Electronic Supplementary Material (ESI) for Energy & Environmental Science.

# Supporting information

# Constructing Canopy-Shaped Molecular Architectures to Create Local Pt Surface Sites with High Tolerant to $H_2S$ and CO for Hydrogen Electrooxidation

Tao Wang,[+] Zhi-Xin Chen,[+] Song Yu, Tian Sheng, Hai-Bin Ma, Lu-Ning Chen, Muhammad Rauf, Hai-Ping Xia, Zhi-You Zhou,[*] Shi-Gang Sun

*Collaborative Innovation Center of Chemistry for Energy Materials, State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China*

## Material and method

### 1. Reagents, solutions, materials and apparatus

20 wt% Pt/C was purchased from Alfa Aesar. Sulfuric acid (98%) were purchased from Merck. 2,6-diacetylpyridine (DAcPy 99%), 2-acetylpyridine (AcPy 99%), pyridine (Py 99.9%) and 1,3-diacetylbenzene (DAcPh 97%) were purchased from Sigma-Aldrich. All chemicals were used as received. The solutions were prepared from super pure water (18 MΩ cm) purified through a Milli-Q Lab system (Nihon Millipore Ltd.). Ar (99.999%) and $H_2$ (99.999%) were purchased from Linde. $H_2$/100ppm CO balance gas and $H_2$/1ppm $H_2S$ balance gas were purchased from Dalian Special Gas Co. , Ltd, China.

Electrochemical preparation and characterization were carried out in a standard three-electrode cell working with on a rotating ring electrode (RDE) system (BAS Inc.) with a CHI-760D bipotentiostats. Counter electrode was a platinum foil and reference electrode was a reversible hydrogen electrode (RHE) and all potentials were quoted versus the RHE scale. Working electrode was a glassy carbon (GC, $\phi = 5$ mm) RDE. Prior to the electrochemical treatment, the GC was polished mechanically by successively using alumina powder of sizes 5, 1, and 0.3 μm, and cleaned in an ultrasonic bath.

### 2. Experiment section

**Preparation of electrodes.** Commercial 20 wt% Pt/C catalyst (1 mg) were dispersed into 0.5 mL water, 0.4 mL ethanol and 0.1 mL 5% Nafion solution under ultrasonic treatment. The ink (10 μL) was pipetted onto the GC electrode and then dried in air, resulting in a Pt loading of 10 μg cm$^{-2}$.

**Electrochemical test.** Electrocatalytic test was carried out at room temperature (~ 25 $^{o}$C). The working electrode was cleaned by potential cycling between 0.03 and 1.26 V at 50 mV s$^{-1}$ in Ar-saturated 0.5 M $H_2SO_4$ until stable cyclic voltammograms were obtained. The electrode was then transferred to 0.5 M $H_2SO_4$ in presence absence of organic molecules for hydrogen oxidation and $H_2S$/CO tolerance tests. The concentrations of DAcPy, AcPy, and Py were 10 mM, and ~3.5 mM for DAcPh (saturation solution). The rotating rate of RDE is 1600 rpm. The potential was scanned between -0.05 and 0.4 V at 10 mV s$^{-1}$ under $H_2$ atmosphere. Long term stability tests were performed at 0.1 V for 5 h. All currents were normalized by geometric area of electrodes.

**Preparation of Pt/C coated with DAcPy.** Pt/C (20 mg) and DAcPy (5mg) were dispersed in 10 mL isopropanol by ultrasonic treatment. And then the suspension was heated at 80 °C for 12 h. After heat treatment, Pt/C were separated by centrifugation and washing.

**X-ray photoelectron spectroscopy (XPS) test.** Pt foil was immersed in 10 mM DAcPy solution for 0.5 h under Ar atmosphere and then transfer to 10 μM $Na_2S$ solution for 0.5 h. The sample was cleaned by water, and dried. Reference sample was prepared by directly immersing Pt foil in 10 μM $Na_2S$ solution for 0.5 h, and then cleaned, and dried. XPS were carried out in an ultrahigh vacuum system using monochromatized Al Kα radiation (1486.6 eV) and an Omicron Sphera II hemispherical electron energy analyzer. Binding energies reported herein are with reference to C 1s at 284.5 eV.

