Research Article

Reexamination of Solvothermal Synthesis of Layered Carbon Nitride

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“Graphitic carbon nitride” synthesized by the solvothermal reaction between cyanuric chloride ($C_3N_3Cl_3$) and sodium amide ($NaNH_2$), which was one of the most common methods reported so far, was carefully examined by several analytical techniques for its chemical and structural characteristics. The chemical quantification by the electron microprobe and combustion methods showed that the product synthesized has a significant amount of hydrogen with a composition $C_3N_5H_3$. Moreover, we found by FT-IR and IR-Raman measurements that the product consists mainly of stacked *s*-triazine units on the basis of the structural framework of cyanuric chloride, suggesting that *s*-triazine-based carbon nitride is more stable than heptazine-based one under a mild temperature condition ($\sim 200^\circ C$). The present study clearly demonstrates that hydrogen-free, pure graphitic C_3N_4 cannot be produced by the present solvothermal reaction proposed by the earlier study.

1. Introduction

Since highly incompressible carbon nitrides with a stoichiometric composition of C_3N_4 were theoretically predicted [1, 2], many efforts have been made to experimentally synthesize the potential superhard phases such as by the chemical vapor deposition (CVD) and high-pressure and high-temperature (HPHT) techniques. According to the first-principle calculation by Teter and Hemley [2], among the five polymorphs predicted, cubic- C_3N_4 is energetically the most favorable under high pressure and could possibly be synthesized from graphitic- C_3N_4 (*g*- C_3N_4) at pressure above 12 GPa. On the other hand, *g*- C_3N_4 is thought to be the most stable form at the ambient condition and consists of two types of structural units, *s*-triazine ring unit [2] and heptazine (tri-*s*-triazine) ring unit [3], which are connected by nitrogen atoms in 3-fold coordination. In the past few decades, *g*- C_3N_4 attracted considerable attention in industrial applications such as photocatalyst (e.g., [4]), hydrogen storage (e.g., [5]), semiconductor (e.g., [6]), and a starting material for synthesizing potential superhard carbon nitride phases (e.g., [7]). A number of reports have been published for the synthesis of *g*- C_3N_4 and even other graphitic forms with nonstoichiometric

compositions on the basis of various techniques such as CVD [8–10], solid reaction [11–17], solvothermal method [18–22], and thermal decomposition of compounds [23–26]. Among these, one of the easiest and simplest ways to obtain a nanocrystalline powder of *g*- C_3N_4 is the solvothermal method, in which the synthesis is achieved through the reaction of chemical sources in a solvent such as benzene and acetonitrile at high temperatures. In particular, a pioneer recipe reported by Guo et al. [18] was commonly used in many previous studies (e.g., [7, 27–29]) to obtain nanocrystalline *g*- C_3N_4 powders of various purposes. Their *g*- C_3N_4 -forming reaction is expressed by the following formula:

According to Guo et al. [18], this reaction proceeds in a step-by-step process as follows:

However, our recent study [7] suggested a strong possibility that such prepared $g\text{-C}_3\text{N}_4$ contains a considerable amount of hydrogen either in its structure or as surface adsorbates. The HPHT experiments using the solvothermally prepared $g\text{-C}_3\text{N}_4$ failed to synthesize any dense carbon nitride phases but instead resulted in the formation of a hydrogen-bearing, carbon nitride imide ($\text{C}_2\text{N}_2(\text{NH})$)-related phase [7]. FT-IR spectrum of the $g\text{-C}_3\text{N}_4$ powder also indicates the presence of hydrogen probably in the form of NH, as clearly mentioned in the original paper by Guo et al. [18] (and also pointed out in our earlier paper [7]), although they did not discuss the origin of hydrogen. It is, therefore, highly questionable whether the product obtained by Guo et al.'s recipe [18] is certainly hydrogen-free graphitic C_3N_4 composed of the stacked layers of *s*-triazine building blocks. Meanwhile, Guo et al.'s solvothermal recipe and characterization of the product by X-ray and electron diffraction and spectroscopic analyses have been cited by recent studies [30–32], where the authors assumed that their carbon nitride products have the ideal graphitic framework composed of *s*-triazine and heptazine units through the comparison with Guo et al.'s result. Thus, the careful reexamination of the solvothermal method and the reaction product is necessary and essential for further scientific and industrial applications of this carbon- and nitrogen-based nanomaterial. This may lead to new insights, such as recently reported work by Miller et al. [33] who reexamined the classic “Pharaoh's serpent reaction,” in which mercury (II) thiocyanate decomposes to HgS, CS_2 , and $g\text{-C}_3\text{N}_4$ through the self-propagating combustion reaction and found that the reaction results in the formation of unique nanocomposite semiconductor material composed of nano-HgS particles and a porous $g\text{-C}_3\text{N}_4$ matrix. In the present study, we carefully synthesized “ $g\text{-C}_3\text{N}_4$ ” by following the solvothermal method and examined the chemical and structural characteristics by means of various techniques in order to clarify the origin of hydrogen and the real process of the solvothermal reaction.

