## Supporting Information

# An archetype of the electron-unobstructed core–shell composite with inherent selectivity: conductive metal– organic frameworks encapsulated with metal nanoparticles

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## **Table of Contents**

Section S1. Experimental Section	3
Chemicals and Materials	3
Instrumentation	3
Synthetic Procedures	5
Section S2. Supporting Tables	8
Table S1. Concentration of as-synthesized metal NPs.	8
Table S2. Loadings of metal NPs in NPs@MOFs composites	9
Section S3. Supporting Figures	10
Fig. S1 SEM image of Pt@Ni <sub>3</sub> (HITP) <sub>2</sub>	.10
Fig. S2 Nitrogen adsorption-desorption isotherms of Ni <sub>3</sub> (HITP) <sub>2</sub> , Pt@Ni <sub>3</sub> (HITP) <sub>2</sub> , and Pt- PVP@Ni <sub>3</sub> (HITP) <sub>2</sub> .	.11
Fig. S3 Elements distribution in Pt@Ni <sub>3</sub> (HITP) <sub>2</sub> .	.12
Fig. S4 Low-mag TEM image of Au@Ni₃(HITP)₂	.13
Fig. S5 Raman spectra of Pt@Ni <sub>3</sub> (HITP) <sub>2</sub> , Pt-PVP@Ni <sub>3</sub> (HITP) <sub>2</sub> , and Ni <sub>3</sub> (HITP) <sub>2</sub>	.14
Fig. S6 Experimental PXRD pattern of Pt-PVP@Ni $_3$ (HITP) $_2$ and simulated PXRD pattern of Ni $_3$ (HITP) $_2$	. 15
Fig. S7 ORR performance of Pt NPs	.16
Fig. S8 Conductivity of Ni <sub>3</sub> (HITP) <sub>2</sub> and Ni <sub>3</sub> (HIB) <sub>2</sub>	.17
Fig. S9 Characterizations for Pt@Ni <sub>3</sub> (HIB) <sub>2</sub>	.18
Fig. S10 ORR performance of Pt@Ni <sub>3</sub> (HIB) <sub>2</sub>	.19
Fig. S12 Characterizations for Pt@UiO-66	.21
Fig. S13 LSV curves of Pt@UiO-66 with sample loading of 0.35, 0.5, and 0.7 mg/cm <sup>2</sup>	.22
Fig. S14 The structure of Pt (100) plane absorbed cMOFs used in the calculations	.23
Fig. S15 TEM image of Au@Ni <sub>3</sub> (HIB) <sub>2</sub> .	.24
Fig. S16 Stereo-selectivity of Au@Ni <sub>3</sub> (HIB) <sub>2</sub> .	.25
Fig. S17 Calculated structures of $Ni_3$ (HITP) <sub>2</sub> and $Ni_3$ (HIB) <sub>2</sub> . Brown, blue, gray, and red sphere represent C, N, Ni, and H atoms, respectively.	es .26
Section S4. References	27

#### **Section S1. Experimental Section**

#### **Chemicals and Materials**

Chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·4H<sub>2</sub>O, Adamas, 99.9%, Pt:37.5%), Chloroauric acid (HAuCl<sub>4</sub>·4H<sub>2</sub>O, Adamas, 99%, Au:50%), sodium borohydride (NaBH<sub>4</sub>, Adamas,  $\geq$ 98%), hexadecyltrimethylammonium bromide (CTAB, Sigma-Aldrich, 99%), ethylene glycol (EG, Aladdin, SP, ≥99%), tetramethylammonium bromide (TMABr, TCI, ≥97.0%), nickel(II) chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O, J&K, 99.9%), 2,3,6,7,10,11-hexaiminoxytriphenylene hydrate (H<sub>6</sub>HITP, Tensus BioTech, >97.0%), hexaiminobenzene (HIB, Hwrk Chem, >95.0%), tetrabutylammonium hexafluorophosphate  $(Bu_4NPF_6)$ Adamas, ≥99%), 3phenylpropionaldehyde (PPA, Adamas, ≥95%), cinnamyl alcohol (CA, J&K, ≥98%), acetonitrile (CH<sub>3</sub>CN, Adamas, PREP, ≥99.9%), hydrochloric acid (HCI, GENERAL-REAGENT, GR, 36~38%), nitric acid (HNO<sub>3</sub>, GENERAL-REAGENT, AR, 65.0~68.0%), and methanol (GENERAL-REAGENT, AR, ≥99.7%) were purchased from the mentioned sources and used without further purification. Deionized water (DI water) used in this study is from Milli-Q Direct 8/16 system.

#### Instrumentation

Transmission electron microscopy (TEM) images and energy-dispersive X-ray elemental mapping images were performed on JEM 2100 plus Electron Microscope operated at 200 kV, JEM 1400 Electron Microscope operated at 120 kV or JEM F200 Electron Microscope operated at 200 kV. Methanol solution containing samples were dropped onto TEM grids and air-dried at room temperature.