**Electrochemical surface enhanced Raman spectroscopy (EC-SERS).** EC-SERS test was carried out with XploRa, France using 638nm laser and the power is 2.1 mW. Au core(55 nm)-Pt shell(1.4 nm) nanoparticles were prepared for SERS. Prior to each experiment, the Au@Pt nanoparticles were transferred to the GC electrode.

**Thermogravimetric analysis (TGA).** TGA was conducted using an SDT Q600TGA thermal gravimetric analyzer in $N_2$ flow at a heating rate of 10 °C/min with 5 mg Pt black adsorbed by DAcPy.

**High-resolved transmission electron microscopy (HRTEM) test.** HRTEM was conducted on JEM-2100 at 200 kV.

**CHN element analysis.** Element analysis of DAcPy-coated Pt black was carried out on Vario EL III elemental analyzer (Elementar Analysen Syetem GmbH, Germany). Two parallel samples were tested.

**Calculation method.** All the DFT calculations were implemented with the Perdew-Burke-Ernzerh (PBE) generalized gradient approximation (GGA) exchange-correlation functional using the Vienna Ab-initio Simulation Package (VASP) [s1-s7]. The projector-augmented-wave (PAW) pseudopotentials were utilized to describe the core electron interaction. The optB88-vdW method as implemented in the VASP code was utilized to describe vdW interactions [s8-s10]. The cut-off energy was set as 400 eV and a 2´ 2´ 1 Monkhorst-Pack *k*-point sampling was used for Brillouin zone. The vacuum region layers were built more than 12 Å to ensure the slab interaction was eliminated. A *p*(4´ 4) Pt(111) supercell was used with three Pt layers. During all the optimization process, the bottom layer atoms were fixed in the slab, while the top two-layers atoms were relaxed. In this work, the adsorption energy was defined as: $E_{ad}$ = E(ad/Pt) - E(ad) - E(Pt), where E(ad/Pt), E(ad), and E(Pt) are the total energies of the adsorbate binding to Pt(111) surface, free adsorbate in gas phase and clean Pt(111), respectively. At the electrode potential of 0 V, pH = 0 ($[H^+]$ = 1M), at 298 K, due to the equilibrium of $H^+ + e^- \rightarrow \frac{1}{2} H_2$, we can use the free energy of ½ $H_2$ in the gas phase to replace that of $H^+ + e^-$. [s11]

