Facile One-Pot Synthesis of Nanoporous Carbon Nitride Solids by Using Soft Templates

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Carbon materials have attracted much attention because they are attractive for a wide range of applications, and also because of the scientific interest in the challenges posed by their synthesis, processing, and characterization.[1] Recently, carbon materials with various morphologies and contain heteroatoms such as nitrogen[2] and boron[3] have been actively pursued and considered as the most promising candidates to complement carbon in materials applications. For example, graphitic carbon nitride (g-C$_3$N$_4$) is a potentially useful substitute for amorphous and graphitic carbon in a variety of applications, such as catalytic supports and gas storage.[4] Because there are many ways to substitute carbon by nitrogen in graphite in a regular fashion, here the term carbon nitrides is understood to comprise a large family of related compounds (e.g., C$_3$N$_4$, C$_3$N$_2$, C$_3$N, C$_5$N, C$_{10}$N$_3$, and others). Accordingly, various strategies have been adopted to prepare the nitrogen-enriched carbon materials. Many groups have succeeded in synthesizing graphitic carbon nitrides via condensation of C-, N-, and H-containing precursors. For example, Kawaguchi synthesized a graphitic hexagonal polymer, (C$_3$N$_3$)$_2$(NH)$_3$, which was found to be stable up to 500 °C.[5] Through a solid-state reaction of 2,4,6-triamino-1,3,5-triazine with 2,4,6-trichloro-1,3,5-triazine in a high pressure-high temperature condition, Wolf et al. obtained a well-characterized and highly crystalline graphitic carbon nitride derivative. The generated HCl played the role of a template by filling the nitridic in-plane pores of a triazine-based condensation pattern.[6] Gao et al. were able to prepare carbon nitride at atmospheric pressure from polymerized (CH$_2$NH$_2$)$_2$ and CCl$_4$.[7] Schnick et al. succeeded in isolating the crystal structure of an intermediate, melem (C$_6$N$_{10}$H$_6$), and proved the existence of melem as an important intermediate during the thermal condensation of melamine as well as of other simple C/N/H precursor compounds.[8] Recently, Park et al. synthesized carbon nitride materials by using a solution-based, stepwise condensation reaction between cyanuric chloride and melamine at low temperature and ambient pressure.[9] In addition, physical and chemical vapor deposition methods are also employed often.[10]

Fewer examples have described the synthesis of nanoporous g-C$_x$N$_y$ (mpg-C$_x$N$_y$). Antonietti[11] and Vinu[12] et al. developed a method for the synthesis of mpg-C$_x$N$_y$ that makes of nanoporous silica host matrices as "hard template." By utilizing this method, the morphological properties of carbon nitride can be controlled to a certain extent by different silica templates, featuring large surface areas. However, the removal of the silica host matrices involves aqueous ammonium bifluoride (NH$_4$HF$_2$) or hydrogen fluoride (HF), which is hazardous and not environmentally friendly. Developing a reliable and facile strategy to synthesize nanoporous graphitic carbon nitride without hard templates is a topic that urgently requires a solution in order to enable larger-scale access to these materials. Therefore, there has been a growing interest over the past few years in the use of surfactants and block polymers as "soft templates" for the production of nanoporous materials, including carbons.[13,14]

Herein, a variety of nonionic surfactants and amphiphilic block polymers (e.g., Triton X-100, P123, F127, Brij30, Brij58, and Brij76) as well as some ionic surfactants are tested as structure-directing agents for the synthesis of mpg-C$_x$N$_y$ (see Scheme S1 in the Supporting Information for structure of the agents).

Ionic liquids (ILs) are organic salts with a low melting point, usually below 100 °C. They possess a high thermal stability, in some cases in excess of 400 °C.[15] Their unique physical and chemical properties make ILs attractive solvents for a wide variety of applications such as catalysis, separation, and electrochemistry.[16] They are also interesting templates for sol–gel synthesis, owing to their special functionality and structure. For example, Dai and Zhou et al. described the synthesis of nanoporous silicas by using imidazolium-based ILs.[17] Because of their high temperature stability and their negligible vapor pressure, ILs are especially promising for high-temperature syntheses. In this work some imidazolium- and pyridine-based ILs (Scheme S1) were also explored as soft templates. To the best of our knowledge, this approach is the first report on the facile synthesis of mpg-C$_x$N$_y$ by a soft-template-mediated synthetic strategy.

