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Electronic Supplementary Material

Synthesis of carbon-supported sub-2 nanometer bimetallic catalysts by strong metal-sulfur interaction

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S1. Methods and syntheses of materials

Chemicals: All chemicals were from commercial sources and used without further purification. Platinum (II) acetylacetonate (97%) and silica template (SiO₂, 7 nm, S5130, 99%) were purchased from Sigma-Aldrich. Tetraammineplatinum (II) hydroxide hydrate (Pt(NH₃)₄(OH)₂, 97%) was purchased from Shanghai Aladdin Bio-Chem Technology Co. Ltd. Pt/C (5 wt%) was purchased from Alfa Aesar. 2,2'-bithiophene (98%) was purchased from J&K Scientific Ltd. All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd., China, including hexachloroplatinic hexahydrate (H₂PtCl₆·6H₂O, 99%), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 98.5%), cobalt chloride hexahydrate (CoCl₂·6H₂O, 99%), cobalt sulfate (CoSO₄·7H₂O), cobalt(II) oxalate dehydrate(CoC₂O₄), rhodium (III) chloride (RhCl₃), ruthenium (III) chloride (RuCl₃), iridium(III) chloride hydrate (IrCl₃·H₂O), sodium hydroxide (NaOH, 96%), sulfuric acid (H₂SO₄, 95%~98%), ethanol absolute (C₂H₅OH, 99.7%), and tetrahydrofuran (THF, 99%). DI water (18.2 MΩ/cm) used in all experiments was prepared by passing through an ultra-pure purification system.

Synthesis of the S-C support: The S-C supports were prepared by the cobalt-assisted carbonization of molecular precursors with silica nanoparticles as hard templates, according to the previously reported method.^{1, 2} Briefly, 0.5 g of 2,2'-bithiophene and 0.25 g of Co(NO₃)₂·6H₂O were first dissolved in 40 mL tetrahydrofuran (THF). Then 0.5 g of SiO₂ fumed powder (7 nm) was added into above solution under stirring to form a homogenous dispersion. THF in the mixed solution was then removed by a rotary evaporator. The obtained dried powder was subsequently carbonized under flowing N₂ at 800 °C for 2 hours. Finally, the carbonized product was treated by alkaline (2.0 M NaOH, room temperature, 48 h) and acidic (0.5 M H₂SO₄, 80 °C, 8 h) leaching successively to remove SiO₂ templates and cobalt species, respectively, to yield the S-C supports. The content of cobalt residue in S-C was lower than 0.1 wt%, as revealed by the inductively coupled plasma atomic emission spectrometry (ICP-AES) measurements.

Synthesis of the sub-2 nm bimetallic NPs catalysts: The sub-2 nm bimetallic NPs catalysts were prepared via a conventional impregnation process with S-C as supports. In a typical synthesis, a certain amount of two metal salt precursors was first dissolved in a suitable solvent before 50 mg S-C was added under stirring to form a homogeneous black dispersion. After removing out the solvent by a rotary evaporator, the obtained metal salts/S-C composite powder was subsequently reduced under flowing H₂/Ar (5 vol% H₂) at 700 °C. The total metal loading for typical samples was controlled to be 5.0 wt%. The molar ratio of two metals could be altered by simply varying the concentration of metal pairs in the impregnation step. Vulcan XC72R and Ketjen Black EC-300J supported bimetallic catalysts were also prepared for comparison by the same process. The detailed synthetic parameters for each sample were summarized in the Tables S2, S3 and S4[†].

