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Electronic Supplementary Information

Synthesis of nitrogen-containing ordered mesoporous carbon as a metal-free catalyst for selective oxidation of ethylbenzene†

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1. Preparation of NOMC

The synthesis was carried out in a basic aqueous phase through a self-assembly process of MAP and F127 according to modified procedures as described in reference¹. Typically, 2.0 g F127 and 0.48 g 1,3,5-trimethylbenzene (TMB) were dissolved in the deionized H₂O. Then, 1.1 g MAP, 0.7 g HMT and 1.3 ml of 28 wt% aqueous ammonia were added to the above solution and the mixture was stirred at room temperature for another hour. After that, the solution was poured into a flask and transferred into an oil bath equipped with a water-cooled condenser at 80 °C stirred for 24 h. The as-made product was collected by sedimentation separation, washed with water and ethanol and dried at 80 °C for 12 h. Carbonization was carried out in a tubular furnace under an Ar atmosphere with the heating rate of 1 °C/min and then keeping the temperature at 350, 600 and 800 °C for 3 h, respectively. The final product was denoted as **NOMC-T**. To obtain NOMC with different nitrogen content, R was added into the mixture to partially displace MAP, denoted **NOMC-x-T**, where x represents the molar ratio of R/MAP and T represents the calcination temperature (here, T=600 and 800).

In comparison, nitrogen-containing ordered mesoporous carbon was also prepared through the similar method with the literatures¹, but carbonized at ammonia (50 ml/min) atmosphere for 3h with a heating rate of 1 °C/min, at 800 °C, denoted as **NH₃-OMC-800**. On the other hand, CMK-3 was fabricated via the hard-templating method² using sucrose as carbon sources and carbonized at 900 °C for 3 h. After the CMK-3 was oxidized at concentrated HNO₃ for 3 h at 60 °C, the product was denoted as **O-CMK-3**.

2. Characterization

Small angle XRD patterns were recorded on a Rigaku D/Max-2500PC diffractometer with a Cu K α radiation operating at 50 kV, 300 mA. The mesostructures of the NOMC was characterized by a FEI T12 transmission electron microscopy (TEM) with an accelerating

voltage of 120 kV. Scanning electron microscopy (SEM) images were taken using an FEI Nano450 scanning electron microscope operated at 15 kV. Nitrogen adsorption-desorption data were measured with a Micromeritics ASAP 3020 analyser at 77 K. Prior to the measurements, the samples were degassed at 120 °C for 12 h. The specific surface areas (S_{BET}) were calculated by the Brunauer-Emmett-Teller (BET) method using adsorption data in a relative pressure range from 0.02 to 0.20. The total pore volumes (V_{T}) were estimated on the basis of the adsorbed amount at a relative pressure of 0.985. The pore size distributions (PSD) was calculated from adsorption data of isotherms using the Barrett-Joyner-Halenda (BJH) model. Surface chemistry of samples was investigated using an ESCALAB 250 instrument with Al K α X-rays (1486.6 eV).

3. Catalytic reaction

Typically, ethylbenzene (1.0 mmol), catalyst (0.050 g), TBHP (3.0 mmol, 65 wt% in water), anisole (110 μL) as internal standard and acetonitrile (2 mL) were added into a 70 mL glass reactor sealed with Teflon lid (Beijing Synthware Glass, Inc. Pressure Vessel, Heavy Wall). The reaction mixture was heated to 80 °C in an oil bath and stirred for 12 h. After that, the reaction vessel was taken out from oil bath and cooled down. Gas chromatography (GC) analysis was performed on an Agilent GC equipped with a 30 m*0.25 mm*0.25 μm HP-5 capillary column and a flame ionization detector.

