Solvent-free synthesis of crystalline carbon nitride compounds

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Abstract

A carbon nitride sample has been successfully synthesized by a chemical reaction between 1,3,5-trichlorotriazine and ammonium chloride at a temperature of $400\,^\circ C$ without any solvent. Through the measurements of X-ray diffraction, transmission electron microscopy (TEM) and electron energy loss spectroscopy, it is convinced that a polycrystalline graphitic carbon nitride phase has been synthesized in the sample. Its determined lattice parameters of a and c are 4.65 Å and 6.48 Å. In addition to the dominant graphitic carbon nitride phase, another structured carbon nitride phase is also observed in TEM. Its determined d values from selected area electron diffraction pattern are in good agreement with the theoretical calculation results of α-C_3N_4, implying that α-C_3N_4 be possibly formed in the obtained sample.
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1. Introduction

In 1989, Liu and Cohen predicted theoretically that the hypothetical material β-C_3N_4 with a structure similar to β-Si_3N_4 could have an extremely high hardness, close to or even harder than that of diamond [1,2]. Since then, this kind of predicted super-hard compound has been intensively investigated both theoretically and experimentally. In 1996, five different structural forms of C_3N_4 were proposed by Teter and Hemley [3], including α-C_3N_4, β-C_3N_4, cubic-C_3N_4, pseudocubic-C_3N_4 and graphitic-C_3N_4. So far, a variety of techniques have been developed to prepare the carbon nitride materials [4–8]. Unfortunately, due to the great thermodynamic stability of N_2, it is difficult to realize the direct synthesis of the predicted covalent carbon nitride of β-C_3N_4. Recently, the graphitic form of carbon nitride (g-C_3N_4) has been paid more and more attention, because of its potential applications in precursors to prepare not only super-hard phases (such as β-C_3N_4), but also carbon nitride nanotubes and nanospheres [3,9,10]. So far, five possible models of graphitic carbon nitride have been presented [3,11–14], and three main techniques such as pyrolysis of melamine [15], electrodeposition [16], and solvothermal synthesis [17] have

been used to synthesize the carbon nitride compound with the graphitic structures. However, in most cases, the synthesized carbon nitride samples have the actual turbostratic structure [17,18]. Lately, solvothermal synthesis routes have been successfully used to prepare the carbon nitride compounds such as polycrystalline α-C_3N_4 and β-C_3N_4 [7,19] and graphitic carbon nitride nanocrystals [20,21], and a high nitrogen content carbon nitride has been synthesized by sodium flux-assisted low-temperature high-pressure synthesis method [22]. In our previous work, we have synthesized the cubic-C_3N_4 crystals [23] and an orthorhombic carbon nitride phase [24] by ion beam sputtering and high-temperature short-time treatment of turbostratic carbon nitride precursor, respectively. Up to now there are few reports on the synthesis of crystalline carbon nitride compounds by solvent-free synthesis route. Due to the merits of nearly free of pollution and economical and technological feasibility, solvent-free synthesis is one of the promising synthesis routes that are suitable for large-scale synthesis in industry. In this paper, we report on the synthesis of crystalline carbon nitride compounds by a facile solvent-free chemical reaction route without any catalysts.

2. Sample preparation and measurement

In the synthesis of carbon nitride compounds, 1,3,5-trichlorotriazine ($C_3N_3Cl_3$) and ammonium chloride (NH_4Cl)

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were chosen as reactants. Five grams $C_3N_3Cl_3$ and 1.5 g NH_4Cl were mixed together and put into a stainless autoclave with 50 ml capacity in a glove box filled with N_2 gas. The autoclave was sealed, and was then heated quickly to 400 °C and kept at this temperature for 48 h. After the reaction, the sample was cooled down to room temperature in the autoclave. The collected powders were washed first with acetone to remove the organic impurities, and were then washed with dilute hydrochloric acid to remove the inorganic impurities. After being rinsed in distilled water, they were dried in vacuum at 100 °C for more than 5 h. After that a yellow powder sample was finally obtained.

The structure of the synthesized sample was checked by powder X-ray diffraction (XRD, Rigaku D/Max-Rb) with Cu Kα radiation and transmission electron microscopy (TEM, JEM-2010). The sample for TEM measurement was prepared by grinding the powder sample in an agate mortar and then dispersing it on holy Cu grids using ethanol. Chemical compositions of the synthetic particles were analyzed using electron energy loss spectroscopy (EELS, Gatan-ENFINA-776). The chemical bond types of the synthesized carbon nitride sample were checked by Flourier transform infrared spectroscopy (FTIR).