Catalytic nitrobenzene hydrogenation: The catalytic hydrogenation reactions were performed in a steel Parr autoclave. Typically, 3 mmol p-chloronitrobenzene and 5 ml of methyl alcohol were added into a reaction glass vial before the catalyst was added in a Pt/substrate molar ratio of 0.1 %. The reaction vial was then placed into a 100 ml Parr autoclave reactor. After that, the autoclave was sealed and purged with H₂ to replace the air three times and pressurized with 2 bar H₂. Subsequently, the reactor was placed in water bath heated to 40 °C. The reaction was carried out for suitable time with magnetic stirring (1500 rpm). After the hydrogenation reaction, o-xylene was added into the reaction system and used as an internal standard. Ten milliliters of ethyl acetate were used to extract the organic compounds in the reaction system. The products were analyzed using a Shimadzu gas chromatograph (GC) with a flame ionization detector and high-purity nitrogen as the carrier gas. For the stability tests, the catalyst was separated by centrifugation, washed with ethanol and acetone several times, and then dried under vacuum at 60 °C overnight. Then the recovered catalyst was used directly for the next run without any reactivation. For the hydrogenation of substituted nitroarenes, 0.5 substrate and 2 ml of methyl alcohol were added into a reaction glass vial and other processes are similar with above. Note that the selectivity of Figure 4a and recycling experiments of Figure 4b was chosen at 2.0 h and 30 min, respectively. TOFs are calculated by Equations 1 and 2 below:

$$TOF = \frac{Conv. (\%) \times n \text{ (substrate)}}{n(\text{metal}) \times t}$$
(1)

$$n \text{ (metal)} = \frac{m(\text{catalyst}) \times w (\%)}{M(\text{metal})}$$
(2)

where n (substrate) is the initial molar of substrate, Conv. (%) is the conversion of substrates at the reaction of t, n (metal) is the molar of Pt atom on catalyst, w (%) is the mass fraction of Pt in catalysts and the result is a quantitative analysis by ICP-OES, M_{metal} is molar mass of Pt.

Characterizations: High-resolution transmission electron microscopy was performed on a JEM-2010F field-emission microscope operated at an accelerating voltage of 200 kV. Low-magnification HAADF-STEM images were obtained on FEI Talos F200X operated at 200 kV. Atomic resolution HAADF-STEM images were obtained on probe aberration-corrected JEM ARM200F operated at 200 kV. Energy dispersive spectroscopy (EDS) mappings and line scan were carried out on FEI Talos F200X, equipped with Super X-EDS system (four systematically arranged windowless silicon drift detectors) at 200 kV. At least two hundred NPs were measured for each sample to give the particle size distribution. N₂ adsorption was determined by BET measurements with a Quantanchrome ASiQ gas sorption analyzer, and the data were collected at liquid nitrogen temperature (77 K). The pore size distribution plot was recorded from the adsorption branch of the isotherm based on the Barrett-Joyner-Halenda model. Powder XRD patterns were collected on a Philips X'pert Pro Super diffractometer with Cu Ka line (λ = 1.5418 Å), radiation source with the operation voltage and operation current being 40 kV and 50 mA, respectively. The content of metal element in the catalysts was measured by ICP-OES (Optima 7300 DV, PerkinElmer). XPS measurements were carried out on an ESCALAB MKII instrument equipped with an Mg Ka source (hv= 1,253.6 eV), operating at 150 W and a spot size of 400mm. For the narrow scans, analyzer pass energy of 30 eV was applied. TPR of all catalysts were performed by using a Quantachrome ASiQ gas sorption analyzer equipped with TCD to measure the consumption of hydrogen. The temperature was set at a ramp rate of 10 °C min⁻¹, and the reducing gas of 10 vol% H₂ balanced Ar was set at a flowrate of 50 ml min⁻¹. X-ray absorption fine structure (XAFS) spectra at Pt/Ir L₃-edge and Co K-edge were obtained on the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF) operated at 2.5 GeV and 250 mA. The Rh L₃-edge XAFS spectra were collected at the beamline 14W1 in the Shanghai Synchrotron Radiation Facility, a 3.5 GeV third-generation synchrotron source, using a Si(111) double-crystal monochromator in transmission mode.



Fig. S1 (a) Nitrogen sorption isotherms and pore size distributions, (b) TEM image, and (c) XPS of S_{2p} region of the S-C support. (d) PXRD of the S-C support and Pt-Co/S-C catalyst.



Fig. S2 Phase diagrams of Pt-Co alloy (data from SGnobl noble metal alloy database).