A synthetic scheme based on the self-condensation of dicyandiamide (DCDA) accompanied by elimination of ammonia to generate carbon nitride solids was employed (Scheme 1a). In a general procedure, the soft templates and DCDA were firstly mixed by dissolving both in water, and then dried at 100 °C in air. The mixture was then heated to form the mpg-CN polymer while simultaneously removing the soft template at the final stage of calcination (Scheme 1c and d).

However, to get ordered porous carbon nitrides by making use of soft templates is very difficult for thermodynamic and physicochemical reasons, similar to how the preparation of

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Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.200900284.
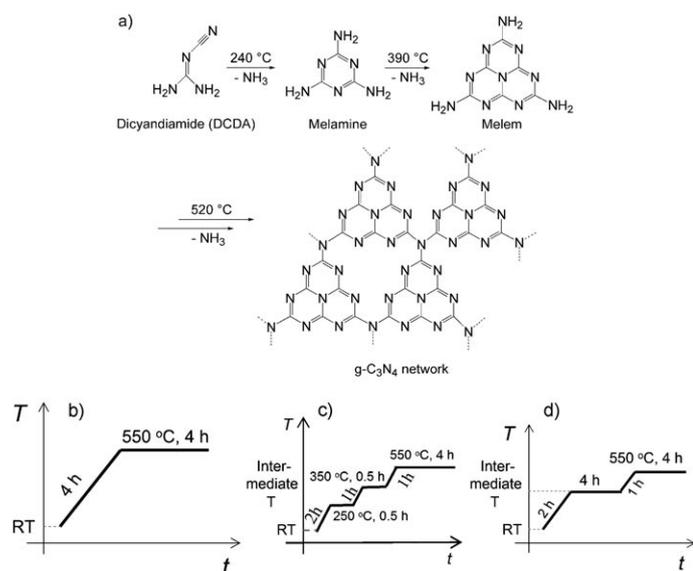
Scheme 1. a) Proposed reaction path from DCDA to graphitic carbon nitride. Typical heating programs for b) a nonporous bulk graphic carbon nitride solid, and c, d) nanoporous carbon nitride solids by using soft templates employed in this study.

other soft porous materials by soft templates is still a challenge. Only very few specific exceptions have been reported to be successful.[21] The technical problem that is faced is that the condensation towards larger extended CN-structures takes place around or above the decomposition temperature of the template. For example, the traditional approach (Scheme 1b) to preparing bulk carbon nitrides was essentially inapplicable to prepare mpg-CN by soft templates, because the addition of surfactant promoted the formation of volatile intermediates, which reduced the product yield to practically zero (e.g., Table 1, mpg-CN-Triton-0.5). Control experiment showed that surfactants did not react with fully condensed carbon nitrides, but decomposed when heated. This indicates that a side-reac-

tion between surfactants and carbon nitride precursors exists, rendering both volatile.

This problem was solved by delicately introducing holding sequences at intermediate temperatures around the template decomposition or each important condensation step (Scheme 1c and d) to suppress volatilization, followed by the final condensation step at 550 °C, at which temperature the template has already decomposed. Structural changes owing to further condensation and rearrangements at this temperature are to be expected. Broader screening experiments indicated that holding temperatures around 350∼400 °C are appropriate (depending on surfactants), while lower and higher temperatures essentially fail (Table S1).

X-ray diffraction (XRD) patterns (Figure 1a and Figure S1) revealed the graphite-like packing of practically all products, showing the typical (002) interlayer-stacking peak around 27°, for example, corresponding to an interlayer distance of $d = 0.336$ nm for mpg-CN-P123-0.7. According to Figure 1, the (002) peak is shifted for all diverse templates to slightly lower angles with the increasing the mass ratio of the template to monomer (r), reflecting an increasing interlayer distance. This is a further indication that the template not only influences textural features, but also enters the materials condensation scheme.

For a further clarification of this effect, the molar carbon to nitrogen ratio (C/N) of the products was determined by elemental analysis (Table 1), and the experimental value varied from 0.82 to 2.06 when using P123. As compared to the theoretical value of C_3N_4 (0.75), this means a significant incorporation of carbon fragments of the template within the aromatic ring systems which is proportional to the template content. In the case of high template concentrations, instead of ideally C_3N_4, nitrogen-doped carbons were obtained. This was also evidenced by the disappearance of the in-plane structural packing motif for typical g-C_3N_4 at ca. 13° in the XRD patterns (Figure 1, $r = 0.7$, 0.8). As compared to ordinary graphite, the nitrogen content was nevertheless extremely high (36–59 wt%). In fact, this positively influenced properties, such as electronic structures (Figure S2). For example, the electric conductivity of mpg-CN-P123-0.8 increased by a factor of 10^4 as compared to bulk g-C_3N_4 (Figure 1b), thus enabling nanoelectronics applications. However, the FTIR spectra (Figure S3) of all samples showed typical C–N heterocycle stretches in the region of ca. 1100–1600 cm^{-1} and the breathing mode of the tri-s-triazine units at 800 cm^{-1} from nonporous bulk g-C_3N_4, evidencing the formation of extended networks of C–N–C bonds.[18]

Table 1. Textural properties of nanoporous carbon nitride solids obtained by using P123 and Triton X-100 as soft templates and the control.