3. Results and discussion

Three temperatures of 350, 400 and 450 °C have been tried in the syntheses of the samples. It has been found that the sample synthesized at 400 °C shows the best crystallization, while the sample synthesized at 450 °C is mainly amorphous. Fig. 1 shows the XRD spectrum of the synthesized carbon nitride sample obtained at 400 °C. Different from the previous works [17–19], in addition to the strongest reflection peak, three more reflection peaks arising from graphitic carbon nitride phase are observed. These four reflection peaks are labeled with number 1–4 as showed in Fig. 1. Their d values have been determined as 0.4122, 0.3243, 0.2019 and 0.1203 nm, matching the theoretically calculated data of g-C_3N_4 [25] for the (1 0 0), (0 0 2), (2 0 0) and (2 2 0) planes (see the list in Table 1), respectively. The strongest reflection peak at the position of $2\theta = 27.48°$ reveals that graphitic carbon nitride phase is dominant in our synthesized sample. Its corresponding d value of 0.3243 nm is close to that of the synthesized graphitic carbon nitride phase in the previous works [18,21,22]. In this work, the determined lattice
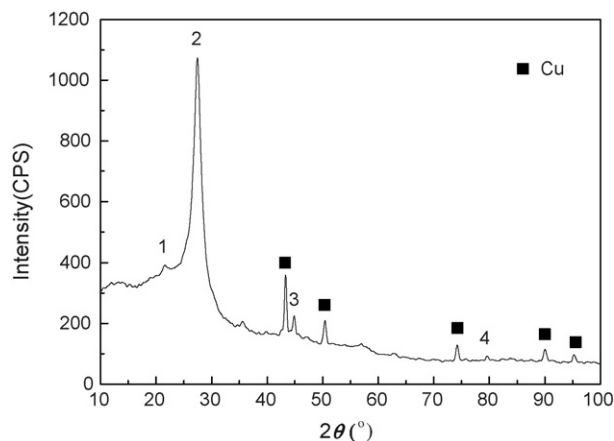

Fig. 1. XRD spectrum of the synthesized carbon nitride sample.

parameters of the graphitic carbon nitride phase from the XRD results are $a = 4.65$ and $c = 6.48$ Å. In addition, the peaks labeled with squares in Fig. 1 are arising from metal Cu, which comes from the Cu plug of the autoclave.

TEM measurements have been performed on a series of the synthesized particles to further check their morphologies and structures. After checking many particles, we find that most of the particles have piece-like morphologies with an irregular shape. Fig. 2a and b show the typical TEM image and selected area electron diffraction (SAED) pattern obtained from one of the observed piece-like particles, respectively. In Fig. 2b, the diffraction rings indicate that these synthesized piece-like particles are polycrystalline. The measured lattice spacing ($d = 0.3216$ nm) of the sharp diffraction ring is smaller than the value of the (0 0 2) plane of the standard graphite (PDF#250284: $d = 0.3348$ nm), being consistent with the result given by the XRD. Thus, it can be indexed as the (0 0 2) plane of the graphitic carbon nitride phase. In addition to the polycrystalline graphitic carbon nitride particles, one more kind of structural particles have also been observed in a small amount, and one typical TEM image and the corresponding SAED pattern have been showed in Fig. 2c and d. In Fig. 2c, there are many piece-like particles, each of which seemed to be of the aggregation of numerous even smaller particles (see the inset in Fig. 2c). The lattice spacings measured directly from the innermost ring

Table 1
The d values taken from XRD (Fig.1) and SAED (Fig. 2e) patterns of our synthesized carbon nitride sample, comparing with the theoretically calculated powder XRD patterns of g-C_3N_4 and α-C_3N_4 in [25]

