# Formation of crystalline carbon nitride powder by a mild solvothermal method

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Crystalline carbon nitride powder has been successfully prepared *via* the liquid–solid reaction between anhydrous $C_3N_3Cl_3$ and $Li_3N$ in benzene at 355 °C and 5–6 MPa for 12 h. X-Ray diffraction (XRD) indicated that the major part of our brown sample was composed mainly of $\alpha$-$C_3N_4$ and $\beta$-$C_3N_4$ with lattice parameters of $a = 6.49$ Å, $c = 4.70$ Å for $\alpha$-$C_3N_4$ and $a = 6.43$ Å, $c = 2.43$ Å for $\beta$-$C_3N_4$. X-Ray photoelectron spectra (XPS), Fourier transform infrared spectroscopy (FTIR), electron energy-loss spectroscopy (EELS) and energy loss near edge structure (ELNES) strongly supported the existence of C–N covalent bonds. The relative N/C ratio is about 0.66. The temperature had an effect on the crystallization of carbon nitride powder. We have shown that the solvothermal technique might hold some promise for synthesizing pure crystalline $\alpha$-$C_3N_4$ and $\beta$-$C_3N_4$.

In this communication, we report the successful synthesis of crystalline carbon nitride materials with potential wide applications ranging from microelectronics to aircraft propulsion *via* a novel solvothermal method. In recent years, there has been considerable interest in the synthesis of crystalline carbon nitride materials suggested by Liu and Cohen.[1–4] So far, five different crystal structures of $C_3N_4$ materials have been proposed:[5–7] the hexagonal $\alpha$-$C_3N_4$ and $\beta$-$C_3N_4$, the cubic and pseudocubic $C_3N_4$ phases, and the graphitic $C_3N_4$. With their potential wide applications, $\alpha$-$C_3N_4$ and $\beta$-$C_3N_4$ have been prepared experimentally from various techniques, such as electron cyclotron resonance plasma enhanced chemical vapor deposition,[8] ion beam and laser ablation processing,[9,10] nitrogen implantation in carbon,[11] ion and vapor deposition methods[12] as well as electrodeposition from an organic liquid,[13–15] *etc.* Of all the above-mentioned techniques, only a few have been found promising for forming polycrystalline carbon nitrides. Therefore the successful synthesis of $\alpha$-$C_3N_4$ and $\beta$-$C_3N_4$ will have an enormous impact not only on basic science but also on technological developments. As a developing synthetic technology, solvothermal synthesis, which is generally conducted at intermediate temperatures (100–500 °C) in a sealed system, has gained much attention.[16–19] Here we apply this novel mild technique to successfully synthesis crystalline $\alpha$-$C_3N_4$, $\beta$-$C_3N_4$ and g-$C_3N_4$ (2H). The reaction can be formulated as follows:

$$C_3N_3Cl_3 + Li_3N \xrightarrow{\text{benzene}} C_3N_4 + 3LiCl$$
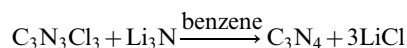
Experimentally, all of the reagents and solvents were analytical grade purity. In a typical synthesis, 32.5 mmol anhydrous $C_3N_3Cl_3$ and 32.5 mmol anhydrous $Li_3N$ were placed into a stainless steel autoclave of 50 ml capacity, which was filled with benzene up to 70% (35 ml) of the total volume. The autoclave was sealed and maintained at 355 °C and 5–6 MPa for 12 h, and then cooled to room temperature naturally. After washing the resulting product with alcohol, dilute acid, dilute alkali and distilled water several times, which were used to remove the unreacted $C_3N_3Cl_3$, $Li_3N$ and the by-product LiCl, a brown precipitate was collected. Finally, the product was desiccated at 100 °C under vacuum for 4 hours. The X-ray powder diffraction (XRD) pattern was recorded on a Japan Rigaku D/Max-J4100 X-ray diffractometer with $CuK_\alpha$ radiation ($\lambda = 1.54178$ Å). X-Ray photoelectron spectra (XPS) were obtained on a Perkin-Elmer PHI5300 ESCA (electron spectrometer for chemical analysis), using nonmonochromatized $MgK_\alpha$ X-ray as the excitation source. Fourier transform infrared spectroscopy (FTIR) was carried out with a Perkin-Elmer (L-710) spectrophotometer. The electron energy-loss spectroscopy (EELS) experimental studies were carried out using a Philips CM200-FEG (field emission gun) transmission electron microscope equipped with a Gatan image filtering (GIF) system, operated at 200 kV.