Scanning electron microscopy (SEM) images were obtained on a JSM-7800F Prime Scanning Electron Microscope. Samples for SEM were dispersed in methanol and dropped onto the silicon wafer and dried in a 65 °C oven.

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 X-ray diffractometer with Cu Kα radiation at room temperature. Samples for XRD were prepared by drying the sample in an oven and scraping the sample powder onto a sample holder.

After activating the samples at 393 K under vacuum overnight, the N<sub>2</sub> adsorption-desorption isotherms were measured at 77 K on a BELSORP-MAXII adsorption instrument.

ICP-OES was performed on a spectrometer ICP-OES Icap7400. Samples for ICP-OES were prepared by dissolving oven-dry powders in nitrohydrochloric acid and diluting them to proper concentrations.

Raman spectra were performed on a SR-500I-D2-1F1 instrument (path length = 200 nm) using a red light-emitting diode laser ( $\lambda$  = 785 nm, 0.5 mW for 150-450 cm<sup>-1</sup>;  $\lambda$  = 532 nm, 0.5 mW for 800-2100 cm<sup>-1</sup>).

X-ray photoelectron spectroscopy (XPS) data was collected on an ESCALAB 250Xi spectrometer with a monochromatic AI X-ray radiation source. The scanning range was from 0 - 10 eV. The C 1s binding energy peak at 284.5 eV was used for Pt/C calibration. The C 1s binding energy peak at 284.8 eV was used for Ni<sub>3</sub>(HITP)<sub>2</sub> relative materials calibration. Core-shell samples are synthesized with thin shells and thermally activated before XPS analysis.

The linear sweep voltammetric (LSV) measurements (using a Bio-Logic VSP) were conducted in 0.1 M KOH electrolyte using a saturated calomel electrode (SCE, 0.99 versus RHE in 0.1 M KOH) as the reference electrode, platinum wire as the counter electrode, and the electrocatalyst-dropped 5-mm diameter glassy carbon electrode as the working electrode. Electrolyte (0.1 M KOH) was saturated with high-purity oxygen at room temperature by bubbling O<sub>2</sub> prior to the measurements for at least 30 min. A flow of O<sub>2</sub> was maintained over the electrolyte during the recording. The working electrode run cyclic voltammetric (CV) measurements at least 20 times before the data were recorded at a scan rate of 100 mV·s<sup>-1</sup>. The presented LSV curves in Figures were subtracted from the background LSV measurements performed in a N<sub>2</sub> saturated electrolyte. 5 mg of electrocatalyst was ultrasonically dispersed in 10  $\mu$ L of Nafion solution (0.5 wt %) and 1 mL of aqueous ethanol solution (ethanol: H<sub>2</sub>O = 1: 1) for about 10 min to form a homogeneous ink. Then, 13.6  $\mu$ L of the as-prepared catalyst ink was dropped on a 0.5 cm-diameter RDE giving a loading of 0.35 mg cm<sup>-2</sup>.

The CV measurements (using a Bio-Logic VSP) of 2 mM 3-pheynylpropionaldehyd/cinnamyl alcohol were conducted in 0.2 M  $Bu_4NPF_6$  electrolyte in CH<sub>3</sub>CN. The working electrode was an electrocatalyst-dropped 5-mm diameter glassy carbon disk, used in conjunction with a

platinum wire auxiliary as counter electrode and a silver wire miniature reference electrode. The electrolyte was saturated with high-purity nitrogen at room temperature by bubbling N<sub>2</sub> prior to the measurements for at least 15 min.

#### Synthetic Procedures

**Pt-CTAB NPs:** The synthesis was carried out following the previous report<sup>1</sup> with some modifications. 10 mL of the aqueous solutions of 0.2 mM H<sub>2</sub>PtCl<sub>6</sub>·4H<sub>2</sub>O and 2 mM CTAB were mixed in a 20-mL vial at room temperature. The mixture was heated at 50 °C for about 5 min until the solution became clear. The vial was capped with a rubber septum immediately after adding 11.4  $\mu$ L of 45 mM ice-cold NaBH<sub>4</sub> and the H<sub>2</sub> gas pressure inside the vial was released through a needle in the septum for 10 min. The needle was then removed and the solution was kept at 50 °C for 6 h. The formed Pt cubes were spun down at 13000 rpm for 20 minutes and re-dispersed in 0.5 mL of 0.1 M CTAB solution for future use.

**Pt-PVP NPs:** The synthesis was carried out following the previous report<sup>2</sup> with some modifications. 12.5 mL of 0.01 M H<sub>2</sub>PtCl<sub>6</sub>·4H<sub>2</sub>O in EG solution, 5 mL of 0.5 M PVP ( $M_w$  = 24000) in EG solution, 3.75 mL of 0.5 M TMABr in EG solution, and 3.75 mL of EG were mixed at 500 rpm in a 100-mL vial at room temperature. The mixture was bubbled with N<sub>2</sub> flow for 5 min, then placed at a 200 °C-oil bath at 350 rpm for about 25 min. The vial was then cooled to room temperature. The formed Pt-PVP cubes were washed with 100 mL acetone and spun down at 5000 rpm for 10 minutes. The solution was washed with hexane and ethanol twice. The final solution was re-dispersed in 25 mL DMF for future use.

