Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Enhanced Catalytic Performance of Cobalt Nanoparticles Coat-ed by a N,P-Codoped Carbon Shell Derived from Biomass for Transfer Hydrogenation of Functionalized Nitroarenes

Yanan Duan, Tao Song, Xiaosu Dong, and Yong Yang*

[†]CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

Corresponding Authors
*Y.Y.: email: yangyong@qibebt.ac.cn

1. General Considerations

Unless otherwise noted, all reagents were purchased commercially from Sigma-Aldrich, or Aladdin and used as received without further purification. The fresh bamboo shoots were obtained from Anhui Taiping Test Centre, International Centre for Bamboo and Rattan, Anhui Province, China. The commercially available activated carbon was purchased from Fujian Xinsen Carbon Coop., Shaowu, Fujian. All operations were carried out in an argon atmosphere using glovebox and Schlenk techniques unless otherwise specified. Anhydrous tetrahydrofuran (THF), hexanes and toluene were obtained from an argon purged solvent purification system comprised of columns of activated alumina and molecular sieves. Anhydrous *N*,*N'*-dimethylformamide (DMF), acetonitrile (CH_3CN), dimethyl sulfoxide (DMSO) and 1,4-dioxane were purchased from Aladdin and used without further purification. Gas chromatography analysis was performed on an Agilent HP-7890 instrument with a flame ionization detector (FID) and an HP-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thicknesses) using helium as the carrier gas. Gas chromatography-mass spectrometry analysis was carried out on an Agilent HP-7890 instrument with an Agilent HP-5975 with triple-axis detector and HP-5 capillary column using helium carrier gas. NMR spectra were from a Bruker DRX-400, or DRX-600, instrument and calibrated using residual non-deuterated solvent ($CDCl_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm; C_6D_6: $\delta_H = 7.16$ ppm, $\delta_C = 128.06$ ppm) as an internal reference.

2. Characterization

The X-ray diffraction (XRD) patterns of all the catalysts were obtained on a Bruker D8 Advance X-ray diffraction diffractometer equipped with Cu Ka radiation (λ= 1.5147 Å). The morphology of catalysts was examined by a H-7600 transmission electron microscopy (TEM), a Tecnai G2 F30 high-resolution TEM (HRTEM) and a FEI Tecnai G2 F20 scanning transmission electron microscopy (STEM). Nitrogen adsorption–desorption data were obtained on a Micromeritics ASAP 2020 static volumetric sorption analyzer. The specific surface area of the samples was calculated by the

Brunauer-Emmet-Teller (BET) method. The micropore volume was calculated by t-plot method. The pore size distributions were determined by non-local density functional theory (NLDFT). The X-ray photoelectron spectroscopy (XPS) data was collected on an ESCALAB 250Xi (Thermo Scientific, UK) instrument equipped with a monochromatized Al Ka line source. All the binding energies obtained were calibrated based on the C 1s peak at 284.8 eV. The elemental composition analysis of the catalysts was conducted on Vario El elemental analyzer. Ion Chromatography was conducted on a Thermo Scientific Dionex ICS-5000 equipped with CS-12 column with methanesulfonic acid (20 mM) as an eluent. Raman spectra were obtained on a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer system using a 532 nm wavelength laser at room temperature. Magnetic measurement was carried out using a SQUID MPMS-XL5 from Quantum Design with the field range of -3 to 3 T in hysteresis mode. The sample was prepared in a gelatine capsule held in a plastic straw under protective atmosphere. The raw data were corrected for the diamagnetic part of the sample holder. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was conducted on a PerkinElmer Optima 5300 DV instrument.

3. Preparation of the catalysts Co@NPC-x and Co@NC-x

The cobalt nanoparticles coated by N,P-codoped carbon shell was prepared in two-steps including hydrothermal treatment and carbonization process. The fresh bamboo shoots were obtained from Anhui Taiping Test Centre, International Centre for Bamboo and Rattan, Anhui Province, China. The Bamboo shoots were firstly cut into slices and dried at 70 °C for 24 h. The dried bamboo shoots (2 g) were then ground into powders and transferred in a 100 mL Teflon-inner stainless-steel autoclave coupled with 18 ml of deionized water. The autoclave was then heated to 180 °C and maintained for 5.5 h. The resulting brown solids were filtered, washed by distilled water thoroughly to remove any residual of soluble metal ions such as Ca^{2+} or K^+ (detected by ion chromatography), dried at room temperature under vacuum for 24 h. After that, 0.5 g of the brown hydrochars were added to 15 mL H_2O involved 0.2 mmol of

