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Ultralow-temperature photochemical synthesis of atomically

dispersed Pt catalysts for hydrogen evolution reaction

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Materials and methods:

1. Materials

Chloroplatinic acid (H₂PtCl₆·6H₂O), sulfuric acid, and isopropyl alcohol were purchased from Sinopharm Chemical Reagent Co. Ltd. Ethyl alcohol was purchased from Aladdin Industrial Corporation. Ultrathin carbon film on holey carbon (400mesh, Cu) was purchased from Ted Pella Inc. Nitrogen-doped mesoporous carbon (NMC) was purchased from Nanjing XFNANO Materials Tech Co. Ltd., and was further annealed at 900 °C in Ar for one hour to remove remained impurities.

2. Preparation of atomically dispersed Pt solution

A 1-mM H_2PtCl_6 mixed solution (20 mL) containing ethyl alcohol and deionized water at a volume ratio of 9:1 was incubated at -60 °C in a thermostat. After the solution was irradiated with UV light (wavelength: 365 nm; power density: 0.89 mW cm⁻² (measured using a PL-MW 2000 radiometer) at -60 °C in a thermostat for one hour, the atomically dispersed Pt solution was obtained.

3. Preparation of Pt₁/NMC

A 10-ml aliquot of 2 mg ml⁻¹ NMC ethyl alcohol solution was mixed with 20 ml of the prepared atomically dispersed Pt solution, and then magnetically stirred for one hour at -60 °C. The mixture was then suction filtered and washed process with mixed wthyl alcohol and water solution at -30 °C. Finally, the resultant atomically dispersed Pt adsorbed in NMC was dried and stored at room temperature.

4. Preparations of Pt nanoparticles dispersion and Pt/NMC

A 1-mM H_2PtCl_6 mixed solution (20 mL) containing ethyl alcohol and deionized water at a volume ratio of 9:1 was incubated at 25 °C in a thermostat. The solution was then irradiated with UV light (with the same density used for the preparation for atomically dispersed Pt) for one hour at 25 °C; the dispersion of Pt nanoparticles was obtained. After that, a 10-ml aliquot of 2 mg ml⁻¹ NMC ethyl alcohol solution was mixed with 20 mL of the Pt nanoparticles dispersion. After the mixture was magnetically stirred for one hour, it was suction filtered, washed and dried at 25 °C; and the Pt/NMC powder was obtained.

5. XRD characterizations

XRD (D/max 2500 V) was performed with a Cu target at 8° min⁻¹ scanning speed. The operation voltage and current were 40 kV and 150 mA, respectively.

6. TEM characterizations

TEM images were recorded on a JEOL-2100F microscope, operated at a voltage of 200 kV.

7. STEM characterizations

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

8. ICP-MS characterizations

The Pt-loading contents of Pt_1/NMC and Pt/NMC were measured by ICP-MS measurements (ELAN DRC-e). As confirmed by the ICP-MS test, the Pt-loading contents of Pt_1/NMC and Pt/NMC were 2.54% and 3.8%, respectively.

9. XPS characterizations

The XPS characterizations of Pt_1 /NMC were carried out using an X-ray photoelectron

spectrometer (Escalab 250Xi) equipped with an Al K α radiation source (1487.6 eV) and a hemispherical analyzer with a pass energy of 30.0 eV and an energy step size of 0.05 eV. The obtained data was corrected by the binding energy of C 1s peak (284.8 eV). The spectral deconvolution was performed by Shirley background subtraction using a Voigt function, and the convolution was carried out by the Gaussian and Lorentzian functions.

10. Electrocatalytic measurements

The catalyst dispersion (or ink) was prepared by mixing commercial Pt/C, Pt/NMC, or Pt₁/NMC with a 1-ml mixture containing 500 ul of isopropyl alcohol, 420 ul of water and 80 ul of 5wt% Nafion solution. For Pt₁/NMC ink, 2 mg of Pt₁/NMC was dispersed in 1-ml mixture solution; this results in Pt with a concentration of 0.1 ug ul⁻¹. After that, 20 ul of the ink was uniformly loaded onto freshly polished glassy carbon electrodes (diameter = 5 mm), and the corresponding loading content of Pt element was 10 ug cm⁻². The same experimental procedures and analyses were applied to Pt/C and Pt/NMC.

