) Pd-fcc, and (d) Pd-hcp site are considered, according to nitrogen atom of NC located on the above site.

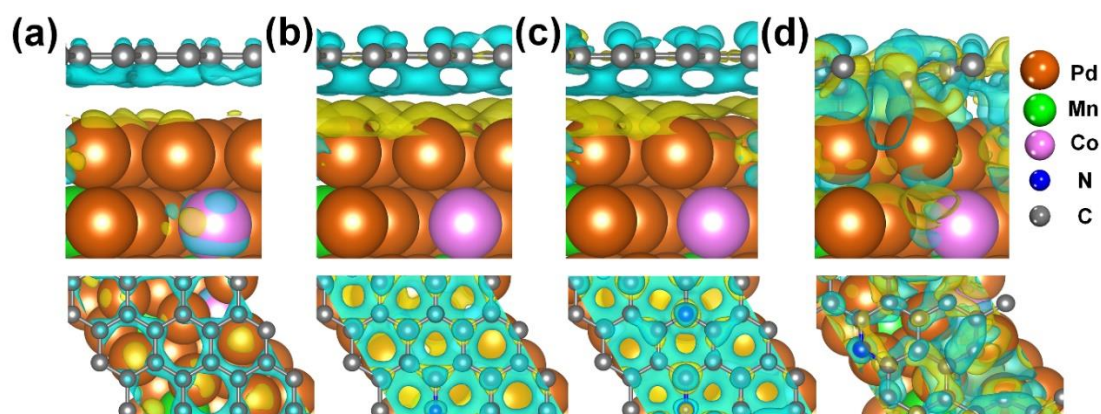


Figure S18. The charge density difference diagram between carbon and PdMnCo system for (a) PdMnCo/C, (b) PdMnCo/NGC, (c) PdMnCo/2NGC and (d) PdMnCo/NPC; yellow and cyan iso-surface represent electron accumulations and electron depletions, respectively; the iso-surface level is $0.0009e/\text{bohr}^3$. Charge density difference (Figure 6d-f, and S17a-c)

combined with Bader analysis (Table S7) confirm that charge-transfer from carbon to PdMnCo surface increases with the augment of nitrogen concentrations, promoting the reduction of adsorbed hydrogen.

3. Supplementary Tables

Table S1. Pd-based catalysts for HER in acid media

Catalyst	Loading amount (mg cm ⁻²)	Counter electrode	Overpotential at 10 mA cm ⁻² (mV)	Reference
Pd-CN _x	0.0723	Pt wire	55	18
Pd ₄ Se	0.28	Pt foil	182	19
Pd/GO	-	Pd wire	>100	20
CoPd@NC	0.285	Pt wire	80	21
PdCu ₃	0.285	Pt wire	>69	22
Ag@PdAg	0.408	Pt foil	93	23
PdPS	1~2	Pt foil	90	24
PdMnCo/NC-2	0.285	Pt foil	34	<i>This work</i>
PdMnCo/NC-2	0.285	Pd wire	38	<i>This work</i>

Table S2. Summary of the Mn 2p, Co 2p, Pd 3d peak-fitting results

Sample	Substrate		PdMnCo/NC	
	K.E. [eV]	At.%	K.E. [eV]	At.%
Mn ⁰	639.02	0.79	639.01	0.32
Mn ²⁺	640.56	2.29	640.99	1.39
Mn ⁴⁺	642.58	1.28	642.59	2.38
Co ⁰	778.43	1.04	778.47	0.56
Co ²⁺	779.79 / 781.89	0.62	780.36 / 782.21	1.41
Pd ⁰	-	0	335.85 / 341.06	1.37
Pd ²⁺	-	0	338.15 / 342.9	0.17

Table S3. The energy and relative energy of five possible PdMnCo configurations basing on PBE functional.

Conf.	<i>E</i> /eV	ΔE /eV
a	-148.82	0.54
b	-148.87	0.51
c	-149.05	0.33
d	-148.4	0.98
e	-149.38	0

Based on this ternary alloy PdMnCo, the five possible sites for hydrogen adsorption and N atom of NGC (N atom substituting C atom in pure carbon) covering on the top of metal surface are considered in Figure S11. The corresponding structure and energy about NGC placing on the top of PdMnCo surface in Figure S12 and Table S3, the difference of energy is very little, among Mn-hcp configuration is lowest of all only by 0.01eV. Therefore, the latterly stable configurations of PdMnCo/C system including PdMnCo/2NGC, PdMnCo/C and PdMnCo/NPC are referring to the stable PdMnCo/NGC system.

Table S4. The energy and relative energy of four configurations for PdMnCo/NGC based on PBE+optB88 functional.

