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

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

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Nitrogen-containing ordered mesoporous carbon (NOMC) was synthesized by using m-aminophenol (MAP) as carbon and nitrogen co-precursor via a co-assembly process with F127 in aqueous phase and exhibited a good catalytic performance for selective oxidation of ethylbenzene.

Ordered mesoporous carbon (OMC) has recently attracted interest because of its high specific surface areas, regular mesoporous structure and tunable pore size.[1-3] To improve their properties, surface modification is necessary and has been extensively investigated.[4] Nitrogen atom is usually induced into the carbon matrix, resulting in the improvement of surface polarity, electron-donor properties of the carbon matrix, and introducing active basic/catalytic sites on the carbon surface.[5] Most Nitrogen-containing ordered mesoporous carbon (NOMC) were synthesized through a hard-templating method using appropriate nitrogen sources,[6] such as acrylonitrile, pyrrole, aniline, melamine-formaldehyde resin and ethylenediamine-carbon tetrachloride. Although the incorporation of nitrogen into the OMC through a hard-templating method is well developed and higher nitrogen content with a C/N molar ratio of 4.3-2.3 can be achieved,[7] there is still a demand of new methods to synthesize NOMC because the hard-templating approach is low in efficiency, high in cost, fussy in process and harmful to health.

In recent years, organic-organic self-assembly method has been successfully used to synthesize OMC through either a “hydrothermal”[8-10] method or evaporation-induced self-assembly (EISA) [11-13] process. These methods provide new opportunities for design and synthesis of OMC and heteroatom-containing OMC. Many studies have revealed that the interaction between carbon precursors and block copolymer plays a vital role in the formation of ordered mesoporous structures in soft-templating method.[14] Therefore, the successful synthesis of NOMC through direct soft-templating method relies much on the co-assembly of proper nitrogen-containing carbon precursors with the block co-polymer. For example, on the basis of EISA method, Wan *et al.*[15] synthesized NOMC via a step-by-step method by using phenol, formaldehyde and m-aminophenol as an extra nitrogen source and F127 as structure-directing agent; Zhao *et al.*[5] successfully obtained NOMC via self-condense of melamine confined in the mesochannels of an OMC matrix synthesized with EISA method; Dai *et al.*[14] demonstrated that the pyrolysis of the soft-templating polymeric composites in ammonia atmosphere was a direct, facile way towards NOMC. Although NOMC could be synthesized according to these methods, the synthesis process is still time-consuming and the process is not the real direct soft-templating strategy for synthesis of NOMC. To our best knowledge, there are still few reports of the direct synthesis of NOMC via one-pot soft-templating method.

Herein, we selected a water-soluble m-aminophenol (MAP) as carbon and nitrogen co-precursor and directly introduced N into the OMC during the co-assembly process between MAP and F127. This strategy took advantage of polymerization between MAP and formaldehyde.[16] We found that the N content of NOMC could be regulated through adding resorcinol (R) to change the molar ratio of R/MAP and changing the carbonization temperature without the loss of ordered mesoporous structure. The produced NOMC performed a better catalytic activity than that of CMK-3 for selective oxidation of ethylbenzene.

Fig. 1 illustrates the synthesis process towards NOMC. In the first stage, MAP molecules interact with the hydrophilic PEO blocks of F127 through the hydrogen-bonding interactions, which also exist among H_2O, NH_3 and MAP. 1,3,5-trimethylbenzene (TMB) is a non-polar molecule and preferentially locates inside the hydrophobic regions (PPO block) of F127, which easily causes the formation of stripe-like micelles.[17] During stirring process at 80 ℃, formaldehyde molecules are gradually produced by the hydrolysis of hexamine (HMT). MAP molecules condensate with formaldehyde molecules forming nitrogen-containing resoles/F127 composites. At the same time, $-NH_2$ groups of MAP can react with the aldehyde groups via elimination to generate Schiff base, which is stable because the -CH=N- bond is conjugated with -CH=CH- bond.[15] During the calcination, most of F127 are removed below 400 ℃ (Fig. S1) and the thermosetting nitrogen-containing resoles are remained forming pore walls. The loss of some small molecules (such as water, NH_4^+)

as well as the decomposition of functional groups due to the elevation of temperature leads to the formation of NOMC. Therefore, the basic principle relies on the polymerization of MAP and HCHO molecules around F127 to form the nitrogen-containing resoles/F127 composites and the removal of F127 to obtain ordered mesoporous structure made of nitrogen-containing pore wall after calcination. Here, for clarity, we take nitrogen-containing ordered mesoporous carbon with molar ratio of R/MAP=0:1 after carbonized at 800 ℃ (denoted as NOMC-800) for example unless special instructions.