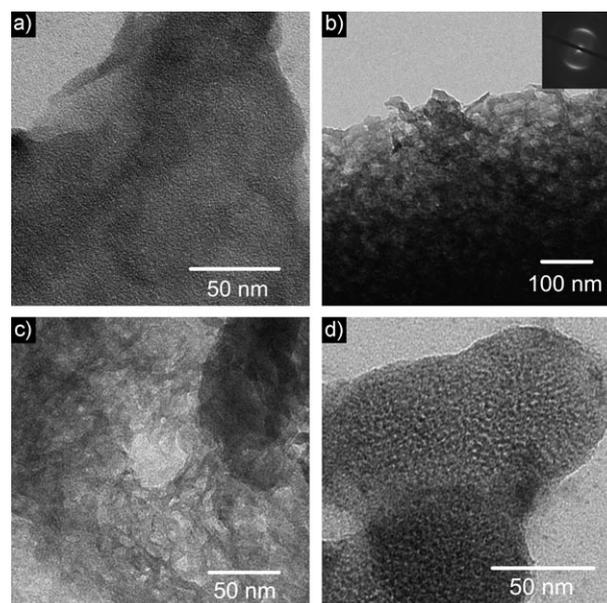| Sample	C/N[a]	Product mass[b] [g]	Surface area[c] [m^2 g^{-1}]	Pore volume[d] [cm^3 g^{-1}]	Pore diameter[e] [nm]
Bulk g-C_3N_4[f]	0.73	0.526	8	–	–
mpg-CN-P123-0.2[g]	0.820	0.325	10	0.031	3.1
mpg-CN-P123-0.5[g]	1.284	0.271	44	0.156	3.4
mpg-CN-P123-0.7[g]	1.711	0.169	187	0.232	3.1
mpg-CN-P123-0.8[g]	2.055	0.093	299	0.128	–
mpg-CN-Triton-0.5[f]	–	0.016	–	–	–
mpg-CN-Triton-0.1[h,i]	0.69	0.465	16	0.046	4.3
mpg-CN-Triton-0.2[h,i]	0.72	0.407	16	0.083	4.2
mpg-CN-Triton-0.4[h,i]	0.77	0.245	55	0.149	3.8
mpg-CN-Triton-0.5[h,i]	0.82	0.108	92	0.263	3.8
mpg-CN-Triton-0.6[h,i]	0.89	0.085	116	0.284	3.8
mpg-CN-BmimDCN-1.5[f]	0.81	0.203	81	0.179	5.6

