Supporting information for:

Direct Immobilized Atomically Dispersed Pt Catalyst by Suppressing

Heterogeneous Nucleation at -40 °C

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Materials and methods:

1. Materials

Chloroplatinic acid (H₂PtCl₆·6H₂O, AR, Pt \geq 37.5%, Aladdin), absolute ethanol (C₂H₅OH, 99.8%, Aladdin), NMC powders (8.0 at.% Nitrogen, XFNANO) and Ultrathin carbon film on holey carbon (400mesh, Cu, Ted Pella Inc) was were used as received without any further purification.

2. Preparation of supported metal catalysts at different temperature.

Typically, NMC or other substrates was dispersed in ethanol absolute by sonication for 30 min forming a homogenous dispersion (~ 2 mg mL⁻¹) and stirring at -40 °C for another 30 min. Then, 300μ L of H₂PtCl₆ solution (0.1 M) was add into pre-cooled NMC ethanol dispersion (~ 2 mg mL⁻¹, -40 °C) by one-shot injection with the final concentration of metal precursors about 0.5 mM. The reaction mixture solution was

then continuously stirred at -40 °C for another 12 h, to ensure the sufficient anchoring of atomic Pt species. Then, this Pt/NMC-LT sample was rinsed and collected by vacuum filtration at -40 °C and dried naturally at RT. Control experiments was conducted for Pt/MMC-RT sample with identical conditions except the reaction temperature of RT. Moreover, Ir/NMC-LT, Ir/NMC-RT, Rh/NMC-LT, Rh/NMC-RT, Pt/MC-LT, Pt/MC-RT, Pt/XC-LT and Pt/XC-RT have been further synthesized analogously.

3. XRD characterizations

Powder XRD patterns were acquired at room temperature and 8° min⁻¹, using an X-ray diffractometer (D/max 2500V) at an operating voltage and current of about 40 kV and 150 mA, respectively.

4. STEM characterizations

Aberration-corrected high-angle annular dark field-STEM images were acquired on a JEM-ARM200F transmission electron microscope operated at 200 kV.

5. ICP-MS characterizations

The Pt-loading contents of Pt/NMC-LT and Pt/NMC-RT were measured by ICP-MS measurements (ELAN DRC-e). As confirmed by the ICP-MS test, the Pt-loading contents were 1.58% and 1.70%, respectively.

6. XPS characterizations

XPS measurements were obtained using an X-ray photoelectron spectrometer (Escalab 250Xi) equipped with an Al K α radiation source (1487.6 eV) and hemispherical analyzer with pass energy of 30.0 eV and an energy step size of 0.05 eV. The binding

energy of the C 1s peak at 284.8 eV was considered as an internal reference. Spectral deconvolution was performed by Shirley background subtraction by using a Voigt function convoluting the Gaussian and Lorentzian functions.

7. XAFS experiments and data processing

XAFS measurements at the Pt L₃-edge were carried out at the BL14W1 station in the Shanghai Synchrotron Radiation Facility (SSRF) and data analysis was performed by the IFEFFIT software package according to the standard data analysis procedures.^[1, 2] And the X-ray absorption data at the Pt L-edge of samples were recorded at room temperature and exposed to air, transmission mode for the Pt foil while and fluorescence mode for the samples. The electron beam energy was 3.5 GeV, and the stored current was 260 mA (top-up). A 38-pole wiggler with a maximum magnetic field of 1.2 T was inserted into the straight section of the storage ring and used. The XAFS data were collected using a fixed-exit, double-crystal Si (111) monochromator. A multi-element (7) Ge solid-state detector was used to collect the fluorescence signals, and the energy was calibrated with Pt foil. The photon flux at the sample position was 2.5×10^{12} photons per second.

After the background subtraction and normalization procedures using standard routines with default parameters, the spectra were calibrated and averaged, the pre-edge background was subtracted, the post-edge was normalized, and the data were phase corrected. The Fourier transformation of the k^2 -weighted EXAFS oscillations, $k^2 \cdot \chi(k)$, from the *k* space to the R space was performed over a range of approximately 3-9 Å⁻¹, to obtain a radial distribution function. In addition, the data fitting was performed by Artemis program available in the IFEFFIT package.

8. Electrocatalytic measurements

For the preparation of catalyst ink, Pt/NMC-LT (10 mg), Pt/NMC-RT (10 mg) and commercial Pt/C (20 wt%, 2 mg) catalysts were dispersed into a mixture solution (800 ul of ethanol, 150 ul of ultrapure water and 50 ul of 5wt% Nafion solution), respectively. Then corresponding amounts (18.6, 17.3 and 14.7 ul) of various catalyst inks were uniformly loaded onto freshly polished glassy carbon electrodes (5 mm in diameter) to form work electrodes, maintaining the loading of Pt element at 15 ug cm⁻².