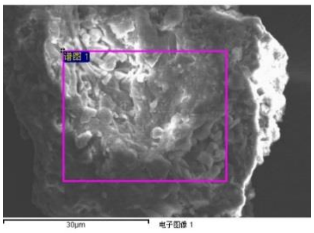
$Co(NO_3)_2.6H_2O$ with 0.1 g of PPh_3, and stirred evenly at 60 ^oC for 2h, then the resultant mixture was dried at 100 ^oC for 10 h, and calcined at 700, 800, and 900^oC for 2 h in N_2 flow with a heating rate of 5 °C min^{-1}. The black powder heteroatom doped porous carbons were obtained and denoted as Co@NPC-x, where x represents the pyrolysis temperature. Accordingly, the catalysts with different P loadings (e.g. 1, 5, 10, 20, 30 wt%) were prepared in same procedure with only changing of the added amount of PPh_3.

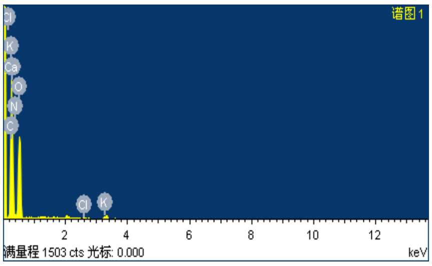
For comparison, the catalyst Co@NC-800 was prepared by pyrolysis of the mixture of brown chars with $Co(NO_3)_2$ without addition of PPh_3 at 800^oC under N_2 flow, other conditions were kept completely same as Co@NPC-800. The catalyst Co@C-800 was prepared by pyrolysis of the mixture of commercially available activated carbon with $Co(NO_3)_2$ under otherwise identical conditions same to Co@NPC-800. The bare support NC-800 was prepared by pyrolysis of the obtained brown chars at 800^oC under N_2 flow. The bare support NPC-800 was prepared by pyrolysis of the obtained brown chars mixed physically with PPh_3 (20 wt% loading) at 800^oC under N_2 flow.

4. Catalytic transfer hydrogenation of functionalized nitroarenes

In a typical procedure, to a sealable Schlenk reaction tube equipped with a magnetic stir bar was charged with 40 mg of Co@NPC-800 catalyst. The tube was then sealed with a rubber septum and was evacuated for a while to remove air. 5 mL solvent, 0.5 mmol of nitrobenzene, and 2.0 mmol of hydrogen donor were injected via syringe into the tube and the reaction was stirred under N_2 balloon at 120^oC. After completion of the reaction, the reaction mixture was filtered or separated using external magnet. The liquid was analysed by GC and GC-MS to determine the conversion and selectivity using dodecane as an internal standard. The verification of each aniline was done by comparing with the corresponding authentic sample by GC and GC-MS.

5. The elemental compositions of dried bamboo-shoots were determined by EDX and C/H/N elemental analysis.





EDX analysis result:

Element	weight%	Atom%
C K	42.86	49.43
N K	14.39	14.23
O K	41.44	35.88
Cl K	0.10	0.04
K K	1.03	0.36
Ca K	0.18	0.06
Total	100.00	

Elemental analysis result for the dried bamboo shoots:

Element	C	N
Atom%	41.7	4.27

6. Optimization of reaction conditions.

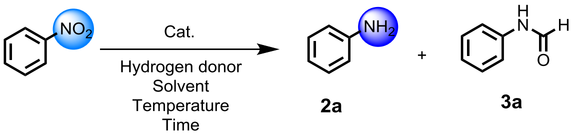


Table S1. The catalytic performance using HCOOH as hydrogen donor[a]

Entry	Amount (mg)	HCOOH (equiv.)	Solvent (v/v)	Time (h)	Conversion (%)[b]	Selectivity (%)[b]	
						2a	**3a**
1	20	12	THF	24	100	5	95
2	20	8	THF	24	68	14	86
3	20	6	THF	24	30	52	48
4	20	4	THF	24	20	66	34
5	20	3	THF	24	28	79	21
6	20	6	THF/H_2O(4.9/0.1)	24	86	50	50
7	20	6	THF/H_2O(4.5/0.5)	24	99	68	32
8	20	6	THF/H_2O(4.0/1.0)	24	100	65	35
9	20	6	THF/H_2O(3.0/2.0)	24	100	59	41
10	20	4	THF/H_2O(4.5/0.5)	24	77	88	12
11	40	4	THF/H_2O(4.5/0.5)	24	82	91	9
12	50	4	THF/H_2O(4.5/0.5)	24	88	96	4
13	60	4	THF/H_2O(4.5/0.5)	24	97	96	4

[a]Reaction condtions: nitrobenzene (0.5 mmol), HCOOH as hydrogen donor with different equivalents with respect to nitrobenzene, Co@NPC-800 (20 - 60 mg) as catalyst, 5 mL solvent, 120°C, 24 h. [b]Conversion and selectivity were determined by GC using dodecane as an internal standard.

