Controllable Coordination of Phosphotungstic Acid-Modified Carbon Matrix for Anchoring Different Sizes of Pt Species: From Single Atoms, Subnanoclusters to Nanoparticles

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Experimental

Materials

Platinum(II) acetylacetonate (Pt(acac)$_2$, 98%), Phosphotungstic Acid (PTA, 98%) were purchased from Energy Chemical. Carbon Black XC-72 and Acetone (AR) were purchased from Macklin. All the chemicals were used without further purification.

Synthesis of Pt/PTA-C Catalysts

Typically, 10 ml acetone solution containing PTA (6.41 μmol) was dripped in 1.0 g of carbon black support and stirred for 10 min. Then, the mixture underwent an ultrasonic treatment for 10 min to form a uniform PTA-carbon black solution. The carbon black modified by PTA was dried in an oven at 70℃ for 60 min and recorded as "PTA-C".

According to an equal volume impregnation method, 2.5 ml acetone solution, containing Pt(acac)$_2$ (25.64 μmol) with a molar ratio of PTA/Pt= 1:4, was dropwise to PTA/C drop by drop. The obtained Pt(acac)$_2$-PTA/C was transferred to an alumina combustion boat for reduction in a 5% H$_2$/N$_2$ atmosphere at 170℃ for 60 min. After cooling, the resulting mixture was ground to a fine power, yielding Pt species supported on the surface of PTA/C with a Pt loading of 0.5 wt%. Similarly, by adjusting the different molar ratios of PTA/Pt (1:1.6, 1:8 and 1:16), Pt/PTA-C catalysts with different loadings were prepared (0.2 wt%, 1.0% and 2.0%).

The pre-catalysts were labelled in the following manner: the form of Pt species in the catalyst (SAs= only single atoms; Mix=single atoms, sub-nanoclusters and nanoparticles; NPs=only nanoparticles), the theoretical loading of Pt (0.2, 0.5, 1.0, 2.0 wt%) and the PTA-C support. For instance, Pt SAs$_{0.5}$/PTA-C refers to 0.5 wt% Pt single atoms supported on the PTA modified carbon black, Pt Mix$_{1.0}$/PTA-C refers to 1.0% Pt species, including single atoms, sub-nanoclusters and nanoparticles, supported on the the PTA modified carbon black, whereas Pt NPs$_{2.0}$/PTA-C refers to 2.0 wt% nanoparticles supported on PTA-C matrix.

As a control, a Pt(0.5)/C catalyst with an unmodified carbon black as the support was synthesized by the same procedures.

Characterization

X-ray diffraction (XRD) patterns were measured on a Bruker D8 Advance X-ray diffractometer using Cu irradiation (λ=0.15418 nm) with a fixed power source (40 kV, 40 mA). XRD patterns were collected at a scanning speed of 4°min^{-1} over a 2θ range of 5°-90°.

Transmission electron microscopy (TEM) images were recorded with a JEM-2100F instrument utilizing an acceleration voltage of 200 kV.

H$_2$ pulsed chemisorption was carried out in Auto Chem II 2920 (Micromeritics Company, USA). 100 mg sample was reduced for 1h in a 10%H$_2$/Ar atmosphere at 300 °C, then switched to Ar for 30min, and then cooled to 50 °C. 10%H$_2$/Ar (pulsed volume exchange 0.5 cc) was injected by pulse until adsorption saturation. The concentration of H$_2$ was determined by the thermal conductivity cell detector.

X-ray photoelectron spectroscopy (XPS) was conducted on a ThermoFischer, ESCALAB 250XI spectrometer with an Al Kα (1486.6 eV) excitation source. The working voltage was 14.6 kV, the filament current was 13.5 mA, and the signals were accumulated over 10 cycles. The C 1s peak at 284.8 eV was used for calibration.

The surface chemistry of the synthesized catalysts was studied with FTIR, which was carried out on a spectrophotometer (TENSOR 27, Bruker). The Pt loadings were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, ThermoFischer, iCAP 7400).

