

Supporting information for

**Mesoporous Nitrogen-Doped Carbons with High Nitrogen Content and  
Ultrahigh Surface Areas: Synthesis and Applications in Catalysis**

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## 1 Methods

### 1.1 Materials and general methods.

Glucose and melamine were purchased from Alfa Aesar. KCl and ZnCl<sub>2</sub> (99%) were acquired from Sinopharm Chemical Reagent. All chemicals were used without further purification.

XRD analysis was performed on a Rigaku D/MAX-2500 diffraction using Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), in range of 3-80° (2 $\theta$ ) with a step width of 0.02°. The morphology of the sample was observed by field emission SEM on a scanning electron microscope (S-4800, Hitachi, Japan) and by TEM on a transmission electron microscope (JEM2011, JEOL, Japan) equipped with energy dispersive spectroscopy (EDS). The SSA and pore structure were investigated with a Quantachrome Quadrasorb SI-MP porosimeter using nitrogen as the adsorbate at 77 K. Prior to determination of the isotherm, the samples were degassed at 300 °C under vacuum for at least 3 h. The value of the total pore volume ( $V_{total}$ ) was determined from the NLDFT kernel at the relative pressure  $P/P_0 = 0.99$ . The micropore

volume ( $V_{micro}$ ) was estimated using the  $\alpha s$  method (M.-M. Titirici, R. J. White, C. Falco and M. Sevilla, *Energy Environ Sci*, 2012, **5**, 6796). The mesopore volume was calculated by subtraction of micropore volume from the total pore volume ( $V_{meso} = V_{total} - V_{micro}$ ). The total SSA ( $S_{total}$ ) was calculated using the Brunauer-Emmett-Teller (BET) method from the nitrogen adsorption data in the relative pressure ( $P/P_0$ ) of 0.03-0.30. X-Ray photoelectron spectroscopy (XPS) data were collected on an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al-K $\alpha$  radiation. The base pressure was about  $3 \times 10^{-9}$  mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. FT-IR analyses of the samples were performed using a Bruker Optic TENSOR-37. All samples were mixed with KBr and determined in the range of 4000-400  $\text{cm}^{-1}$  wavenumbers. The elemental contents of the samples were determined using Flash EA1112 from Thermo. All gas chromatography (GC) experiments were carried out and recorded by GC (Agilent Technologies, GC 7890B).

### **1.2 Synthesis of mesoporous N-doped carbon materials.**

In a typical experiment, melamine (1.5 g) and glucose (1.0 g) were mixed with PZ (12.0 g) by grinding at room temperature. The porogen salt PZ mixture containing 51 mol% KCl and 49 mol%  $\text{ZnCl}_2$  was first prepared by grinding. Subsequently, the mixture was transferred into a ceramic boat, and moved to a tubular furnace for carbonization under nitrogen atmosphere with a flow rate of 100 mL/min. Gradient heating mode was adopted. The sample was heated with a heating rate of 3  $^{\circ}\text{C}/\text{min}$  from room temperature to 240  $^{\circ}\text{C}$  and held at this temperature for 4 h; then the temperature was further increased to the final calcination temperature (e.g., 800  $^{\circ}\text{C}$ ) with a heating rate of 1  $^{\circ}\text{C}/\text{min}$ , and maintained at the final temperature for 6 h. Afterwards, the tubular furnace was allowed to cool down to room temperature under nitrogen atmosphere. The resultant mixture was ground into powder in an agate mortar, and washed with sufficient deionized water at room temperature to remove the salts until there was no  $\text{Cl}^-$  detected in the supernatant. The resultant sample was dried under vacuum at 60  $^{\circ}\text{C}$  for 12 h. Different samples using glucose and melamine as the carbon and nitrogen resources were obtained via changing the mass ratio of glucose to melamine and the final calcination temperature. In addition, NDCs using the cellulose and lignin as the carbon precursor were also prepared with the ratio of melamine/cellulose or lignin = 1.5.

### **1.3 Catalytic oxidation of hydrocarbons.**

In a typical oxidation, substrate (1.0 mmol), catalyst (12 mg), TBHP (3.48 mmol, 70 wt % in water), and water (3 mL) were added into a 15 mL glass reactor sealed with Teflon lid (Beijing Synthware Glass, Inc. Pressure Vessel, Heavy Wall). The reaction mixture was heated to the designated temperature in an oil bath with magnetic stirring (stirring rate: 1000 r. p. m.) and kept at that temperature for a period of time. After that, 0.07 g n-dodecane was added to the system as an internal standard and then 9 mL  $\text{CH}_2\text{Cl}_2$  was added to extract organic compounds in the reaction system. Finally,

the organic phase was analysed by Agilent 7890B GC with a HP-INNOWAX capillary column (30 m × 0.25 mm × 0.25 μm). The catalyst NDC was recycled by filtration, washed with THF and ethanol, and then dried under vacuum at 100 °C for 12 h, followed by being reused for the next run.