2. Experimental Methods

Nanocrystalline “graphitic” carbon nitride was prepared through the solvothermal reaction (1) between cyanuric chloride ($\text{C}_3\text{N}_3\text{Cl}_3$) and sodium amide (NaNH_2) by following the procedure reported by Guo et al. [18]. Cyanuric chloride (99 %) and sodium amide (98 %) reagents purchased from Sigma-Aldrich Co. LLC were used. Since sodium amide is highly sensitive to moisture and readily decomposes to produce sodium hydroxide and ammonia when hydrated, it was kept carefully under nitrogen atmosphere to avoid a potential alteration caused by moisture. The two reactants (0.003 mol each) were introduced into a Teflon inner vessel of an autoclave together with 45 ml of benzene (99 %). The autoclave was then placed in an oven and heated at 200°C for a duration of 6, 12, 24, 48, or 72 hours. The recovered product was first washed three times with acetone to remove any organic impurities and further washed three times with distilled water to remove sodium chloride, which is a byproduct of reaction (1). The final product obtained was a slightly yellowish white powder similar to that synthesized

by Guo et al. [18]. It was dried at 100°C in a vacuum condition for at least 24 hours before measurements, in which no change in color was observed.

The chemical composition of the synthetic products was analyzed by electron microprobe using field emission-scanning electron microscope (FE-SEM, JEOL JSM-7000F) equipped with an energy-dispersive X-ray spectrometer (EDS, Oxford Instruments, X-Max 20) and also checked by combustion elemental analysis using a CHN analyzer (Yanaco Co. Ltd., MT-5). It has previously been technically difficult to accurately quantify light elements such as C and N by EDS due to high attenuation nature of the low-energy characteristic X-rays in the volume excited by electron beam. However, we recently demonstrated that a surface conductive coating of thin osmium layer is effective for EDS quantitative analysis particularly of light elements such as C, N, and O in both inorganic and organic materials [7, 38]. The validity of this method for carbon nitride analysis was indeed shown in Kojima and Ohfuji [7], in which the accuracy of quantification for C and N was evaluated to be less than 0.5%. For quantitative analysis, powdered carbon nitride samples were pelletized by using a hydraulic press and coated with a 5 nm thick osmium layer. Pure SiC and cubic BN standards with the same surface coating were used for quantitative calibration of carbon and nitrogen, respectively. Measurements were made carefully by beam-scanning on each target area of the products (at 1 nA and 15 kV) to avoid potential damage by the electron beam [38], which might result in modification of the C/N ratio. Since EDS cannot technically detect hydrogen, the amount of hydrogen in the products was estimated from the result of the combustion analysis.

Powder XRD profiles of the products were collected by using an X-ray diffractometer (Rigaku Co. Ltd., Ultima IV) equipped with a copper anode and a high speed and highly sensitive semiconductor detector (Rigaku, D/tex Ultra 250). The use of this detector was found to be very effective to obtain XRD patterns with better S/N ratio even from the poorly crystalline carbon nitride products. The FT-IR measurement was carried out by using a FT-IR spectrometer (Spectrum One, Perkin-Elmer, Inc.) with a resolution of 4 cm^{-1} . The sample was pelletized with KBr prism material at the weight ratio of 1:50 for the measurement. Raman spectroscopic measurements were performed by using a confocal Raman microscope system (JASCO Co., Ltd., NRS-5000) with green (532 nm) and near-infrared (1064 nm) lasers. However, in the present case, the excitation by the green laser was found to be unsuitable for Raman spectroscopy due to a strong green fluorescence emitted from the carbon nitride samples. Peak fitting of XRD, FT-IR, and Raman profiles was carried out by using PeakFit ver. 4.12 software (HULINKS).

3. Results and Discussion

Table 1 shows the chemical quantification data of the carbon nitride product (synthesized by heating for 24 hours) obtained by EDS and combustion elemental analyses. The EDS spectra showed the presence of no other elements including sodium and chlorine (NaCl), which was produced

TABLE 1: The results of chemical quantification analysis by EDS and by combustion method (using organic elemental analyzer).

