Mesoporous Materials

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# Boron- and Fluorine-Containing Mesoporous Carbon Nitride Polymers: Metal-Free Catalysts for Cyclohexane Oxidation**

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Recently, various lightweight materials with diverse nanomorphologies that contain heteroatoms such as nitrogen, boron, or fluorine have been actively pursued because of their unusual properties, such as in catalytic applications or as semiconductors.[1] For example, ordered and disordered modifications of carbon nitride ($C_3N_4$) extend the property profile of carbon nanostructures and have numerous potential areas of applications ranging from semiconductors to fuel cells.[1a]

A large number of reports deals with the synthesis of different modifications of bulk $C_xN_y$ materials.[2] The synthesis of these nitrogen-rich species generally includes thermal condensation of nitrogen-rich precursors, often from molecules containing or generating triazine rings. For example, through a solid-state reaction of 2,4,6-triamino-1,3,5-triazine with 2,4,6-trichloro-1,3,5-triazine at high pressure and high temperature, Wolf and co-workers obtained a well-characterized and highly crystalline graphitic carbon nitride derivative.[3] However, it was shown that the more ideal bulk carbon nitride solids perform rather weakly in some catalytic processes, while more disordered, polymeric versions showed nice activity, as structural defects or surface terminations seemed to play a key role for the catalytic activation.[4] To enhance the performance of carbon nitride both as a support and as a catalyst, the specific surface had to be enhanced, and nanocasting with hard templates using porous silicas has been explored recently for the replication of porous carbon nitride materials with controlled mesopore structures.[5]

This nanocasting method is good for the proof of principle, but it is hardly transferable to a practical process, as the templates have to be removed in an extra step involving aqueous ammonium bifluoride ($NH_4HF_2$) or hydrogen fluoride (HF), which are hazardous and not environmentally friendly and also prohibit further functionalization. A general and robust method for the synthesis of porous polymeric carbon nitrides without the extra step of removing hard templating silica structures has yet to be developed.

Ionic liquids are an especially promising choice to achieve this aim. Ionic liquids are generally defined as organic salts with a low melting point, usually below 100 °C. They inherit many features of inorganic molten salts, such as excellent chemical and thermal stability (in some cases in excess of 400 °C) and negligibly small vapor pressure, with the convenience of being liquid under ambient conditions. They have found application in numerous fields, for example as solvents or catalysts in organic synthesis, as electrolytes, or in chemical separations.[6] Recently, the advantages of ionic liquids in inorganic synthesis have been gradually realized and have received more and more attention. For instance, they turned out to be interesting solvents in the synthesis of nanoparticles owing to their special solvent structure that derives from the ion–ion interaction and extended hydrogen-bonding motifs.[7] From the many different available ionic liquids, we chose a class with $BF_4^-$ counterions, as the anion might enter the C–N condensation scheme, while boron and fluorine doping could improve the catalytic activity of the discussed systems and contribute to the performance of such materials.

Herein we demonstrate that the simple, commercially available room-temperature ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) is a unique soft template for the easy synthesis of boron- and fluorine-enriched mesoporous polymeric carbon nitride, in which an organic precursor, for example dicyandiamide (DCDA), self-condensed into carbon nitride solids in the presence of $BmimBF_4$. We show that the resulting materials possess high nitrogen, boron, and fluorine contents, high surface area, local graphitic order, and an excellent photoconductivity under visible light. We also demonstrate the catalytic properties of these CNBF materials in the heterogeneous, metal-free oxidation of cyclohexane. The CNBF materials show nice performance in the oxidation of cyclohexane with good conversion and excellent cyclohexanone selectivity.

