Supporting Information

The metal-free nitrogen-doped carbon nanosheets: a catalyst for directly synthesis imines under mild conditions

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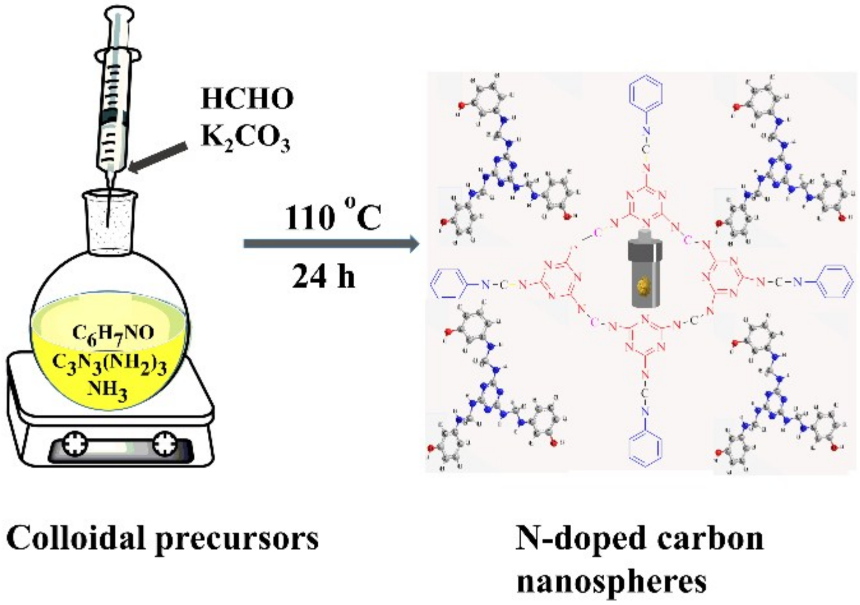
1. Catalyst Characterization

In this study, these catalysts were in detail characterization to know its properties of physical and chemical. X-ray diffraction (XRD) was performed on a Rigaku D/max-2400 advanced X-ray diffractometer using Cu-Kα radiation (λ=1.5406 Å) with the 2 thate range between 10-60°. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM, FEI Tecnai F30) were utilized to observe the surface morphologies of the catalysts. Nitrogen physisorption isotherms were carried out the pore size distribution and pore volume on a static volumetric instrument (TriStar II 3020 V 1.04). The specific surface area was analyzed by the Brunauer-Emmett-Teller (BET) method. X-ray photoelectron spectroscopy (XPS) was measured valence state and bonding energy of samples, conducted on the PHI-5702 instruments with an Mg anode (Mg K_α h_υ = 1253.6 eV) at a base pressure of 5×10^{-8} mbar. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained on a Bruker spectrometer (VERTEX 70). Elemental analysis (EA, CHNS) was detected the content of C, H, and N elements in catalysts. UV-Vis absorption spectra was conducted by an Agilent Cary 5000 UV-Vis spectrophotometer. Thermogravimetric analysis (TGA, TA-Q50) measured the mass change of N-doped carbon material, heated from 25 to 800 °C under N_2 atmosphere at a heating rate of 2 °C min^{-1}.

2. Catalyst Synthesis route and synthesis mechanism

For the synthesis of the porous N-doped carbon nanosheets, 3-Aminophenol, ethanol and deionized water were thoroughly dissolved in a 50 mL round-bottomed flask by ultrasound. Then, $NH_3{\cdot}H_2O$ was dropwise added to the mixture, and it was dramatically stirred at 30 ˚C for 0.5 h. Subsequently, formalin (10 mL) was drop by drop added to the mixture, and the colloid was aged at 30 ˚C for 4 h. Sequentially, melamine and K_2CO_3 were added into the flask. After stirring for a further 0.5 h, a homogeneous precursor solution was obtained. The obtained solution was collected into a 50 mL stainless steel teflon autoclave and kept in an electric oven at 110 °C for 24 h. After cooling down naturally, the yellow precipitates were collected by filtration and followed by drying in a vacuum oven at 60 °C for 12 h, and it was named as NPC-110. Later, the dried precursor particles carbonized at a series of temperatures i.e. 500, 600, 700, 800, 900 ˚C for 120 min each, under Ar (8% H_2) atmosphere at a heating rate of 2 $^{\circ}C{\cdot}min^{-1}$. The carbonized particles were washed several times using deionized water in the ultrasonic irradiation to promote the dissolve of K ions. Finally, the nanosheets particles were dried in a vacuum oven at 60 ˚C overnight.



Scheme S1. Synthesis route and idealized structure.