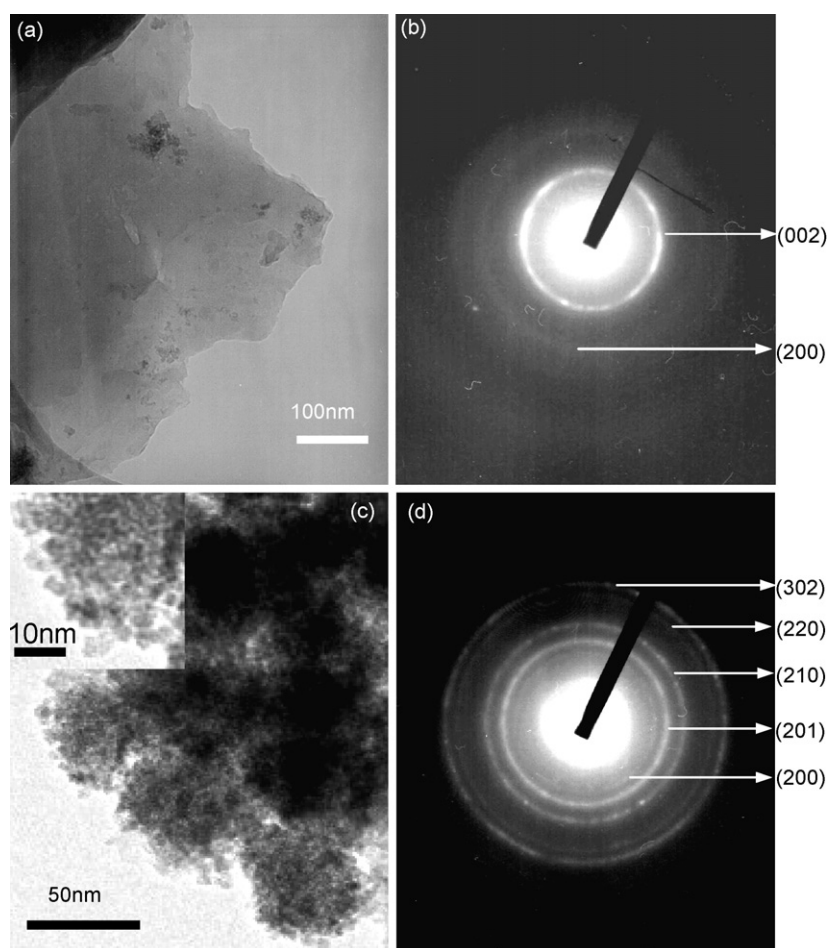| No.	XRD		SAED (Fig. 2d)	g-C_3N_4 [25]		α-C_3N_4 [25]	
	d (nm)	I (%)	d (nm)	d (nm)	$h k l$	d (nm)	$h k l$
1	0.4122	5.9		0.4107	1 0 0		
2	0.3243	100		0.3360	0 0 2		
			0.2802			0.2800	2 0 0
			0.2456			0.2407	2 0 1
			0.2098			0.2117	2 1 0
3	0.2019	22.2		0.2053	2 0 0		
			0.1614			0.1617	2 2 0
			0.1464			0.1463	3 0 2
4	0.1203	6.3		0.1186	2 2 0		

Fig. 2. Typical TEM images of the synthesized polycrystalline piece-like graphitic carbon nitride particle (a); possible α-C_3N_4 particles (c); and their corresponding SAED patterns (b and d).

to the outermost one (Fig. 3d) have been listed in Table 1. They are well coincident with the theoretically calculated α-C_3N_4 data in literature [25], implying that the α-C_3N_4 phase be possibly obtained in our synthesized sample. However, as the quantity of the possible α-C_3N_4 phase is so low in the synthesized sample, detection of the signals from these particles becomes impossible in the XRD measurements. That is why the graphitic carbon nitride phase was observed in the XRD spectra, and the possible α-C_3N_4 phase was not. From the SAED results, the determined lattice parameters of possible α-C_3N_4 phase are $a = 6.47$ and $c = 4.71$ Å, being coincident well with the *ab initio* calculations ($a = 6.47$, $c = 4.72$ Å) of α-C_3N_4 by Teter and Hemley [3].

