Activation of ordered mesoporous carbon nitride prepared via soft-template for CO$_2$ adsorption

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Abstract. A mesoporous carbon nitride material (MCN) was nanocasted by using a soft-template of triblock surfactant Pluronic F127, a carbon resource from resol and dicyandiamide (DCDA) as a nitrogen precursor. The obtained MCN was activated to improve its porous channel (AMCN). A reference sample of mesoporous carbon (MC) material was also prepared in the same protocol without DCDA. The tunable mesostructures (p6m symmetry) was proved by X-ray diffraction, transmission electron microscopy images and nitrogen adsorption-desorption isotherms. Fourier transformation infrared spectroscopy and energy dispersive X-ray spectroscopy presented about 3.1 wt% of doped-nitrogen in the obtained MCN. In comparison to the MC, a significant increase of BET surface area (333 m$^2$/g for MC, 414 m$^2$/g for MCN and 951 m$^2$/g for AMCN) and an enlargement of pore volume (0.23 cm$^3$/g for MC, 0.25 cm$^3$/g for MCN and 0.33 cm$^3$/g for AMCN), which contributed to a noticeable enhancement of the room temperature CO$_2$ uptake from 1.8 mmol/g (for MC) to 3.7 mmol/g (for MCN) and 4.1 mmol/g (for AMCN). This work emphasized that the assistance of DCDA and further activation resulted in enlargement of both pore volume and BET surface area promising a feasible application of MCN and AMCN in adsorption technology.

1. Introduction
Ordered mesoporous carbons have received considerable attention due to outstanding features such as their large surface area, porous structure, physical-chemical stability and good conductivity. However, synthesized mesoporous carbons show hydrophobic surfaces and lack of active sites, which limit their application [1, 2]. To enhance the properties of the material, nitrogen-doped mesoporous carbons could be a good strategy. Mesoporous carbon nitrides (MCN) could improve the surface polarity and electric conductivity which enables their application in electric double-layer capacitors, fuel cells, and catalytic processes. Similar to synthesis of mesoporous carbons, Meng et al. [3] developed a soft-template method to facile preparation of MCN. Triblock polymers like P123, F127 can be used as soft templates for appropriate carbon and nitrogen precursors. Resol resin is an excellent carbon precursor for this method [3]. For nitrogen doping, various nitrogen precursors have been studied [1]. Wei et al. [4] investigated dicyandiamide (C$_2$H$_4$N$_4$) as a nitrogen precursor and obtained uniform mesopores as well as basic groups in the MCN. This compound possesses high nitrogen content (66.6 wt%), small size and weight. Therefore, resol resin and DCDA were selected as precursors for the current research.

It is well known that CO$_2$ causes greenhouse effect and global warming, leading to serious climate change. Therefore, much effort has been done to develop many chemical and physical methods for
CO₂ capture and sequestration as a means of alleviating this problem [4]. Due to high specific surface areas, high total pore volume, large pore size and basic nitrogen sites, MCN could be a promising material for CO₂ adsorption.

2. Materials and method

2.1. Preparation of mesoporous carbon nitride
To prepare MCN, the resol was firstly prepared from phenol and formaldehyde in a base catalyzed process according to previous reports [3]. For a typical preparation, 0.70 g of phenol was melted at 40 °C, then 0.13 g of 20 wt% NaOH solution was slowly added under stirring. After 10 min, 1.05 g of formalin (37 wt%) was added dropwise, and the mixture was stirred at 70 °C for 1 h. Upon cooling down to room temperature, the pH value was adjusted to around 7.0 using 0.6 M HCl solution. Water was then removed under vacuum at 50 °C. The obtained resol was redissolved in ethanol (20 wt% resol); thereby separating sodium chloride as a precipitate at the same time.

MCN was prepared according to previous procedures [4]. Typically, 1.00 g F127 and 1.00 g dicyandiamide (DCDA) were dissolved in the solution of 20.0 g ethanol and 10.0 g water. Subsequently, 5.00 g of resol (20 wt%) in ethanol solution was added. After stirring for 30 min, the mixture was let evaporate ethanol at room temperature for 12 h, followed by drying in an oven at 100 °C for 24 h. The composite products were crushed into powders. Calcination was carried out in a tube furnace under N₂ atmosphere at 250 °C for 2 h, then raised to 600 °C and kept for 3 h with a heating rate of 1 °C/min. Moreover, a MC sample which was prepared in the same procedure without DCDA was used as reference one.