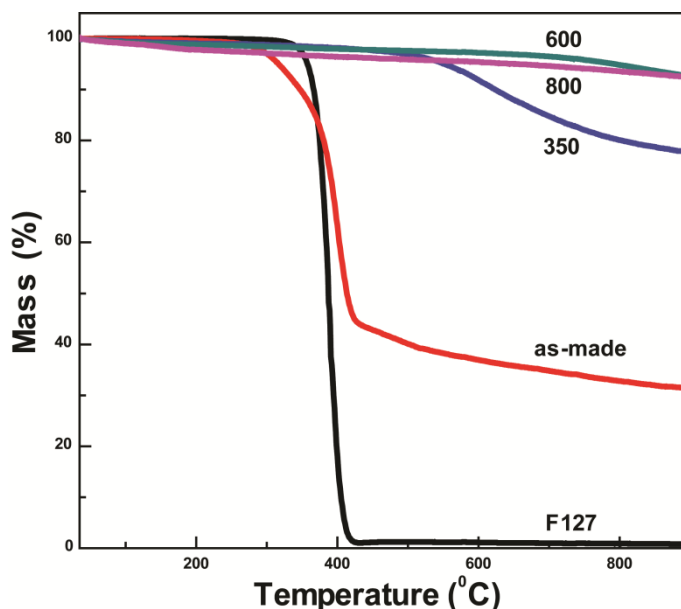


Fig. S1 The degradation behavior of pure co-polymer F127, as-made nitrogen-containing resoles/F127 composites and NOMC-350,600,800. A majority of F127 can be removed after carbonized at 600 °C or above.

Table S1 The textural property of NOMC-x-T, where x represents the mole ratio of R/MAP and T is the carbonization temperature.

R/MAP (mole ratio)	Carbonization Temperature (°C)	S_{BET} (m^2/g)	D (nm)	V_{micro} (cm^3/g)	V_{t} (cm^3/g)
0:1	600	524	5.1	0.15	0.44
1:2	600	563	5.8	0.15	0.40
1:1	600	535	4.4	0.15	0.35
2:1	600	619	5.1	0.16	0.43
1:0	600	668	5.1	0.18	0.47
0:1	800	857	5.1	0.27	0.64
1:2	800	886	5.1	0.26	0.60
1:1	800	867	4.4	0.27	0.54
2:1	800	794	5.1	0.24	0.53
1:0	800	891	4.7	0.27	0.58

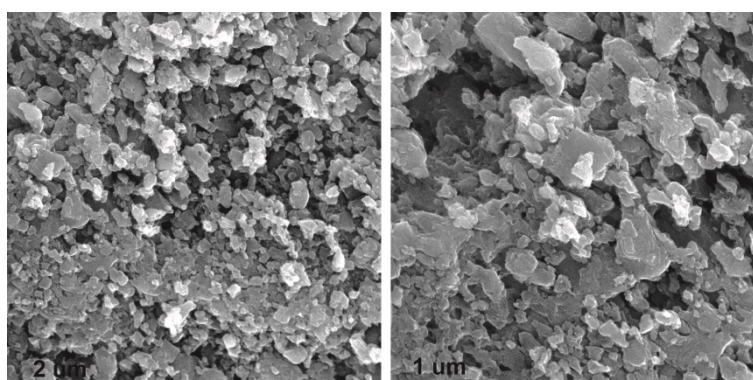


Fig. S2 SEM images at different magnification times of NOMC-800.

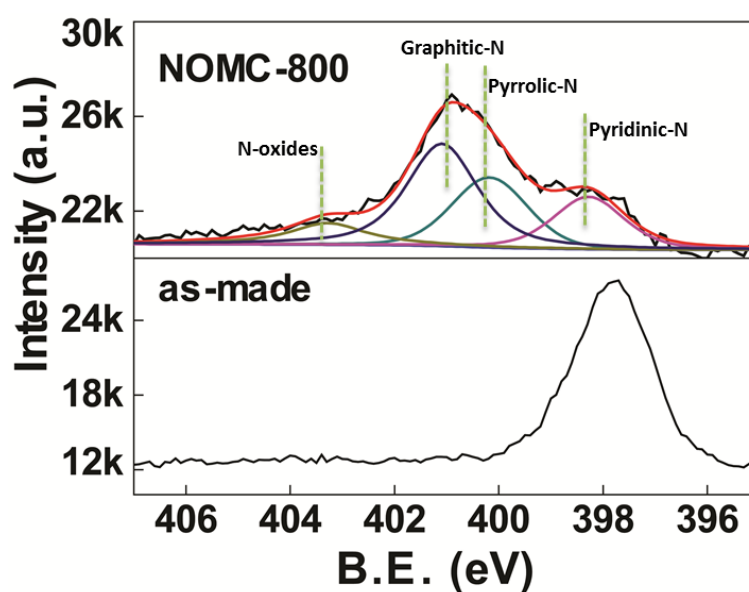


Fig. S3 N1s spectra of as-made sample and NOMC-800.

