Carbon Nitride Nanoparticles

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Highly Ordered Mesoporous Carbon Nitride Nanoparticles with High Nitrogen Content: A Metal-Free Basic Catalyst**

*Xin Jin, Veerappan V. Balasubramanian, Sakthivel T. Selvan, Dhanashri P. Sawant, Murugulla A. Chari, G. Q. Lu, and Ajayan Vinu**

Mesoporous silica nanoparticles (MSNs) with controlled size, morphology, and tunable porosity have been receiving much attention due to their applications in the fields of drug delivery, catalysis, adsorption, separation, and fuel cells.[1–3] Various MSNs with different functional groups and structures have been prepared and utilized for drug and gene delivery,[4,5] while mesoporous nanoparticles composed of carbon and nitrogen are of particular interest for basic catalysis and the capture of carbon dioxide. Carbon nitride (CN) is a well known and fascinating material that has attracted worldwide attention because the incorporation of nitrogen atoms in the carbon nanostructure can enhance the mechanical, conducting, field-emission, and energy-storage properties.[6–14] Mesoporous CN (MCN) materials with large surface areas, small particle sizes, and tunable pore diameters promise access to an even wider range of applications due to their interesting electrical and conducting properties. Recently, Vinu et al. reported the preparation of mesoporous carbon nitride with tunable pore size using mesoporous silica SBA-15 as template.[15–17] Unfortunately, the materials had a low nitrogen content due to their low thermal stability and exhibited a large particle size.

Ultrafine mesoporous nanoparticles are expected to provide excellent textural parameters and high chemical, thermal, and mechanical stability, which may help to achieve high nitrogen content in the walls of the CN framework. Controlling the nitrogen content in the mesoporous carbon matrix is extremely important, as the nitrogen atoms in the wall structure of MCN can offer basic sites in the form of amine or imine groups which dictate the basic character and basic catalytic performance of the materials. However, to the best of our knowledge, there has been no report on the preparation of MCNs with high nitrogen content and their application in base-catalyzed reactions. Herein we report for the first time on the preparation of well-ordered mesoporous CN nanoparticles with a size smaller than 150 nm (MCN-3) and a high nitrogen content (C_4N_2) by using mesoporous ultrasmall silica nanoparticles as template. The nitrogen content of MCN-3 is twice that of MCN-1 and MCN-2, which were prepared from SBA-15 and SBA-16, respectively.[15–17] We also demonstrate for the first time the basic catalytic properties of MCN-3, which is the first highly ordered, mesoporous, metal-free basic catalyst, in the transesterification of β-keto esters; MCN-3 shows superior performance in the transesterification of β-keto esters with excellent conversion and 100 % product selectivity.

The templates for the fabrication of MCN-3 are ultrasmall mesoporous silica nanoparticles, which were prepared by a process mediated by fluorocarbon polymer and Pluronic P123 surfactant, reported by Ying et al., and denoted IBN-4.[18] IBN-4 has two-dimensional hexagonally ordered mesoporous structure with a channel-type pore system and rod-shaped morphology. The interesting feature of this material is its small particle size, in the range of 150–300 nm long and 50–150 nm wide.[18] The detailed procedure for the synthesis of IBN-4 is given in the Experimental Section.

Figure 1 shows the powder XRD patterns of MCN-3 and its parent silica template IBN-4. MCN-3 exhibits three well-resolved peaks, which could respectively be indexed as the 100, 110, and 200 diffractions of *p6m* symmetry with a lattice constant of 10.95 nm. The shape of the XRD pattern of MCN-3 is similar to that of the parent silica template, which has a two-dimensional structure with *p6m* symmetry. However, the

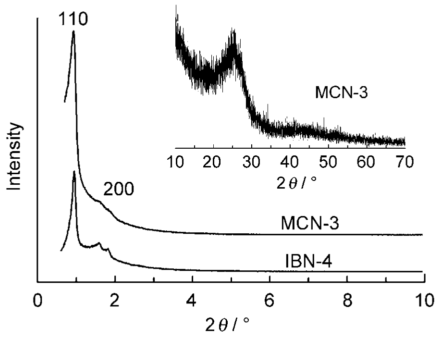

Figure 1. Powder XRD patterns of MCN-3 and IBN-4. Inset: Higher angle XRD pattern of MCN-3.