All electrochemical tests were performed in a conventional three-electrode electrochemical cell using an Autolab potentiostat (PGSTAT-204N) equipped with the Nova 1.11 software in 0.5 M H₂SO₄. A rotating-disk glassy-carbon electrode was used as the working electrode, 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 potentials measurements were calibrated to the reversible hydrogen electrode according to the following equation: $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059^{*}$ pH. To accelerate the diffusion of H₂ gas bubbles formed at the catalyst surface during the hydrogen evolution reaction, the polarization curves were recorded using a rotating-disk electrode with 90% IR compensation at the rotation rate of 1600 rpm. To test the stabilities of Pt₁/NMC, Pt/NMC and Pt/C catalysts, a total of 1000 or 5000 cyclic voltammetry sweeps were carried out at the voltage range of +0.3 to -0.1 V (versus RHE) with a scan rate of 100 mV s⁻¹ in 0.5 M H₂SO₄

11. XAFS experiments and data processing

XAFS measurements at the Pt L₃-edge were carried out in both transmission (for the Pt foil) and fluorescence (for the samples) modes at the BL14W1⁻¹ in the Shanghai Synchrotron Radiation Facility (SSRF). And the X-ray absorption data at the Pt L-edge of samples were recorded at room temperature and exposed to air. 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.

The raw data analysis was performed using the IFEFFIT software package according to the standard data analysis procedures ². The background subtraction and normalization procedures were carried out using standard routines with default parameters determined by the Athena program in the IFEFFIT software package, in which the spectra were calibrated and averaged, the pre-edge background was

subtracted, and the post-edge was normalized. Meanwhile, 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.

12. Computational Methods

DFT calculations. Our 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}. Electronic exchange-correlation effects were treated by the Perdew-Burke-Ernzerhof parameterized functional in generalized gradient approximation (PBE-GGA) ⁷. Electronic wave functions were expanded by plane wave basis sets with a kinetic energy cutoff of 450 eV.

Periodic boundary conditions were used to construct models of nitrogen-doped mesoporous carbon without defects, and with edge vacancy defects, double vacancy defects and single vacancy defects, as shown in Fig-HS1. The thickness of vacuum layers was set to at least 18 Å to avoid periodic interactions. During the geometrical optimization, DFT-D3 method was adopted to include van der Waals interactions ⁸. The convergence criterion for the self-consistent electronic minimization loop was set to 10^{-5} eV, and the ionic relaxations were performed until the force on each atom was less than 0.02 eV Å⁻¹. During the structure relaxations for Pt adsorption in NMC substrate, the Brillouin zone was sampled using a Monkhorst-Pack scheme ⁹ (3 × 3 × 1 grid meshes were used for NMC without defects and NMC with edge vacancy defects, and $4 \times 4 \times 1$ grid meshes were used for NMC with double vacancy defects and single vacancy defects). Bader charge analysis ^{10,11} was carried out to quantitatively calculate the charge transfer between the NMC substrate, adsorbed Pt atoms and adsorbed H atoms, as well as between Pt atoms and ethanol molecules.

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 AIMD simulations were performed within the NVT ensemble at a temperature of 213 K or 239 K. The initial volume of liquid ethanol at different temperatures was obtained by the relationship between ethanol density and temperature (ρ [g/cm³] = – 8.4618 × 10⁻⁴ T [°C] + 0.8063; R² = 0.99999) ¹². To better describe the reaction at steady state, AIMD simulations were carried out at the target temperature for 30 ps, 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 the atomic simulation environment (ASE) ^{13,14}, has been shown to accurately evaluate the reaction barriers in various catalytic reactions ^{15,16}. Thus, we used this technique to calculate the activation barriers of Pt-Pt dimerization in liquid ethanol as well as the H-H association barriers on single Pt atom adsorbed at NMC-SV/DV/EV site. Force convergence criteria was set to 0.05 eV Å⁻¹, and the search for the transition state was conducted at 0.02 Å step.