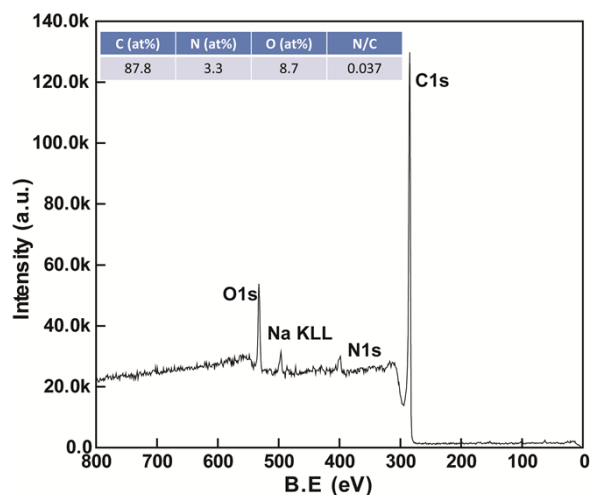


Fig. S4 XPS spectra of the product synthesized using HCHO and NaOH to displace HMT and ammonia water, respectively. Condition: 1.1 g MAP, 0.48 g TMB, 2.96 ml 37 wt% formaldehyde, 0.2g 20 wt% sodium hydroxide aqueous solution. Carbonization temperature: 800 °C. The atom ratio of N/C is about 0.037, which is in accordance with the NOMC-800 (N/C=0.034) synthesized using HMT and ammonia water. Therefore, we propose that the main N source of NOMC comes from MAP instead of HMT. Nevertheless, we could not exclude the contribution of HMT and/or ammonia water.

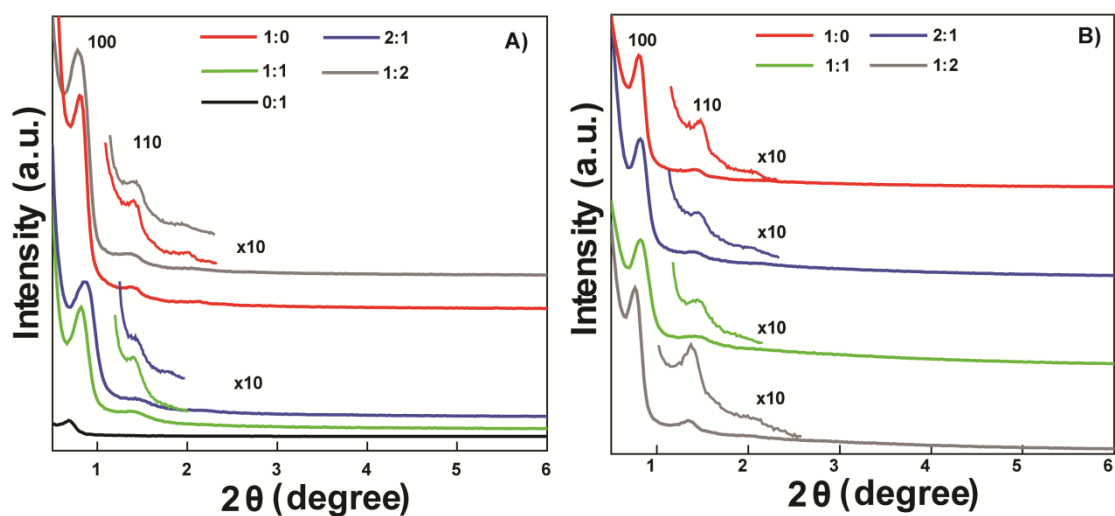


Fig. S5 XRD patterns of NOMC-x-600 (A) and NOMC-x-800 (B). The XRD patterns of all these samples show two resolved peaks peak at $2\theta=0.6-2.0$. The d-spacing value ratios for the two peaks are about $1:1/\sqrt{3}$ and can be indexed as (100) and (110) reflections of 2-D hexagonal $p6mm$ symmetry. However, the XRD pattern of NOMC-0:1-600 has only one weak peak at ~ 0.68 . We propose that it may be attributed to low contrast between pore walls and pore, because after carbonized at 800 °C, two clear peaks can be observed (**Fig. 3A in paper**). Moreover, combining results of N_2 adsorption-desorption curves and TEM images, we believe that NOMC-0:1-600 also has 2-D hexagonal $p6mm$ symmetry.