Method		C	N	H	O
EDS	At. %	35.67	59.90	-	4.17
	Molar ratio*	3	5.04	-	0.35
CHN	At. %	23.19	38.28	38.53	-
	Molar ratio*	3	4.95	4.98	-

* The amount of carbon is fixed to be 3.

as a by-product in reaction (1), removed by the postsynthesis treatment as mentioned above. Both methods gave a C/N ratio of 3 to 5 for the product, which clearly differs from the stoichiometry of C_3N_4 . The combustion analysis revealed that the product contains a considerable amount of hydrogen equivalent to approximately 5 moles when the molar amount of carbon is assumed to be 3. Therefore, the chemical formula of the product obtained in this study can be written as $C_3N_5H_5$. We also conducted additional runs with shorter/longer heating durations, but no clear changes were observed in the composition of the products (Figure 1), indicating that the reaction between cyanuric chloride and sodium amide has completed in a short time period and no further changes occurred. It should, however, be noted that the amount of hydrogen measured by the combustion analysis may have been overestimated due to contamination of H_2O molecules that were potentially trapped at the surface of the poorly crystalline sample. Taking these points into account, the chemical reaction formula (1) proposed for the solvothermal method by Guo et al. [18] should be rewritten as follows:

where the molar content of hydrogen in the carbon nitride product is assumed to be 3 based on the stoichiometry of the reaction. This means that the reaction does not involve the decomposition of $NaNH_2$ to form Na_3N , and the step-by-step process (formulas (2) to (4)) proposed by Guo et al. [18] is unlikely, as discussed later.

Figure 2 shows the FT-IR spectrum of the sample synthesized by heating for 24 hours following the recipe of Guo et al. [18], in which strong absorptions are observed in the range of 800-1800 and 2800-3600 cm^{-1} . Since in-plane C-N stretching and bending vibration modes of the s-triazine-based g- C_3N_4 show broad bands at 1150-1650 cm^{-1} region [8, 35], the several bands observed in the 1400-1600 cm^{-1} region (two intense peaks at 1432 and 1568 cm^{-1}) are likely attributed to the stretching vibration mode of CN as well as the deformation mode of NH_2 [14, 35]. Although Larkin et al. [37] pointed out that CN ring deformation mode generates the IR absorption peaks at 675 and 748 cm^{-1} , these peaks were not observed in this study. On the other hand, the peak at 814 cm^{-1} can be assigned to the out-of-plane bending mode of the s-triazine and/or heptazine ring vibration [37, 39]. The bands at 1249 and 1316 cm^{-1} indicate the presence of C-N chain bonds between the heptazine rings and NH groups associated with C-NH-C units [14, 40]

FIGURE 1: The atomic concentrations of carbon, nitrogen, and hydrogen in the products synthesized at various heating durations, determined by combustion method.

FIGURE 2: FT-IR spectrum of the sample obtained after heating for 24 hours.

(Table 2), suggesting that the polymerization of aromatic rings has occurred during the reaction. A shoulder peak at 1647 cm^{-1} and the broad peaks in 3200-3400 cm^{-1} region are assigned to the deformation and stretching modes of bridging $-NH-$ and terminal $-NH_2$ groups, respectively [34, 35]. The origin of hydrogen is likely from NH_2 and/or OH molecules, which are derived from the $NaNH_2$ precursor and water (moisture) adsorbed on the surface. The small peak at 2181 cm^{-1} band is originated from $C\equiv N$ bonds [10, 12, 15, 17, 36], which probably terminate dangling bonds as is the case of NH_2 group. Figure 3(a) shows the Raman spectra of the product collected with an excitation wavelength of 1064 nm, and Figure 3(b) shows the same spectra after background subtraction. Raman peak position of the present product and

TABLE 2: The observed IR vibrational modes in comparison with melem, melon, and melamine as references. The abbreviations in the assignment column are as follows, b.: bending; def.: deformation; str.: stretching.

This study	Melem ^a	Melon ^a	Melamine ^b	Assignment
814	804	808 887	810	out-of-plane b. [34, 35] Unassigned
	1101		1022	def. (ring) + def. (NH ₂) [35] Unassigned
1163			1170 1194	def. (ring)+ def. (NH ₂) [35]
1249		1246		str. (CN) associated with C-NH-C unit [10, 35]
1316	1308	1321		
1432		1418	1432	str. (CN) + b. (NH ₂) [34]
	1487	1456	1465	
			1526	str. (CN) + b. (NH ₂) [34]
1568		1570	1567	
1605	1616	1632	1626	b. (NH ₂) [34]
1647			1646	
2181				C≡N [10, 12, 15, 17, 36]
	3126	3163	3123	
3249			3178	
			3323	str. (NH) [34, 35]
	3420		3417	
3453			3468	