The structures of these hybrid materials were investigated by powder X-ray diffraction (XRD), nitrogen gas adsorption, and transmission electron microscopy (TEM) measurements. The XRD pattern, for example of CNBF-0.3 ($r = 0.3$, $r$ denotes the mass ratio of $BmimBF_4$ to DCDA), is dominated by the (002) interlayer-stacking peak of carbon nitrides,

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corresponding to an interlayer distance of $d = 0.338$ nm (Figure 1). In our reaction conditions, the (002) peak is shifted to slightly lower angles compared with bulk melon ($d = 0.326$ nm), thus indicating a small expansion of the interlayer. This finding suggests disturbance of the packing and potential undulations of the single layers by doping units, which also explains the increased width of the (002) peak. A typical TEM image of CNBF-0.5 is shown in Figure 1 b. The TEM picture clearly reflects the presence of a well-developed, sponge-like mesopore structure within the CNBF-0.5 generated by self-assembly of the BmimBF$_4$ template towards regular, approximately 9.5 nm large micellar units. The whole structure nicely resembles a nanoscopic morel mushroom.

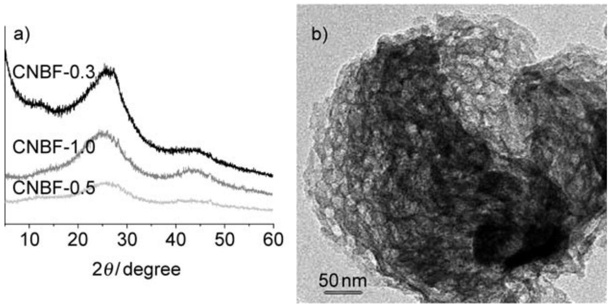

***Figure 1.*** a) XRD patterns of CNBF-*r* (*r* is the mass ratio of BmimBF$_4$ to DCDA, $r = 0.3$, 0.5, or 0.7). b) Typical TEM image of CNBF-0.5.

The surface area of the CN materials could be controlled by changing the ratio of the template to the DCDA precursor. Some nitrogen adsorption isotherms of CNBF are shown in Figure 2. CNBF-0.5 exhibits the largest specific Brunauer–Emmett–Teller (BET) surface area (444 m$^2$g$^{-1}$) and a total pore volume of 0.32 m$^2$g$^{-1}$, while micropores are essentially absent in these materials. The relation of the BET surface area with the content of the template is, however, not at all linear. First, it strongly increases with *r*, then it decreases again, presumably owing to structural pore collapse (Table S1 in the Supporting Information).

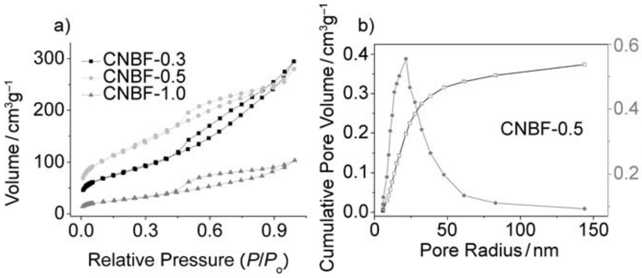

***Figure 2.*** N$_2$ adsorption/desorption isotherms and corresponding Barrett–Joyner–Halenda (BJH) pore-size distribution curve determined from the sorption branch of the isotherm of CNBF-0.5. $R$ = pore radius, $v$ = pore volume.

The carbon and nitrogen stoichiometry determined by elemental analysis shows that the products are highly enriched in nitrogen, even compared to ideal C$_3$N$_4$ (the C/N ratios are around 0.65, the theoretical C/N ratio of bulk C$_3$N$_4$ material is 0.75, see Table S1 in the Supporting Information). X-ray photoelectron spectroscopy (XPS) results indicate that both boron and fluorine atoms have been incorporated into the CN matrix. The boron contents are near 20 mol %, while the fluorine content is near 4 mol % (Figure S2 in the Supporting Information). Therefore, the ionic liquid template not only influences textural features but also enters the materials' condensation scheme. Most probably, the B atoms enter C sites in polymeric C–N structures (thus balancing stoichiometry), with F saturating residual bonds. Note that BN is also an extremely stable covalent material.