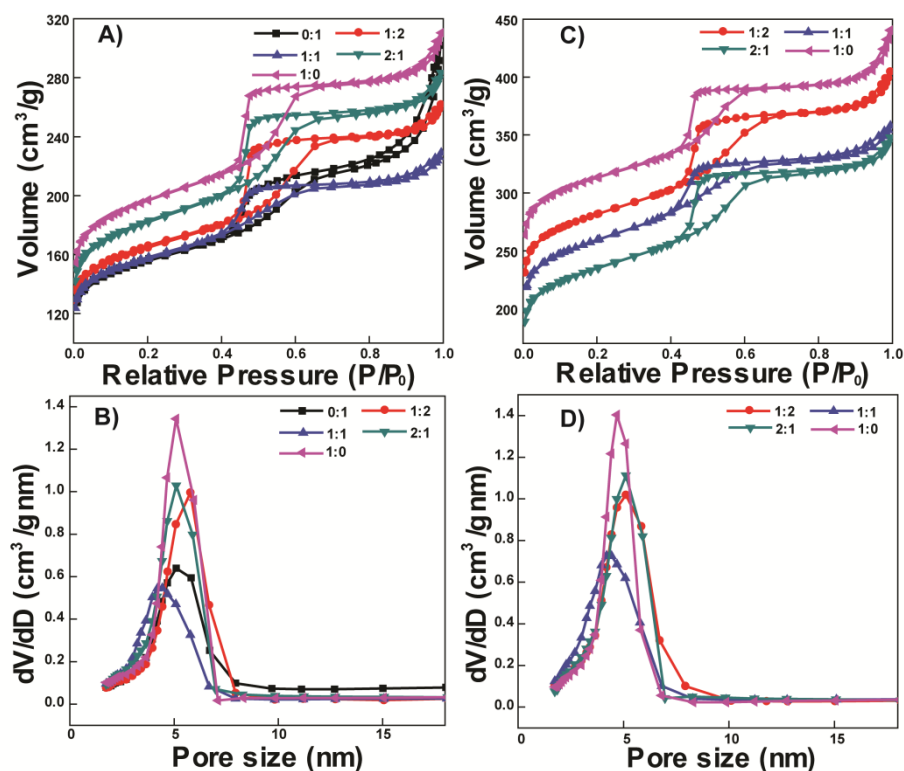


Fig. S6 N₂ adsorption-desorption isotherm curves (A and C) and BJH model pore size distributions (B and D) for NOMC-x-600 (A and B) and NOMC-x-800 (C and D), respectively. The isotherms of 1:2 and 1:0 in Fig. S6 C are offset vertically by 20 and 50 cm³/g for clarity, respectively. N₂ adsorption-desorption isotherm curves of the materials show typical type-IV curves, according to the IUPAC classification, with a clear capillary condensation steps at P/P₀=0.35-0.6, implying uniform mesopore distributions. Moreover, all of the isotherms do not give a perfect H1-type hysteresis loop, implying that the pore channels may be blocked partially. A very strong increase of the adsorbed nitrogen volume can be observed at a relative pressure greater than 0.9, representing unrestricted monolayer-multilayer adsorption resulted from interparticle pores and voids.