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[*] Dr. V. V. Balasubramanian, Dr. S. T. Selvan, Dr. D. P. Sawant, Dr. M. A. Chari, Dr. A. Vinu
International Center for Materials Nanoarchitectonics, World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science
1-1 Namiki, Tsukuba 305-0044, Ibaraki (Japan)
Fax: (+81) 29-860-4706
E-mail: vinu.ajayan@nims.go.jp
Homepage: http://www.nims.go.jp/super/HP/vinu/websitevinu/V-top.htm
X. Jin, Dr. G. Q. Lu
ARC Center for Functional Nanomaterials
University of Queensland, Queensland 4072 (Australia)

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intensity of the (100) peak of MCN-3 is higher than that of IBN-4, that is, the structural order of the material is improved after the replication process, and the negative replica of IBN-4 was successfully obtained. As expected, thermogravimetric analysis (TGA) of MCN-3 showed little silica residue after combustion of the CN framework at temperatures higher than 600 °C in the presence of air (less than 1 wt %), that is, the intense XRD peak with *p*6*m* symmetry does not result from the IBN-4 silica template. To check whether the CN wall structure of MCN is crystalline or amorphous, the material was characterized by wide-angle XRD analysis. The wide-angle XRD pattern of MCN-3 (Figure 1 inset) exhibits a peak at 25.3 with a *d* spacing of 0.351, which is almost the same as that obtained for nonporous carbon nitrides, that is, the wall structure of the samples is composed of carbon and nitrogen that are arranged in a turbostratic form. Formation of turbostratic ordering in the wall structure of carbon nitride materials is highly important, as it gives information about their electrical, electronic, and basic catalytic properties.

High-resolution TEM images taken along the [100] direction confirm that hexagonally ordered pores arranged in a linear array are present in the sample. Interestingly, the rodlike morphology similar to that of the parent template and small particle size were retained even after the replication process (Figure 2 A and B). The particle length of 150–250 nm and width of 80–150 nm are almost 10–15 times smaller than those of MCN-1.[15] The size of the MCN nanoparticles was also confirmed by HRSEM measurements (Figure 2 C and Figure 1S, Supporting Information). Thus, MCN materials in the form of small nanoparticles with rod-shaped morphology can be easily obtained by using IBN-4 as hard template. Figure 2 D displays the electron energy-loss (EEL) spectrum of MCN-3. The sample exhibits C and N K-edges at 284 and 401 eV, respectively. The peak at 284 eV is due to 1s–π* electron transitions and is a fingerprint of a sp^2-hybridized carbon bonded to nitrogen, whereas the peak at 401 eV is attributed to sp^2-hybridized nitrogen atoms which are present with carbon atoms in the wall structure. Similar results have been also obtained for MCN-1 prepared with SBA-15 as template.[15,16]

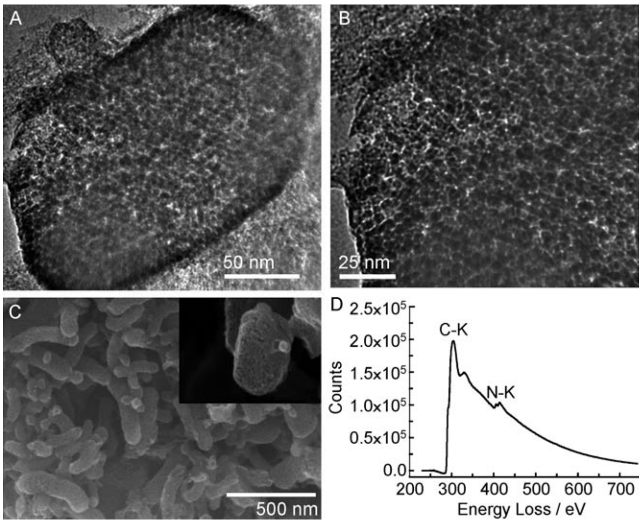

Figure 2. A, B) HRTEM and C) HRSEM images and D) EEL spectrum of MCN-3.

The nitrogen-adsorption isotherm of MCN-3 is a type IV curve with a sharp capillary condensation step at high relative pressure and an H1 hysteresis loop, which is typically observed for samples with a large mesopores and cylindrical channels (Figure 3). These results also reveal that MCN-3 has a well-ordered pore structure similar to that of the IBN-4 silica template. The total pore volume of 0.67 cm^3 g^{-1} and specific BET surface area of 645 m^2 g^{-1} of MCN-3 are much higher than those of MCN-1. The BJH pore size distribution calculated from the adsorption branch of the nitrogen isotherm confirms that the pores of MCN-3 are highly uniform and have a narrow pore size distribution. The calculated pore diameter of 3.8 nm is smaller than that of the IBN-4 silica template.