The reaction was performed using formic acid (FA) as hydrogen doror in the presence of the catalyst Co@NPC-800. Initially, a larger excess of FA (12 equiv.) was employed with 20 mg of the catalyst in THF for the reaction. Complete conversion of nitrobenzene was achieved with **3a** as the main product (entry 1). Decreasing the amout of FA used led to signiciant enhancement to **2a** selectivity but condiserably slowed the reaction efficiency (entries 2-5). We found that addition of a certain amout of water in the reaction mixture could not only sharply improve the reaction efficiency but also influenced the selectivity to a some extent (entries 6-9), and the best result in term of both activity and selectivity was obtained using 4.5/0.5 (v/v, 5 mL) of THF/H_2O as solvent. Subsequent studies showed that the catalytic actvity could be further improved by increasing the amount of the catalyst and the selectivity to **2a** could be significantly tuned with 4 equivalent of FA (entries 10-13).

Table S2. Effect of type of hydrogen donor[a]

Entry	Reductant (equiv)	Time (h)	Conversion (%)[b]	Selectivity (%)[b]	
				2a	**3a**
1	$NaBH_4$ (4)	12	100	100	0
2	$PhMe_2SiH$ (4)	24	59	100	0
3	HCOOH (4)	24	89	90	10
4	$HCOONH_4$ (4)	12	100	97	3

[a]Reaction conditions: nitrobenzene (0.5 mmol), hydrogen donor (2.0 mmol), Co@NPC-800 (40 mg), THF/H_2O (4.5/0.5, v/v), 120°C. [b]determined by GC-FID using dodecane as an internal standard.

Based on the screening results obtained of using FA as hydrogen donor, we next investigated the reduction using a fixed amount of the catalyst Co@NPC-800 (40 mg) and 4 equivalent of hydrogen donor (with respect to nitrobenzene) in THF/H_2O (4.5/0.5, v/v) as solvent. Other 3 types of reductants, which are frequently used for catalytic transfer hydrogenation reactions, were studied, respectively. $NaBH_4$ showed the best catalytic efficiency, while it was not preferable choice due to its price, air-sensitive, and relative toxic features. Under otherwise identical conditions, ammonium formate outperformed superior activity and selectivity to its analogous FA. Therefore, ammonium formate was chosen as our choice for further studies.

Table S3. Effect of solvent[a]

Entry	Solvent	Time (h)	Conversion (%)[b]	Selectivity (%)[b]	
				2a	**3a**
1[c]	THF	24	75	88	12
2[d]	THF/H_2O	12	100	97	3
3[d]	1,4-dioxane/H_2O	12(24)	84(100)	99	1
4[d]	MeCN/H_2O	24	85	>99	<1
5[d]	DMSO/H_2O	24	61	98	2
6[d]	Toluene/H_2O	24	43	99	1
7[e]	H_2O	24	3	100	0

[a]Reaction conditions: nitrobenzene (0.5 mmol), $HCOONH_4$ (2.0 mmol), Co@NPC-800 (40 mg), solvent (5 mL), 120°C. [b]determined by GC-FID using dodecane as an internal standard.[c]THF (5 mL). [d]the volume ratio equals to 4.5/0.5, v/v. [e]H_2O (5 mL).

Several different solvents were employed for the reaction. Apparently, THF/H_2O was the best choice among all solvents investigated. While other mixed solvents also showed excellent selectivity to **2a**, considerably lower activities were observed compared with THF/H_2O (entries 2-6). However, the reaction exhibited significantly poorer activity in either pure THF or H_2O as solvent (entries 1 and 7).