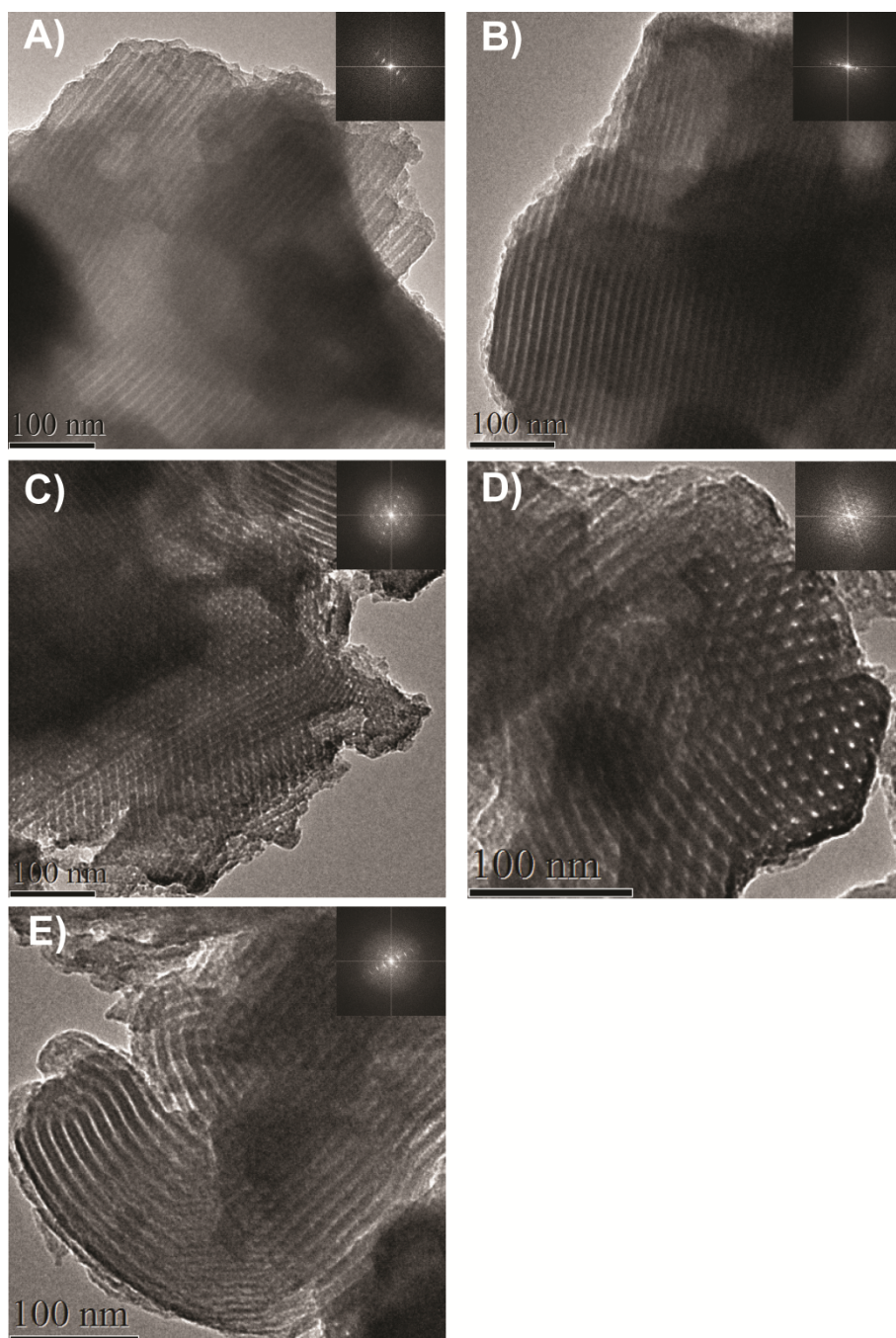


Fig. S7 TEM images of NOMC-x-600 **A)** $x=1:0$, **B)** $x=2:1$, **C)** $x=1:1$, **D)** $x=1:2$ and **E)** $x=1:0$. The insets are the corresponding fast Fourier transform (FFT) patterns. These images show the stripe-like mesostructures, indicating adding R to displace partially the MAP could also form the ordered mesoporous structure.