Fig. 1 shows the XRD pattern of a typical product prepared by solvothermal process. We did not find any correlation of our XRD results with those of diamond and graphite, leaving C–N solid structures as the remaining possibility. Table 1 lists all of the observed interplanar spacing data found in our XRD spectrum with those theoretically calculated by Wang *et al.*[20] The sample with the strongest peak of $\alpha(110)$ at a $d$ spacing of 3.29 Å is an $\alpha$-$C_3N_4$-rich powder. The fact that $\alpha$-$C_3N_4$ is
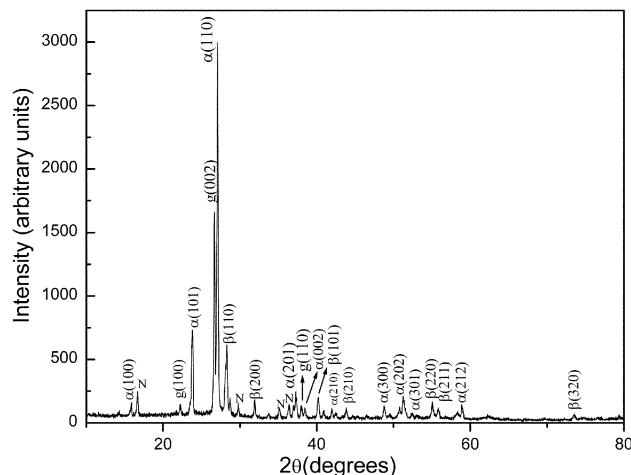


**Fig. 1** Typical XRD pattern of the powder.

**Table 1** Comparison of experimental XRD data with the latest theoretical results of ref. 20

| $d_{exp}/\text{Å}$ | $I/I_0$ | α-C$_3$N$_4$ | | β-C$_3$N$_4$ | | g-C$_3$N$_4$ (2H) | |
|---|---|---|---|---|---|---|---|
| | | $d_{theo}/\text{Å}$ | hkl | $d_{theo}/\text{Å}$ | hkl | $d_{theo}/\text{Å}$ | hkl |
| 5.60 | 5 | 5.60 | 100 | | | | |
| 5.32 | 6 | | | | | | |
| 4.03 | 5 | | | | | 4.10 | 100 |
| 3.70 | 22 | 3.60 | 101 | | | | |
| 3.36 | 58 | | | | | 3.36 | 002 |
| 3.29 | 100 | 3.23 | 110 | | | | |
| 3.18 | 14 | | | 3.22 | 110 | | |
| 3.00 | 3 | | | | | | |
| 2.79 | 6 | | | 2.79 | 200 | | |
| 2.46 | 4 | | | | | | |
| 2.43 | 4 | | | | | | |
| 2.41 | 8 | 2.41 | 201 | | | | |
| 2.37 | 4 | | | | | 2.37 | 110 |
| 2.34 | 4 | 2.35 | 002 | | | | |
| 2.24 | 6 | | | 2.26 | 101 | | |
| 2.13 | 4 | 2.12 | 210 | | | | |
| 2.09 | 4 | | | 2.11 | 210 | | |
| 1.87 | 4 | 1.87 | 300 | | | | |
| 1.80 | 7 | 1.80 | 202 | | | | |
| 1.75 | 2 | 1.74 | 301 | | | | |
| 1.61 | 4 | | | 1.61 | 220 | | |
| 1.59 | 3 | | | 1.60 | 211 | | |
| 1.28 | 2 | | | 1.28 | 320 | | |



**Fig. 2** XPS measurements showing (a) the powder is composed primarily of C and N with a small amount of O, and deconvoluted spectra of (b) C$_{1s}$ and (c) N$_{1s}$.

predominant over β-C$_3$N$_4$ implies that the former is thermodynamically more stable than the latter, which agrees with the theoretically predicted structures of these two phases, with N strongly nonplanar in α-C$_3$N$_4$ and planar in β-C$_3$N$_4$.[6] So, from the energy point of view, α-C$_3$N$_4$ is more favorable to be formed than β-C$_3$N$_4$. The lattice parameters of $a = 6.49$ Å, $c = 4.70$ Å for α-C$_3$N$_4$ and $a = 6.43$ Å, $c = 2.43$ Å for β-C$_3$N$_4$ were obtained from Fig. 1, and are in close agreement with the *ab-initio* calculations ($a = 6.47$ Å, $c = 4.72$ Å for α-C$_3$N$_4$, $a = 6.40$ Å, $c = 2.40$ Å for β-C$_3$N$_4$) by Teter and Hemley.[7] It is clear that the experimental values for α-C$_3$N$_4$ and β-C$_3$N$_4$ agree with the theoretical values well, except for $d = 4.03$ Å, 3.36 Å, 2.37 Å which correspond to g-C$_3$N$_4$ (2H)[20] and $d = 5.32$ Å, 3.00 Å, 2.46 Å, 2.43 Å which are assigned to some unknown crystalline C–N phases (indexed by N in Fig. 1). Since most of the low index, high intensity peaks of α-C$_3$N$_4$ and β-C$_3$N$_4$ show up in the experimental results, we can conclude with confidence that our powder mainly consists of crystalline α-C$_3$N$_4$ and β-C$_3$N$_4$.