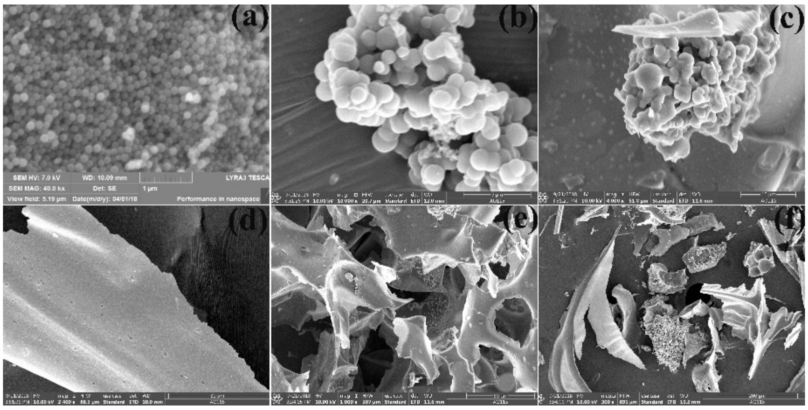
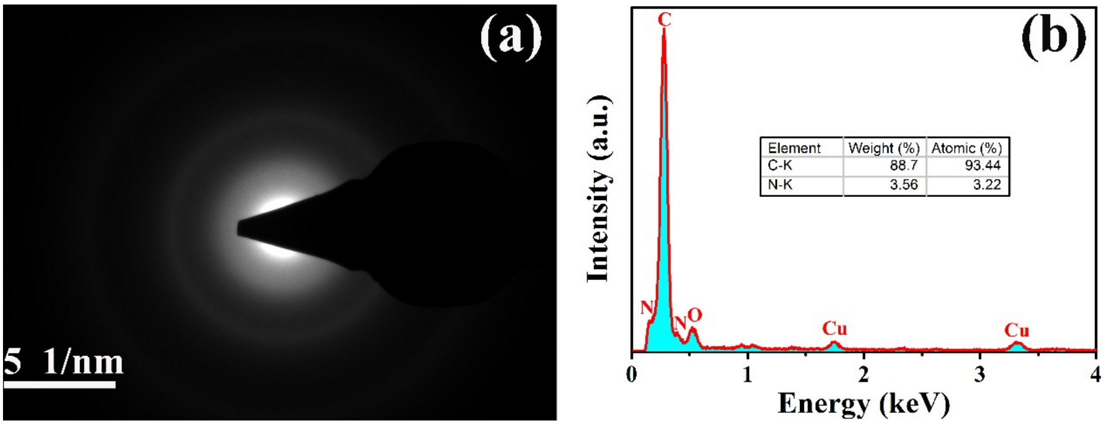


Fig. S1 SEM images of NC-110 (a), NC-500 (b), NC-600 (c), NC-700 (d), NC-800 (e) and NC-900 (f).



Element	Weight (%)	Atomic (%)
C-K	88.7	93.44
N-K	3.56	3.22

Fig. S2 Selected-area diffraction image (a), and the EDX (b) of NC-800

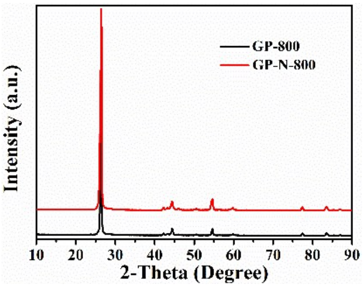


Fig. S3 The XRD pattern of GP-CN-800 and GP-800.

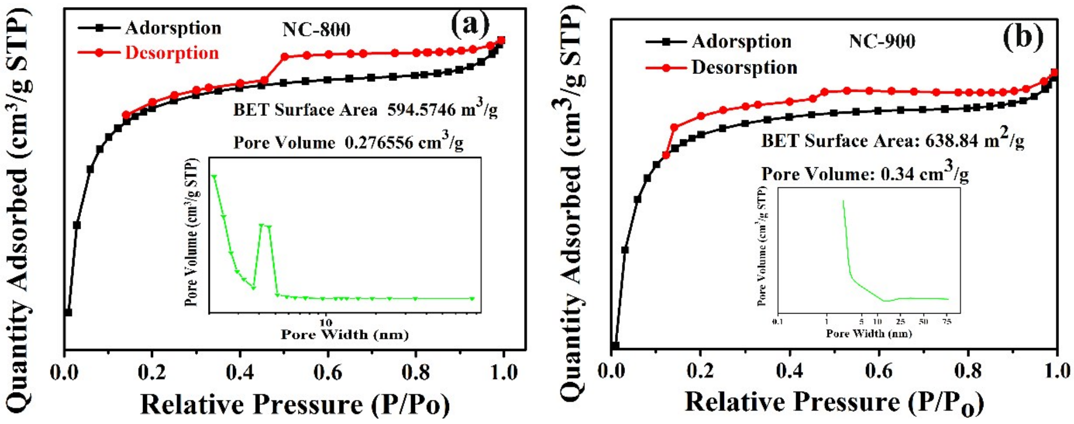


Fig. S4 Nitrogen adsorption-desorption isotherms of NC-800 (a), and NC-900 (b).