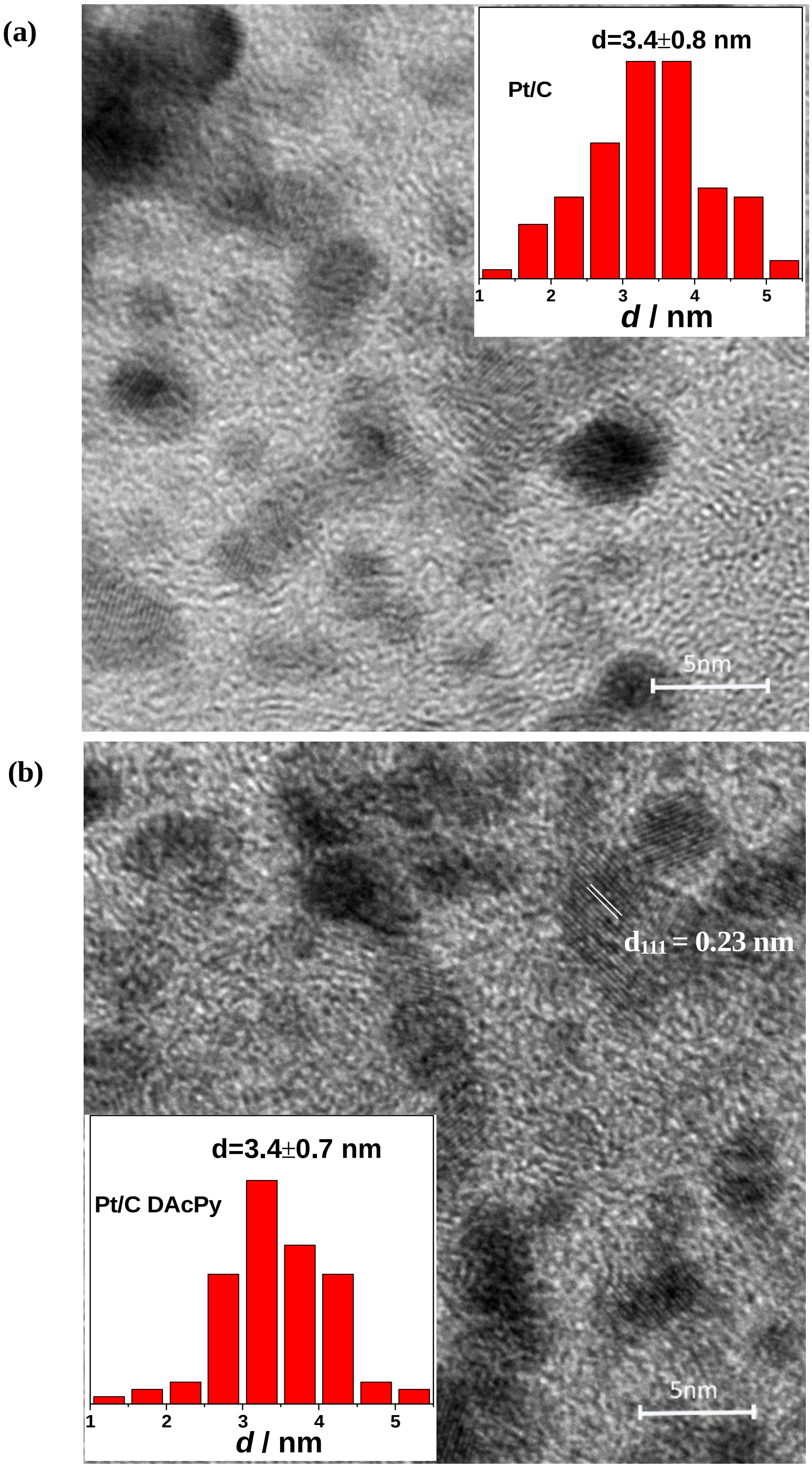


**Fig. S1** HRTEM images of Pt/C (a) and DAcPy-coated Pt/C (b). Size histograms were inset. The lattice space of 0.23 nm, corresponding to (111) diffraction of Pt could be observed.