All HER-related electrochemical tests were performed in a conventional threeelectrode electrochemical cell using an Autolab potentiostat (PGSTAT-204N) equipped with the Nova 1.11 software in 0.5 M H₂SO₄. To accelerate the diffusion of H₂ gas bubbles formed at the catalyst surface, a rotating-disk glassy-carbon electrode was used as the working electrode at 1600 rpm, while a carbon rod electrode and Ag/AgCl (with saturated KCl as the filling solution) were used as the counter and reference electrodes, respectively. All polarization curves were calibrated to the reversible hydrogen electrode according to the following equation: $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059*pH$, with an IR compensation level of 90%. In addition, accelerated durability test (ADT) were carried out at the voltage range of +0.3 to -0.1 V (vs. RHE) for 5000 cyclic voltammetry cycles with a scan rate of 100 mV s⁻¹ in 0.5 M H₂SO₄.

Supplementary Text:

1. DFT calculations.

First-principles calculations were performed based on density functional theory (DFT) as implemented in the Vienna *ab-initio* simulation package (VASP).^[3, 4] The projector-augmented-wave (PAW) method was utilized to describe the interactions between the ionic cores and the valence electrons.^[5, 6] The general gradient approximation of Perdew-Burke-Ernzerhof (PBE-GGA) was employed to treat the electronic exchange-correlation effects.^[7] Electronic wave functions were expanded using a plane wave basis set with an energy cutoff of 450 eV. Bader charge analysis was also performed to quantitatively estimate the charge transfer for reaction configurations.^[8, 9]

Periodic boundary conditions were used to construct models of nitrogen-doped mesoporous carbon without vacancy defects (WVD), with single point defects (SPD), double point defects (DPD) and hole vacancy defects (HVD). The thickness of vacuum layer was set to be at least 18 Å to avoid periodic interactions. During the geometrical optimization, the DFT-D3 method was adopted to include van der Waals interactions.^[10] During structure relaxations for Pt adsorption on NMC substrate, the Brillouin zone was sampled using a Monkhorst-Pack scheme.^[11] The ionic relaxations were performed until the force on each atom was less than 0.05 eV Å⁻¹ and convergence criterion for the self-consistent electronic minimization loop was set to 10⁻⁵ eV. Bader charge analysis was carried out to quantitatively calculate the charge transfer for Pt atoms in reaction with ethanol molecules in the reaction mixture.^[12, 13]

2. Ab-initio molecular dynamics (AIMD) simulations.

Our AIMD simulations were performed based on the Born-Oppenheimer approximation using a Nose–Hoover thermostat, with a time step of 1 fs. All the AIMD

simulations were performed within the NVT ensemble at a temperature of -40 °C or RT. The initial volume of ethanol liquid at different temperatures was obtained by the relation between ethanol density and temperature ($\rho[g/cm^3] = -8.4618 \times 10^{-4} T [^{\circ}C] + 0.8063$, R² = 0.99999). ^[14] The dangling bonds of NMC substrate in simulations were hydrogen saturated. To better describe the reaction at steady state, AIMD simulations were carried out at the target temperature for 30 ps, and the time that has been observed to be sufficient for simulating Pt diffusions and initial nucleation process from which Pt-Pt dimer is formed.

The constrained minimization technique, as implemented in Atomic Simulation Environment (ASE),^[15, 16] has been shown to be accurate for evaluating the reaction barriers in various catalytic reactions.^[17-19] Thus, we have used the technique to calculate nucleation barriers of Pt-Pt dimerization in the ethanol and NMC substrate reaction mixture and H-H association barriers on Pt@NMC-SPD site. Force convergence criteria was set to 0.08 eV Å⁻¹, and a 0.03 Å step was used during searching the transition state.

3. Binding energy of Pt atom in direct interaction with ethanol molecules.

$$\Delta E_{\rm PE} = [E_{\rm DFT}(\text{Pt in } \text{Pt}_{3c}/\text{Pt}_{4c}) - E_{\rm DFT}(\text{ethanol}+\text{NMC}) - E_{\rm DFT}(\text{Pt})]$$

where $E_{DFT}(Pt \text{ in } Pt_{3c}/Pt_{4c})$, $E_{DFT}(ethanol+NMC)$ and $E_{DFT}(Pt)$ are the DFT calculated total energies of Pt in Pt_{3c} or Pt_{4c} configurations in the ethanol and NMC reaction mixture, ethanol and NMC reaction mixture and isolated Pt atom, respectively. The atomic configurations of Pt atom in the reaction mixture were randomly selected from the AIMD simulations after the system reached a steady state.