Pt L$_3$-edge X-ray absorption spectra were collected on the beamline 7-3 in Stanford Synchrotron Radiation Laboratory (SSRL), and were provided technical support by Ceshigo Research Service "www.ceshigo.com". The radiation was monochromatized by a Si (111) double-crystal monochromator. The obtained XAFS data was processed in Athena (version 0.9.25) for background, pre-edge line and post-edge line calibrations. Then Fourier transformed fitting was carried out in Artemis (version 0.9.25). The k^3-weighted EXAFS oscillation in the range of 3-12 Å^{-1} and R range of 1-3

Å was used for fitting. For Wavelet Transform analysis, the χ(k) exported from Athena was imported into the Hama Fortran code.

Catalytic Performance Test

In a typical run, the prepared catalyst (2.5 μmol) was added to the aromatic nitro-compounds (5.0 mmol) in a mixed solution of ethanol and ethyl acetate (EtOH/EA: 15 ml/ 15 ml). The reaction mixture was transferred into an autoclave, stirred at room temperature for 10 min for full mixing, and then purged with hydrogen three times at a pressure of 1 MPa and then retained at room temperature. The resulting solution was filtered with a PTFE syringe filter (pore size 0.45 μm) and analyzed by GC and GC-MS.

After completion of the reaction, the catalyst was collected by centrifugation. The collected solid was washed with ethanol three times, dried under vacuum and reused for the next run.