The residual boron and fluorine content is not to be seen as an impurity; instead, it provides potential utility for these porous CNBF materials in photocatalysis, extending melon as a polymeric semiconductor.

UV/Vis spectra (Figure 3 a) indicate that the optical band gap and thereby the semiconductor properties of the CNBF have indeed changed, with a significant extension of the spectrum towards absorption in the visible range, which we attribute to dopant states within the band gap. The PL spectra (Figure 3 b) under 420 nm excitation show broad and strong photoluminescence, which speaks for an effective separation of charges and weak thermal relaxation of the excited states. The CNBF material is obviously still an effective semiconductor like the undoped parent material melon. The luminescence is weakened with increasing specific surface area, thus indicating improved charge localization on the surface terminal sites, which is believed to promote the catalytic redox functions.

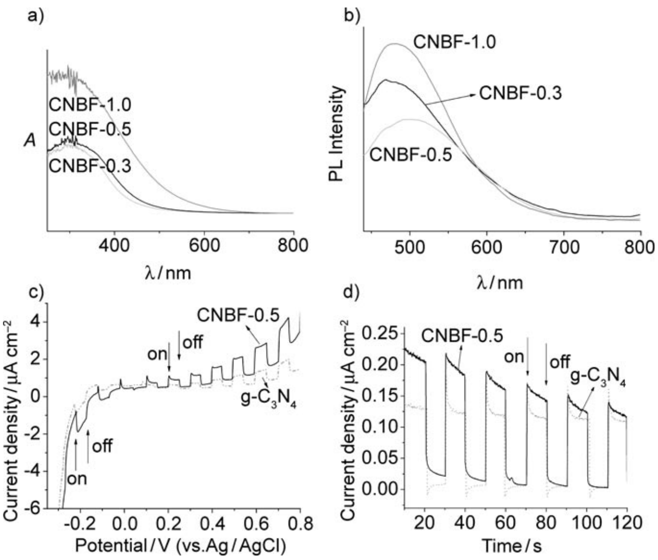

***Figure 3.*** a) UV/Vis spectra and b) photoluminescence spectra under 420 nm excitation at 298 K for CNBF. c) Current–potential curves and d) current–time curves under chopped illumination ($\lambda > 420$ nm) for CNBF-0.5 (dashed line) and bulk melon (solid line) electrodes in 0.2 M aqueous Na$_2$SO$_4$.

Figure 3 c shows the photocurrent response of the CNBF electrode in a 0.2 M Na$_2$SO$_4$ aqueous solution. Visible light illumination ($\lambda > 420$ nm) of CNBF layers cast on indium tin oxide (ITO) glass plates can generate a photocurrent which has been remarkably improved as compared to melon. The material, however, turns out to be electrochemically active against water, which leads to a decreasing photocurrent with time. As the reasons for this decrease can be manifold (including photochemical water splitting), work focusing on this aspect is ongoing.

To illustrate the usefulness of this organic semiconductor, selective oxidation of cycloalkanes was tested. The selective oxidation of cyclohexane is a very important industrial process, for example in the production of adipic acid and caprolactam, which in turn are the starting materials for the synthesis of nylon-6 and nylon-66 polymers, respectively.[8] The industrial process uses homogeneous metal catalysts and dioxygen as oxidant at temperatures above 150 °C.[9] Apart from low conversion, this process also produces several by-products, such as mono- and dicarboxylic acids, esters, and other oxygenated materials. This low conversion and selectivity, leaching of metal, and over-oxidation of products in the existing catalytic systems reinforce the need for new systems using reinforce the need for new catalytic systems, including heterogeneous catalyst and clean oxidant.[10] Herein, we used the metal-free CNBF materials as oxidation catalysts and hydrogen peroxide as oxidant for the highly selective oxidation of cyclohexane.