Parallel EELS measurements have been performed on the synthesized particles to check their chemical compositions. After checking many synthesized particles, we find that with just a small amount of the particles being formed by pure carbon, most of them are formed by two elements of carbon and nitrogen. As for the piece-like particles with the graphitic structure, their compositions are not definite, ranging from 55~76 at.% C to 24~45 at.% N. While for the possible α-C_3N_4 particles, their compositions varied just slightly. Fig. 3a and b show the EELS spectra obtained from two typical carbon nitride particles as shown in Fig. 2a and c, respectively. No other elements such as Cu and Cl were detected in both of the two carbon

nitride phases, implying that the detected Cu in XRD measurement did not bond with the synthesized carbon nitride phases. The quantified compositions determined from Fig. 3a and b are found to be 58.6 at.% C and 41.4 at.% N and 63.4 at.% C and 36.6 at.% N, respectively. At the reaction condition mentioned above, the organic reactant $C_3N_3Cl_3$ could be partly decomposed and carbonized to create pure carbon, so the existence of a small amount of amorphous carbon particles has been confirmed in EELS measurements. Therefore, the obtained products actually are mixture of the amorphous carbon and the polycrystalline carbon nitride particles. Because we have not found a suitable method to separate the carbon nitride from the mixture, the carbon concentrations determined from EELS measurements in Fig. 3a and b are higher than that in C_3N_4.

On the other hand, as shown in Fig. 3c, the particles of the possible α-C_3N_4 aggregate together, and it is not possible to separate just one particle to do the EELS measurement because the e-beam size used in our measurements is about 100 nm. Thus, in the EELS measurement on the possible α-C_3N_4 particles, the detected signal is not only from the possible α-C_3N_4 but also from the other possible phases such as graphitic carbon nitride and amorphous carbon. That is the most possible reason for which the two EELS spectra look similar to each other. However, in the EELS spectrum, only the signals from C
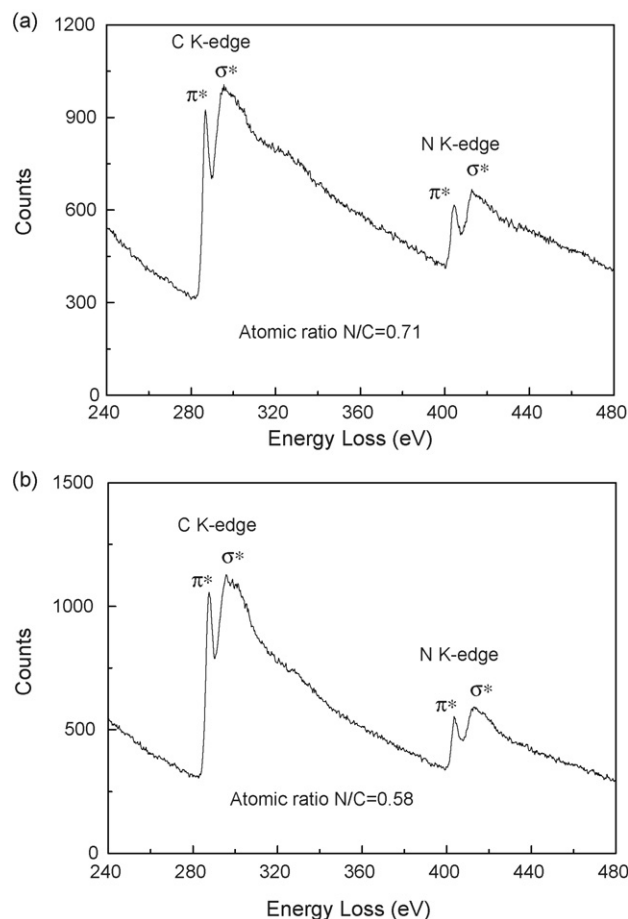
Fig. 3. Typical EELS spectra for the synthesized polycrystalline graphitic carbon nitride (a) and possible α-C$_3$N$_4$ (b) corresponding to the particles showed in Fig. 2a and c, respectively. Both spectra exhibit the characteristics of carbon nitride compound with definite core-loss edges at 284 and 401 eV, corresponding to C and N singles, respectively.

and N have been observed, implying at least that the detected phase is one kind of C–N phase. By further considering that no other compositional C–N phases are found up to now to have α structure except for α-C$_3$N$_4$, moreover the parallel SAED and EELS measurements have been performed on the same area of possible α-C$_3$N$_4$ and the determined d values from SAED pattern are in good agreement with that of the theoretical calculation results of α-C$_3$N$_4$ [25], we think that α-C$_3$N$_4$ has been possibly formed in our synthesis procedure, though in a small amount.