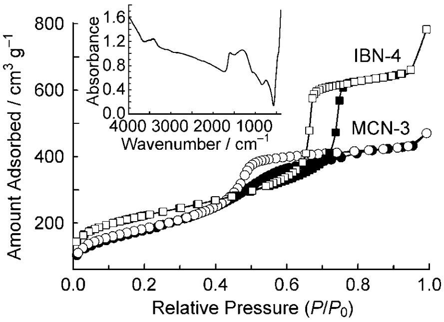

Figure 3. Nitrogen adsorption/desorption isotherms of MCN-3 in comparison with IBN-4. Inset: FTIR spectrum of MCN-3.

X-ray photoelectron survey spectra reveal that MCN-3 is mainly composed of carbon and nitrogen with a small amount of hydrogen and oxygen, and that different kinds of carbon and nitrogen are present in the mesoporous wall structure. Although the nitrogen content of the sample is higher than that of MCN-1, the C 1s and N 1s spectra confirm that the nature and coordination of the carbon and nitrogen species are similar to those of MCN-1 (Figure 2S, Supporting Information).[15,16] The nature of the carbon and nitrogen atoms in MCN-3 was also investigated by FTIR spectroscopy. The sample exhibits four major bands centered at 760, 1209.5, 1590.7, and 3415 cm^{-1} (Figure 3, inset). The bands at 1209.5 and 1590.7 cm^{-1} are assigned to aromatic C–N stretching and aromatic ring modes, respectively, while the broad peak centered at 3415 cm^{-1} is attributed to the stretching mode of NH groups in the aromatic ring. The band at 760 cm^{-1} is due to rings containing nitrogen, such as a cyanogen ring (C_3N_3).[19,20] This result suggests that the material contains numerous cyanogen rings, which are composed of sp^2 C–N bonds, stabilize the wall structure, and prevent loss of nitrogen during high-temperature treatment. The band at 760 cm^{-1} was not observed for MCN-1, which has a low nitrogen content, that is, MCN-3 is highly stable at a high temperature owing to its small particle size.

An interesting feature of this material is its nitrogen content. Electron energy-loss, energy-dispersive X-ray, and CHN analyses reveal that the carbon-to-nitrogen atomic ratio of MCN-3 is about 2.3, which is almost two times lower than that of MCN-1 prepared by the same chemical polymerization technique. Previously, we succeeded in decreasing the carbon-to-nitrogen atomic ratio of MCN-1 from 4.5 to 3.3 by simply adjusting the amount of nitrogen source in the synthesis. However, the textural parameter of MCN-1 is significantly affected, and material with a carbon-to-nitrogen ratio of less than 3.3 cannot be prepared by this process. In the case of MCN-3, without making any changes in the synthesis procedure, material with a carbon-to-nitrogen atomic ratio of 2.3 could easily be obtained without any adverse affect on the textural parameters, which are indeed much better than those of MCN-1. These results clearly suggest that the small size of MCN-3 nanoparticles prevents loss of nitrogen atoms from the CN network in the mesoporous wall structure during the carbonization process. It is well known that high energy is required to break the bonds between atoms in nanoparticles. We surmise that this could be the reason for the high nitrogen content of MCN-3. To the best of our knowledge, this is the first report on the fabrication of mesoporous carbon nitride nanoparticles with a carbon-to-nitrogen ratio as low as 2.3. As mentioned in the previous section, the nitrogen content in the MCN materials is highly critical as it dictates their basic properties. We investigated the base-catalysis performance of MCN-3 in the transesterification of β-keto esters.