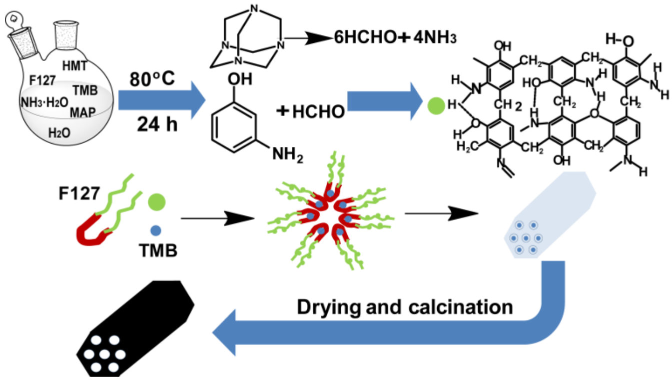

Fig. 1 Schematic representation of the synthesis route towards NOMC.

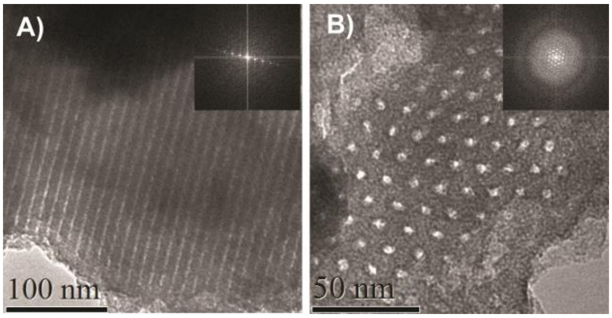

Fig. 2 TEM images of NOMC-800 with its ordered hexagonal mesoporous structure viewed from the A) [110] and B) [001] directions. The insets are the corresponding fast Fourier transform (FFT) patterns.

TEM images (Fig. 2) reveal that NOMC-800 is of an ordered 2-D hexagonal mesoporous structure. The cell parameter, a (the distance between the two adjacent pore centres), is estimated from the TEM images to be ~12.7nm. SEM images (Fig. S2) of the sample indicate that the sample is composed of irregularly polyhedral particles with the size ranging from hundreds of nanometres to a few micrometres.

The ordered mesoporous structure could be further confirmed by small angle XRD pattern (Fig. 3A). XRD pattern of NOMC-800 shows two resolved peaks at 2θ= 0.6-2.0. The d-spacing value ratio for these peaks is about $1:1/\sqrt{3}$ and can be indexed as (100), and (110) reflections associated with 2-D hexagonal p6mm symmetry. The cell parameter, a, is calculated using the formula $a=2d_{100}/\sqrt{3}$, where d_{100} represents the d-spacing values of the (100) diffraction, to be ~13nm, consistent with above TEM results. N_2 adsorption-desorption isotherms of NOMC-800 show typical type-IV curves, with a clear condensation step at P/P_0=0.4-0.6, suggesting a uniform mesopore (Fig. 3B). It should be noticed here that the isotherms do not give a good H1-type hysteresis loop, suggesting that some pore distortion may exist and partially block the channels.[11] According to Brunauer-Emmett-Teller (BET) method, the specific BET surface area is calculated to be as high as 857 m^2/g. The micropore and mesopore volumes are 0.27 and 0.64 cm^3/g, respectively. The pore size calculated from adsorption branch by Barett-Joyner-Halenda (BJH) model is about ~5.1nm (see Table S1).

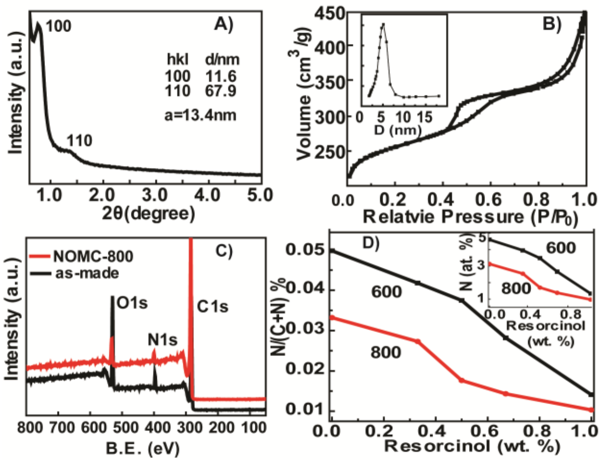

Fig. 3 A) small angle XRD pattern and B) N_2 adsorption-desorption isotherms with the pore size distribution (inset) of the NOMC-800. C) XPS spectra of the as-made and NOMC-800 and D) The variation of nitrogen content with the molar ratio of R/MAP and carbonization temperature.