4. Energy difference for detachment of Pt atom from ethanol to NMC

$$\Delta E_{\rm PD} = E_{\rm DFT}({\rm Pt}@{\rm NMC} + {\rm ethanol}) - E_{\rm DFT}({\rm Pt}@{\rm ethanol} + {\rm NMC})$$

where $E_{DFT}(Pt@NMC + ethanol)$ and $E_{DFT}(Pt@ethanol + NMC)$ are the DFT calculated total energies of one Pt adsorbed on NMC with surrounding ethanol and Pt in ethanol with NMC substrate, respectively.

5. DFT calculations of adsorption energy of single Pt atom or Pt dimer on NMC

$$\Delta E_{\text{Pt}} = E_{\text{DFT}}(\text{Pt-dimer}@\text{NMC}) - E_{\text{DFT}}(2\text{Pt}@\text{NMC})$$

where E_{DFT} (Pt-dimer@NMC) and E_{DFT} (2Pt@NMC) are the DFT calculated total energies of Pt dimer on NMC substrate and two isolated Pt atoms on NMC substrate, respectively.

6. DFT calculations of Hydrogen Gibbs free energy.

Generally, the overall HER (H⁺ + e⁻ \rightarrow 1/2H₂) can be separated into two pathways described by either the Volmer-Heyrovsky or the Volmer-Tafel mechanism.^[20, 21] The Gibbs free energy of adsorbed H atom (ΔG_H) in the HER is widely used to assess the catalytic activity of a catalyst, and the closer to zero, the better performance a catalyst will show. The ΔG_H can be evaluated by the formula:

$$\Delta G_{\rm H} = \Delta E({\rm H}) + \Delta E_{\rm ZPE} - T\Delta S_{\rm H}$$

where $\Delta E(H)$, ΔE_{zPE} and ΔS_{H} are the adsorption energy, zero-point energy (ZPE) change and entropy change of adsorbed H atom, respectively. Here, the first term is

$$\Delta E(\mathbf{H}) = [E_{\text{DFT}}(n\mathbf{H} @ \text{surface}) - E_{\text{DFT}}(\text{surface}) - \frac{n}{2}E_{\text{DFT}}(\mathbf{H}_2)] / n$$

where $E_{\text{DFT}}(n\text{H}@\text{surface})$ and $E_{\text{DFT}}(\text{surface})$ are the total energies of the surface with and without H atom adsorption, and *n* is the number of the adsorbed H atoms on the catalyst

surface. The ZPE change is calculated as $\Delta E_{_{ZPE}} = E_{_{ZPE}}(H^*) - 1/2E_{_{ZPE}}(H_2)$, in which $E_{_{ZPE}}(H^*)$ and $E_{_{ZPE}}(H_2)$ are the ZPE of an adsorbed H atom and H₂ in the gas phase, and our calculated ZPE of H₂ molecule is about 0.277 eV, in good agreement with previous theoretical results.^[22, 23] In view of the negligible vibrational entropy of the adsorbed H atom (normally only several meV), the entropy change is mostly from the contribution of H₂ molecule, $\Delta S_{_{H}} = S(H^*) - 1/2S_{_{H_2}}^0 \approx -1/2S_{_{H_2}}^0$, where $S_{_{H_2}}^0$ is the entropy of H₂ molecule in the gas phase at standard condition. For comparison, the (4 × 4) four layers Pt (111) slab, with the bottom two layers fixed, was used to calculate the activity of typical Pt catalyst. Our calculated $\Delta G_{_{H}} \sim -0.094$ eV, with hydrogen adsorbed on fcc-hollow site, was in good agreement with previous theoretical work.^[24]



Figure S1. HAADF-STEM images of (a) Ir/NMC-LT, (b) Ir/NMC-RT, (c) Rh/NMC-LT and (d) Rh/NMC-RT, scale bar: 2 nm.



Figure S2. HAADF-STEM images of (a, b) Pt/MC-LT, (c, d) Pt/MC-RT, scale bar: 10 nm for (a) and (c); 2 nm for (b) and (d).



Figure S3. HAADF-STEM images of (a, b) Pt/XC-LT, (c, d) Pt/XC-RT, scale bar: 10 nm for (a) and (c); 2 nm for (b) and (d).