β-Keto esters are important synthons prepared by reaction of highly reactive and unstable diketene with various alcohols.[21–23] They can be transformed into chiral building blocks by chemical and enzymatic transformation and can be used as a tool for chain-extension reactions. Transesterification of β-keto esters is an effective and important method of ester synthesis and has wide applications in both academic and industrial research. Protic acids, Lewis acids, and bases are generally employed as catalysts for transesterification of β-keto esters.[21–25] Here we used the first metal-free MCN with huge surface area as basic catalyst for the transesterification of β-keto esters (Figure 4). The catalyst is highly active and affords high alcohol conversion in a short time. Interestingly, even the less reactive long-chain primary alcohols gave the corresponding keto esters, which are often-used starting materials for the polymer industry, in good yield, although the reaction time is a little longer than those of the alcohols with a short alkyl chain. This could mainly be due to the fact that the catalyst has a huge number of strongly basic sites originating from nitrogen functional groups such as NH, NH_2, and/or N bonded with the carbon matrix in the wall structure of MCN-3. Aryl and cyclic alcohols also underwent transesterification affording the corresponding esters, which have a high commercial value, in high yield. In addition, the catalyst was recycled four times without much change in activity. This indicates that the catalyst is highly stable and can be reused for several cycles, which are prerequisites for commercialization. Furthermore, this catalyst is expected to give excellent results in other base-catalyzed organic reactions, as it has high surface area, large pore diameter, and large pore volume with a huge number of nitrogen functional groups on the surface.

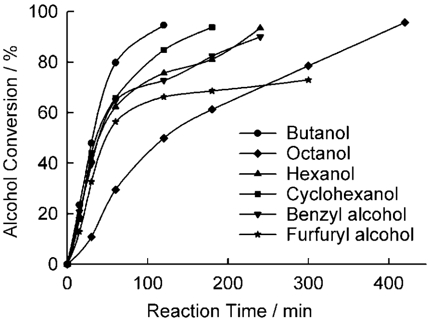

Figure 4. Basic catalytic performance of MCN-3 in the transesterification of β-keto esters of different alcohols. Reaction conditions: β-Keto ester/alcohol molar ratio 1.2:1, catalyst MCN-3 (10 wt% of total reaction mixture), solvent toluene, reaction temperature 110°C.

In summary, we have demonstrated for the first time the preparation of highly ordered, discrete, monodisperse, mesoporous carbon nitride nanoparticles smaller than 150 nm with high nitrogen content by using ultrasmall silica nanoparticles with well-ordered mesostructure as template for a simple polymerization reaction between ethylenediamine and carbon tetrachloride inside the nanochannels of the template. Characterization by XRD, nitrogen adsorption, CHN analysis, spectroscopic techniques such as EELS and FTIR, HRTEM, and HRSEM showed that the material has an excellent mesostructural order with uniform mesostructure, small particle size, high surface area, and a large pore volume. The nitrogen content of MCN-3 is almost twice that of our previously reported mesoporous carbon nitrides prepared from SBA-15 and SBA-16 templates, the particle sizes of which are in the micrometer range. We tested the performance of MCN-3 in the base-catalyzed transesterification of β-keto esters of aryl, aliphatic, and cyclic primary alcohols. The catalyst is highly active and affords a high yield of the corresponding esters in a short reaction time. It is also highly stable and could be recycled several times. Moreover, we believe that the current synthetic protocol can be generalized to prepare various MCNs with different particle sizes by using different templates, and that MCN-3 could be employed in various base-catalyzed organic transformations, act as a novel candidate for future drug-delivery systems and as an adsorbent for capturing CO_2.

Experimental Section

Preparation of mesoporous silica and mesoporous carbon nitride nanoparticles with high nitrogen content: In a typical synthesis of IBN-4, 0.25 g of Pluronic P123 and 0.7 g of Fluorocarbon-4 (FC-4) were dissolved in 40 mL of 0.02 M HCl solution at 30°C. Then 1.0 g of TEOS was added to the solution under stirring at 30°C for 20 h, and the mixture was transferred to an autoclave and heated at 100°C for 24 h. The final product was calcined at 550°C for 24 h under air. The sample was denoted IBN-4.

Mesoporous carbon nitride nanoparticles with high nitrogen content (MCN-3) were prepared by using IBN-4 as a template. In a typical synthesis, 0.5 g of calcined IBN-4 was added to a mixture of ethylenediamine (EDA) (1.35 g) and carbon tetrachloride (3 g). The resultant mixture was heated at reflux (90°C) and stirred for 6 h. Then, the resulting dark brown solid mixture was placed in a drying oven for 12 h and ground into fine powder. The template/carbon nitride polymer composite was then treated in a nitrogen flow of 50 mL min^{-1} at 600°C at a heating rate of 3.0°C min^{-1} and kept under these conditions for 5 h to carbonize the polymer. MCN-3 was obtained by dissolution of the silica framework in 5 wt% hydrofluoric acid, isolated by filtration, washed several times with ethanol, and dried at 100 °C.

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