2.2. Activation of mesoporous carbon nitride
The MCN was placed in the centre of a quartz tube and heated to 950 °C with heating rate of 5 °C/min under nitrogen. Next, the nitrogen stream was switched to CO₂ one (50 cm³/min) for activation. Finally, the tube was cooled to room temperature under nitrogen. With different activation time of 1 h, 2 h, activated MCN samples were denoted as AMCN-1h, AMCN-2h.

2.3. CO₂ adsorption
MCN and MC samples were degassed at 300 °C in 2.0 h. CO₂ adsorption was conducted at 0 - 40 °C and 1 atm on an adsorption apparatus by laboratory set-up.

2.4. Characterization
The structure of MCN was characterized by X-ray powder diffraction (XRD) using Brucker AXS D8 diffractometer over the small angle. Cu-Kα radiation was used as the target (λ = 1.5418 Å). Nitrogen adsorption and desorption isotherms were conducted at 77 K on a Surface Area & Pore Size Analyzer (Quantachrome NovaWin version 11.0). All samples were degassed in 2 h at 160 °C. Pore size distribution and pore volume were calculated by BJH method. Transmission electron microscopy (TEM) images were collected by JEOL JEM-1400 at 100kV. The FTIR spectra of MCN and MC samples were analyzed by using a Tensor 27 spectrometer (Bruker Optics, Germany). The elemental analysis was performed by using a JSM-7401F microscope and JED-2300 energy dispersive spectroscopy.

3. Results and discussion

3.1. Small-angle X-ray diffraction
The structure of MCN was studied by small-angle XRD (Figure 1). The XRD pattern presents several diffraction peaks at 2θ = 0.5-2, which can be indexed to (1 0), (2 0) with d = 150 Å and 72 Å, respectively. They represent reflections of an ordered hexagonal mesostructure. Compared to previous research, this result is totally sensible and suitable with the 2-D hexagonal structure of FDU-15 [2, 3]. The intense (10) peak reflects a d-spacing of 150 Å, which corresponds to a unit-cell parameter of 17.3 nm.
3.2. Nitrogen adsorption-desorption isotherms of MCN

Figure 2 shows nitrogen adsorption and desorption isotherms for as-prepared MCN. It is found to be the typical IV isotherm with distinct hysteresis loops at relative pressure (P/P₀) from 0.4 to 0.7, relating to the uniformity of the mesopores. This hysteresis loop could be H1-type which represents uniform cylindrical pores of 2-D hexagonal structure. The pore size distribution of MCN by using the BJH model shows uniform mesopores and micropores on its wall (Fig. 2b). In addition, the highest distribution at 3.2 nm, the S_{BET} of 414 m²/g and the pore volume of 0.25 cm³/g for MCN are shown in Table 1.

3.3. TEM images of MCN

The TEM images of MCN are illustrated in Figure 4. The (1 0 0) and (1 1 0) planes demonstrated that the well-ordered hexagonal mesostructure was obtained. This result is similar to previous reports for FDU-15 and other 2-D hexagonal structures [3, 4].
Figure 3. TEM images of MCN with (a) (1 0 0) and (b) (1 1 0) planes

3.4. FTIR spectra of MCN

Figure 4 shows the FTIR spectra of MC and MCN. The MC sample does not show any clear band. It demonstrates that the surface of MC could be less functional groups. Conversely, the result of MCN presents broad peaks of -NH$_2$, -NH, C-N bonds at 3425, 1586, 1118 cm$^{-1}$, respectively. The sharp band at 2361 cm$^{-1}$ can be assigned to CO$_2$ adsorption by basic sites from the nitrogen group on the
surface of MCNs [5]. Furthermore, EDX analysis indicated the presence of 3.13 wt% nitrogen element on the surface of MCN (Table 1).