The composition and the nature of chemical bonding of the prepared powder were studied by XPS measurement. The shift of C$_{1s}$ binding energy to a higher value compared to that of the C–C bond in diamond is primarily due to a high nitrogen content, and also confirms chemical bonding of carbon with more electronegative nitrogen. A typical wide-scan XPS spectrum and the deconvoluted C$_{1s}$ and N$_{1s}$ spectra are shown in Fig. 2(a), (b) and (c). Fig. 2(a) shows that our product predominantly consists of C and N elements with a small amount of O (C: 56.6%, N: 37.6%, O: 5.8%) which is obvious from the surface absorption. The gross chemical composition estimated from XPS results gave a N/C ratio about 0.66, lower than the stoichiometry of the theoretical material C$_3$N$_4$ (1.33). It was suggested[21,22] that the N fraction in β-C$_3$N$_4$ should be substantially lower than 1.33 due to repulsion between the nonbonded N atoms and their consequent partial replacement by C–C bonded dimers. The C$_{1s}$ and N$_{1s}$ spectra are deconvoluted into various lines, each associated with a different binding energy (as shown in Fig. 2(b) and (c)). We assign the C$_{1s}$ peak at 287.9 eV to the sp$^3$-type C–N bonds, the peak at 286.6 eV to the sp$^2$-type C=N bonds and the peak at 284.5 eV to the C–C bonds. The N$_{1s}$ peak is comprised of two
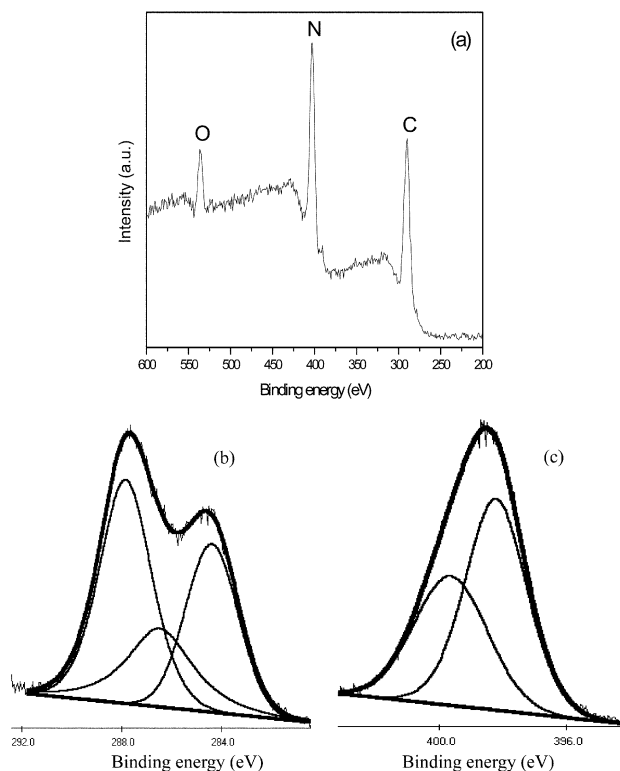
components centered at 398.3 eV and 399.7 eV, which are identified as originating from sp$^3$ C–N and sp$^2$ C=N bonding respectively.[23] The absence of C≡N indicates that our product has a good inorganic network structure. From the analysis of XPS, it can be said that there is a significant amount of C–N bonds for N and C atoms in the prepared crystalline powder, favoring the formation of α-C$_3$N$_4$ and β-C$_3$N$_4$ crystalline phases.

The FTIR adsorption spectrum of our crystalline carbon nitride powder displayed in Fig. 3 clearly shows several peaks at frequencies characteristic of vibrational modes related to the chemical bonding between carbon and nitrogen. The absorption peaks at 1620 cm$^{-1}$ and 1508 cm$^{-1}$ are due to C=N bonds,[22,24] while the other sharp peaks at 1301 cm$^{-1}$, 1258 cm$^{-1}$ and 1093 cm$^{-1}$ correspond to the characteristic
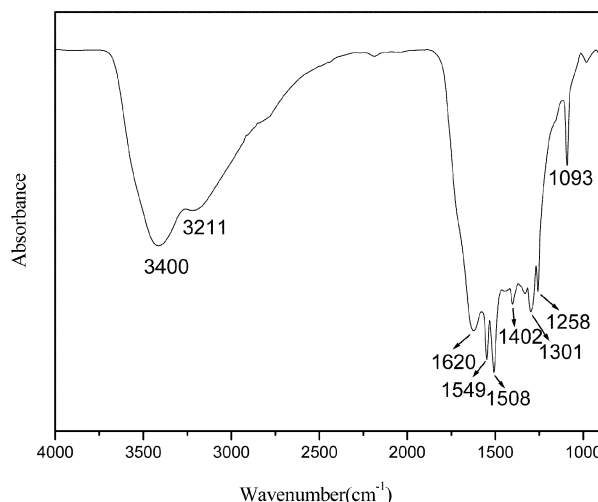