[a] Molar ratio. [b] 1 g of DCDA. [c] BET surface area. [d] Barrett–Joyner–Halenda (BJH) adsorption pore volume. [e] BJH adsorption pore size considering only the pore contribution, which might be minor. [f, g, h] Heating programs according to Scheme 1b, c, and d, respectively; intermediate temperature 400 °C. [i] With extra air flow (2 bar).
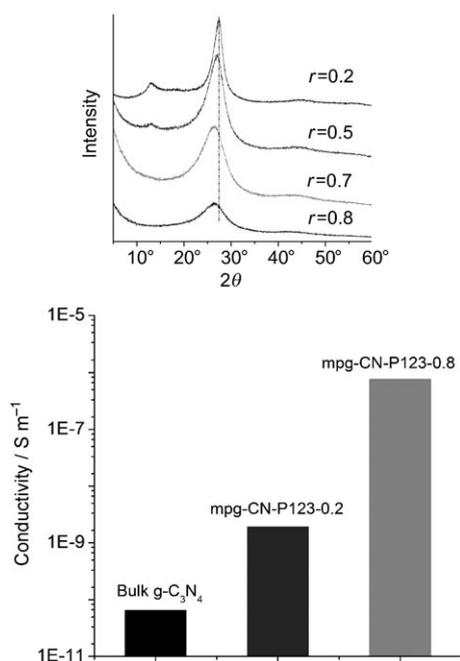
Figure 1. a) Powder XRD patterns of mpg-CN-P123-r ($r = 0.2$, 0.5, 0.7 and 0.8), and b) the electric conductivities of bulk g-C_3N_4, mpg-CN-P123-0.2, and mpg-CN-P123-0.8.
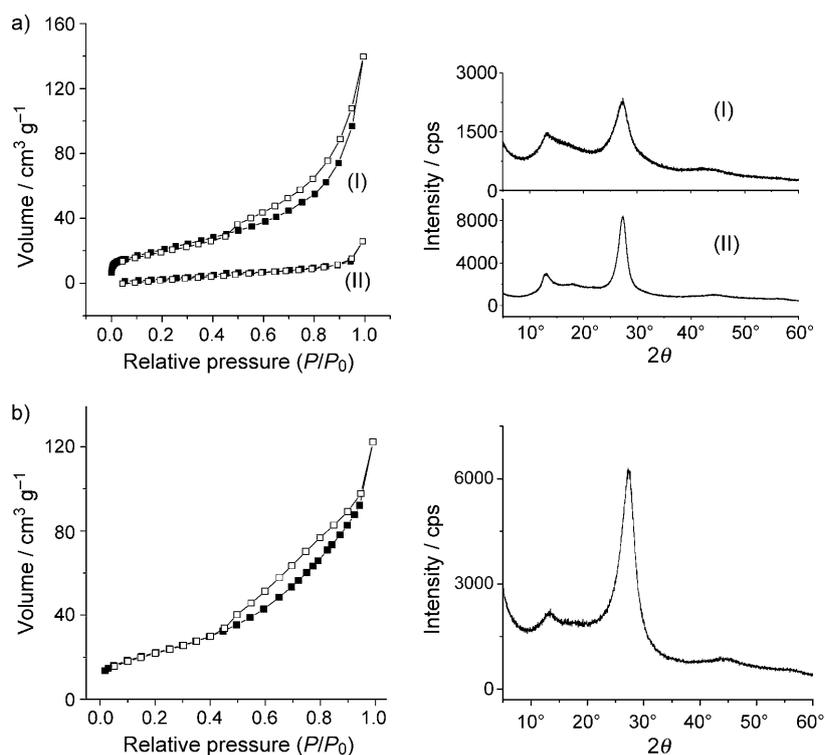

Figure 2. TEM images of nanoporous carbon nitride solids prepared by using soft templates. a) P123, $r = 0.7$; b) Triton X-100, $r = 0.1$; c) Triton X-100, $r = 0.5$; d) BmimPF$_6$, $r = 0.1$. The variable r is the mass ratio of templates to DCDA. The heating programs for (a), (b–c), and (d) are Scheme 1 c, d, and b, respectively.

A transmission electron microscopy (TEM) image of an mpg-CN-P123-0.7 sample is shown in Figure 2 a, reflecting the pore structures within the Pluronic-based CN-material. The porosity of the samples was further quantified by nitrogen sorption measurements. These isotherms (Figure S3) were however of type IV, according to the International Union of Pure and Applied Chemistry (IUPAC) classification, and do not agree with a uniform mesopore system. Some information about the pore structures was determined from the Brunauer–Emmett–Teller (BET) isotherms, and is summarized in Table 1 (see also Table S1). The surface areas of mpg-CN-P123 were between 10.0 and 299 m^{2}g^{-1}, depending on the template content. Absolute pore volume and pore size also did not appear to agree to the TEM data and the amount of template added. These materials are essentially only microporous.

Obviously, the amphiphilic contrast of the Pluronic materials was not large enough to enable a sufficiently robust self-assembly within the materials matrix. To understand the role of the chemical nature of the template for more successful templating, a variety of other amphiphilic block copolymers and surfactants were investigated. It was reasonable to assume that PEO-based surfactants are a meaningful choice, because dicyandiamide acts as both proton acceptor and donor and interacts with the PEO blocks via strong hydrogen bonds, providing compatibility between the template and condensing material matrix. However, low-molecular-weight non-ionic templates, for example Brij30, but also the ionic surfactants cetyltrimethylammonium chloride (CTAC) and cetyltrimethylammonium bromide (CTAB) only lead to maximal surface areas of ca. 80 m^{2}g^{-1} (Table S1). In TEM, the starting development of disordered, textural pores can be partly observed, but experimental-

ly, mainly micropores are accessed. The formation of micropores can be attributed to the chemical reaction of template fragments with the condensing carbon nitride (bulk g-C_3N_4 by heating program b was never found to be microporous, but is a dense material instead).

For this reason we think that the large pore system is in principle closed: the formation of carbon nitride sheets after a slightly too early removal of the template seals the pores again. Addition and chemical incorporation of the template makes the wall material microporous and thereby allows indirect access to at least some of the pores.