Figure S4. Atomic configurations of the three-coordinated-Pt (Pt_{3c}) and fourcoordinated-Pt (Pt_{4c}) structures. C, H, Pt and O atoms are depicted by gray, white, blue and red spheres, respectively. Rest of the atoms in the ethanol liquid are shown by stick model. The structures in (a) and (b) are obtained by AIMD simulations when the systems reach steady state.



Figure S5. (a) Schematic illustration of the AIMD configuration of one Pt in Pt_{3c} configuration and the other Pt in Pt_{4c} configuration in the reaction mixture. (b) and (c) show the distance (red line) between two Pt atoms and the fluctuation of the total energy (blue line) as a function of simulation time at temperature -40 °C and RT, respectively. During the 30 ps AIMD simulations, the potential energy quickly decreases and gradually reach convergence, indicating that the simulation time is sufficient for the reaction system to reach equilibrium state.



Figure S6. Comparison of the nucleation kinetic rate constant. The rate constant was calculated by equation $k \sim k_B T/h \cdot exp(-\Delta E_a/k_B T)$ (k_B is Boltzmann constant, T is reaction temperature, *h* is Planck constant, E_a is transition state barrier) and the scale factor *R* was defined as k_{RT}/k_{-40} °_C. Here, $E_a(-40 \text{ °C})$ and $E_a(\text{RT})$ were defined as Pt-Pt dimer nucleation barrier at -40 °C and RT, respectively. (a), (b), (c) and (d) show the scale factor *R* for different relations between $E_a(-40 \text{ °C})$ and $E_a(\text{RT})$ as a function of barrier $E_a(\text{RT})$. Obviously, the nucleation reaction at RT possessed extremely large kinetic rate constants than that at -40 °C, which indicating that the low temperature condition could effectively suppress the Pt nucleation formation in the reaction mixture.



Figure S7. AIMD simulations of one Pt surrounded by ethanol and another Pt located on NMC substrate in the reaction mixture. (a)/(d) and (b)/(e) show the initial/final atomic configurations for AIMD simulations at temperatures -40 °C and RT, respectively. (c) and (f) show the distance (red line) between two Pt atoms and the fluctuation of the total energy (blue line) as a function of simulation time at temperatures -40 °C and RT, respectively.



Figure S8. The SEAD patterns and corresponding HAADF-STEM images of (a, d) Pt/NMC-LT, (b, e) Pt/NMC-LT and (c, f) pure NMC, scale bar: 10 nm for (a), (b) and (c); 2 nm for (d), (e) and (f).



Figure S9. N 1s XPS spectra of Pt/NMC-LT and Pt/NMC-RT.



Figure S10. Schematic diagrams of Pt single atom from Pt_{3c} configuration to NMC substrate. (a) Top and side view of Pt from Pt_{3c} configuration to NMC-SPD site. (b) Top and side view of Pt from Pt_{3c} configuration to NMC-DPD site. C, N, Pt, O and H atoms are represented as brown, blue, light blue, red and white spheres, respectively.



Figure S11. Schematic diagrams of Pt single atom from Pt_{4c} configuration to NMC substrate. (a) Top and side view of Pt from Pt_{4c} configuration to NMC-SPD site. (b) Top and side view of Pt from Pt_{4c} configuration to NMC-DPD site. C, N, Pt, O and H atoms are represented as brown, blue, light blue, red and white spheres, respectively.



Figure S12. The EIS spectra of Pt/NMC-LT, Pt/NMC-RT and Pt/C catalysts under HER reaction conditions in $0.5 \text{ M H}_2\text{SO}_4$ solution.



Figure S13. HAADF-STEM images of Pt/MXC-LT after ADT tests, scale bar: 10 nm for (a); 2 nm for (b).



Figure S14. Polarization curves of Pt/C (collected before and after 5000 CV cycles) in $0.5M H_2SO_4$.



Figure S15. Tafel plots of the Pt/NMC-LT, Pt/NMC-RT and Pt/C (collected before and after 5000 CV cycles) in 0.5M H₂SO₄.



Figure S16. Schematic of various defected SPD/DPD/HVD configurations of NMC substrate that are considered for studying the high HER activity of the Pt/NMC system. C and N atoms are represented as brown and blue spheres, respectively.