Table S4. Effect of amount of HCOONH4[a]

Entry	Reduct (equiv.)	Time (h)	Conversion (%)[b]	Selectivity (%)[b]	
				2a	**3a**
1	$HCOONH_4$ (4)	12	100	97	3
2	$HCOONH_4$ (3)	24	99	>99	<1
3	$HCOONH_4$ (2)	24	49	100	0
4	$HCOONH_4$ (1)	24	25	100	0
5	$HCOONH_4$ (0)	24	0	0	0
6	HCOOH (6)	24	99	68	32
7	HCOOH (4)	24	89	90	10

[a]Reaction conditions: nitrobenzene (0.5 mmol), Co@NPC-800 (40 mg), THF/H_2O (4.5/0.5, v/v), 120°C. [b]determined by GC-FID using dodecane as an internal standard.

Further investigation showed that a decrease the amount of ammonium formate used for the reaction considerably prolonged the reaction times to achieve complete conversion albeit with negligible influence on selectivity to **2a** (entries 1-4). However, no reaction took place in the absence of ammonium formate (entry 5).

Table S5. Effect of amount of Co@NPC-800[a]

Entry	Amount (mg)	Time (h)	Conversion (%)[b]	Selectivity (%)[b]	
				2a	**3a**
1	60	6(12)	100(100)	99(99)	1
2	50	6(12)	100(100)	99(99)	1
3	40	12	100	97	3
4	20	24	98	90	10

[a]Reaction conditions: nitrobenzene (0.5 mmol), $HCOONH_4$ (2.0 mmol), Co@NPC-800 (20-60 mg), THF/H_2O (4.5/0.5, v/v), 120°C. [b]determined by GC-FID using dodecane as an internal standard.

Table S6. Effect of Temperature[a]

Entry	Temperature (°C)	Time (h)	Conversion (%)[b]	Selectivity (%)[b]	
				2a	**3a**
1	120	12	100	97	3
2	100	12	85	98	2
3	80	12	30	100	0

[a]Reaction conditions: nitrobenzene (0.5 mmol), $HCOONH_4$ (2.0 mmol), Co@NPC-800 (40 mg), THF/H_2O (4.5/0.5, v/v), 80-120°C. [b]determined by GC-FID using dodecane as an internal standard.

7. Characterization Results

Table S7. The results of elemental analysis and texture properties of the different catalysts

Sample	**Co content (wt%)**[a]	**XPS analysis**					**BET analysis**		
		N(%)	O(%)	C(%)	P(%)	Co(%)	S_{BET}(m^2/g)[b]	V_{total} (cm^3/g)[c]	d_{DFT} (nm)[b]
Co@C-800	2.48	-	8.71	90.22	-	1.07	1124	0.234	2.5
Co@NC-800	4.04	2.81	6.07	90.83	-	0.29	223	0.134	3.5
Co@NPC-700	2.14	4.54	7.48	87.04	0.46	0.48	383	0.076	2.4
Co@NPC-800	3.54	2.74	8.73	87.49	0.52	0.52	400	0.158	3.5
Co@NPC-900	4.04	2.69	8.68	87.78	0.46	0.39	434	0.160	3.4

[a] Determined by ICP-OES. [b] Specific surface areas were determined by the BET multipoint method. [c] Average pore sizes were obtained by the BJH method

Table S8. The results of XPS analysis of the catalyst Co@NPC-800 with different PPh_3 added amounts

Amount of added PPh_3 (wt%)	**XPS analysis**				
	Co (wt%)	C (wt%)	N (wt%)	P (wt%)	O (wt%)
0	0.29	90.83	2.81	-	6.07
1	0.29	88.89	2.49	0.18	8.15
5	0.29	88.26	2.79	0.22	8.47
10	0.27	87.47	2.83	0.33	9.37
20	0.52	87.49	2.74	0.52	8.73
30	0.45	87.68	3.07	0.46	8.34

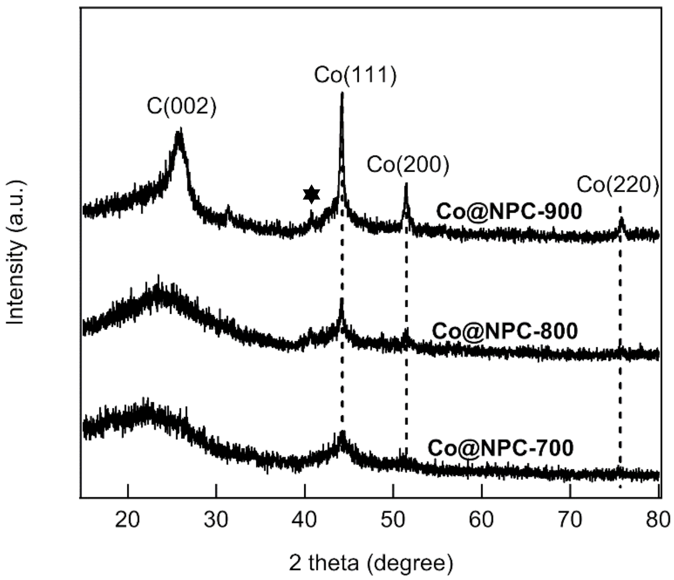


Figure S1. X-ray diffraction patterns for the catalyst Co@NPC with different pyrolysis temperature at 700, 800, and 900°C.