XPS spectra were employed to detect the surface chemistry property of these samples. Fig. 3C shows the spectra of NOMC-800 and as-made sample (the sample was synthesized without carbonization, namely, nitrogen-containing resoles/F127 composites) and clear signals from C, N, O of these two samples are observed. The N content of the as-made sample is about 5.1 at%, suggesting that N can be induced into the resoles/F127 composites via polymerization of MAP and HCHO around F127. After carbonized at 800 ℃, the N content decreases to 3.3 at% and the O content decreases from 20.6 to 5.7 at% because of the decomposition of many oxygen and nitrogen functional groups and the removal of F127. Interestingly, noticeable change of N type is observed after carbonized at 800 ℃ (Fig. S3). In the case of the as-made sample, there is one obvious peak at ~397.6 eV. After carbonized at 800 ℃, the N1s peak shifts to higher binding energy, indicating the obvious change of N types which is originated from rearrangement and transformation of the different N species.[18,19] The N1s spectra of NOMC-800 could be fitted to four components, pyridinic-N (398.3 eV), pyrrolic-N (400.2 eV), graphitic-N (401.1 eV) and nitrogen-oxides (403.3 eV).[14,18,19] In order to regulate nitrogen content, resorcinol (R) was added into the reaction system, because R was usually used to synthesize OMC.[17,20,21] The N content decreases with the rise of carbonization temperature and the molar ratio of R/MAP (Fig. 3D). For example, the N content of NOMC-800 changes from 3.3 to 0.9 at% with tuning the weight fraction of R from 0 to 100 wt%. We propose that NH_3 from ammonia water or the hydrolysis of HMT also partially involved in the polymerization and/or co-assembly.[22] Therefore, there is still some N remained when only R is used. Nevertheless, the main source of N comes from MAP molecules (Fig. S4). Alternatively, small XRD patterns (Fig. S5), N_2 adsorption-desorption isotherms (Fig. S6), TEM images (Fig. S7 and Fig. S9) and XPS characterizations (Fig. S8 and Fig. S10) of other products in ESI also confirm that we successfully synthesize NOMC with tunable N content.

NOMC has been used in adsorption, separation, energy storage/conversion, but there are few reports of NOMC as a metal-free catalyst.[4,23] It has been demonstrated that N in N-doped graphene plays a vital role in the C-H activation.[24] Such progress encourages us to test the produced NOMC in selective liquid-phase oxidation of ethylbenzene. The results of various carbon catalysts are summarized in Table 1. In our experiment, acetophenone (AcPO) is the main product with benzaldehyde, benzoic acid and 1-phenyl-ethylalcohol as the by-products, which is in line with CNTs and/or N-doped graphene as catalysts.[24,25] The blank test indicates that there is a low reaction activity because of the EB autoxidation.[26] CMK-3 exhibits higher catalytic performance than that of blank test, indicating that mesoporous carbon materials itself has a certain catalytic ability for the formation of AcPO. However, O-CMK-3 (CMK-3 treated by HNO_3) has a lower activity than that of CMK-3, which may be attributed to the side-effects of oxygen-functional groups introduced via HNO_3-treatment.[25,27] There is an obvious increase of catalytic performance when NOMC-800 is used as a catalyst. We propose that N introduced into the OMC plays a very important role in the reaction, which is in agreement with previous report.[24] Moreover, although NOMC prepared via similar method with the literature[14] exhibits approximate activity (see property of the NH_3-OMC-800 in Table S2), in the view of the synthesis process, NOMC-800 prepared in this work has an advantage over the NH_3 treatment. It is worth noting that there is no metal induced into the materials which is very important for the carbon catalysis research to exclude the effects of the metal impurities in the carbon catalyst.[28]

Table 1 Catalytic activity of different carbon materials for the liquid phase oxidation of ethylbenzene[a].

Sample	Conversion (%)	Selectivity (%)	R_s[b] ($\mu mol\ m^{-2}\ h^{-1}$)
Blank	13.8	14.1	-
CMK-3	40.8	40.2	40.8
O-CMK-3[c]	34.9	30.7	39.1
NOMC-800	63.3	84.1	168.7
NH_3-OMC-800	63.1	86.1	108.1

a) the conversion and selectivity for (AcPO) were determined by GC; b) Yield rate of AcPO per m^2 of catalyst surface at 12h. c) CMK-3 is treated by concentrated HNO_3 for 3h, at 60 ℃ and denoted as O-CMK-3.

In conclusion, using MAP as carbon and nitrogen co-precursor, the nitrogen-containing ordered mesoporous carbon has been successfully synthesized via co-assembly process between MAP with F127. Our results show that this approach is simple for direct introduction of nitrogen into the OMC comparing with traditional NH_3 post-treatment, step-by-step strategies and other hard-templating methods. Furthermore, this work enlarges the application of OMC in catalysis especially using OMC as a metal-free catalyst.

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Notes and references

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†Electronic Supplementary Information (ESI) available: materials preparation, Characterization methods, additional figures and references. See DOI: 10.1039/c000000x/

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