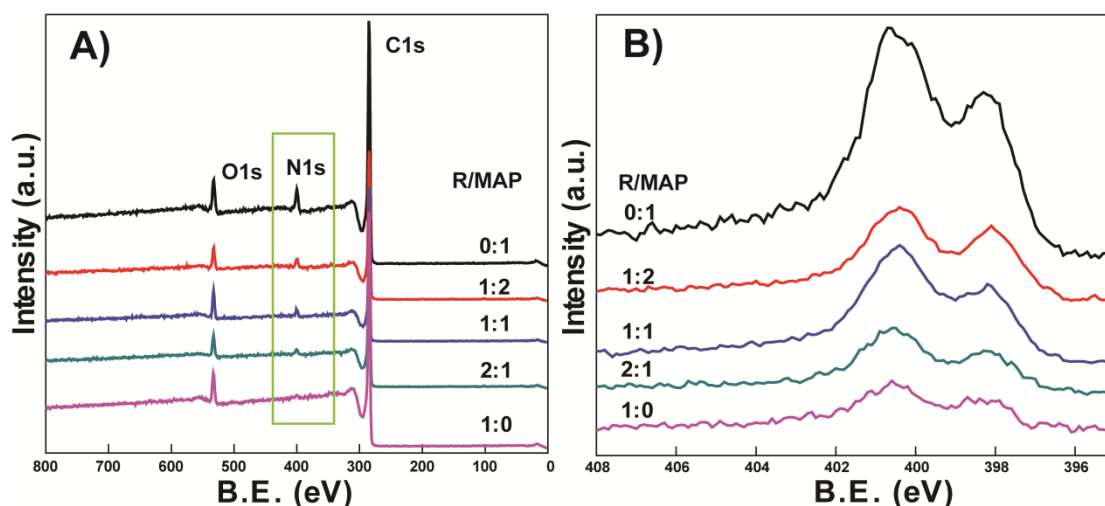


Fig. S8 XPS spectra (A) and N1s spectra of NOMC-x-600 (B). The evolution of nitrogen content can be changed by simply regulate the mole ratio of R/MAP, from 1.3 at% to 4.6 at% along with the changing of the mole ratio of R/MAP from 1:0 to 0:1. The evolution of the N1s XPS spectra of NOMC-x-600 has obvious two peaks, indicating that all these materials have similar nitrogen types. For the sample of NOMC-1:0-600, there is still 1.3 at% nitrogen remained in the ordered mesoporous carbon, indicating that ammonia involved in the polymerization and/or co-assembly.

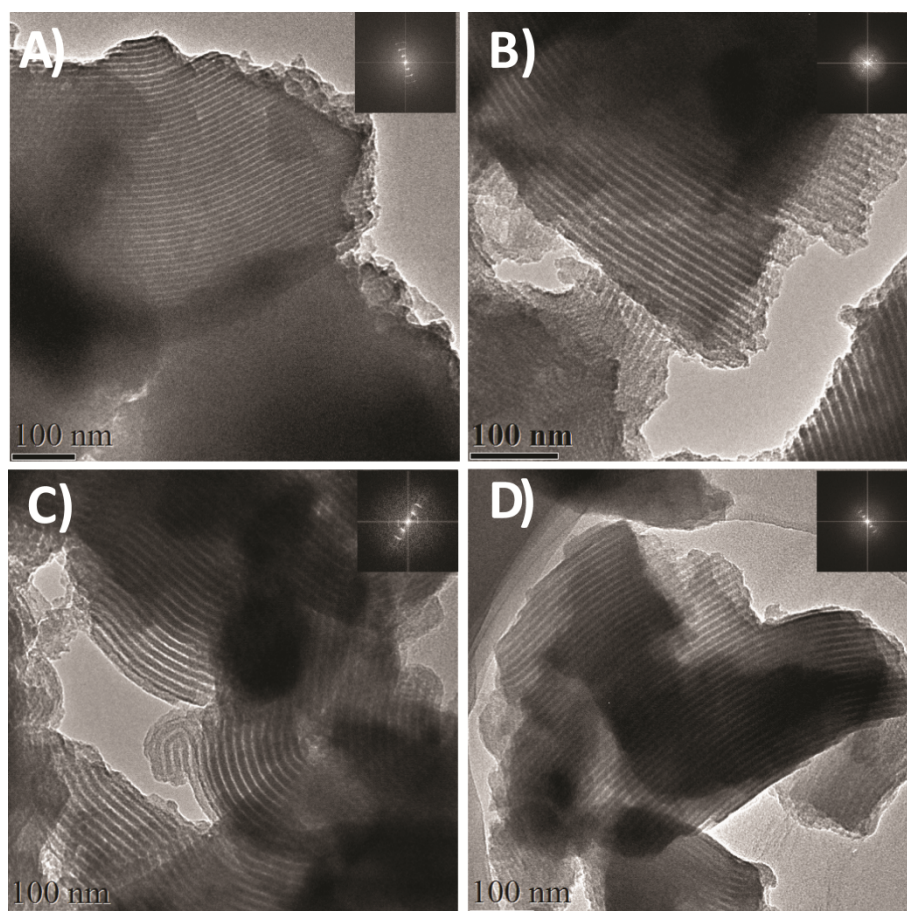


Fig. S9 TEM images of NOMC-x-800 A) x=1:0, B) x=2:1, C) x=1:1 and D) x=1:2. The insets are the corresponding fast Fourier transform (FFT) patterns. These images show the stripe-like

mesostructures, indicating adding R to displace partially the MAP could also form the ordered mesoporous structure even if carbonized at 800 °C.

