Carbon nanotube-supported Au-Pd alloy with cooperative effect of metal nanoparticles and organic ketone/quinone groups as a highly efficient catalyst for aerobic oxidation of amines

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Electronic Supplementary Information

1. Experimental details

1.1. Materials and catalyst preparation

Metal oxides including SiO₂, Al₂O₃, TiO₂, ZrO₂, CeO₂ and MgO with purities >99% were purchased from Sinopharm Chemical Reagent Co. Ltd. or Alfa Aesar. Activated carbon (AC) was obtained from Sinopharm Chemical Reagent Co. Ltd. XC-72, an extra-conduction carbon black, was purchased from Shanghai Cabot Chemical Co. Ltd. Multiwalled carbon nanotubes (CNTs) with outer diameters of 20-60 nm and inner diameters of 3-5 nm were synthesized by a method reported previously.¹ The CNTs were typically treated by 68 wt% HNO₃ at 373 K under refluxing conditions for 12 h to remove the remaining Ni catalyst used for the synthesis of CNTs or other possible metal impurities and to create oxygen-containing functional groups on the surface. To study the effect of functional groups on CNTs, 37 wt% HCI (at 353 K under refluxing conditions for 12 h), 55 wt% HNO₃ (at 373 K under refluxing conditions for 12 h) and the Fenton reagent were also exploited to treat the CNTs. After the treatment by an acid solution, the CNTs were recovered by filtration, followed by washing with deionized water (till pH = 7 or no Cl⁻) and drying at 373 K. The CNTs pretreated by 37 wt% HCl, which did not possess oxidation ability, were used as a reference and were expected to contain a low concentration of oxygen-containing functional groups. For the pretreatment by the Fenton reagent, the CNTs were first pretreated by 37 wt% HCl to remove possible metal impurities, and then the sample was suspended in an aqueous solution of $FeSO_4$ (1.0 M). Subsequently, H_2O_2 aqueous solution with a concentration of 30 wt% and a volume of 50 mL was added

dropwise to the suspension in about 2 h under stirring. The suspension was stirred for another 2 h. The solid product was recovered by filtration, followed by washing with aqueous solution of HCI (3.0 M) to remove possible iron impurities and then deionized water until no CI⁻ could be detected. The washed CNTs were then dried at 373 K. The ICP analysis showed that about 20 ppm of Fe residues remained on CNTs.

Colloidal Au-Pd nanoparticles stabilized with polyvinyl alcohol (PVA) were synthesized by addition of 1.0 wt% PVA (Aldrich, MW = 10000) aqueous solution into a mixed solution of PdCl₂ and HAuCl₄. The ratio of PVA to (Au + Pd) was controlled at 1.2/1. A freshly prepared NaBH₄ solution was added into the mixture rapidly, forming a dark-brown sol containing the colloidal Au-Pd nanoparticles. The molar ratio of NaBH₄ to (Au + Pd) was regulated to be 5/1. Other monometallic or bimetallic particles stabilized by PVA were prepared by the same procedure.

The supported Au-Pd bimetallic nanoparticles were prepared by immobilization of the PVA-stabilized colloidal Au-Pd nanoparticles onto different supports. Typically, the powdery support was added into the dark-brown sol. After vigorous stirring for 6 h, the solid catalyst was recovered by filtration and washed repeatedly with hot distilled water (3.0 L) to remove the PVA stabilizer. The resultant was dried at 373 K overnight and was further treated in flow O_2 at 573 K for 2 h. After cooling down to room temperature, H_2 was introduced and the sample was further reduced in H_2 at 573 K. The supported monometallic or other bimetallic catalysts were prepared with the same procedure. The total loading of the metals was fixed at 10 µmol g(cat)⁻¹ for each sample, and the loading amount was confirmed by Inductively coupled plasma mass spectrometry (ICP-MS) analysis.