**Au-CTAB NPs:** The synthesis was carried out following the previous report<sup>3</sup>. 550 mg CTAB was dissolved in 97 mL DI H<sub>2</sub>O, followed by adding 2.50 mL 0.01 M HAuCl<sub>4</sub> and 0.50 mL 0.1 M trisodium citrate. The mixture solution was transferred into a 200 mL pressure vessel and heated at 110 °C for 24 hours. The formed Au octahedrons were spun down at 6000 rpm for 20 minutes and re-dispersed in 3 mL of 0.1 M CTAB solution for future use.

**Ni<sub>3</sub>(HITP)<sub>2</sub>:** The synthesis was carried out following the previous report with some modifications<sup>4</sup>. 1.32 mg of NiCl<sub>2</sub>·6H<sub>2</sub>O and 60  $\mu$ L of NH<sub>4</sub>OH were dissolved in 0.6 mL of DI water by sonification. 1 mL of the aqueous solution containing 2.0 mg HITP·6HCI was added.

The open vial was placed in the 65 °C-oil bath and stirred for 30 min. Then it was sealed and left undisturbed for 6 h. The as-synthesized  $Ni_3(HITP)_2$  was centrifuged and washed with DI water twice and methanol twice, respectively. The collected product was oven-dried under 65 °C for future use.

**Pt@Ni<sub>3</sub>(HITP)<sub>2</sub>:** 1.32 mg of NiCl<sub>2</sub>·6H<sub>2</sub>O and 60  $\mu$ L of NH<sub>4</sub>OH were dissolved in 0.6 mL of DI water by sonification. 1 mL of the aqueous solution containing 2.0 mg of HITP·6HCI was added. The solution was stirred in an open vial for 2 min at 65 °C. 0.5 mL of Pt-CTAB NPs were added to the solution and mixed adequately. The open vial was placed in the 65 °C-oil bath and stirred for 30 min. Then it was sealed and left undisturbed for 6 h. The assynthesized Pt@Ni<sub>3</sub>(HITP)<sub>2</sub> was centrifuged and washed with DI water twice and methanol twice, respectively. The collected product was oven-dried under 65 °C for future use.

**Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub>:** The synthesis of Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub> was similar to the synthesis of Pt@Ni<sub>3</sub>(HITP)<sub>2</sub>. Instead of using 0.5 mL of Pt-CTAB NPs, 0.5 mL of Pd-PVP NPs were used for the coating.

**Au@Ni<sub>3</sub>(HITP)<sub>2</sub>:** The synthesis of Au@Ni<sub>3</sub>(HITP)<sub>2</sub> was similar to the synthesis of Pt@Ni<sub>3</sub>(HITP)<sub>2</sub>. Instead of using 0.5 mL of Pt-CTAB NPs, 0.5 mL of Au-CTAB NPs were used for the coating.

 $Ni_3(HIB)_2$ : The synthesis was carried out following the previous report with some modifications.<sup>5</sup> A solution of 40 mg of Ni(NO<sub>3</sub>)<sub>2</sub>· 6H<sub>2</sub>O in 2.5 ml of DI water and 0.4 ml of concentrated aqueous NH<sub>4</sub>OH was added to a solution of 15 mg of HIB· 3HCl in 2.5 ml of DI water. This mixture was stirred in a 20 mL-open vial for 30min at room temperature and left undisturbed for 1.5 h. The resulting black powder was centrifuged at 6000 rpm, and then washed with water and 6 M NH<sub>4</sub>OH at 100 °C. Finally, the collected product was washed with acetone and dried under the vacuum at 100 °C.

**Pt@Ni<sub>3</sub>(HIB)<sub>2</sub>:** A solution of 40 mg of Ni(NO<sub>3</sub>)<sub>2</sub>· 6H<sub>2</sub>O in 2.5 ml of DI water and 0.4 ml of concentrated aqueous NH<sub>4</sub>OH was added to a solution of 15 mg of HIB· 3HCl in 2.5 ml of DI water. This mixture was stirred in a 20 mL-open vial for 2min at room temperature. 0.5 mL of Pt-CTAB NPs were added to the solution and stirred for another 30 min. Then it was left undisturbed for 1.5 h at room temperature. The resulting black powder was centrifuged at

6000 rpm, and then washed with water and 6 M NH₄OH at 100 °C. Finally, the collected product was washed with acetone and dried under the vacuum at 100 °C.