Fig. S3 (a) Fourier transforms of EXAFS spectra of bimetallic Pt-Co and reference samples at the Co K edge. (b-c) Fourier transforms of EXAFS spectra of bimetallic Ir-Co and Rh-Co and reference samples at the Ir L_3 edge (b) and Rh L_3 edge (c).



Fig. S4 (a) EDS line scans, (b) HAADF-STEM images, and (c) size distribution of Rh-Co bimetallic NPs.



Fig. S5 (a) EDS line scans, (b) STEM-HAADF images, and (c) size distribution of Ir-Co bimetallic NPs.



Fig. S6 PXRD patterns of Pt-Co bimetallic NPs prepared with different metal precursors.



Fig. S7 STEM-EDS line scans of Pt-Co bimetallic NPs prepared with different precursors: (a) $Pt(NH_3)_4(OH)_2$ -CoCl₂, (b) H_2PtCl_6 -Co(NO₃)₂,(c) H_2PtCl_6 -CoC₂O₄, (d) H_2PtCl_6 -CoSO₄, and (e) $Pt(acac)_2$ -CoCl₂.



Fig. S8 HAADF-STEM images and size distribution of (a) 10 wt% and (b) 20 wt% Pt-Co bimetallic NPs, respectively. (c) PXRD patterns of high-loading Pt-Co bimetallic NPs.



Fig. S9 STEM-EDS line scans of 20 wt% Pt-Co bimetallic NPs.



Fig. S10 Reduction pathways for P-chloronitrobenzene. Reaction conditions: 3 mmol substrate, 0.1 mol% Pt, 40 °C, 2.0 bar H_2 , 2.0 h, methanol as solvent.



Fig. S11 Kinetic profiles of nitrobenzene reduction on (a) Pt/C, (b) Pt/S-C, (c) Pt-Co/S-C (Pt/Co=1), (d) Pt-Co/S-C (Pt/Co=3), (e) Pt-Co/S-C (Pt/Co=5), (f) Pt-Co/K-300J (Pt/Co=5).



Fig. S12 HAADF-STEM images of the catalysts for the catalytic hydrogenation of nitroarenes.



Fig. S13 PXRD patterns of Pt-Co/S-C catalyst before and after 5 recycles for the nitroarenes hydrogenation.



Fig. S14 (a) STEM-EDS line scans, (b) HAADF-STEM images, and (c) size distribution of Pt-Co/S-C (Pt/Co=5) bimetallic NPs.



Fig. S15 (a) STEM-EDS line scans, (b) HAADF-STEM images, and (c) size distribution of Pt-Co/S-C (Pt/Co=5) bimetallic NPs after 5 recycles.

S3. Supporting Tables

Sample	C (wt%)	N (wt%)	S (wt%)	Molar ratio of S/C
S-C	54.35	0.75	12.72	0.08
Pt-Co/S-C	73.56	0.48	5.52	0.03
S-C-1000	81.35	0.87	2.35	0.01

 Table S1 Elemental analysis results of the S-C support and the bimetallic Pt-Co catalyst.

Sample	Metal pairs		Solvent	M1/M2	Temperature/time	Average
Sumple	M2	M1	Borvent	ratio	(°C/h)	size (nm)
Pt-Co		H ₂ PtCl ₆			700/8.0	1.4±0.3
Rh-Co	CoCl ₂	RhCl ₃	water	1/2	700/8.0	1.4±0.3
Ir-Co		IrCl ₃			700/8.0	0.9±0.3

 Table S2 Synthesis recipes of bimetallic NPs on S-C with total metal loading of 5 wt%.