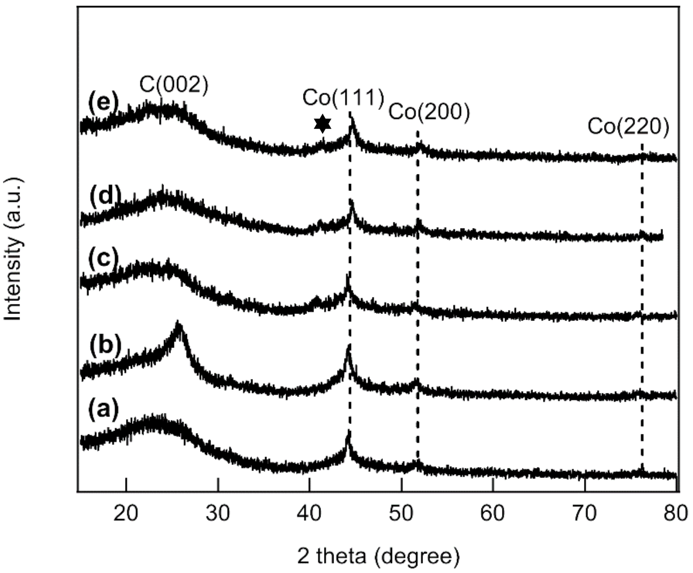


Figure S2. X-ray diffraction patterns for the catalyst Co@NPC with different added amount of PPh_3. (a) 1 wt%; (b) 5 wt%; (c) 10 wt%; (d) 20 wt%; and (e) 30 wt%.