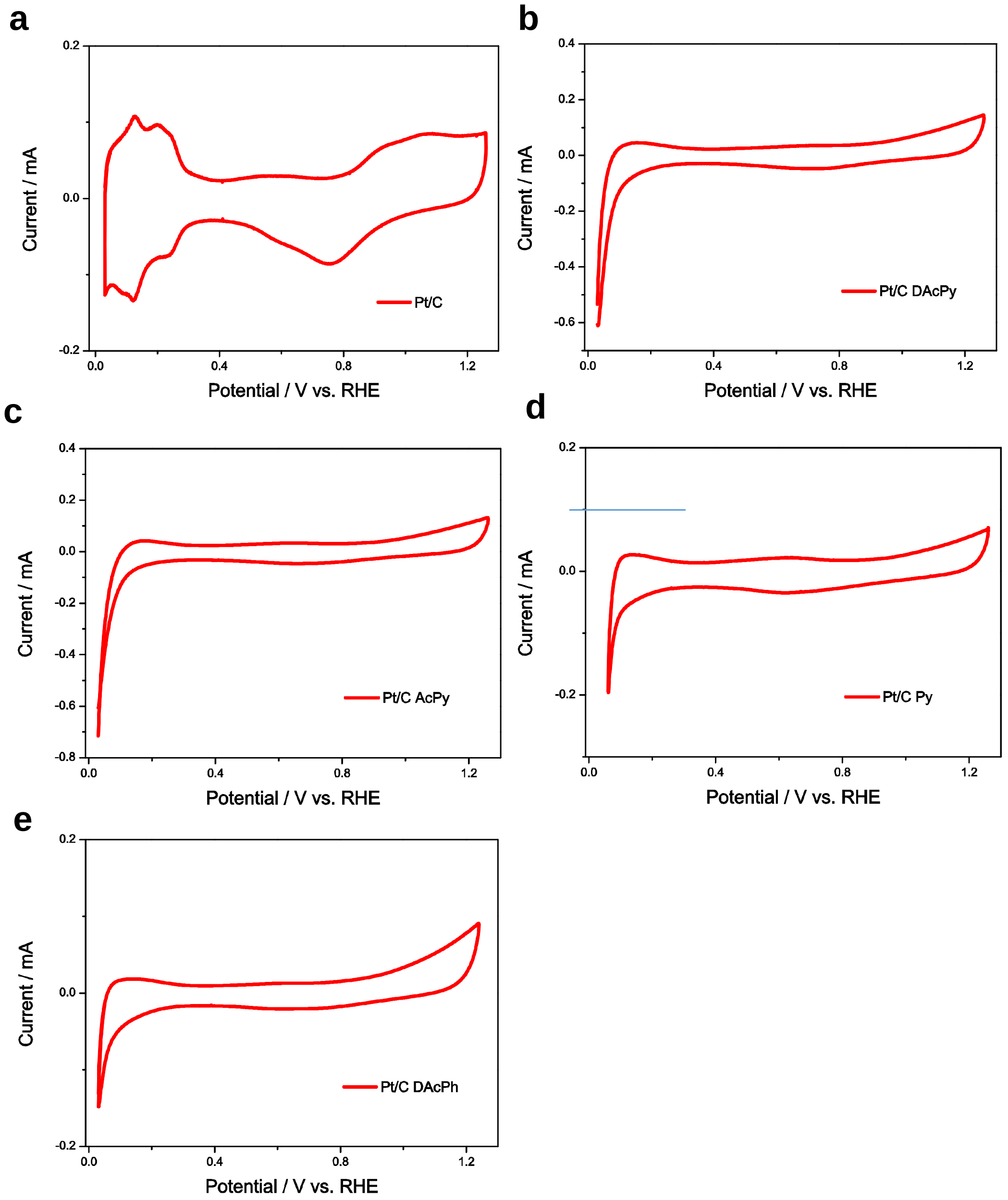


**Fig S2.** Cyclic voltammograms of Pt/C in 0.5 M $H_2SO_4$ (a) and with DAcPy (b), AcPy (c), Py (d), and DAcPh (e). The concentrations of DAcPy, AcPy, and Py were 10 mM, but about 3.5 mM for DAcPh (saturated solution). Clearly, all of these organic molecules can be adsorbed on the Pt surface, since hydrogen adsorption/desorption current (0.05~0.35 V) is suppressed greatly.