**Pt-PVP@Ni<sub>3</sub>(HIB)<sub>2</sub>:** The synthesis of Pt-PVP@Ni<sub>3</sub>(HIB)<sub>2</sub> was similar to the synthesis of Au@Ni<sub>3</sub>(HIB)<sub>2</sub>. Instead of using 0.5 mL of Pt-CTAB NPs, 0.5 mL of Pt-PVP NPs were used for the coating.

**Pt-PVP@UiO-66:** The synthesis of Pt-PVP@Ni<sub>3</sub>(HIB)<sub>2</sub> was similar to the previous report<sup>6</sup>. 29.0 mg of BDC and 35.0 mg of ZrCl<sub>4</sub> were dissolved in 10 mL of DMF by sonification. 0.4 mL of Pt-PVP NPs and 0.3 mL of acetic acid were added to the mixed solution. Then the solution was left undisturbed at 120 °C for 12 h. The resulting grey powder was centrifuged at 6000 rpm and washed with DMF and methanol three times, respectively. Finally, the collected powder was dried under vacuum at 100 °C.

**Au@Ni<sub>3</sub>(HIB)<sub>2</sub>:** A solution of 40 mg of Ni(NO<sub>3</sub>)<sub>2</sub>·  $6H_2O$  in 2.5 ml of DI water and 0.4 ml of concentrated aqueous NH<sub>4</sub>OH was added to a solution of 15 mg of HIB· 3HCl in 2.5 ml of DI water. This mixture was stirred in a 20 mL-open vial for 2min at room temperature. 0.5 mL of Au-CTAB NPs were added to the solution and stirred for another 30 min. Then it was left undisturbed for 1.5 h at room temperature. The resulting black powder was centrifuged at 6000 rpm, and then washed with water and 6 M NH<sub>4</sub>OH at 100 °C. Finally, the collected product was washed with acetone and dried under the vacuum at 100 °C.

### Section S2. Supporting Tables

**Table S1.** Concentration of as-synthesized metal NPs. Theoretical and actual concentrationsof metal NPs CTAB aqueous solution.

Sample	Theoretical concentration (mM)	Actual Concentration (mM)
Pt-CTAB	4.0	1.05
Pt-PVP	5.0	4.9
Au-CTAB	8.3	4.5

The theoretical concentrations of metal NPs CTAB aqueous solution were calculated based on the complete reduction of the input corresponding metal salt precursors. The actual concentrations were based on the ICP-OES measurement. **Table S2.** Loadings of metal NPs in NPs@MOFs composites. Theoretical and actual loadings of Pt in Pt@Ni<sub>3</sub>(HITP)<sub>2</sub>/ Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub>/ Pt@Ni<sub>3</sub>(HIB)<sub>2</sub>/ Pt-PVP@Ni<sub>3</sub>(HIB)<sub>2</sub>/ Pt-PVP@UiO-66, Au in Au@Ni<sub>3</sub>(HITP)<sub>2</sub>/ Au@Ni<sub>3</sub>(HIB)<sub>2</sub>.

Sample	Theoretical Value (wt.	Actual Value (wt. %)
	%)	
Pt in Pt@Ni₃(HITP)₂	1.47	1.90
Pt in Pt-	1.55	2.03
PVP@Ni <sub>3</sub> (HITP) <sub>2</sub>		
Pt in Pt@Ni <sub>3</sub> (HIB) <sub>2</sub>	0.71	1.95
Pt in Pt-PVP@Ni <sub>3</sub> (HIB) <sub>2</sub>	0.75	2.05
Pt in Pt-PVP@UiO-66	0.92	1.96
Au in Au@Ni <sub>3</sub> (HITP) <sub>2</sub>	6.0	7.1
Au in Au@Ni <sub>3</sub> (HIB) <sub>2</sub> .	3.0	7.4

The theoretical loadings of metal NPs were calculated based on the complete reaction of the input corresponding HITP·6HCI or HIB·3HCI precursors. The actual loadings were based on the ICP-OES measurement.

### Section S3. Supporting Figures



**Fig. S1** SEM image of Pt@Ni<sub>3</sub>(HITP)<sub>2</sub>. The acquiring condition was 5.0 kV, LED, WD 10.3 mm.

The SEM image presented the uniform morphology of  $Pt@Ni_3(HITP)_2$ . It showed that the Pt NPs were fully embedded within  $Ni_3(HITP)_2$ .



**Fig. S2** Nitrogen adsorption–desorption isotherms of Ni<sub>3</sub>(HITP)<sub>2</sub>, Pt@Ni<sub>3</sub>(HITP)<sub>2</sub>, and Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub>.