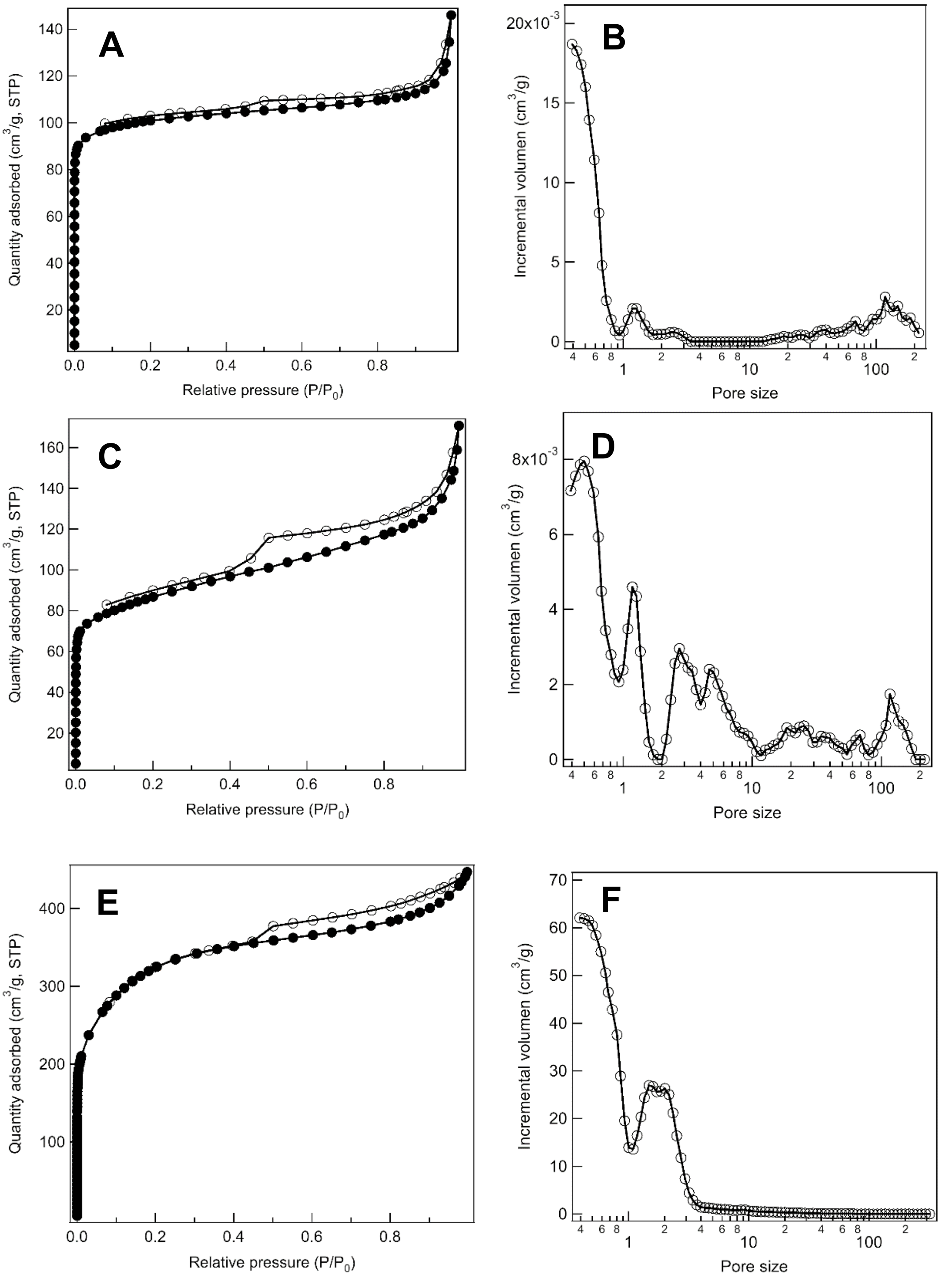


Figure S3. N_2 sorption isotherms and pore size distribution of the catalysts (A &B) Co@NPC-700; (C&D) Co@NPC-900; and (E&F) Co@C-800 at 77 K. The pore size distributions calculated using a nonlocal density function theory (NLDFT) method.

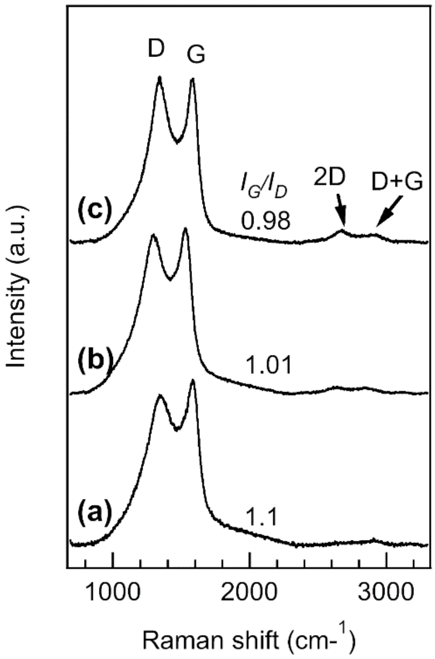


Figure S4. Raman spectroscopy for the catalyst Co@NPC with different pyrolysis temperature at (a) 700, (b) 800, and (c) 900°C.

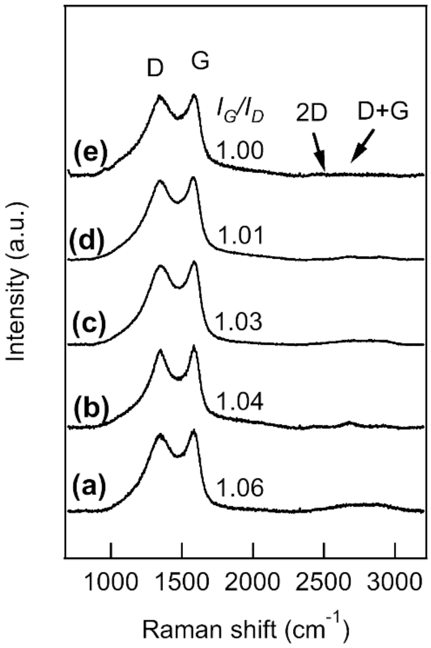


Figure S5. Raman spectroscopy for the catalyst Co@NPC with different added amount of PPh_3. (a) 1 wt%; (b) 5 wt%; (c) 10 wt%; (d) 20 wt%; and (e) 30 wt%.