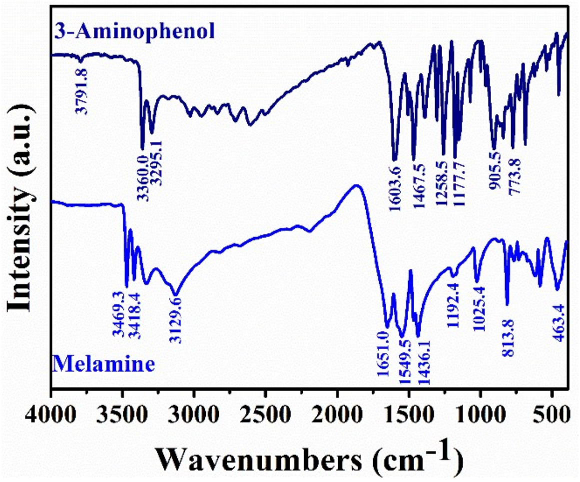


Fig. S5 The FT-IR of 3-Aminophenol and melamine.

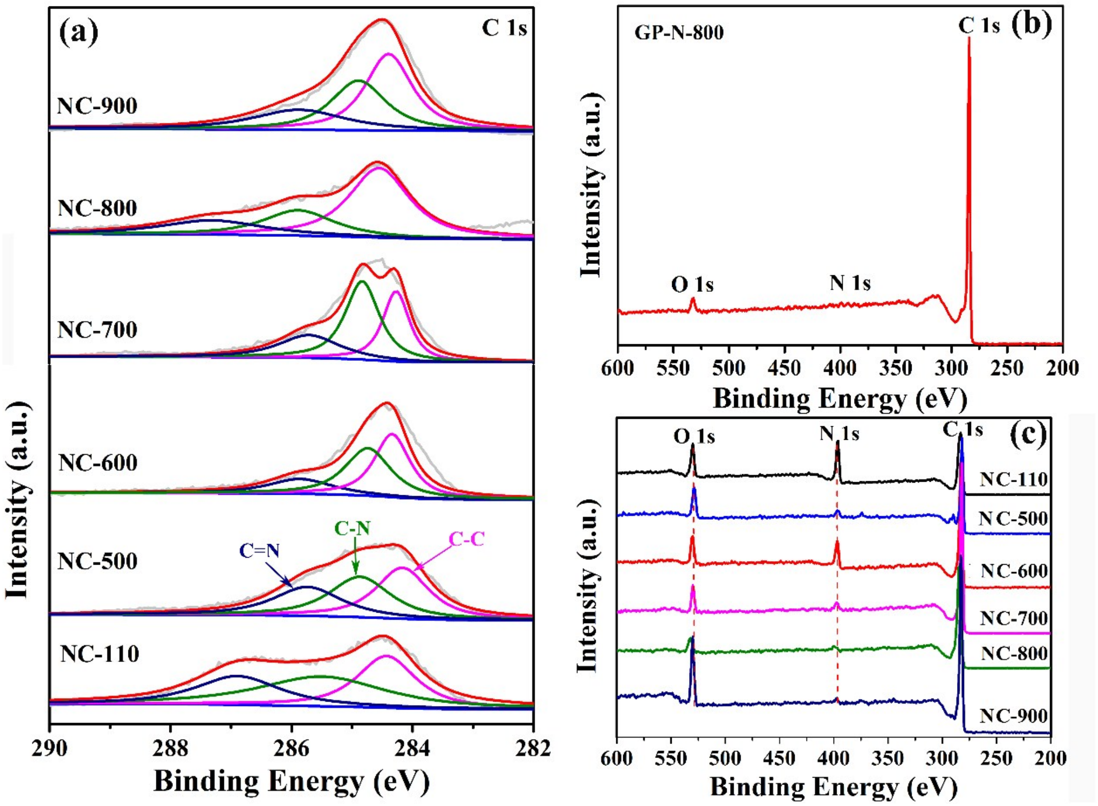


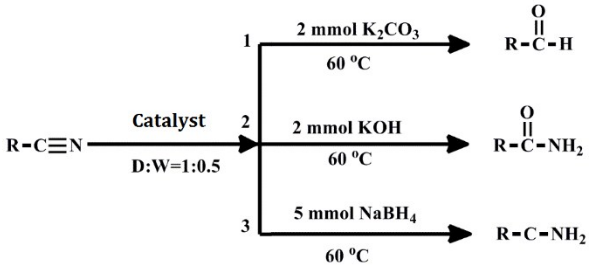
Fig. S6 High-resolution C 1s spectra (a), XPS wide-scan spectra of GP-N-800 (b), and NC 110-900 (c).