#### 1.4 Preparation of noble metal/ mesoporous N-doped carbon materials.

In a typical experiment to prepare the Pd/ mesoporous N-doped carbon materials, 5.26 mg Pd(OAc)<sub>2</sub> was dissolved in 270 μL dichloromethane (DCM), then mixed with 50 mg NDCs. The mixture was dried under vacuum at 60 °C for 2 h, then put into a quartz tube and heated to 300 °C under H<sub>2</sub> atmosphere and maintained for 2 h. The resulting Pd catalyst was named as 5% Pd/M-G-1.5-800. Using similar procedures, other noble metal/M-G-1.5-800 (including Rh, Pt and Ru) composites with metal loading at different weight (Rh 5%, Pt 3%, Ru 5%) were prepared as well by varying metal precursors (e.g., RhCl<sub>3</sub>·3H<sub>2</sub>O, HPtCl<sub>4</sub> and RuCl<sub>3</sub>·3H<sub>2</sub>O dissolved in CH<sub>3</sub>CH<sub>2</sub>OH). Noteworthy, the final H<sub>2</sub> reduction temperature of Ru is 200 °C for 2 h. The metal carbon composites were names as: 5% Rh/M-G-1.5-800, 3% Pt/M-G-1.5-800, and 5% Ru/M-G-1.5-800.

## 2 Characterizations

### 2.1 The nitrogen content results of the different NDCs.

Table S1 Nitrogen content for different NDCs carbonized at 800 °C.

Sample	Yield/%	Elemental content			Pyridinic-N/% 398.4 eV	Pyrrolic-N/% 399.3 eV	Quaternary-N/% 401.2 eV
		N/%	C/%	H/%			
G-800	20.9	1.1	92.12	1.30	23.04	61.16	15.80
M-G-0.33-800	21.9	4.4	85.03	1.74	28.05	57.12	14.83
M-G-0.67-800	24.0	8.6	73.45	2.10	26.87	60.03	13.10
M-G-1-800	25.2	10.3	74.44	1.79	37.42	33.98	28.60
M-G-1.5-800	27.4	11.4	73.56	1.58	36.32	33.25	30.43
M-G-3-800	19.6	11.9	70.77	1.41	45.98	28.80	25.23
M-C-1.5-800	27.3	9.5	64.01	2.89	-	-	-
M-L-1.5-800	22.5	8.9	64.51	2.48	-	-	-

Table S2 Nitrogen contents for NDCs carbonized at different temperature.

Sample	Yield/%	Elemental content			Pyridinic-N/% 398.4 eV	Pyrrolic-N/% 399.3 eV	Quaternary-N/ % 401.2 eV
		N/%	C/%	H/%			
M-G-1.5-240		29.2	43.17	2.61			
M-G-1.5-400	42.4	30.9	47.26	2.52	43.51	56.49	0.00
M-G-1.5-500	36.0	27.4	49.07	2.55	45.69	54.31	0.00
M-G-1.5-600	33.2	25.0	50.50	2.75	44.15	55.85	0.00
M-G-1.5-800	27.4	11.4	73.56	1.58	36.32	33.25	30.43