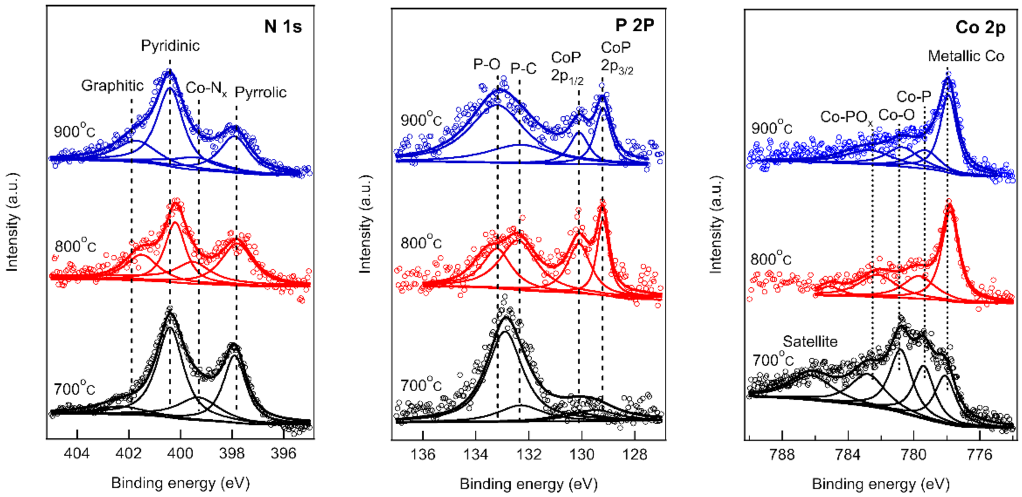


Figure S6. N 1s, P 2p, and Co 2p XPS spectra for the catalyst Co@NPC prepared at 700, 800, and 900°C.

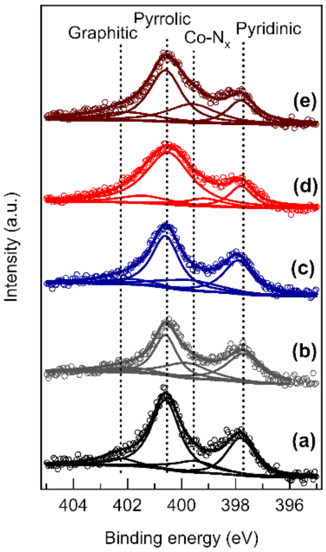


Figure S7. N 1s XPS spectra for the catalyst (a) Co@NC-800 and Co@NPC-800 with different added amount of PPh_3 (b) 1 wt%; (c) 5 wt%; (d) 10 wt%; and (e) 30 wt%.

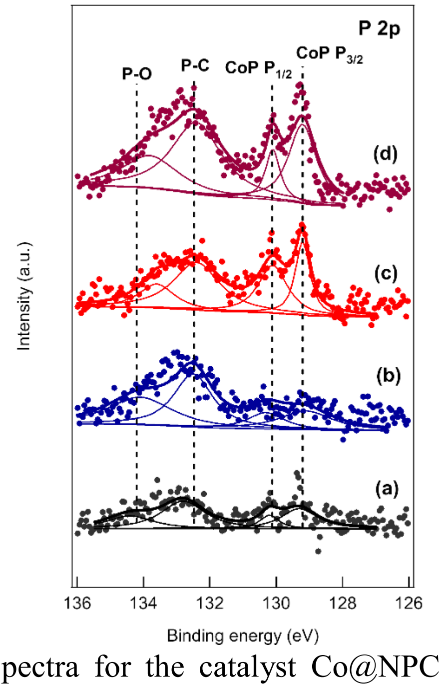


Figure S8. P 2p XPS spectra for the catalyst Co@NPC-800 with different added amount of PPh_3 (a) 1 wt%; (b) 5 wt%; (c) 10 wt%; and (d) 30 wt%.

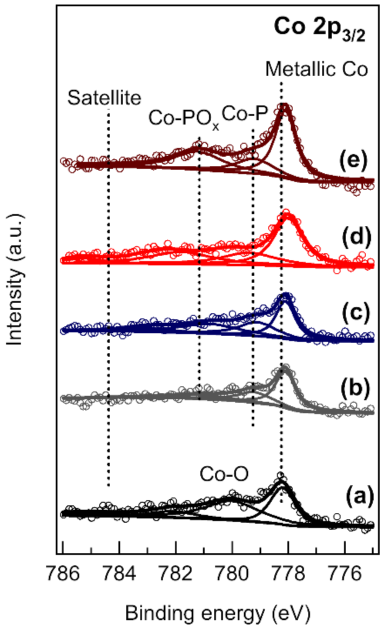


Figure S9. Co 2p$_{3/2}$ XPS spectra for the catalyst (a) Co@NC-800 and Co@NPC-800 with different added amount of PPh$_3$ (b) 1 wt%; (c) 5 wt%; (d) 10 wt%; and (e) 30 wt%.