Calculated details

Firstly, according to the literatures and estimation on HAADF images, the sub-nanocluster of 0.2-0.5 nm contains 10 single atoms, the sub-nanocluster of 0.5-1.0 nm contains 20 single atoms, and the nanoparticles of 1-2 nm has about 60 single atoms. Based on the frequencies of different size as shown in Fig. 2k , the ratio of Pt NPs to all Pt species in the hybrid Pt $Mix_{1.0}$/PTA-C catalyst is as follows: $\dfrac{6.2\% \times 60}{56.3\% \times 1 + 19.1\% \times 1 + 18.4\% \times 20 + 6.2\% \times 60}$; Secondly, the weight percentage of NPs in the Pt $Mix_{1.0}$/PTA-C catalyst was 0.3768%; Finally, from the catalytic performance test shown in Fig. 8, the activity afforded by nanoparticles was only 6.68%, Pt NPs in the hybrid catalyst contribute around 8.29% to the total nitrobenzene conversion. That is to say, single Pt atoms and nanoclusters (<1 nm) in the hybrid Pt $Mix_{1.0}$/PTA-C catalyst dominate their more than 90% of total activities. It is a strong evidence that the Pt single atoms and nanoclusters are the most important active sites herein.
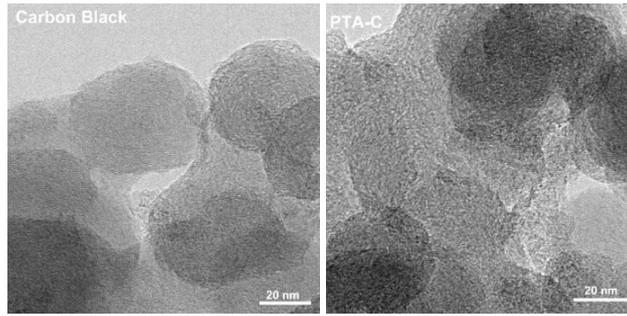
Fig. S1. TEM images of carbon black and PTA-C.
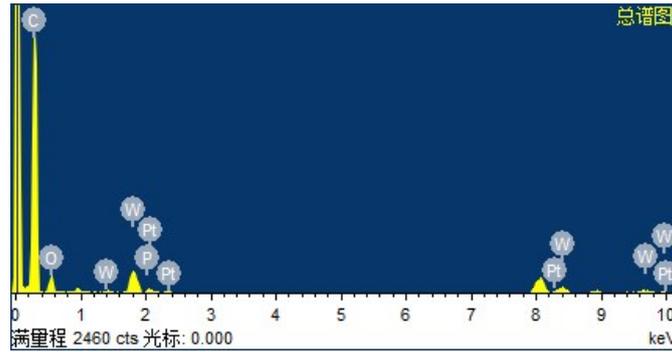
Fig. S2. EDS spectrum of Pt $SAs_{0.5}$/PTA-C catalyst.
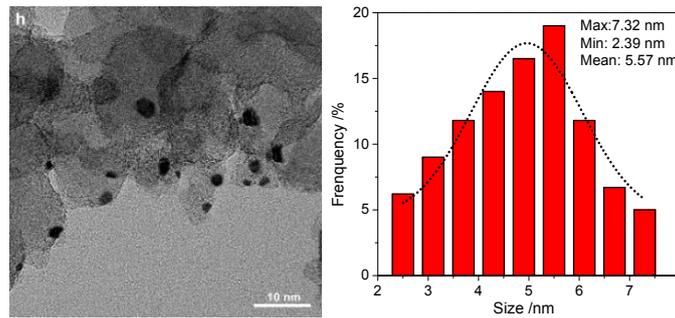
Fig. S3. TEM image and the corresponding size distribution of Pt(0.5)/C catalyst.
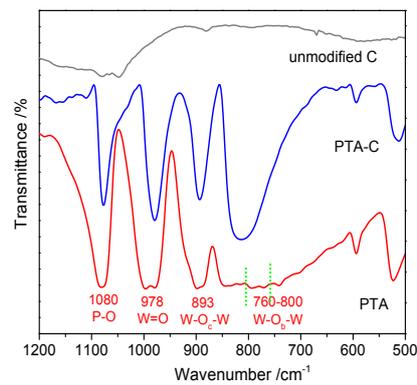
Fig. S4. FTIR spectra of unmodified carbon support, PTA and PTA-C.
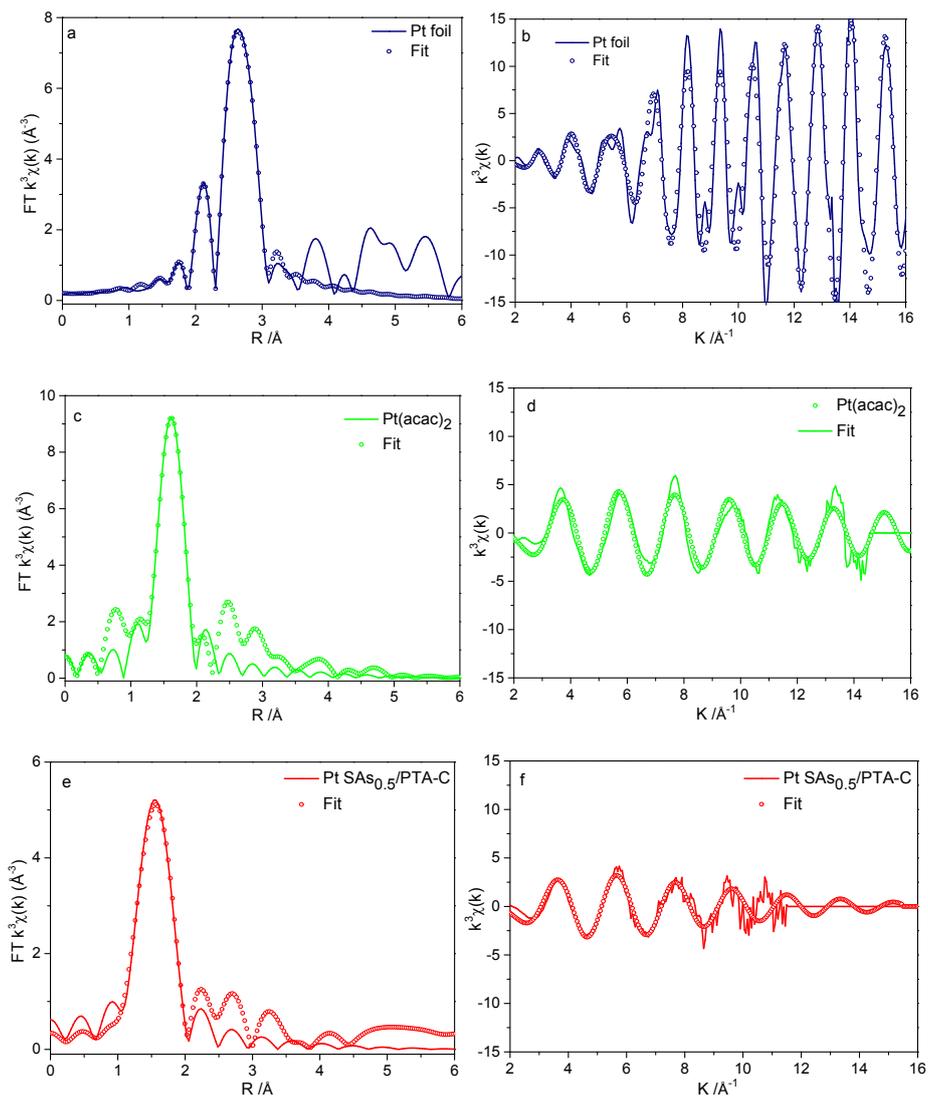
Fig. S5. FT-EXAFS curves between the experimental data and the fitting curve (a, c and e); and inverse FT-EXAFS fitting result (b, d and f) of the K-edge spectra for Pt foil (a and b), Pt(acac)$_2$ (c and d) and Pt SAs$_{0.5}$/PTA-C catalyst (e and f).
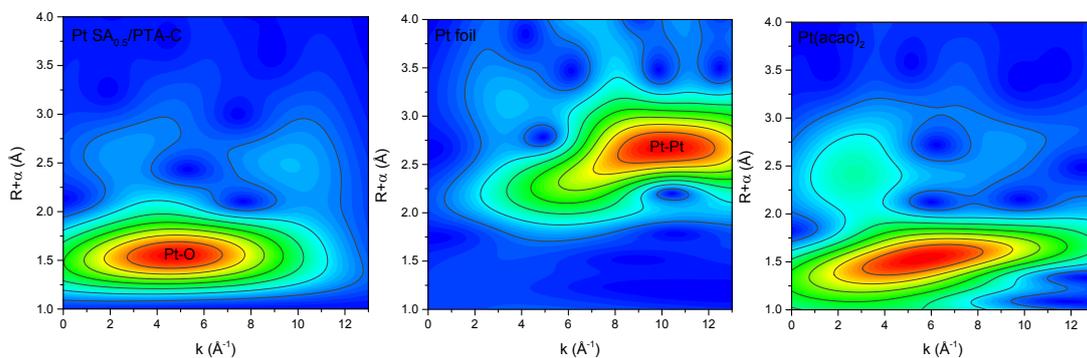
Fig. S6. Wavelet transformed (WT) k^3-weighted χ(k)-function of the Pt-L edge EXAFS spectrum for Pt foil and Pt(acac)$_2$.