Triton X-100 (Table 1) is a favorable exception as a soft template for nanostructured carbon nitride solids. TEM images of these samples show a nicely developed pore texture in the final carbon nitride solids (Figure 2, b and c), which reflects the geometric properties of the original surfactants supramolecular aggregates. In addition, the intense electron diffraction arcs from a selected area proved the high organization of the pore walls. Figure 3 shows nitrogen adsorption isotherms of as-prepared mpg-CN-Triton-0.5, and the corresponding BJH pore-size distribution curves revealed dominant pores with a size of 3.8 nm as well as some bigger pores up to 15 nm. The BET surface area was 76 m^{2}g^{-1}, while micropores were essentially absent in this material. In the presence of extra air flow, also the C/N-ratio could be kept remarkably low (0.7–0.9) and in most cases, higher yields of mpg-CN were obtained. This means that the elimination of thermal gas-products, for example, fragments of surfactants and the ammonia, would effectively prohibit the aforementioned unwanted side-reactions between surfactant fragments and the carbon nitride intermediates.

Figure 3. N_2 adsorption/desorption isotherms and XRD patterns. a) trace I: mpg-CN-Triton-0.5; trace II: bulk nonporous carbon nitride solid. b) mpg-CN-BmimDCN-1.5.

and excludes the use of HF to remove silica hard templates. Here the "greener" soft template method indeed would pave the way for the emerging applications of carbon nitride solids in the sustainable energy field.[2a, b, 19] Moreover, owing to thermodynamic and physicochemical reasons, preparing soft porous materials by soft templates is still a challenge.[21] We have illustrated another "exceptional" example here. Further work on catalysis, photocatalysis, and photoelectrochemistry of these nanostructured carbon nitrides is currently ongoing.

Experimental Section

All reagents were obtained from Sigma–Aldrich, Acros, or Merck, unless specified otherwise. In a typical synthetic procedure, aqueous solutions of templates and dicyandiamide were first mixed, and then the mixture was heated in an oil bath at 100 °C until removal of water and formation of solids. The solids were then transferred into a crucible and heated according to different heating programs, which are illustrated in Scheme 1 b–c. BET surface areas and pore volumes were obtained from 77 K N_2 adsorption/desorption isotherms using an ASAP 2010 instrument. Samples were outgassed at 200 °C for 10 h to a residual pressure $< 10^{-4}$ Pa. TEM images were recorded on a Zeiss EM91 microscope. WAXS spectra were recorded on a Bruker D8 Advance diffractometer and FTIR spectra were recorded on a BioRad FTS 6000 spectrometer, equipped with an attenuated total reflection (ATR) setup. Elemental analyses (C, N, H) were performed on a Vario EL Elementar (Elementar Analyzen-System, Hanau, Germany). Conductivity measurements were carried out by confining the sample between two platinum discs and measuring the electrical resistance of the respective sample by Ohm's law using a Gamry Reference 600 potentiostat system.

The most favorable behavior, in our opinion, was however found for ionic liquids as soft templates. Even without elaborated temperature holding procedures, nanoporous textures were observed by TEM (Figure 2 d) and in the N_2 adsorption/desorption isotherms (Figure 3 b and Table 1). We attribute this behavior to the missing volatility of the primary products. Perfect graphitic structure was found for hexafluorophosphate as a counterion (BmimPF$_6$). Because we felt biased about the whereabouts of the fluoride-based anions in the final materials, we also worked on all-organic ionic liquids, namely one containing a dicyanamide counterion (BmimDCN) and, as a variation of the cation, butylpyridiniumdicyanamide (BuPyDCN). The latter two ionic liquids gave good nanoporous structures with acceptable porosity. For example, mpg-CN-BmimDCN-1.5 showed a pore size of 5.6 nm, a BET surface area of 80.7 m^2 g^{-1}, and an interlayer-stacking structure typical of bulk nonporous g-C$_3$N$_4$ (Figure 3 b). It has been reported that the dicyanide-based ILs can have significant carbon yields because of the polymerization of anions.[20] Compared with the carbon materials, the relative larger surface area and higher C/N ratio of mpg-CN-BmimDCN-1.5 indicate that the dicyanamide-based ILs mainly act as soft template in our reactions.

In summary, nanoporous graphitic carbon nitride has been synthesized by using different soft and direct templates through the self-polymerization reaction of dicyandiamide. Most as-prepared CN-materials possess a high surface area, but the development of a useful pore system is only found for some selected templates, for example Triton X-100 and ionic liquids. The proposed synthetic route is unique in its simplicity

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