Figure S17. DFT calculated binding energies of H adsorption on NMC-SPD sites as a function of the H coverage. The optimized structures were also shown as insets. C, N, Pt and H atoms are represented as brown, blue, light blue and white spheres, respectively. Here, for comparison, we also show the configurations (black dotted squares) discussed in our previous work.^[25]



Figure S18. The calculated activation barriers of H-H association reactions for Pt single atom located at NMC-SPD sites. (a) and (b) correspond to different NMC-SPD atomic structures. The DFT optimized structures of initial state (IS), transition state (TS) and final state (FS) are shown. C, N, Pt and H atoms are represented as brown, blue, blue and white spheres, respectively. Here, the pathway resented in panel (b) have been discussed in our previous work,^[25] and is shown here for comparison.

Table S1. Pt L_3 -edge EXAFS fitting results for Pt_1 /NMC and the reference of Pt/NMC and Pt foil. N, coordination number, R, distance between absorber and backscatter atoms.

Sample	Path	Ν	R(Å)
Pt/NMC-LT	Pt-C (N,O)	5.9	1.98(5)
Pt/NMC-RT	Pt-Pt Pt-C (N,O)	7.2	2.25(6)
Pt foil	Pt-Pt	12	2.76(3)

Configuration	$\Delta E_{\rm PE}({ m eV})$	Bader charge (<i>e</i>)	Boi	nd-Length	(Å)
-40 °C-Pt _{3c}	-3.809603	-0.056036	Pt-C	Pt-O	Pt-H
			2.0335	2.2212	1.5405
RT-Pt _{3c}	-3.827816	-0.058525	Pt-C	Pt-O	Pt-H
			2.0320	2.2189	1.5376
-40 °C-Pt _{4c}	-4.067643	-0.148411	Pt-C	Pt-O	Pt-H
			2.0369	2.2377	1.5499
				2.2740	
RT-Pt _{4c}	-4.105732	-0.155778	Pt-C	Pt-O	Pt-H
			2.03205	2.2311	1.5478
				2.2574	

Table S2. The DFT calculated binding energy, Bader charge and bond-length for Pt in Pt_{3c} and Pt_{4c} configurations at -40 °C and RT, respectively. A positive Bader charge indicates loss of electrons, where a negative value denotes gain of electrons.

Table S3. The fitted data of Nyquist plots. Corresponding equivalent circuits $[R_s([R_{ct}(R_1Q_1)]Q_2)]$. R_s is the solution resistance, and R_{ct} is associated with the charge-transfer resistances through electrode-electrolyte interface.

Sample	R _s	R _{ct}
Pt/NMC-LT	8.05	6.00
Pt/NMC-RT	8.16	8.30
Pt foil	8.00	11.50

Table S4. HER activity for recently reported noble metal catalysts and other atomically dispersed metal catalysts in 0.5 M H_2SO_4 (* represents 0.1M H_2SO_4). For the noble metal based catalysts, the loading was corresponding to the total content of Pt, Pd and Ru. For other kinds of catalysts, the loading was corresponding to the whole quality of catalysts.

Catalyst	Loading	Tafel slope	Overpotential	Overpotential	Ref.
			at 10 mA cm ⁻²	at 100 mA cm ⁻²	
	(mg cm ⁻²)	(mV dec ⁻¹)	(mV)	(mV)	
Pt/NMC-LT	0.010	26.3	17.0	49.8	This
					work
Pd/Cu-Pt	0.0408	25	22.8	~45	1
nanorings					
ALD Pt/NGN	0.0017	29	~38	N/A	26
SWNT/ Pt	N/A	38	27	130	27
Pt ₁ @Fe-N-C	0.0084	42	60	~90	28
Pt-GDY2	0.0047	46.6	~70	N/A	29
Pt@GTs	0.0014	24	18	N/A	30
Pt-MoS ₂ *	0.018	96	~140	N/A	31
Pt ₁ /MC	0.010	26	25	65	32
Pt-CNSs/RGO	0.0799	29	75	N/A	33
nanohybrids					
Pd@I-PtCu	N/A	20	~115	N/A	34
Ru SACs@PN	0.0033	38	24	~100	35
Ru-C ₃ N ₄ /rGO	0.0202	55	80	N/A	36
A-Ni-C	0.283	41	~50	~115	37
Co-NG	0.0901	82	147	N/A	38
Ni-doped	N/A	45	~170	N/A	39
graphene					
CoN _x /C	2.0	57	N/A	133	40
$Mo_2TiC_2T_x$ -	0.012	30	30	77	41
Pt _{SA}					
2D MoS _{2-x} O _x	N/A	67	~265	N/A	42
NiO@1T-	N/A	~150	~220	N/A	43
MoS ₂ /CFP					
monolayer	N/A	73	136	N/A	44
MoS_2					
Pt ₁ /hNCNC-	0.003	24	15	N/A	45
2.92					

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