The catalysts are active and afford remarkably high selectivity towards the formation of cyclohexanone in a short time. For example, using CNBF-0.3 as catalyst in acetonitrile, the total conversion of cyclohexane was 7.8 % and the selectivity towards cyclohexanone was as high as 91 % after 4 h (Table 1). Interestingly, the CNBF-1.0 catalyst afforded 100 % selectivity towards the formation of cyclohexanone, although the conversion of cyclohexane is lower than observed for CNBF-0.3 and CNBF-0.5 catalysts. The products of all the reactions were analyzed, but no over-oxidation by-product was detected in the GC-MS analysis. This result indicates that, in contrast to the previous metal catalysts, the CNBF materials are highly selective oxidation catalysts and do not produce any adipic acid or valeric acid under these conditions.

*Table 1:* Conversion and selectivity of cyclohexane oxidation over CNBF catalysts.[a]

| Catalyst | Total conv. [%] | Selectivity [%] for one[b] | one/ol[b] | Selectivity [%] for $H_2O_2$ |
|---|---|---|---|---|
| g-$C_3N_4$[c] | 1.6 | > 99 | – | 10 |
| CNBF-0.3 | 7.8 | 91 | 10.1 | 43 |
| CNBF-0.5 | 7.5 | 89 | 8.4 | 33 |
| CNBF-1.0 | 5.3 | > 99 | – | 36 |

[a] No products were detected without the carbon nitride catalyst. Reaction conditions: cyclohexane 0.8 mL, $H_2O_2$ (30 % in water solution) 0.51 mL, catalyst 50 mg, temperature 150 °C, time 4 h. [b] cyclohexanone = one, cyclohexanol = ol. [c] Graphitic $C_3N_4$.

Furthermore, the catalysts can easily be separated from the reaction solution by simple filtration. The samples are highly stable (in the absence of light) and can be reused for several cycles without losing activity, which is a prerequisite for practical applications. Furthermore, this catalyst is expected to give excellent results in other organic reactions, as it has a large surface area and suitable pore volume with a large number of boron functional groups on the surface, which might act as strong Lewis acid sites, thus complementing the basic nitrogen sites.

In conclusion, a new kind of boron- and fluorine-enriched polymeric carbon nitride solid has been successfully synthesized. Notably, the resulting materials show a technically advantageous "morel-like" mesopore structure with narrow pore size distribution and improved photoactivity under visible-light illumination. Surprisingly, these materials exhibit good catalytic performance for the selective oxidation of cycloalkanes. The catalysts afford a remarkably high selectivity towards the formation of cyclohexanone, are highly stable, and could be recycled several times. Moreover, we believe that the current ionic-liquid-based strategy to control structure and composition can be extended to incorporate other heteroatoms by changing the anion or cation of the ionic liquids into C,N-based materials. This approach may widen the materials' application range.

## Experimental Section

Synthesis of CNBF: In a typical synthetic procedure, $BmimBF_4$ (0.5 g) was dissolved in water (6 mL) and stirred for 5 min. Then dicyandiamide (1 g) was added into the aqueous solution and the mixture was heated in an oil bath at 100 °C until the water had completely evaporated and a white solid had formed. The white solid was then transferred into a crucible and slowly heated over 2 h to a temperature of 350 °C. The material was tempered at this temperature for 4 h, heated over 1 h from 350 °C to 550 °C, and tempered at this higher temperature for another 4 h. Then, the sample was allowed to cool in the oven to room temperature.

Catalytic tests and analytical procedures: The oxidation of cyclohexane over CNBF samples was carried out in a Teflon-lined stainless steel batch reactor (40 mL total volume) using acetonitrile as the reaction solvent. Cyclohexane (0.8 mL), catalyst (0.05 g), 30 % hydrogen peroxide in water solution (0.51 mL), and acetonitrile (8 mL) were introduced into the reactor. The reactor was heated to 150 °C over 30 min with stirring, and the reactor was held at this temperature for 4 h. The products were analyzed on a GC-MS instrument (Agilent Technologies, GC6890N, MS5970).

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