Steep nitrogen gas uptakes at a lower relative pressure (P/P<sub>0</sub><0.001) indicated abundant micropore structures<sup>7</sup>. This is consistent with the structure of Ni<sub>3</sub>(HITP)<sub>2</sub>, which possessed an aperture size of 1.8 nm. The sharp rises at medium and high relative pressure regions (P/P<sub>0</sub>=0.8–1.0) indicated the presence of macropores in these materials, contributed by the stacked crystals. The N<sub>2</sub> uptake of Pt@Ni<sub>3</sub>(HITP)<sub>2</sub> and Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub> were similar and the slightly decreased N<sub>2</sub> uptake in Pt@Ni<sub>3</sub>(HITP)<sub>2</sub> and Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub> compared with Ni<sub>3</sub>(HITP)<sub>2</sub> came from the encapsulation of the heavier Pt NPs. This result demonstrated that most of the channels and cavities in Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub> were not obstructed by the residual PVP molecules.



**Fig. S3** Elements distribution in Pt@Ni<sub>3</sub>(HITP)<sub>2</sub>. a) EDS mapping images of Pt@Ni<sub>3</sub>(HITP)<sub>2</sub>. b) EDS spectrum of Pt@Ni<sub>3</sub>(HITP)<sub>2</sub>.

The lack of Br element in EDS data (Fig. S3) demonstrated the Br-free in  $Pt@Ni_3(HITP)_2$  composite, which provides extra evidence for the formation of direct interfaces. For reference, the Si element might come from silicone grease, O might come from the carbon film and the Cu might be due to the Cu TEM grid.



Fig. S4 Low-mag TEM image of Au@Ni<sub>3</sub>(HITP)<sub>2</sub>.

The Au NPs excited by the laser beam with molecular vibration, resulted in an enhanced Raman scattering for the molecules adsorbed on Au surfaces. Thus, Au NPs were embedded in  $Ni_3(HITP)_2$  for surface-enhanced Raman spectroscopy (SERS) studies.



Fig. S5 Raman spectra of Pt@Ni<sub>3</sub>(HITP)<sub>2</sub>, Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub>, and Ni<sub>3</sub>(HITP)<sub>2</sub>.

The Raman spectra of Pt@Ni<sub>3</sub>(HITP)<sub>2</sub>, Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub>, and Ni<sub>3</sub>(HITP)<sub>2</sub> were collected to analyze the interaction between NPs and cMOFs. Two featured peaks<sup>8</sup> around 1570 and 1365 cm<sup>-1</sup> are assigned to the  $E_{2g}$  phonon of sp<sup>2</sup> C atoms of the HITP ligands at G-band and the breathing mode of  $\kappa$ -point phonon at D-band, respectively. The blue-shifted featured peaks for Pt@Ni<sub>3</sub>(HITP)<sub>2</sub> compared with Ni<sub>3</sub>(HITP)<sub>2</sub> and PVP@Ni<sub>3</sub>(HITP)<sub>2</sub> resembled the reported NPs-matrix composites<sup>9, 10</sup>. This also proved the interaction between metal NPs and cMOFs with direct interfaces was enhanced than that of the indirect interfaces.



**Fig. S6** Experimental PXRD pattern of Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub> and simulated PXRD pattern of Ni<sub>3</sub>(HITP)<sub>2</sub>.

The PXRD patterns of Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub> were shown above, and it was confirmed to be  $Ni_3(HITP)_2$  with a known structure<sup>11</sup>. The crystallinity of  $Ni_3(HITP)_2$  was well maintained after the encapsulation of Pt-PVP NPs.



**Fig. S7** ORR performance of Pt NPs. a) LSV curves of 0.3 wt% Pt-CTAB/C and b) LSV curves of 0.3 wt% Pt-PVP/C.

Pt-CTAB/C and Pt-PVP/C were Pt-CTAB NPs and Pt-PVP NPs dispersed carbon black, respectively. The LSV curves of Pt-CTAB NPs and Pt-PVP NPs dispersed carbon black were collected for reference. The onset potentials were 0.83 and 0.87 (*versus* RHE), respectively.



**Fig. S8** Conductivity of  $Ni_3(HITP)_2$  and  $Ni_3(HIB)_2$ . a) Nyquist plots and (b) the zoom-in Nyquist plots of the high-frequency part for  $Ni_3(HITP)_2$  and  $Ni_3(HIB)_2$ .

At high frequencies, the charge transfer is limited by electronic conductivity<sup>12</sup>. Here, we used  $R_{ct}$  to evaluate the electronic conductivity of the materials. The  $R_{ct}$  value of Ni<sub>3</sub>(HITP)<sub>2</sub> was 2.3  $\Omega$ , which is lower than 7.4  $\Omega$  for Ni<sub>3</sub>(HIB)<sub>2</sub>, showing higher electronic conductivity.



**Fig. S9** Characterizations for Pt@Ni<sub>3</sub>(HIB)<sub>2</sub>. a) PXRD for Pt@Ni<sub>3</sub>(HIB)<sub>2</sub>, Pt-PVP@Ni<sub>3</sub>(HIB)<sub>2</sub>, and Ni<sub>3</sub>(HIB)<sub>2</sub>. b) TEM image and c) EDS mappings for Pt@Ni<sub>3</sub>(HIB)<sub>2</sub>.