1.2. Catalyst characterization

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed with an Agilent ICP-MS 4500 instrument to measure the actual loadings of Au and Pd in each sample. Transmission electron microscopy (TEM) measurements were performed on a JEM-2100 electron microscope operated at an acceleration voltage of 200 kV. High-resolution TEM (HRTEM) and energy-dispersive X-ray spectroscopy (EDS) line scanning measurements were performed on Philips Analytical FEI Tecnai 20 electron microscopy operated at an acceleration voltage of 200 kV. Samples for TEM measurements were suspended in ethanol and dispersed ultrasonically. Drops of suspensions were applied on a copper grid coated with carbon. Powder X-ray diffraction

(XRD) patterns were recorded on a Panalytical X'Pert Pro Super X-ray diffractometer equipped with X'Celerator detection system. The Cu K α radiation (40 kV and 30 mA) was used as the X-ray source. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Quantum 2000 Scanning ESCA Microprobe (Physical Electronics) using Al-K $_{\alpha}$ radiation (1846.6 eV) as the X-ray source. The adsorption amounts of benzylamine on the CNTs pretreated by different methods were measured by addition of the CNT (0.20 g) into a *p*-xylene solution of benzylamine (0.10 M, 5 mL). The suspension was stirred for 4 h at room temperature. The amount of benzylamine remaining in the supernate was measured by gas chromatography (Shimazu, GC-14B) after addition of *n*-hexane as an internal standard to determine the adsorption amount.

1.3. Catalytic reaction

The aerobic oxidation of amines was carried out by using a batch-type reaction vessel equipped with a magnetic stirrer and a reflux condenser. Typically, the powdery catalyst (typically 0.10 g with 1.0 µmol of metal) was added into the reactor pre-charged with amine (1.0 mmol) and solvent (*p*-xylene, 2.0 mL). Then, O_2 (99.9%) was bubbled into the mixture. The reactor was placed into a pre-heated oil bath and the reaction was started when the temperature reached the desired one (typically 393 K). The flow rate of O_2 was controlled at 3.0 mL min⁻¹. After a fixed reaction time, the reactor was cooled in ice water. The catalyst was filtered off and the products were analysed by gas chromatograph (Shimazu GC-16B) with a capillary column (RTX-5) and an FID detector. *n*-Hexane was used as an internal standard. For the solvent-free catalytic reactions, typically, 18.2 mmol of substrate was used without solvent. The product was separated by centrifugation and was purified by passing through a silica gel column (*n*-hexane/ethyl acetate = 10:3 as eluent). The final product was collected and was analysed both qualitatively and quantitatively after rotate evaporation.



2. TEM images of Au-Pd alloy nanoparticles loaded on various supports

Fig. S1 TEM images of Au-Pd alloy nanoparticles loaded on various supports. (a) Au-Pd/SiO₂. (b) Au-Pd/Al₂O₃. (c) Au-Pd/TiO₂. (d) Au-Pd/ZrO₂. (e) Au-Pd/CeO₂. (f) Au-Pd/MgO. (g) Au-Pd/AC. (h) Au-Pd/graphite. (i) Au-Pd/XC-72. (j) Au-Pd/CNT.

3. Catalytic performances of CNT-supported monometallic and bimetallic nanoparticles loaded on CNTs for oxidative homocoupling of benzylamine

Catalyst	Conversion	Selectivity (%)	Selectivity (%)		
	(%)	PhC=N-CPh	PhCHO	(%)	
Au/CNT	33	>99	0	33	
Ru/CNT	25	97	2.8	24	
Pd/CNT	60	98	2.0	59	
Pt/CNT	24	95	0	21	
Ag/CNT	15	99	0	15	
Au-Pd/CNT ^b	95	98	1.6	93	
Au-Pt/CNT	68	>99	0	68	
Au-Ag/CNT	22	>99	0	22	
Au-Cu/CNT	72	>99	0	72	
Au-Ni/CNT	66	>99	0	66	
Au-Co/CNT	49	>99	0	49	
Au-Fe/CNT	63	>99	0	63	
Au-Ru/CNT	51	91	8.8	46	
Pd-Ag/CNT	22	98	1.9	21	
Pd-Pt/CNT	77	>99	0	77	
Pd-Ru/CNT	66	92	8.0	61	
CNT ^c	2.0	90	9.6	1.8	