Conf.	E/eV	$\Delta E/\text{eV}$
fcc	-258.77	0.01
hcp	-258.77	0.01
Co-hcp	-258.77	0.01
Mn-hcp	-258.78	0

The possible adsorption sites of hydrogen atom on the metal surface are referred to Figure S11, and the corresponding adsorption energies are summed to Table S4 based on the PBE functional firstly. To compare hydrogen adsorption energy with PdMnCo/NC system conveniently, the stable hydrogen adsorption sites of metal surface are computed again based on PBE+optB88 functional in Table S5.

Table S5. The adsorption energy (ΔE), Gibbs free energy (ΔG) and bond length (d) between hydrogen atom and Pd atom by PBE functional for graphene, Pt (111), Pd (111), and PdMnCo system.

System	site	$\Delta E/\text{eV}$	$\Delta G/\text{eV}$	$d/\text{\AA}$
Graphene	top	1.45	1.69	1.13
Pt (111)	fcc	-0.49	-0.25	1.87
	hcp	-0.43	-0.19	1.87
Pd (111)	fcc	-0.58	-0.34	1.81
	hcp	-0.53	-0.29	1.81
PdMnCo	fcc	-0.55	-0.31	1.79
	hcp	-0.48	-0.24	1.78
	Mn-hcp	-0.51	-0.27	1.79
	Co-hcp	-0.45	-0.21	1.78
	Mn-fcc	-0.48	-0.24	1.77

Table S6. The adsorption energy (ΔE), Gibbs free energy (ΔG) and bond length(d) of hydrogen atom by PBE+optB88 functional for graphene, Pt (111), Pd (111), PdMnCo, PdMnCo/C, PdMnCo/NGC, PdMnCo/2NGC and system.

System	site	$\Delta E/\text{eV}$	$\Delta G/\text{eV}$	$d/\text{\AA}$
Graphene	top	1.49	1.73	1.13
Pt (111)	fcc	-0.39	-0.15	1.88
Pd (111)	fcc	-0.5	-0.26	1.82
PdMnCo	fcc	-0.48	-0.24	1.8
PdMnCo/C	fcc	-0.42	-0.18	1.78
	hcp	-0.35	-0.11	1.78
	Mn-hcp	-0.33	-0.09	1.79
	Co-hcp	-0.3	-0.07	1.78
	Mn-fcc	-0.36	-0.12	1.77
PdMnCo/NGC	fcc	-0.42	-0.18	1.79
	hcp	-0.35	-0.11	1.78
	Mn-hcp	-0.36	-0.12	1.79
	Co-hcp	-0.31	-0.07	1.78
	Mn-fcc	-0.36	-0.12	1.77
PdMnCo/2NGC	fcc	-0.39	-0.15	1.79
	hcp	-0.32	-0.08	1.78
	Mn-hcp	-0.33	-0.09	1.79
	Co-hcp	-0.29	-0.05	1.79
	Mn-fcc	-0.34	-0.1	1.77
PdMnCo/NPC	fcc	-0.03	0.21	1.71

hcp	-0.14	0.1	1.73
Mn-hcp	-0.11	0.13	1.76
Co-hcp	0.04	0.28	1.73
Mn-fcc	-0.24	0	1.74

Table S7. Difference of interlayer spacing with and without hydrogen atom for the PdMnCo/C, PdMnCo/NGC, PdMnCo/NPC by PBE+optB88 functional. $d_{\text{PdMnCo/C w/o H}}$ and $d_{\text{PdMnCo/C w H}}$ are the distance between graphene (NG, NP) and PdMnCo without and with hydrogen at the interface, respectively.

No./e	PdMnCo/C	PdMnCo/NGC	PdMnCo/2NGC	PdMnCo/NPC
$d_{\text{PdMnCo/C w/o H}} (\text{\AA})$	3.22	3.22	3.25	2.95
$d_{\text{PdMnCo/C w H}} (\text{\AA})$	3.39	3.4	3.41	3.03

Table S8. Charge change of hydrogen atom, three Pd atoms connected with hydrogen atom, Mn&Co atoms, carbon or NC by PBE+optB88 functional. Positive (+) and negative (-) number represent accumulated and depleted electrons, respectively. “/” indicates none.

No./e	Pd (111)	PdMnCo	PdMnCo/C	PdMnCo/NGC	PdMnCo/2NGC	PdMnCo/NPC
H	0.09	0.09	0.09	0.1	0.1	0.08
Pd	-0.03	0.17	0.18	0.24	0.25	0.09
Mn&Co	/	-2.15	-2.15	-2.14	-2.14	-2.14
C/N	/	/	-0.05	-0.26	-0.3	0.2

Reference

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