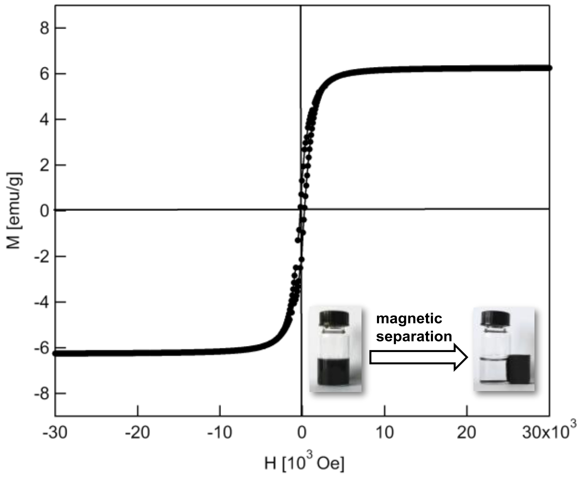
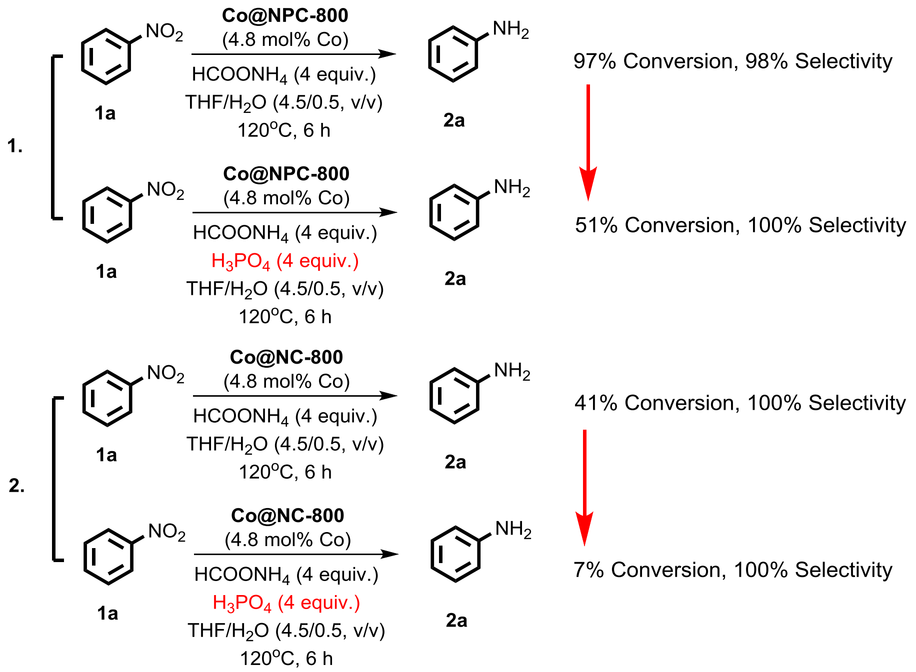


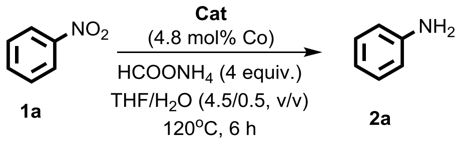
Figure S10. Magnetic hysteresis loops of the catalyst Co@NPC-800 at 300 K, and the inset is the illustration of magnetic separation of the catalyst from solution with external magnet.

Scheme S1. Control experiments.

Nitrogen role in the catalysts

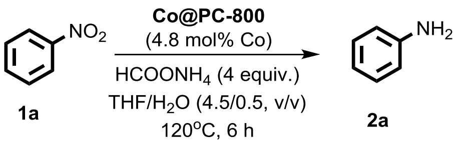


3. The catalytic performance for the catalyst pyrolyzed of the mixture of activated carbon, $CoCl_2$ and external N source melamine at 800°C



Catalyst	N content (wt%)	Conv. (Selectivity)
Co@C-800	0	8% (100%)
with 1 wt% melamine	0.36	17% (100%)
with 5 wt% melamine	1.52	26% (100%)
with 20 wt% melamine	2.97	48% (100%)

Phosphorus role in the catalysts



79% Conversion, 100% Selectivity