Table S1 Comparative chart of catalytic activity of NC-800 in amine to imine reaction.

Catalysts/mg	Temp.	Time	Additives (mmol)		Conv.	Sel.	Yield
	(°C)	(h)	KCl	NaCl	(%)	(%)	(%)
NC-800/15	120	8	2	-	99.9	96.0	96.0
NC-800/15	120	8	-	2	99.9	93.0	93.0
None	120	10	2	-	Trace	Trace	Trace
None	120	8	-	2	Trace	Trace	Trace
GP -800/20	120	9	2	-	Trace	Trace	Trace
GP-800/20	120	10	-	2	Trace	Trace	Trace
CNTs/20	120	10	2	-	Trace	Trace	Trace
CNTs/20	120	10	-	2	Trace	Trace	Trace

[a] Reaction conditions: 1 mmol benzylnitrile, 15 mg NC-800 catalyst and 1.5 mL solvent (D:W=1:0.5) reacted in the closed the high pressure reaction tube at 60℃. The conversion and selectivity were detected by GC-MS.

Table S2 Comparative chart of catalytic activity of the transfer hydrogenation of benzylnitrile. [a]



Catalysts/mg	Temp.	Time	Additives (mmol)			Yield of transfer hydrogenation reaction of benzylnitrile (%)		
	(°C)	(h)	K_2CO_3	KOH	$NaBH_4$	1	2	3
NC-800/20	60	8	2	2	5	99.9	99.9	99.9 (6h)
NC-800/15[b]	60	8	2	2	5	84.0	93.0	99.9
None	60	10	2	2	5	Trace	28.0	60.0
NC-900/20	60	8	2	2	5	30.0	52.0	77.0
NC-700/20	60	8	2	2	5	40.0	61.0	82.0
GP-N-800/20	60	9	2	2	5	26.0	39.0	70.0

GP-800/20	60	10	2	2	5	Trace	32.0	55.0
CNTs/20	60	10	2	2	5	Trace	35.0	60.0
NC-800/20	60	8	1	1	2.5	63.0	79.0	86.0

[a] Reaction conditions: 1 mmol benzylnitrile, 20 mg NC-800 catalyst and 1.5 mL solvent (D:W=1:0.5) reacted in the closed the high pressure reaction tube at 60℃. The conversion and selectivity were detected by GC-MS. [b] 15 mg NC-800 catalyst.

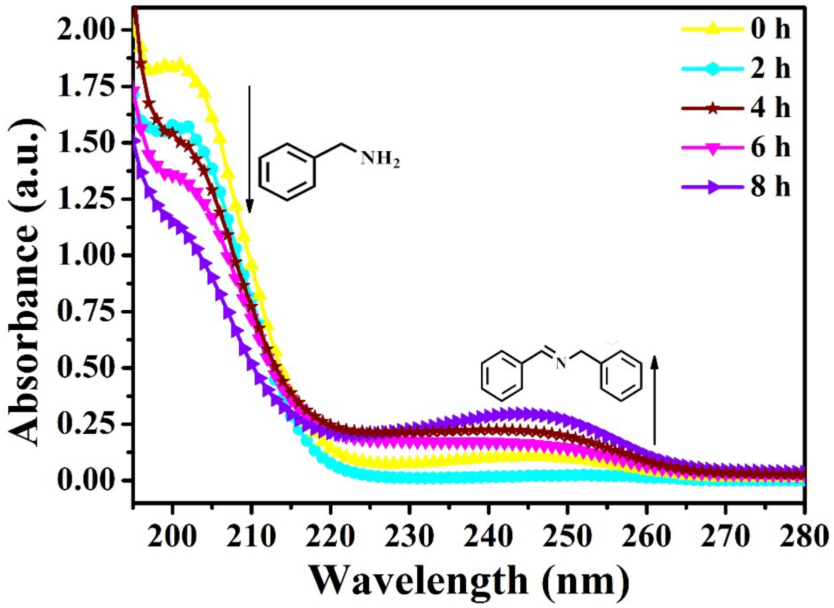


Fig. S7 UV-Vis of the imine reaction rate.