Table S1. The parameters at the Pt foil, Pt(acac)$_2$ and Pt SAs$_{0.5}$/PTA-C catalyst

Sample	Shell	N^a	$R(\text{Å})^b$	$\sigma^2 \times 10^3 (\text{Å}^2)^c$	$\Delta E_0 (\text{eV})^d$	R factor
Pt foil	Pt-Pt	12	2.76±0.01	4.6±0.8	7.8±0.3	0.001
Pt(acac)$_2$	Pt-O	3.5±0.5	1.98±0.01	1.7±1.1	6.5±1.0	0.014
Pt SAs$_{0.5}$/PTA-C	Pt-O	3.3±0.6	1.97±0.01	4.9±1.9	7.6±2.3	0.010

[a] N: coordination numbers; [b] R: bond distance; [c] σ^2: Debye-Waller factors; [d] ΔE_0: the inner potential correction. R factor: goodness of fit.
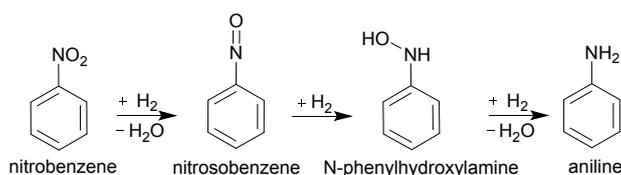
Scheme S1. Nitro-nitroso-hydroxylamine pathway of nitroarenes on Pt/PTA-C catalysts.
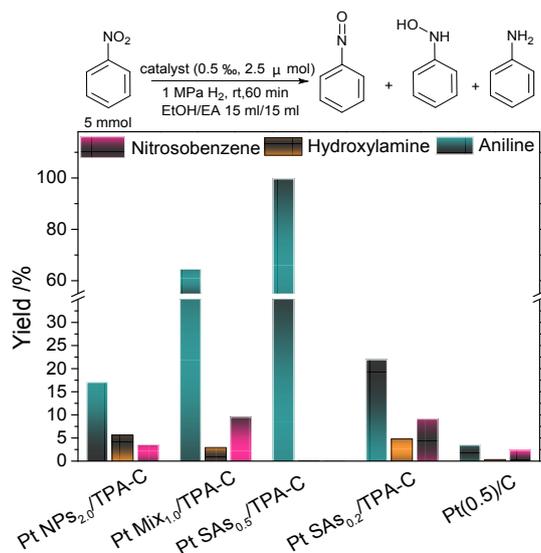
Fig. S7. Hydrogenation reactions of nitrobenzene to aniline over various catalysts.
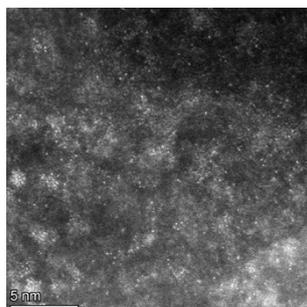
Fig. S8. HAADF-STEM image of Pt SAs$_{0.5}$/PTA-C catalyst after five runs.

Table S2. The conversion, physicochemical parameters of various catalyst

Samples[a]	Pt species	D_M [b]/ %	Con[c]/ %	TOF[d]/h^{-1}
Pt SAs$_{0.5}$/PTA-C	Single atoms	97	99.9	2062
Pt Mix$_{1.0}$/PTA-C	Single atoms and sub-clusters	79	74.2	1857
Pt NPs$_{2.0}$/PTA-C	Nanoparticles (1.56 nm)	51	35.4	1388
Pt (0.5)/C	Nanoparticles (5.57 nm)	24	12.7	1058

[a] Reaction conditions: nitrobenzene (5 mmol), catalyst (0.5 mmol‰ Pt), 1 MPa of H_2 pressure, room temperature, 1 h, EtOH/EA 15 mL/15 mL. [b] Dispersion of metallic Pt was measured based on hydrogen hydrogen pulse adsorption. [c] The conversion is based on nitroaromatic substrates and analysed by GC. [d] The TOF value was evaluated by moles of initial nitrobenzene converted per mole of surface Pt atoms per hour.

Table S3. Comparison of our work and previous reports.

Catalyst	Substrate	Reaction conditions				Yield/ %	TOF/h^{-1}	Selectivity
		P/MPa	T/°C	t/h	Catalyst amount [a]			
Pt SAs$_{0.5}$/PTA-C (this work)	**Nitrobenzene**	**1**	**25**	**1**	**0.5 ‰**	**99.71%**	**2062**	**99%**
Pt/PMA-AC (Ref [33])	Nitrobenzene	1	25	1	0.5 ‰	33.33%	774	>99%(sole product)
Ru/MN270 (Ref [34])	Nitrobenzene	≈1	180	0.5	3%	97%		98%
Au/TiO$_2$ (Ref [35])	Nitrobenzene	4	25	7	1%	93.3%		-
Au/SiO$_2$ (Ref [35])		4	25	7	1%	67.4%		
Pd$_{0.18}$Cu$_{15}$/Al$_2$O$_3$ (Ref [36])	Styrene	≈0.7	25	3.3	0.18%	90%		94%

[a] Defined as the radio of molar quantity of metal species relative to the molar quantity of substrate.