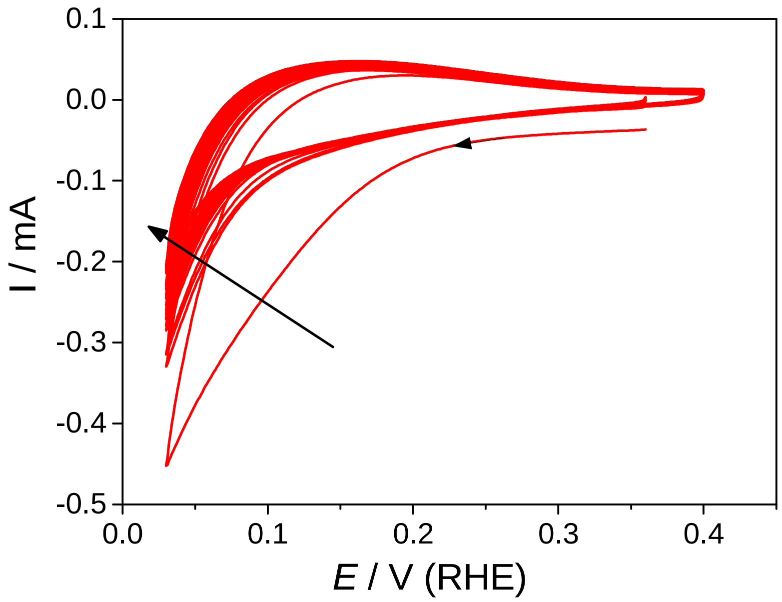
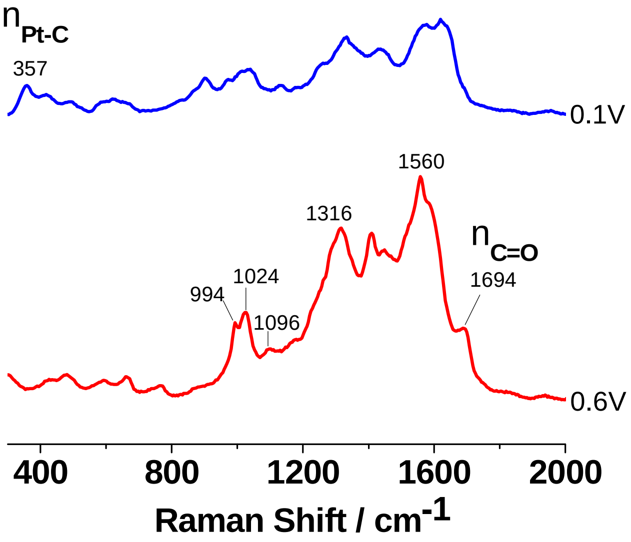


**Fig. S3.** Cyclic voltammograms of Pt/C in 0.5 M $H_2SO_4$ + 10 mM DAcPy. Considerable reduction current could be observed in the first cycle, but it declined quickly in the following cycles.

**Table S1** Assignment of Raman peaks of DAcPy adsorbed on Au@Pt core-shell nanoparticles

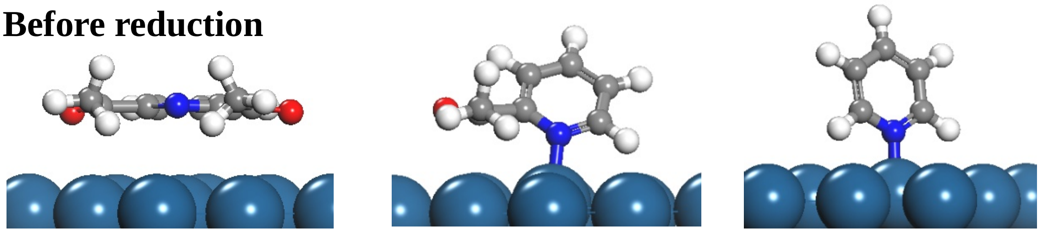
| Wave number ($cm^{-1}$) | Assignment |
|---|---|
| 357 | $\nu_{Pt-C}$ |
| 994 | $\alpha_{CCC}$<br>Ring breathing mode |
| 1024 | $\alpha_{CCC}$<br>Symmetric ring deformation mode |
| 1316 | $\nu_{CrCx}$ |
| 1560 | $\nu_{CC/CN}$<br>Ring C-C stretching mode |
| 1694 | $\nu_{C=O}$ |

ν, stretching; α, in-plane ring bending; Cr, ring carbon atom; Cx, carbon atom of carbonyl group;