**Fig. 3** The FTIR spectrum of the typical as-prepared crystalline carbon nitride powder.
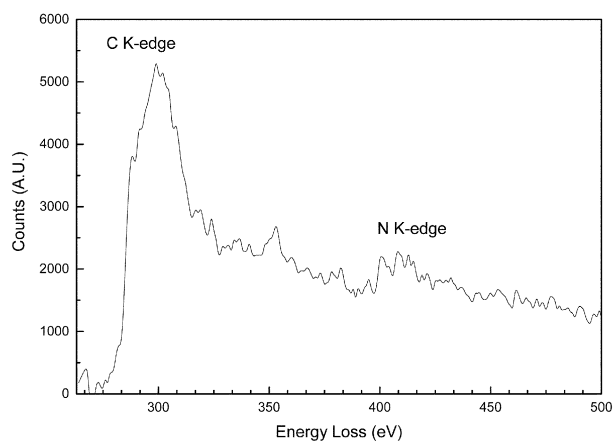
**Fig. 4** ELNES spectrum of carbon- and nitrogen-containing crystallites, showing characteristic K-edges, indicating diamond-like $sp^3$ bonding.

absorbances of single C–N bonds.[24–26] The absorption at 3100–3400 cm$^{-1}$ is assigned to the NH$_2$ asymmetric and symmetric stretching modes, and the absorption at 1549 cm$^{-1}$ corresponds to the NH$_2$ symmetric bending mode.[27] The weak 1402 cm$^{-1}$ peak is attributed to amorphous $sp^3$ C-C bonds.[26] The fact that no significant peak around 2200 cm$^{-1}$ corresponding to C≡N is found is consistent with the analysis of XPS, showing that our powder has a good inorganic network structure.

In order to cross check the nitrogen content and the bonding state between carbon and nitrogen atoms, electron energy-loss spectroscopy (EELS) experimental studies were carried out. Spatially resolved EELS on different areas of the sample reveals the inhomogeneity of the sample. We searched for a likely crystalline area to analyze. The characteristic energy loss near edge structure (ELNES) is displayed in Fig. 4. The π* resonance at 285 eV characteristic of unsaturated (sp or $sp^2$) bonds is almost absent and the broad σ* feature above 288 eV is significant, which suggests that the carbon atom is mainly $sp^3$ bonded in the sample. The corresponding N/C ratio was estimated to be 0.60 by determining the integrated intensity in the C and N ionization K edges after background subtraction, which is consistent well with the XPS analysis. All the results once again indicate the existence of chemical bonding with no significant physical bonding between C and N.

Owing to the fact that crystalline carbon nitrides are metastable materials, benzene in supercritical conditions (critical parameters $T_c$ and $P_c$ being: $T_c = 288.9$ °C, $P_c = 4.86$ MPa[28]) seems to play an important role in the synthetic progress. Under supercritical conditions, benzene can dissolve and disperse C$_3$N$_3$Cl$_3$ effectively and activate Li$_3$N powder, which favors the crystallization of carbon nitride. The effect of reaction temperature on the crystallization of carbon nitride powder was also studied. Lower temperatures lead to amorphous products. Higher temperatures are helpful in crystallization of the powder, but may lead to decomposition of the solvent benzene. So we selected a moderate temperature at 350 °C, which is above the critical temperature of benzene. Moreover, in supercritical benzene small changes of pressure give rise to large changes in both density and solubility.[29] Thereby the optimization of working pressure and temperature in the reactor allows the formation of crystalline powders. The narrow $P,T$ domain for preparing C$_3$N$_4$ suggests that the

kinetics effects could be predominant. The detailed results and formation mechanism of crystalline carbon nitride under different operating conditions are still under research and will be reported later.

In conclusion, crystalline C–N powders mainly consisting of α- and β-C$_3$N$_4$ have been successfully synthesized by a novel benzene-thermal reaction. Although much effort is required to know and control the reaction kinetics, we still believe that this solvothermal reaction is potentially capable of obtaining pure crystalline carbon nitride phases by optimization of our process parameters and providing us a promising synthetic route to obtain some important metastable materials in the near future.

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