DFT calculations of Gibbs free energy of hydrogen. In general, the overall HER (H⁺ + e⁻ \rightarrow 1/2H₂) can be divided into two pathways according to the Volmer-Heyrovsky mechanism or the Volmer-Tafel mechanism ^{17,18}. The Gibbs free energy of adsorbed H atom ($\Delta G_{\rm H}$) in HER is widely used to assess the catalytic activity of a catalyst: a catalyst with $\Delta G_{\rm H}$ closer to zero has better performance than that with $\Delta G_{\rm H}$ farther from zero. The $\Delta G_{\rm H}$ can be calculated by the following equation:

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

Where $\Delta E(H)$, ΔE_{zPE} and ΔS_{H} are the adsorption energy, the zero point energy (ZPE)

change and the entropy change of adsorbed H atom, respectively. And $\Delta E(H)$ is described as:

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

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, respectively, and *n* is the number of adsorbed H atoms on the catalyst surface. The ZPE change can be calculated by $\Delta E_{\text{ZPE}} = E_{\text{ZPE}}(\text{H}^*) - 1/2E_{\text{ZPE}}(\text{H}_2)$;

where $E_{ZPE}(H^*)$ and $E_{ZPE}(H_2)$ are the ZPE of adsorbed H atom and H₂ in gas phase,

respectively. Our calculated ZPE of H_2 molecule is about 0.277 eV, which is in good agreement with the previous theoretical results ^{19,20}. The vibrational entropy of the adsorbed H atom (normally within several meV range) is negligible; thus, the entropy change, which is mostly due to H_2 molecule, can be calculated as follows:

 $\Delta S_{_{H}} = S(\mathrm{H}^*) - 1/2S^{_0}_{_{\mathrm{H}_2}} \approx -1/2S^{_0}_{_{\mathrm{H}_2}}$; where $S^{_0}_{_{\mathrm{H}_2}}$ is the entropy of H₂ molecule in gas phase at

standard condition. For comparison, four layers of (4×4) Pt (111) slab (bottom two layers were fixed) were used to calculate the activity of a typical Pt catalyst. As shown in Fig-H5, the calculated ΔG_H with hydrogen adsorbed on fcc-hollow site is – 0.094 eV, which is in good agreement with the previously reported data ²¹.

Binding energy of Pt atom in liquid ethanol.

 $\Delta E_{\rm PE} = [E_{\rm DFT} (n {\rm Pt} @ {\rm ethanol liquid}) - E_{\rm DFT} ({\rm ethanol liquid}) - nE_{\rm DFT} ({\rm Pt})] / n$

Where $E_{DFT}(Pt@ethanol liquid)$, $E_{DFT}(ethanol liquid)$ and $E_{DFT}(Pt)$ are the DFTcalculated total energies of Pt in liquid ethanol, liquid ethanol and isolated Pt atom, respectively, and *n* is number of Pt atom in liquid ethanol.

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

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

Where $E_{DFT}(Pt@NMC)$, $E_{DFT}(Pt@ethanol liquid)$, $E_{DFT}(NMC)$ and $E_{DFT}(ethanol liquid)$ are the DFT-calculated total energies of Pt in NMC substrate, Pt in ethanol

liquid, NMC substrate and ethanol liquid, respectively. The atomic configurations of Pt atom in ethanol liquid were randomly selected from the AIMD simulations after the system reached a steady state. NMC substrates, including NMC structures with edge vacancy defects, double vacancy defects and single vacancy defects, were used.