## 2.2 Reaction condition optimization results of the oxidation of ethylbenzene.

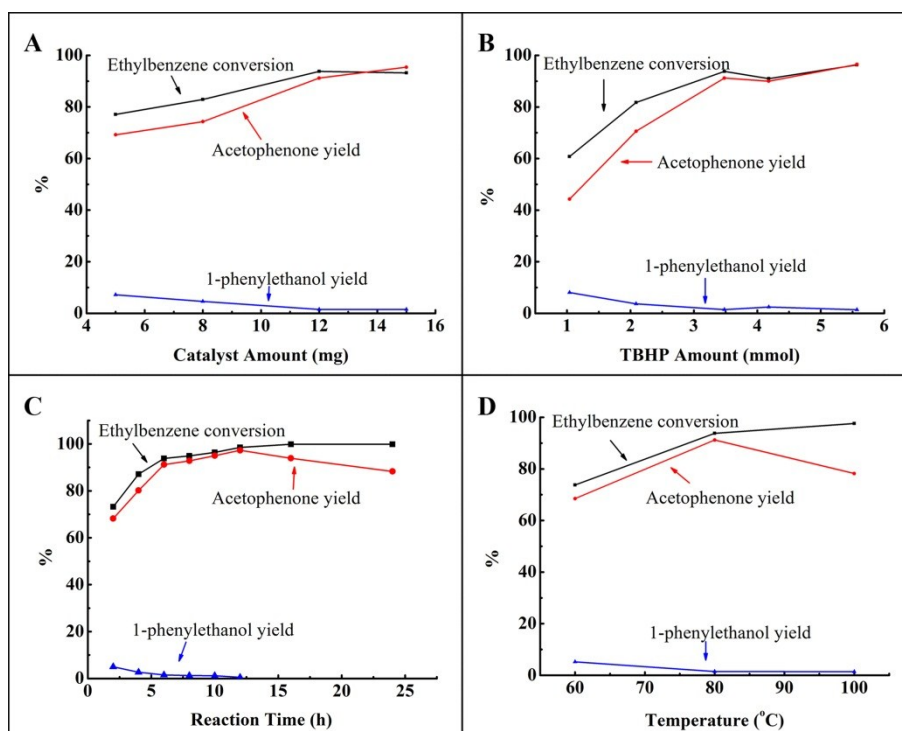


Figure S1 Reaction conditions optimization of the oxidation of ethylbenzene in aqueous phase. The reaction conditions: substrate (1.0 mmol), solvent ( $\text{H}_2\text{O}$ , 3 mL). (A) Catalyst amount optimization under 80 °C, 3.48 mmol TBHP and reacted for 6 h; (B) TBHP amount optimization under 80 °C, 12 mg catalyst and reacted for 6 h; (C) Reaction time optimization under 80 °C, 3.48 mmol TBHP and 12 mg catalyst, and (D) Reaction temperature optimization with 3.48 mmol TBHP, 12 mg catalyst and reacted for 6 h. (Note: When the reaction time  $\geq 16$  h, the product 1-phenylethanol will disappear and the main product acetophenone will be further oxidized to another product benzoic acid thus resulted in the decrease of acetophenone yield.)

### 2.3 Characterizations of the noble metal (Rh, Pt, Ru)/mesoporous NDCs composites.

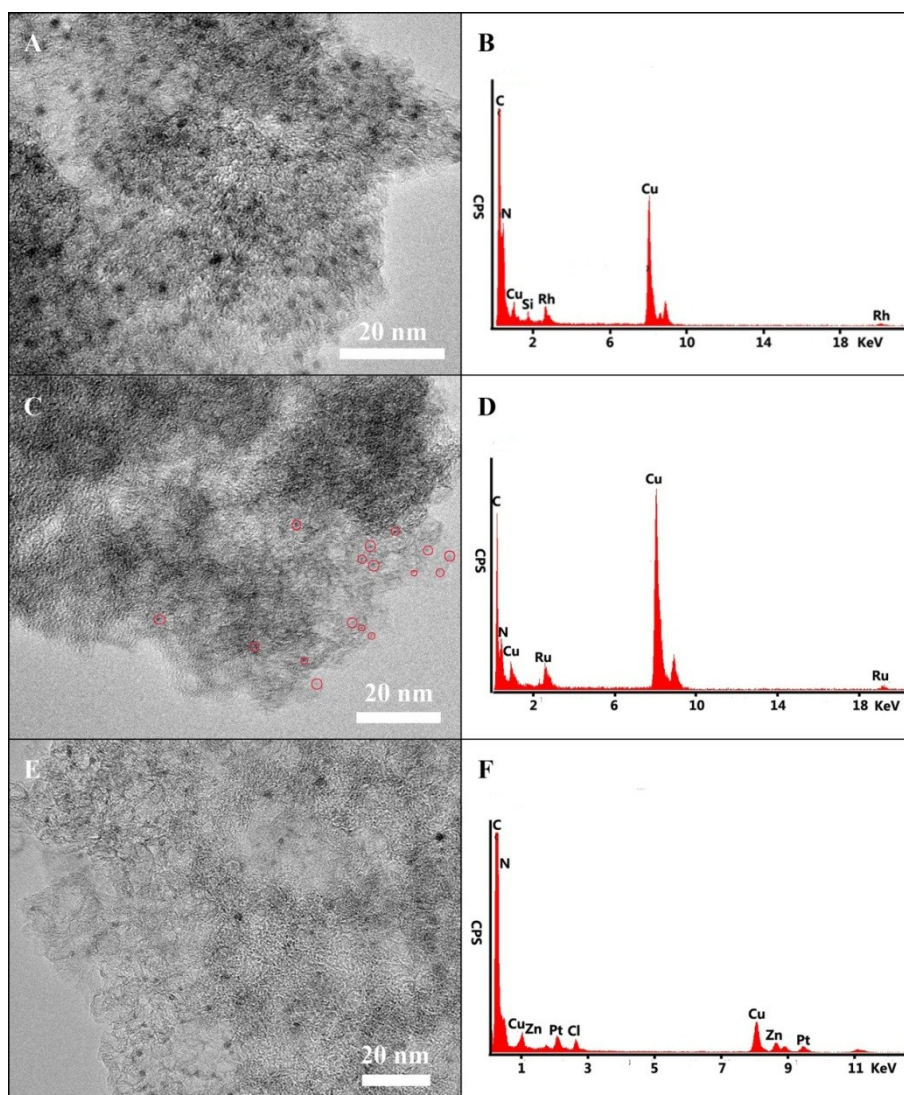


Figure S2 (A) TEM image and (B) EDS profile of 5% Rh/M-G-1.5-800 composite; (C) TEM image and (D) EDS profile of 5% Ru/M-G-1.5-800 composite; (E) TEM image and (F) EDS profile of 3% Pt/M-G-1.5-800 composite.