Pt	Co precursor	Pt/Co	Loading	Temperature/time	Average size
precursor	_	ratio	(wt%)	(°C/h)	(nm)
H ₂ PtCl ₆	CoCl ₂	1/2	5	700/8.0	1.4±0.3
H ₂ PtCl ₆	CoSO ₄	1/2	5	700/8.0	1.2±0.4
H ₂ PtCl ₆	$Co(NO_3)_2$	1/2	5	700/8.0	1.1±0.3
$Pt(acac)_2$	CoCl ₂	1/2	5	700/8.0	1.2±0.3
H ₂ PtCl ₆	CoC_2O_4	1/2	5	700/8.0	1.2±0.3
Pt(NH ₄) ₃ Cl ₂	CoCl ₂	1/2	5	700/2.0	1.4±0.3
H ₂ PtCl ₆	CoCl ₂	1/2	10	700/2.0	1.1±0.3
H ₂ PtCl ₆	CoCl ₂	1/2	20	500/2.0	1.1±0.3

Table S3 Synthesis recipes of small-sized Pt-Co NPs with various precursors andloadings on S-C.

Catalyst	Pt	Co	Co Pt/Co		Temperature/time
Catalyst	Precursors	Precursors	ratio	(wt%)	(°C/h)
Co/S-C	/	CoCl ₂	/	5	700/8.0
Pt/S-C	H ₂ PtCl ₆	/	/	5	700/8.0
Pt-Co/S-C (Pt/Co=5)	H ₂ PtCl ₆	CoCl ₂	5	5	700/8.0
Pt-Co/S-C (Pt/Co=3)	H_2PtCl_6	CoCl ₂	3	5	700/8.0
Pt-Co/S-C (Pt/Co=1)	H ₂ PtCl ₆	CoCl ₂	1	5	700/8.0
Pt-Co/K- 300J (Pt/Co=5)	H ₂ PtCl ₆	CoCl ₂	5	5	700/8.0

Table S4. Synthesis recipes of the catalysts for hydrogenation of *p*-chloronitrobenzene.

Catalyst	Pt (wt%)	Co (wt%)	TOF (h ⁻¹)
Pt/S-C	6.16	/	1789
Pt/C	4.9	/	1814
Pt-Co/S-C (Pt/Co=5)	4.59	0.49	1589
Pt-Co/S-C (Pt/Co=3)	2.81	1.09	1311
Pt-Co/K-300J (Pt/Co=5)	5.09	0.31	943
Pt-Co/S-C (Pt/Co=1)	5.03	2.08	478
Co/S-C	/	5.07	0

Table S5. Catalytic performance for the hydrogenation of *p*-chloronitrobenzene.

Entry	Substrate	Product	Time (h)	Conv. (%)	Sel. (%)
1	F NO ₂	F NH ₂	0.5	>99	>99
2	NO ₂	NH ₂ CI	0.5	>99	>99
3	Br NO ₂	Br NH ₂	1	>99	>99
4	NO ₂	NH ₂	1	>99	>99
5	H_2N	H ₂ N O	2	>99	>98
6	EtONO2	EtO NH ₂	1	>99	>99
7	N ^C NO ₂	N ^{∉C} NH ₂	1	>99	>99
8	NO ₂	NH ₂	2	>99	>99
9	NO ₂	NH ₂	2	>99	>99
10	NO ₂	NH ₂	3	>99	>99

 Table S6. Catalytic performance of Pt-Co/S-C (Pt/Co=5) for the hydrogenation of substituted nitroarenes.

Table S7. Comparisons of the S-C and N-doped carbon (N-C) supports for loading bimetallic Pt-Co nanoparticles. The data of Pt-Co/N-C (PtCo@NHPC_3 were copied from the literature³, and the number of TOF were calculated by equations 1 and 2 based on the complete reaction condition.

Catalyst	$S_{BET} \ (m^2/g)$	Heteroatom content (wt%)	Metal loading (wt %)	Particle size (nm)	Complete reaction conditions	TOF (h ⁻¹)
PtCo@NHPC_3	1230	N-4.6	3.74	4.9	0.84 mol‰ Pt catalyst, 50 °C; 6.8 bar H ₂ , 40 min	1785
PtCo/S- C(Pt/Co=5)	1324	S-5.2	5.08	1.4	0.96 mol‰ Pt catalyst, 40 °C, 2 bar H ₂ , 30 min	2083

S4. References

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