FTIR spectrum (Fig. 4) was used to check the chemical bond types of the synthesized carbon nitride powders. Because of the use of the H-included reactant of NH$_4$Cl, the absorption bands associated with H are observed in the FTIR spectrum near 2900 and 3384 cm^{-1}, which belong to CH$_x$ ($x = 1, 2, 3$) and NH$_x$ ($x = 1, 2$), respectively. The band at 2360 cm^{-1} is attributed to the environmental CO$_2$ background inside the spectrometer. The bands in the 1041–1600 cm^{-1} region are due to the CN heterocycles [24]. The peak at 798 cm^{-1} is attribute to out-of-plane bending modes of CN heterocycles and the strong peak at 1600 cm^{-1} corresponds to C=N in the synthesized graphitic carbon nitride phase [21].
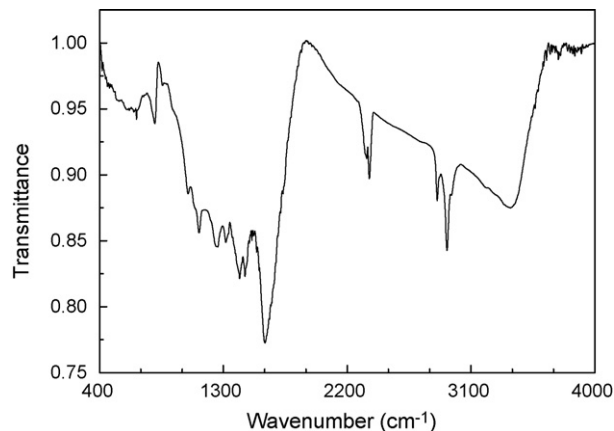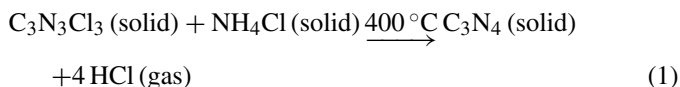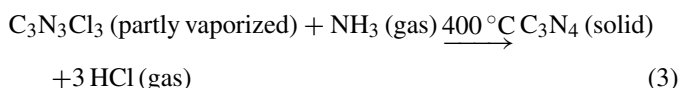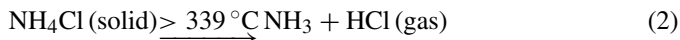

Fig. 4. FTIR spectrum of the synthesized carbon nitride sample.

According to the experimental results in this work, the presumed chemical reaction process for the synthesis of carbon nitride compounds can be expressed as

$$C_3N_3Cl_3 \,(\text{solid}) + NH_4Cl \,(\text{solid}) \xrightarrow{400\,°C} C_3N_4 \,(\text{solid})$$
$$+\,4\,HCl \,(\text{gas}) \tag{1}$$

By further considering the pyrogenation of NH$_4$Cl over the temperature of 339 °C, we can also express the reaction process as the following two steps,

$$NH_4Cl \,(\text{solid}) \xrightarrow{> 339\,°C} NH_3 + HCl \,(\text{gas}) \tag{2}$$

$$C_3N_3Cl_3 \,(\text{partly vaporized}) + NH_3 \,(\text{gas}) \xrightarrow{400\,°C} C_3N_4 \,(\text{solid})$$
$$+\,3\,HCl \,(\text{gas}) \tag{3}$$

Based on the ideal gas law ($PV = nRT$), we estimate that the pressure in the autoclave should be about 5.6–8 MPa. Such a moderate pressure could be favorable to the formation of carbon nitride compounds. In our synthesis procedure, higher reaction temperature will increase the decomposition and carbonization of C$_3$N$_3$Cl$_3$ to create pure carbon. We think this may be the main reason for that the sample prepared at 450 °C is mainly composed by amorphous phase.

4. Conclusions

In summary, crystalline carbon nitride phases have been successfully synthesized by a facile solvent-free chemical reaction rout by using C$_3$N$_3$Cl$_3$ and NH$_4$Cl as reactants at the temperature of 400 °C. The dominant phase in the obtained sample is polycrystalline graphitic carbon nitride with piece-like morphology. In addition to the dominant graphitic carbon nitride phase, a possible α-C$_3$N$_4$ phase has also been detected by SAED measurement. The determined lattice parameters a and c are 4.65 and 6.48 Å for the graphitic carbon nitride phase and 6.47 and 4.71 Å for the possible α-C$_3$N$_4$ phase. Due to the mild reaction conditions and simple manipulation, such a solvent-free

synthetic method has provided a promising route to obtain the attractive carbon nitride compounds.

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