The crystallinity of  $Pt@Ni_3(HIB)_2$  was confirmed by the PXRD data and the core-shell structure was also verified by the TEM image and EDS mappings.



**Fig. S10** ORR performance of Pt@Ni<sub>3</sub>(HIB)<sub>2</sub>. a) LSV curves and b) the corresponding Tafel slope of Pt@Ni<sub>3</sub>(HIB)<sub>2</sub> and Pt-PVP@Ni<sub>3</sub>(HIB)<sub>2</sub> in 0.1M KOH aqueous solution at a scan rate of 100 mV s<sup>-1</sup>, sample loading: 0.35 mg/cm<sup>-2</sup>.

The interface structures were also influential in  $Pt@Ni_3(HIB)_2$  and  $Pt-PVP@Ni_3(HIB)_2$ , possessing the onset potential (Fig. S10a) of 0.77 V and 0.69 V (*versus* RHE), respectively. The Tafel slopes (Fig. S10b) of direct and indirect interfaces were also near 60 mV·dec<sup>-1</sup> and 120 mV·dec<sup>-1</sup>, suggesting the different reaction mechanisms resulting from interface structures.



**Fig. S11 Interaction analysis of NPs and cMOFs via XPS.** High-resolution XPS spectra of a) Pt 4f and b) N 1s orbitals of Pt@Ni<sub>3</sub>(HITP)<sub>2</sub> and Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub>.

The oxide state  $Pt^{2+}$  is commonly observed in small nanoparticles<sup>13</sup>. We have demonstrated the direct interfaces between Pt NPs and Ni<sub>3</sub>(HITP)<sub>2</sub> from SERS (Fig. 1d) and EDS (Fig. S5). That meant the direct interfacial structures of Pt@Ni<sub>3</sub>(HITP)<sub>2</sub> possessed smaller interaction between Pt NPs and Ni<sub>3</sub>(HITP)<sub>2</sub> (Pt-MOF interaction) than the interaction between Pt NPs and PVP (Pt-PVP interaction). The decreased ORR activity of Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub> also demonstrated the PVP molecules hindered the electrons transfer from MOFs to NPs in Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub> than that in Pt@Ni<sub>3</sub>(HITP)<sub>2</sub>.

The N 1s peaks in Pt@Ni<sub>3</sub>(HITP)<sub>2</sub> of -NH- shift negatively by 0.3 eV compared with Pt-PVP@Ni<sub>3</sub>(HITP)<sub>2</sub>, which resembles the reported changes<sup>14</sup>. This might be because of the presence of Pt-N coordination bond at 397.9 eV, which attribute to the electron migration from Pt to Ni<sub>3</sub>(HITP)<sub>2</sub><sup>15</sup>.



**Fig. S12** Characterizations for Pt@UiO-66. a) Low-mag TEM image of Pt@UiO-66. b) Experimental PXRD pattern of Pt@UiO-66 and simulated PXRD pattern of UiO-66.

This is the extreme case of Pt encapsulated in non-conducting MOF. UiO-66 was chosen as an insulating MOF with rigid structures of hard metal (Zr) nodes and un-conjugated organic ligands (1,4-benzenedicarboxylic acid) <sup>16</sup>. The morphology of the core-shell Pt@UiO-66 was shown in Fig. S12a. The structure and crystallinity of Pt@UiO-66 were verified by PXRD (Fig. S12b).



Fig. S13 LSV curves of Pt@UiO-66 with sample loading of 0.35, 0.5, and 0.7 mg/cm<sup>2</sup>.

The ORR activity of Pt@UiO-66 is shown above. It is much lower than  $Pt@Ni_3(HITP)_2$  both in onset potentials and limiting currents. When the sample loading arrived at 0.7 mg/cm<sup>2</sup>, the ORR activity even decreased than the sample loading of 0.5 mg/cm<sup>2</sup>. Thus, non-conducting shell materials obstructed the electron's transfer in the electrocatalytic reaction.



Pt absorbed Ni<sub>3</sub>(HITP)<sub>2</sub>



Fig. S14 The structure of Pt (100) plane absorbed cMOFs used in the calculations.

The morphology of Pt nanoparticles mainly was cubic, thus we constructed the models with Pt(100) planes. First-principles calculations were performed using the CP2K software package with the projector augmented wave method (PAW). A spin-polarized generalized gradient approximation (GGA) was employed to the revised Perdew–Burke–Ernzerhof (RPBE) functional for the exchange correlation potentials. We build  $3\times3\times3$  Pt(100) slab models with the single-layer Ni<sub>3</sub>(HITP)<sub>2</sub> and Ni<sub>3</sub>(HIB)<sub>2</sub> on the surface respectively. The vacuum layers in z-direction were set to more than 15 Å to ensure the slab interaction was eliminated. In geometry optimizations, the cut-off energy of the plane wave basis set was 400 eV, all the atomic coordinates were fully relaxed up to the residual atomic forces smaller than 0.05 eV/Å, and the total energy was converged to  $10^{-5}$  eV. The Monkhorst mesh was  $3\times3\times1$ . The d-band center was thus obtained by averaging over the eigenenergy multiplied by the d-band contribution on the eigenstate of the surface Pt up to E<sub>f</sub>.