DFT calculations of adsorption energy of Pt atom or Pt dimer in NMC substrate. The adsorption energy of Pt atom in NMC substrate is defined as:

$$\Delta E_{\rm Pt} = [E_{\rm DFT} (n {\rm Pt} @ {\rm NMC}) - E_{\rm DFT} ({\rm NMC}) - n E_{\rm DFT} ({\rm Pt})] / n$$

Where $E_{DFT}(nPt@NMC)$, $E_{DFT}(NMC)$ and $E_{DFT}(Pt)$ are the DFT-calculated total energies of Pt in NMC substrate, NMC substrate and isolated Pt atom, respectively, and *n* is number of Pt atom. For instance, the energy difference between one Pt dimer and dispersive two Pt atoms in NMC substrate can be described as:

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

where $E_{DFT}(Pt@NMC)$, $E_{DFT}(Pt_{dimer}@NMC)$ and $E_{DFT}(NMC)$ are the DFT-calculated total energies of Pt atom in NMC substrate, Pt dimer in NMC substrate and NMC substrate, respectively.



Fig. S1. STEM images of Pt_1 /NMC. Examination of different regions revealed that almost no clusters or small particles were present in the vicinity of the isolated atoms.



Fig. S2. Size of isolated Pt for Pt_1/NMC . The size of Pt atoms was approximately 0.1 nm.



Fig. S3. XRD results of NMC, Pt_1/NMC and Pt/NMC. It was indicated that there was no nanaparticles were observed in Pt_1/NMC



Fig. S4. TEM images of (a, b) Pt/NMC and (c, d) Pt₁/NMC. Any Pt nanocrystals cannot be detected in the HRTEM images.



Fig. S5. N 1*s* XPS spectra of Pt_1/NMC . The dominant nitrogen species were pyridinic-N and graphitic-N, which served as anchored points for isolated Pt atoms.



Fig. S6. Pt 4*f* XPS spectra of Pt₁/NMC. The binding energy of Pt 4*f*_{7/2} and 4*f*_{5/2} for Pt₁/NMC is corresponded to Pt^{$\delta+$}, indicating the positive charge on Pt for Pt₁/NMC.



Fig. S7. STEM images of atomically dispersed Pt synthesized in pure ethanol solvent via the ultralow-temperature photochemical reaction.



Fig. S8. AIMD simulations of single Pt atom in ethanol liquid at (a) T = 213 K and (b) T = 298 K. Left panels: atomic configurations of Pt-three-coordinated (Pt_{3c}) model resolved by AIMD simulations when the systems reached steady state. The C, H, Pt and O atoms are depicted by gray, white, blue and red spheres, respectively. Rest of the atoms in the ethanol liquid were shown by stick model. Right panels: partial density of states of Pt *d*-orbitals, C *s* and *p* orbitals, H *s* orbital and O *s* and *p* orbitals in the beside Pt_{3c} configuration.



Fig. S9. Pt-four-coordinated (Pt_{4c}) configuration of single Pt atom in ethanol liquid at (a) T= 213 K and (b) T = 298 K. PDOS was shown as well in the right panels.



Fig. S10. Pt-Pt dimer formation barrier when two separating Pt atoms are both in Pt_{4c} configuration. Energy diagram of forming Pt-Pt dimer at 213 K at (a) 213K and (b) 298K. The initial state, transition state and final state are shown from left to right. The C, H, O and Pt atoms are depicted by gray, white, red and light blue spheres, respectively.



Fig. S11. Pt-Pt dimer formation barrier when two separate Pt atoms are both in Pt_{3c} configuration. Energy diagram of forming Pt-Pt dimer at 213 K at (a) 213K and (b) 298K. The initial state, transition state and final state were shown from left to right. The initial state, transition state and final state are shown from left to right. The C, H, O and Pt atoms are depicted by gray, white, red and light blue spheres, respectively.



Fig. S12. The Overpotential of Pt_1/NMC , Pt/NMC and Pt/C at various current density.



Fig. S13. HER activities for Pt/NMC before and after 1000 CV cycles.



Fig. S14. HER activities of commercial Pt/C before and after 1000 CV cycles.



Fig. S15. STEM images of Pt₁/NMC after stability tests.



Fig. S16. Mass activities of NMC, Pt_1/NMC , Pt/NMC, and Pt/C with same Pt loading content. The mass activity of Pt_1/MC was superior to traditional Pt/C electrode.



Fig. S17. Mass activities ratio of Pt_1/NMC and Pt/C, Pt_1/NMC and Pt/NMC before stability cycling test, respectively. The mass activity of Pt_1/NMC was more than three times greater than those of Pt/C and Pt/NMC from 40 mV to 60 mV overpotential versus RHE.