Table S1 Catalytic performances of monometallic and bimetallic nanoparticles loaded on CNTs for oxidative homocoupling of benzylamine^a

^a Reaction conditions: benzylamine, 1.0 mmol; metal/substrate molar ratio, 1/1000; temperature, 393 K; solvent, *p*-xylene (2.0 cm³); O₂ flow rate, 3 cm³ min⁻¹; time, 4 h. For bimetallic catalyst, metal A/metal B molar ratio = 1/1. ^{*b*}We have conducted three parallel experiments for this catalyst under the same reaction conditions. The results from these parallel reactions are close to each other and the average values from these experiments were listed here. ^{*c*} CNT, 0.10 g.

4. Catalytic behaviours of CNT-supported Au-Pd bimetallic nanoparticles with different Au/Pd molar ratios for the oxidative homocoupling of benzylamine

Table S2 Catalytic behaviours of CNT-supported Au-Pd alloy nanoparticles with different

 Au/Pd molar ratios for the aerobic oxidative homocoupling of benzylamine^a

Catalyst ^b	Mean size ^c	Conversion	Selectivity (%	b)	PhC=N-CPh
	(nm)	(%)	PhC=N-CPh	PhCHO	yield (%)
Au/CNT	3.6	33	>99	0	33
Au-Pd(11/1)/CNT	3.0	55	>99	0	55
Au-Pd(2.8/1)/CNT	3.4	76	>99	0	76
Au-Pd(1/1)/CNT	3.0	95	98	1.6	93
Au-Pd(0.43/1)/CNT	3.1	86	96	3.7	83
Au-Pd(0.11/1)/CNT	3.0	74	97	3.4	72
Pd/CNT	2.7	60	98	2.1	59

^{*a*} Reaction conditions: catalyst, 0.10 g; benzylamine, 1.0 mmol; (Au + Pd)/substrate molar ratio, 1/1000; temperature, 393 K; solvent, p-xylene (2.0 cm³); O₂, 1 atm and flow rate of 3 cm³ min⁻¹; time, 4 h. ^{*b*} The ratio in the parenthesis denotes the molar ratio of Au/Pd. ^{*c*} Measured by TEM.

5. XRD patterns for Pd, Au, and Au-Pd alloy (Au/Pd = 1/1) nanoparticles loaded on CNTs



Fig. S2 XRD patterns of CNT and CNT-supported Pd, Au, and Au-Pd (Au/Pd = 1/1) nanoparticles. Metal [Au, Pd or (Au + Pd)] loadings: (A) 0.15 wt%, (B) 2.0 wt%.

The three diffraction peaks for the catalysts with a lower metal loading (0.15 wt%) could be ascribed to CNTs (Fig. S2A). No diffraction peaks assignable to Au, Pd or Au-Pd crystalline phases could be observed for these catalysts probably because of the low metal loading. We also measured the XRD patterns for the CNT-supported Au-Pd nanoparticles with a higher (Au + Pd) loading (2.0 wt%). The result is displayed in Fig. S2B. The XRD patterns for Pd/CNT and Au/CNT samples with a metal loading of 2.0 wt% are also shown in Fig. S2B. The XRD peaks belonging to metallic Pd and Au at 2 θ of 40.0° and 38.1° were clearly observed for the 2.0 wt% Pd/CNT and 2.0 wt% Au/CNT samples, respectively. A diffraction peak at 2 θ of 38.9°, which could be ascribed to the Au-Pd alloy,² was observed for the 2.0 wt% Au-Pd/CNT, indicating the formation of Au-Pd alloy.

6. Catalytic performances of Au-Pd/CNT for aerobic oxidation of substituted benzylamines and dibenzylamine

Entry	Substrate	Time (h)	Imine yield (%)	TOF (h ⁻¹)
1	NH ₂	8	91	2070
2	Me NH ₂	8	88	2000
3	MeO NH ₂	8	66	1500
4	CI NH2	12	75	1140
5	F NH ₂	12	80	1210
6		16	97	1100

Table S3 Catalytic performances of Au-Pd/CNT for aerobic oxidation of substituted benzyl

 amines and dibenzylamine^a

^a Reaction conditions: substrate, 18.2 mmol; catalyst, 0.10 g; (Au + Pd) amount, 1.0 μ mol; temperature, 393 K; O₂ flow rate, 3 cm³ min⁻¹. TOF was calculated based on the formation rate of imines per molar of (Au + Pd).