The increment of Pt@Ni<sub>3</sub>(HITP)<sub>2</sub> activity than Pt@Ni<sub>3</sub>(HIB)<sub>2</sub> was comparable to the reported value<sup>17</sup>. The theoretical model of Pt@Ni<sub>3</sub>(HIB)<sub>2</sub> resembled that of Pt quite well. However, the onset potential of Pt@Ni<sub>3</sub>(HIB)<sub>2</sub> (0.77 *versus* RHE) was much lower than Pt NPs (0.83 V *versus* RHE). This might result from the grain boundaries of the core-shell structures, which could hinder the conduction of electrons, causing mediocre performance of Pt@Ni<sub>3</sub>(HIB)<sub>2</sub>.



Fig. S15 TEM image of Au@Ni<sub>3</sub>(HIB)<sub>2</sub>.

Since the 1.8-nm aperture size of  $Ni_3(HITP)_2$  is too large for the selective reaction measurement and synthesizing CTAB capped Au NPs in large amounts is easier than Pt-CTAB NPs, Au@Ni\_3(HIB)\_2 was synthesized to demonstrate reaction stereo-selectivity in electrocatalysis. The TEM image is shown above.



**Fig. S16** Stereo-selectivity of Au@Ni<sub>3</sub>(HIB)<sub>2</sub>. Cyclic voltammograms of 2 mM 3pheynylpropionaldehyd (PPA)/cinnamyl alcohol (CA) in CH<sub>3</sub>CN containing 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>, recorded at 295 (±2) K using a 5-mm diameter planar GC disk electrode a) with 5 mg·cm<sup>-2</sup> of Au@Ni<sub>3</sub>(HIB)<sub>2</sub> coated and b) without coating at 0.1 V·s<sup>-1</sup> at 0.1 V·s<sup>-1</sup>.

The reduction peaks in the cyclic voltammograms were the reduction products of CA or PPA over pure GCE electrode and Au@Ni<sub>3</sub>(HIB)<sub>2</sub>. The charge amount, referring to the production yield, could be integrated and calculated according to the reduction peaks.



**Fig. S17 Calculated structures of** Ni<sub>3</sub>(HITP)<sub>2</sub> and Ni<sub>3</sub>(HIB)<sub>2</sub>. Brown, blue, gray, and red spheres represent C, N, Ni, and H atoms, respectively.

The calculated structures of two conductive MOFs,  $Ni_3(HITP)_2^{18}$  and  $Ni_3(HIB)_2^{19}$  were shown in Fig S17 to show the difference of two MOF structures.

#### Section S4. References

(1) Lee, H.; Habas, S. E.; Kweskin, S.; Butcher, D.; Somorjai, G. A.; Yang, P., Morphological control of catalytically active platinum nanocrystals. *Angew. Chem. Int. Ed. Engl.* **2006**, *45* (46), 7824-8.

(2) Chia-Kuang Tsung, J. N. K., Wenyu Huang, Cesar Aliaga, Ling-I Hung, Gabor A. Somorjai, and Peidong Yang, Sub-10 nm Platinum Nanocrystals with Size and Shape Control: Catalytic Study for Ethylene and Pyrrole Hydrogenation. *J. Am. Chem. Soc.* **2009**, *131*, 5816-5822.

(3) Chang, C.-C.; Wu, H.-L.; Kuo, C.-H.; Huang, M. H., Hydrothermal Synthesis of Monodispersed Octahedral Gold Nanocrystals with Five Different Size Ranges and Their Self-Assembled Structures. *Chem. Mater.* **2008**, *20* (24), 7570-7574.

(4) Sheberla, D.; Bachman, J. C.; Elias, J. S.; Sun, C.-J.; Shao-Horn, Y.; Dincă, M., Conductive MOF electrodes for stable supercapacitors with high areal capacitance. *Nat. Mater.* **2017**, *16* (2), 220-224.

(5) Feng, D.; Lei, T.; Lukatskaya, M. R.; Park, J.; Huang, Z.; Lee, M.; Shaw, L.; Chen, S.; Yakovenko, A. A.; Kulkarni, A.; Xiao, J.; Fredrickson, K.; Tok, J. B.; Zou, X.; Cui, Y.; Bao, Z., Robust and Conductive Two-Dimensional Metal–Organic Frameworks with Exceptionally High Volumetric and Areal Capacitance. *Nat. Energy* **2018**, *3* (1), 30-36.