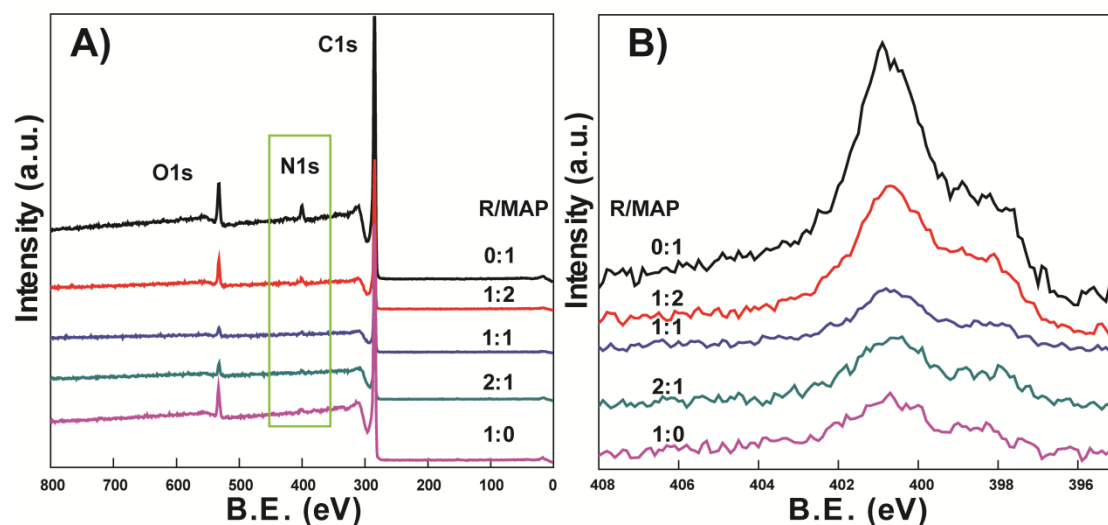


Fig. S10 XPS spectra (A) and N1s spectra of NOMC-x-800 (B). The evolution of nitrogen content can be changed by simply regulate the mole ratio of R/MAP, from 0.9 at% to 3.3 at% along with the changing of the mole ratio of R/MAP from 1:0 to 0:1. Obviously, nitrogen content not only depends on the mole ratio of R/MAP, but also the carbonization temperature. The evolution of the N1s XPS spectra of NOMC-x-800 in **Fig. S10 B** has obvious two peaks, indicating that all these materials have similar nitrogen types. For the sample of NOMC-1:0-800, there is still 0.9 at% nitrogen remained in the ordered mesoporous carbon, indicating that ammonia involved in the polymerization and/or co-assembly.

Table S2 The textural property and chemical composition ^a.

Sample	S _{BET} (m ² /g)	D (nm)	V _{micro} (cm ³ /g)	V _t (cm ³ /g)	C (at%)	O (at%)	N (at%)
NOMC-800 ^b	857	5.1	0.27	0.64	91.2	5.7	3.3
CMK-3	1153	3.9	0.13	1.09	95.4	4.3	0.2
O-CMK-3	721	3.9	0.03	0.68	87.7	11.4	0.8
NH ₃ -OMC-800	1379	4.4	0.17	0.88	93.4	3.8	2.8

Note: a) measured from XPS spectra b) the mole ratio of R/MAP is 0:1.

Reference:

- 1 D. Liu, J.-H. Lei, L.-P. Guo, D. Qu, Y. Li and B.-L. Su, *Carbon*, 2012, **50**, 476.
- 2 Shinae Jun, Sang Hoon Joo, Ryong Ryoo, Michal Kruk, Mietek Jaroniec, Zheng Liu, Tetsu Ohsuna and Osamu Terasaki, *J.Am.Chem.Soc*, 2000, **122**, 10712.