7. TEM image of Au-Pd alloy (Au/Pd = 1/1) nanoparticles loaded on CNTs pretreated by different methods



Fig. S3 TEM images of Au-Pd (Au/Pd = 1/1) alloy nanoparticles loaded on CNTs pretreated by different methods. CNT pretreatment: (a) 37 wt% HCl, (b) 55 wt% HNO₃, (c) 68 wt% HNO₃, (d) Fenton reagent.

8. Relative concentrations of functional groups over Au-Pd/CNT catalysts with CNTs pretreated by different methods and benzylamine adsorption

CNT	Normalized concentrations of functional groups at				Benzylamine
pretreatment	different O1s BEs ^a (%)				_adsorption ^f
	531.1 eV [♭]	532.3 eV ^c	533.3 eV ^d	534.2 eV ^e	(mmol g⁻¹)
37 wt% HCI	14	36	69	13	0.13
55 wt% HNO ₃	35	86	72	73	0.81
68 wt% HNO ₃	93	100	100	100	1.5
Fenton reagent	100	91	92	7.9	1.0

Table S4 Relative concentrations of functional groups over the Au-Pd/CNT catalysts with CNTs pretreated by different methods and benzylamine adsorption^a

^{*a*} The normalization has been performed for each functional group. The relative concentration of the strongest peak among the four catalysts was normalized to 100%; BE denotes binding energy. ^{*b*} Oxygen in ketone/quinone groups. ^{*C*} Carbonyl oxygen in ester or anhydride groups. ^{*d*} Oxygen in ether/hydroxyl or non-carbonyl oxygen in ester/anhydride groups. ^{*e*} Oxygen in carboxyl groups. ^{*f*} The adsorption was performed by addition of 0.20 g support into 5.0 mL *p*-xylene solution containing 0.1 M benzylamine at room temperature.

9. Effect of 4-*tert*-butylcatechol on aerobic oxidative homocoupling of benzylamine catalysed by supported Au-Pd alloy nanoparticles

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Catalyst	Molar ratio of 4-tert-butylcatechol to	PhC=N-CPh yield		
	benzylamine (%)			
None	1.0	1.4		
Au-Pd/SiO ₂	0	8.4		
Au-Pd/Al ₂ O ₃	0	11		
Au-Pd/CNT	0	40		
Au-Pd/SiO ₂	0.3	46		
Au-Pd/Al ₂ O ₃	0.3	91		
Au-Pd/CNT	0.3	98		
^a Reaction conditions:	benzyl amine, 1.0 mmol; metal/substrate	e molar ratio, 1/1000;		
temperature, 333 K; solvent, p-xylene (2.0 cm ³); O ₂ flow rate, 3 cm ³ min ⁻¹ ; time, 8 h.				

Table S5 Catalytic performances of supported Au-Pd alloy nanoparticles for the aerobic

 oxidation of benzylamine with and without addition of 4-*tert*-butylcatechol^a

10. Conversion of 4-tert-butylcatechol under the reaction conditions used for the oxidative homocoupling of benzylamine in the presence of the Au-Pd/CNT catalyst



Fig. S4 Results from the gas chromatography for the conversion of 4-*tert*-butylcatechol in the presence of Au-Pd/CNT catalyst. (a) In the absence of benzylamine; 4-*tert*-butylcatechol, 0.3 mmol. (b) In the presence of benzylamine; 4-*tert*-butylcatechol, 0.3 mmol, 4-*tert*-butylcatechol/benzylamine = 0.3/1 (molar ratio). Reaction conditions: metal/substrate molar ratio, 1/1000; temperature, 333 K; solvent, *p*-xylene (2.0 cm³); O₂ flow rate, 3 cm³ min⁻¹; time, 8 h.

References

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