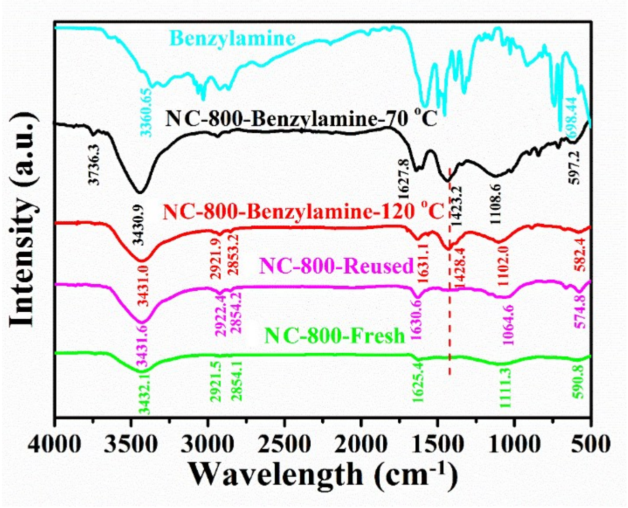


Fig. S8. FT-IR of the fresh, reused, and absorption of substrate of catalyst.

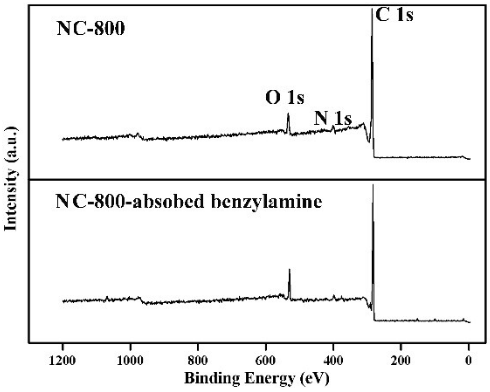


Fig. S9 The comparison of wide-scan XPS of NC-800 and the absorption of benzylamine of NC-800.

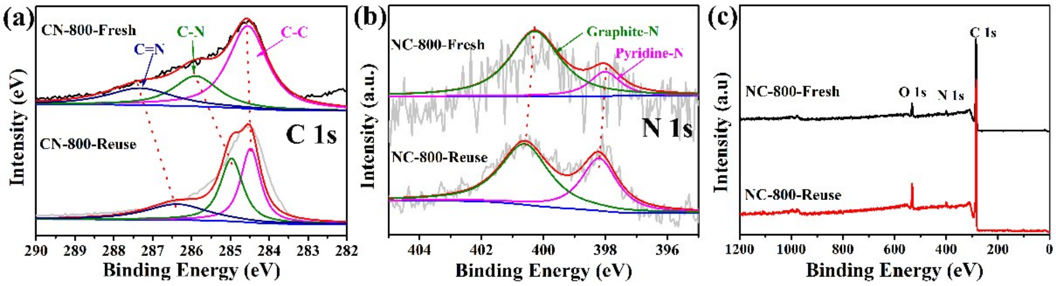


Fig. S10 The comparison of XPS of NC-800 and the reused NC-800.

Table S3 Comparative chart of catalytic activity of NC-800 with other reported catalysts.

Catalysts/mg	Temp. (°C)	Time (h)	Yield of imines (%)	Ea (kJ/mol)	TOF (h^{-1})	Ref.
NC-800/15	**60**	**40**	**99.9**	**67.39**	**1.65×10^{-3} （mol /(g·h)）**	**This work**
PdCu /10	110	3	86.5	-	-	1
Cu NH_4Br/10 -1 equiv.	100	13	100	-	-	2
MoOx/CeO_2-ZrO_2/100	110	6	99.8	-	-	3
0.8 wt% Au/C/-	100	1	99	-	280	4
1.5 wt% Au/TiO_2/-	100	30	92	-	70	4
Pd(II)–P$(Oquin)_3$/-	80	14	100	-	5.6	5
[Ru(H)(Cl)(CO)$(PCy_3)_2$]/-	120	24	63	-	-	6

Fe/MOF/25	100	24	67	-	-	7
Al(20)-MS/50	160	6	100	-	-	8
Ce–Sm/SiO$_2$/200	120	6	100	-	-	9
FeCu@NPC	120	3	99.9	55.52	-	10
PdZn/Al$_2$O$_3$ /100	110	0.5	99	96	-	11
Pc-Ludox-8/20	100	5	90.9	47.6	-	12
α -MnO2/ 0.05 mmol	25	4	95	62.8	-	13

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