Fig. S18. Structures of the nitrogen-doped mesoporous carbon, (a) none defect (ND), (b) with edge vacancy defect (EV), (c) with double vacancy defect (DV), (d) with single vacancy defect (SV). The C and N atoms are depicted by brown and blue spheres, respectively.

Fig. S19. Reaction mechanism for the HER, the best optimized free energy ΔG_H diagrams for atomic H adsorption on Pt single atom at NMC-DV/EV sites. The free energy of hydrogen evolution on Pt (111) was included for comparison. The lower and upper Pt_{EV} red lines represented the cases with different concentrations of two and three atoms, respectively.

Fig. S20. The free energy diagram of hydrogen evolution on Pt (111) surface by our DFT result and from other DFT work ²⁰.

Fig. S21. The DFT calculated adsorption energies of H atom adsorbed on Pt_1/NMC -SV system as a function of the H coverages and the corresponding DFT optimized structures. The brown, blue, light blue and red spheres represent C, N, Pt and H atoms, respectively.

Fig. S22. PDOS of the atomically dispersed Pt adsorbed at NMC-DV site (a) before and (b) after H adsorption. The *s* and *p* orbitals of C atom, *p* orbitals of N atom, *d* orbitals of Pt atom and *s* orbital of H atom were considered. The Fermi level was shifted to zero in each panel.

Fig. S23. PDOS of the Pt adsorbed at NMC-EV site (a) without H adsorption and (b) after H adsorption. The *s* and *p* orbitals of C atom, *d* orbitals of Pt atom and *s* orbital of H atom are considered. The Fermi level is shifted to zero in each panel.

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	R factor
Pt ₁ /NMC	Pt-C (N,O)	6.3	2.06(5)	0.000368
Pt/NMC	Pt-Pt	9.8	2.75(6)	0.00106
Pt foil	Pt-Pt	12	2.76(3)	0.000860

Table S2. The binding energy of single and double Pt atoms for various forms (Pt_{3c} , Pt_{4c} , Pt_{3c} + Pt_{3c} , Pt_{3c} + Pt_{4c} , Pt_{4c} + Pt_{4c} , Pt dimer) in ethanol liquid (ΔE_{PE} in unit of eV per Pt atom) at 213 K and 298 K. The atomic configurations were selected from the typical AIMD simulations as the reaction systems reach steady state, and then the selected atomic configurations were relaxed to a local energy minimum.

System	(213K) $\Delta E_{\rm PE}$	(298K) $\Delta E_{\rm PE}$
Pt _{3c}	-3.830	-3.985
Pt_{4c}	-4.079	-4.372
$Pt_{3c} + Pt_{3c}$	-3.403	-3.667
$Pt_{4c} + Pt_{3c}$	-3.682	-3.728
$Pt_{4c} + Pt_{4c}$	-4.067	-4.085
Pt dimer	-3.871	-4.077

Table S3. The Bader charge of single Pt atom in configurations of Pt_{3c} and Pt_{4c} at 213K and 298K, respectively. The positive Bader charge indicates the loss of electrons, where a negative value indicates that the electrons are gained.

System	213K	298K
Pt-in-Pt _{3c}	+0.063 eV	+0.024 eV
Pt-in-Pt _{4c}	+0.167 eV	+0.134 eV

Table S4. HER activity for different atomically dispersed metal catalysts and Ptbased catalysts in 0.5 M H_2SO_4 . For the Pt-based catalysts, the loading was corresponding to the content of Pt loading, meanwhile, the loading of other catalysts was the whole quality of catalysts. It indicated superior HER activity for Pt₁/MC in our work with respect to previous catalysts. (*The loading of all Pt-based HER catalysts is referring to Pt element).