(6) Luo, L.; Lo, W.-S.; Si, X.; Li, H.; Wu, Y.; An, Y.; Zhu, Q.; Chou, L.-Y.; Li, T.; Tsung, C.-K., Directional Engraving within Single Crystalline Metal–Organic Framework Particles via Oxidative Linker Cleaving. *J. Am. Chem. Soc.* **2019**, *141* (51), 20365-20370.

(7) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W., Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87* (9-10), 1051-1069.

(8) Cai, D.; Lu, M.; Li, L.; Cao, J.; Chen, D.; Tu, H.; Li, J.; Han, W., A Highly Conductive MOF of Graphene Analogue Ni3(HITP)2 as a Sulfur Host for High-Performance Lithium–Sulfur Batteries. *Small* **2019**, *15* (44), 1902605.

(9) Raïssi, M.; Vignau, L.; Cloutet, E.; Ratier, B., Soluble Carbon Nanotubes/Phthalocyanines Transparent Electrode and Interconnection Layers for Flexible Inverted Polymer Tandem Solar Cells. *Org. Electron.* **2015**, *21*, 86-91.

(10) Iqbal, M. W.; Singh, A. K.; Iqbal, M. Z.; Eom, J., Raman Fingerprint of Doping due to Metal Adsorbates on Graphene. *Condens. Matter.* **2012**, *24*, 335301.

(11) Hmadeh, M.; Lu, Z.; Liu, Z.; Gándara, F.; Furukawa, H.; Wan, S.; Augustyn, V.; Chang, R.; Liao, L.; Zhou, F.; Perre, E.; Ozolins, V.; Suenaga, K.; Duan, X.; Dunn, B.; Yamamto, Y.; Terasaki, O.; Yaghi, O. M., New Porous Crystals of Extended Metal-Catecholates. *Chem. Mater.* **2012**, *24* (18), 3511-3513.

(12) Warriner, K.; Namvar, A., 4.54 - Biosensors for Foodborne Pathogen Detection. In *Comprehensive Biotechnology (Second Edition)*, Moo-Young, M., Ed. Academic Press: Burlington, 2011; pp 659-674.

(13) Ma, J.; Habrioux, A.; Luo, Y.; Ramos-Sanchez, G.; Calvillo, L.; Granozzi, G.; Balbuena, P. B.; Alonso-Vante, N., Electronic Interaction between Platinum Nanoparticles and Nitrogen-Doped Reduced Graphene Oxide: Effect on the Oxygen Reduction Reaction. *J. Mater. Chem. A* **2015**, *3* (22), 11891-11904.

(14) Melke, J.; Peter, B.; Habereder, A.; Ziegler, J.; Fasel, C.; Nefedov, A.; Sezen, H.; Wöll, C.; Ehrenberg, H.; Roth, C., Metal–Support Interactions of Platinum Nanoparticles Decorated N-Doped Carbon Nanofibers for the Oxygen Reduction Reaction. *ACS Appl. Mater. Interfaces* **2016**, *8* (1), 82-90.

(15) Sim, H. Y. F.; Chen, J. R. T.; Koh, C. S. L.; Lee, H. K.; Han, X.; Phan-Quang, G. C.; Pang, J. Y.; Lay, C. L.; Pedireddy, S.; Phang, I. Y.; Yeow, E. K. L.; Ling, X. Y., ZIF-Induced d-Band Modification

in a Bimetallic Nanocatalyst: Achieving Over 44 % Efficiency in the Ambient Nitrogen Reduction Reaction. *Angew. Chem. Int. Ed. Engl.* **2020**, *59* (39), 16997-17003.

(16) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P., A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *J. Am. Chem. Soc.* **2008**, *130* (42), 13850-13851.

(17) Zhu, X.; Tan, X.; Wu, K.-H.; Haw, S.-C.; Pao, C.-W.; Su, B.-J.; Jiang, J.; Smith, S. C.; Chen, J.-M.; Amal, R.; Lu, X., Intrinsic ORR Activity Enhancement of Pt Atomic Sites by Engineering the d-Band Center via Local Coordination Tuning. *Angew. Chem. Int. Ed. Engl.* **2021**, *60* (40), 21911-21917.

(18) Sheberla, D.; Sun, L.; Blood-Forsythe, M. A.; Er, S.; Wade, C. R.; Brozek, C. K.; Aspuru-Guzik, A.; Dincă, M., High Electrical Conductivity in Ni3(2,3,6,7,10,11-hexaiminotriphenylene)2, a Semiconducting Metal–Organic Graphene Analogue. J. Am. Chem. Soc. **2014**, *136* (25), 8859-8862.

(19) Dou, J.-H.; Sun, L.; Ge, Y.; Li, W.; Hendon, C. H.; Li, J.; Gul, S.; Yano, J.; Stach, E. A.; Dincă, M., Signature of Metallic Behavior in the Metal-Organic Frameworks M3(hexaiminobenzene)2 (M = Ni, Cu). J. Am. Chem. Soc. 2017, 139 (39), 13608-13611.