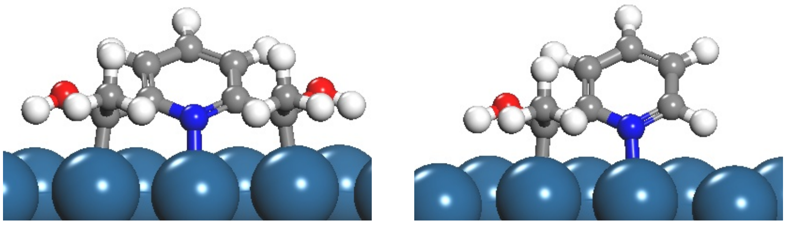
In the Raman spectrum collected at 0.60 V, the bands at 994 $cm^{-1}$ and 1024 $cm^{-1}$ were assigned to ring breathing mode and symmetric ring deformation mode in pyridinic ring, respectively.[s12, s13] And the band at 1316 $cm^{-1}$ was assigned to C-C stretching between pyridinic ring and carbonyl group; the bands at 1560 $cm^{-1}$ was assigned to pyridinic ring C-C stretching mode.[s12] Besides, the band at 1694 $cm^{-1}$ was assigned to C=O stretching of carbonyl group.[s12] In the Raman spectrum collected at 0.10 V, the band at 357 $cm^{-1}$ was assigned to Pt-C stretching. In addition, the band at 1410 $cm^{-1}$ is unknown currently.

## Before reduction



**DAcPy** **AcPy** **Py**

## After reduction

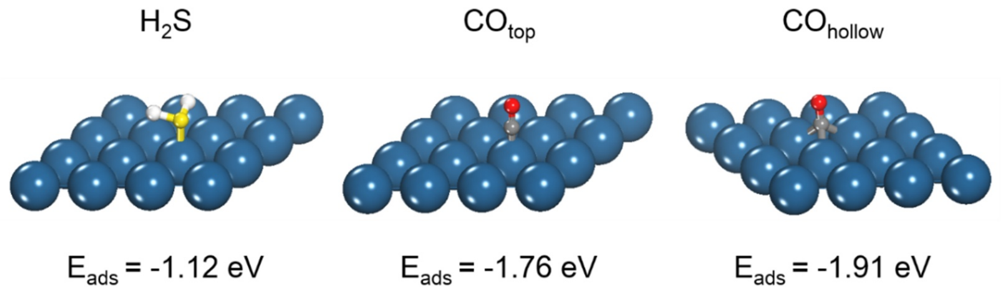


**DAcPy** **AcPy**

**Fig. S4.** Calculated adsorption configurations of DAcPy, AcPy, and Py on Pt(111). DAcPy and AcPy have two adsorption configurations: pristine adsorption and reductive adsorption.

**Table S1.** Calculated adsorption energies of DAcPy, AcPy, and Py on Pt(111) surface.

| | $E_{ads}$ / eV | $E_{ads}$ after reduction / eV |
|---|---|---|
| DAcPy | -1.40 | -3.50 |
| AcPy | -1.22 | -2.51 |
| Py | -1.61 | |



Optimized structures for $H_2S$ and CO adsorption on Pt(111). Blue: Pt; yellow: S; white: H; grey: C; red: O.