Catalyst	Loading* (mg cm ⁻²)	Tafel slope (mV dec ⁻¹)	Overpotential at 10 mA cm ⁻² (mV)	Overpotential at 100 mA cm ⁻² (mV)	Ref.
Pt ₁ /NMC	0.01	26	29	55	This
Pt-MoS ₂	0.027	40	52	N/A	work (22)
ALD50Pt	0.0076	29	~45	N/A	(23)
A-Ni-C	0.283	41	34	112	(24)
Co-NG	0.285	82	147	NA	(25)
CoNx/C	2.0	57	N/A	133	(26)
Ni-doped Gr	N/A	45	~180	N/A	(27)
Pt+MoS ₂	0.018	96	12	N/A	(28)
Pt-CNSs/RGO	0.078	29	~75	N/A A	(29)
Pt/MoS ₂ /CC	N/A	49	18	~75	(30)
Pt ₁ /MC	0.010	26	25	65	(31)
Pt@Te-RGO/P	PI N/A	55	100	NA	(32)
PtNiCu nanochains	0.06	28	~23	~60	(33)
Pt-Pd-Gr	0.01	10	N/A	65	(34)
Pt/carbon nanofibers	N/A	32	55	N/A	(35)
Cuboid-like Pt CNSs/rGO	- 0.17	29	75	N/A	(36)
PtNPS/CNFs	0.0149	50	175	N/A	(37)
Pd@I-PtCu	0.16	20	~115	N/A	(38)

Table S5. The energy difference for the process of Pt atom detaching from ethanol liquid to the NMC substrates (ΔE_{PD} in unit of eV per Pt atom). Negative values of ΔE_{DP} indicate that Pt atom prefers to stay in NMC substrate rather than in ethanol liquid. Both Pt_{3c} and Pt_{4c} configurations are considered, and the NMC substrate with SV/DV/EV defect sites are carefully checked.

Initial state	Final state	$\Delta E_{\rm PD} \left({\rm Pt}_{\rm 3c} \right)$	$\Delta E_{\rm PD} \left({\rm Pt}_{\rm 4c} \right)$
Pt in ethanol	Pt ₁ /NMC-SV	-1.959	-1.710
liquid			
Pt in ethanol	Pt ₁ /NMC-DV	-4.681	-4.432
liquid			
Pt in ethanol	Pt ₁ /NMC-EV	-5.326	-5.077
liquid			

Table S6. The binding energy of Pt (ΔE_{Pt} in unit of eV per Pt atom) and Bader charge of Pt single atom in NMC substrate with ND/SV/DV/EV sites. A positive Bader charge indicates a loss of electrons, whereas a negative value denotes a gain of electrons.

System	$\Delta E_{ m Pt}$	Bader charge (e)
Pt ₁ /NMC-ND	-3.087	-0.185
Pt ₁ /NMC-SV	-5.790	+0.278
Pt ₁ /NMC-DV	-8.511	+0.502
Pt ₁ /NMC-EV	-9.156	+0.319

Table S7. The calculated bond-length and Bader charge of the $Pt_1/NMC-DV$ system before and after one H atom adsorption. Here, the three C and one N atoms refers to the atoms in direct bonding state with Pt atom.

Dt /NIMC DV	Bond-Length (Å)			Bader-Charge (e)			
Pt ₁ /INMC-DV	Pt-C	Pt-N	Pt-H	C	N	Pt	Н
Before H-adsorption	1.946	2.056		-0.041	-1.194	+0.50 2	
	1.966			-0.091			
	1.982			-0.098			
After H-adsorption	1.981	2.051	1.555	-0.131	-1.158	+0.49	10.12
	1.995			-0.184			+0.12
	2.004			-0.132		5	0

Table S8. The calculated bond-length and Bader charge of the Pt_1/NMC -EV system before and after one H atom adsorption. Here, the two C atoms refer to the atoms in direct bonding state with Pt atom.

Dt /NIMC EV	Bond-Length (Å)		Bader-Charge (e)		
Pt ₁ /INIVIC-EV	Pt-C	Pt-H	С	Pt	Н
Before	2.227		-0.065	+0.211	
H-adsorption	1.888		-0.081	+0.311	
After	2.275	1 5 1 0	-0.078	10 422	10.144
H-adsorption	1.943	1.318	-0.077	+0.433	+0.144

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