3.5. Activation of MCN

| Sample     | \( S_{\text{BET}} \) (m\(^2\)/g) | \( V \) (cm\(^3\)/g) | \( d_{\text{max}} \) (nm) | N content (wt%) |
|------------|----------------------------------|-----------------------|-----------------------------|-----------------|
| MC         | 333                              | 0.23                  | 3.2                         | -               |
| MCN        | 414                              | 0.25                  | 3.2                         | 3.13            |
| AMCN-1h    | 738                              | 0.28                  | -                           | -               |
| AMCN-2h    | 951                              | 0.33                  | -                           | -               |

As presented in Table 1, the activation of MCN improved its specific surface areas, the total pore volumes remarkably. The surface area increased from 414 m\(^2\)/g for MCN to 738 m\(^2\)/g for AMCN-1h, 951 m\(^2\)/g. Likewise, the total pore volumes gradually increased from 0.25 to 0.28 and 0.33 cm\(^3\)/g for MCN and those activated samples, respectively. The great enhancement is probably due to the fact that the pre-existent pores are further widened, new narrow micropores are formed and the closed pores are opened during activation.

3.6. \( \text{CO}_2 \) adsorption on MCN

![Figure 5. \( \text{CO}_2 \) adsorption on MCN, AMCN-2h and MC](image)

The \( \text{CO}_2 \) uptake of non-activated, activated mesoporous carbon nitrides, and mesoporous carbon at room temperature and atmospheric pressure was presented in Figure 5 and Table 2. The \( \text{CO}_2 \) uptakes on two MCN samples are much higher than that of MC at different pressures. The presence of basic sites from nitrogen groups (\(-\text{NH_2}, -\text{NH_3}\)) could improve the adsorption. Although the activation of MCN extended its nanoporous, \( \text{CO}_2 \) uptake for MCN-2h only improved slightly at 1 atm, from 3.7 for MC and 4.1 mmol/g for AMCN-2h. Nitrogen amount rather than pore size may play important role at this pressure range.

In comparison with other absorbents, the \( \text{CO}_2 \) uptake of MCNs is higher than those of H-NMC-2.5, activated carbon, zeolite Cu-SSZ-13, zeolite CsX (Table 2). Moreover, MCN have high hydrothermal stability, high attrition resistance, fast kinetics for \( \text{CO}_2 \) adsorption, stable over many cycles, easy
regeneration, capable capacity at ambient temperature and pressure [4, 8]. Thus, MCNs would be expected to become adsorbents suitable for CO$_2$ storage capacity and other gases.

| Sample                  | $S_{BET}$ (m$^2$/g) | $V_t$ (cm$^3$/g) | CO$_2$ uptake (mmol/g) | Condition          |
|-------------------------|---------------------|------------------|------------------------|-------------------|
| MC                      | 333                 | 0.23             | 1.8                    | 30 °C/1 atm       |
| MCN                     | 413                 | 0.26             | 3.7                    | 30 °C/1 atm       |
| AMCN-2h                 | 951                 | 0.33             | 4.1                    | 30 °C/1 atm       |
| H-NMC-2.5 [4]           | 537                 | 0.27             | 2.8                    | 25 °C/1 bar       |
| Activated carbon [4]    | -                   | -                | 2.1–2.5                | 25 °C/1 bar       |
| Zeolite Cu-SSZ-13 [6]   | 710                 | -                | 3.7                    | 25 °C/1 bar       |
| Zeolite CsX [7]         | -                   | -                | ~ 3                    | 25 °C/1 bar       |

4. Conclusion
MCN was synthesized via soft-template method using Pluronic F127 as surfactant to navigate the structure. XRD, TEM and nitrogen adsorption – desorption isotherms demonstrated that the obtained MCN possesses orderly tunable mesostructures (p6m symmetry) with pore volume of 0.25 cm$^3$/g, specific surface area of 414 m$^2$/g and nitrogen content of 3.1 wt%. FTIR indicated basic sites from nitrogen groups on the surface of MCN. Moreover, the activation of MCN improved its nanoporous significantly, from 414 to 951 m$^2$/g and volume pore from 0.25 to 0.33 cm$^3$/g. For CO$_2$ adsorption, the CO$_2$ uptakes of non-activated and activated mesoporous carbon nitrides at room temperature and atmospheric pressure were 2.7-fold (3.7 mmol/g), and 3.0-fold (4.1 mmol/g) higher than that of MC (1.8 mmol/g), respectively. Thus, MCN could be a potential material for CO$_2$ storage and separation.

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