**Fig. S5.** Calculated adsorption configurations and adsorption energy of CO and $H_2S$ on Pt(111).

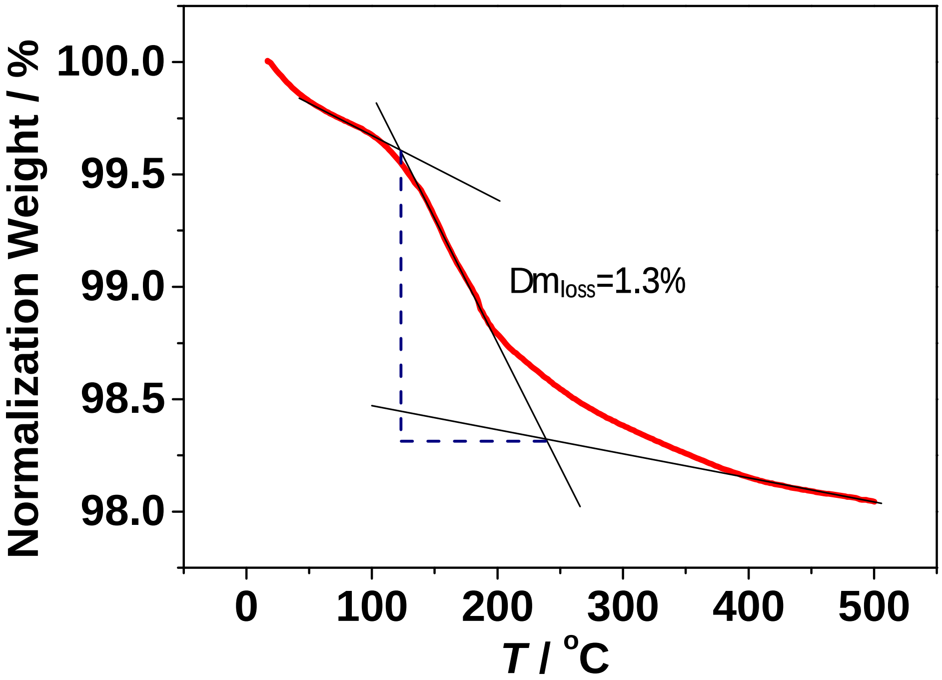


**Fig. S6.** Thermogravimetric curve of DAcPy adsorbed on commercial Pt black in $N_2$ flow at 10 °C $min^{-1}$. The mass of Pt black was 5 mg, and the specific surface area of Pt black was 20.7 $m^2$ $g^{-1}$ determined by electrochemical hydrogen adsorption/desorption in 0.5 M $H_2SO_4$.

**Table S3** CHN element analysis of DAcPy-coated Pt black[a]

| Weight content /% | C | N | H | DAcPy[c] |
|---|---|---|---|---|
| 1# | 1.163 | 0.220 | 0.176 | |
| 2# | 1.153 | 0.195 | 0.179 | |
| Average value | 1.158 | 0.208 | 0.178 | |
| Background | 0.000 | 0.046[b] | 0.020 | |
| Background-corrected average value | 1.158 | 0.162 | 0.158 | 1.75 |

a Due to the low content of DAcPy, two parallel samples were tested to check the measurement accuracy and repeatability.

b The N single in the background test (without sample) may mainly come from $N_2$ in the atmosphere.

c DAcPy content was calculated according to C content.

## References

(s1) G. Kresse, J. Hafner, Ab initio molecular dynamics for open-shell transition metals, Phys. Rev. B. 48 (1993) 13115-13118.

(s2) G. Kresse, J. Furthmuler, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169-11186.

(s3) G. Kresse, J. Hafner, Ab initio molecular-dynamics for liquid metals, Phys. Rev. B 47 (1993) 558-561.

(s4) G. Kresse, J. Hafnre, Ab initio molecular-dynamics simulation of the liquid-metal amorphous-semiconductor transition in germanium, Phys. Rev. B 49 (1994) 14251-14269.

(s5) G. Kresse, J. Furthmuller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci. 6 (1996) 15-50.

(s6) P. E. Blochl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953-17979.

(s7) G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, Phys. Rev. B 59 (1999) 1758-1775.

(s8) W. Liu, J. Carrasco, B. Santra, A. Michaelides, M. Scheffler, A. Tkatchenko, Benzene adsorbed on metals: Concerted effect of covalency and van der Waals bonding, Phys. Rev. B 86 (2012) 245405.

(s9) J. Klimes, D. R. Bowler, A. Michaelides, Chemical accuracy for the van der Waals density functional, J. Phys.: Cond Matt. 22 (2010) 022201.

(s10) J. Klimes, D. R. Bowler, A. Michelides, Van der Waals density functionals applied to solids, Phys. Rev. B. 83 (2011) 195131.

(s11) J. K. Norskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jonsson, *J. Phys. Chem. B*, 2004, **108,** 1520.

(s12) P. Sett, S. Chattopadhyay and P. K. Mallick, *Vib. Spectrosc*, 2009, 49, 84-95.

(s13) D. Y. Wu, X. M. Liu, S. Duan, X. Xu, B. Ren, S. H. Lin and Z. Q. Tian, *J. Phys. Chem. C*, 2008, 112, 4195-4204.