^aRef. [14]; ^bRef. [34]

the reported peak positions of melem [13], melon [13], and melamine [34] are listed in Table 3. The peaks at 691, 983, 1156, and 1527 cm⁻¹ observed from our sample are assigned to the ring breathing mode, bending mode of CNC and NCN, deformation mode of the ring and NH₂, and a combination of CN stretching mode and NH₂ bending mode, respectively [34], which are also observed at almost the same positions for the reference materials (Table 3). The broad peaks at 1307, 1407, and 1605 cm⁻¹ are assigned to the bending mode of NH, CH, and NH₂, respectively [34, 40]. The presence of 1165 cm⁻¹ band in IR spectra from the sample and melamine implies that our product has *s*-triazine ring units, while the ring mode at 747 cm⁻¹ in Raman spectra, which is commonly observed for melem and melon, suggests the presence of the heptazine ring unit in the product. This means that the carbon nitride obtained through the solvothermal reaction is made up of not only *s*-triazine ring units but also heptazine ring units, suggesting that it is an intermediate product during the polymerization of *s*-triazine ring to heptazine ring. However, the degree of polymerization may not be so high due to the dominance of N-H, C-H, and C≡N bonds terminating the bonded chains.

Figure 4 shows the XRD profile of the product obtained by heating for 24 hours, where two intense broad peaks are seen at 2θ around 11° and 27°. The latter, most intense peak can be deconvoluted into three peaks centered at 26.79, 27.24, and 27.77°, respectively (Figure 4(a), inset). The strongest second peak ($d = 3.27$ Å) is likely attributed to

the stacking of conjugated *s*-triazine ring layers, as its d-spacing corresponds well to the interlayer (002) spacing of the precursor cyanuric chloride ($d = 3.26$ Å) [41]. The first broad peak at 26.79° ($d = 3.32$ Å) can be assigned as the 310 reflection associated with the alignment of the aromatic rings of the structural framework of cyanuric chloride. On the other hand, the peak position of the third peak ($d = 3.21$ Å) corresponds to that of 002 ($d = 3.24$ Å) of graphitic carbon nitride (*g*-C₃N₄) composed of the stacked layers of heptazine building blocks [26, 39]. Since the Raman and FT-IR spectra both showed peaks derived from *s*-triazine and heptazine ring units (Figure 2), the formation of *g*-C₃N₄ is also partly expected. The weak peaks in the low-angle region (centered at 10.89 and 12.12°, corresponding to $d = 8.11$ and 7.29 Å) may be attributed to (100) plane of heptazine-based carbon nitride, which is comparable to the in-plane structural packing motif such as the hole-to-hole distance of nitrogen pores [42, 43]. These peaks derived from the heptazine layers were detected from all the products synthesized with various heating durations (6-72 hours). Figure 5 shows the *d*-values and full width at half maximum (FWHM) of each observed peak and the relative intensity of 002 reflection of the *s*-triazine-based and heptazine-based layers ($I_{\text{hep002}}/I_{\text{tri002}}$) versus heating time. The products obtained by heating for less than 24 hours showed more or less larger *d*-values and FWHM, which seem to have decreased with heating time. This implies that the *s*-triazine and heptazine layers were constructed gradually based on the structural framework of

(a)

(b)

FIGURE 3: IR-Raman spectrum of the sample obtained after heating for 24 hours before (a) and after (b) background correction.

cyanuric chloride during heating. On the other hand, the d -values and FWHM values became constant after longer (> 24 hours) heating, suggesting that the construction of the layered structure had been completed. Since $I_{\text{hep002}}/I_{\text{tri002}}$ decreased with heating duration (Figure 5(c)), the layered structure is considered to consist mainly of s -triazine-based network. However, a first-principle calculation [3] reported that heptazine-based carbon nitride is thermodynamically more stable than the s -triazine-based one, and some experimental studies also showed the production of the heptazine-based carbon nitride under high temperatures [13, 42, 44, 45]. Thomas et al. [43] reported that the condensation of s -triazine ring unit to heptazine ring unit occurred at above 390°C through the elimination of ammonia. It is known that heptazine-based polymers are formed (rearranged) from s -triazine-based compounds such as melamine via several intermediate components such as melam, melem, and melon [43]. The result of the present study suggests that the s -triazine-based carbon nitride is more stable at the mild temperature of around 200°C than heptazine-based carbon

(a)

(b)

FIGURE 4: (a) XRD profile of the sample obtained after 24-hour heating. The strongest peak at around 27° can be deconvoluted into three peaks drawn by red dotted line (inset). (b) Comparison of the strongest peak of each product synthesized at different heating durations with the peaks of the $\text{C}_3\text{N}_3\text{Cl}_3$ precursor.

nitride. Therefore, the products obtained by shorter heating (< 24 hours) include the metastable heptazine-based carbon nitride, which then transformed to triazine-based carbon nitride by further heating for more than 24 hours.

According to Guo et al. [18], the solvothermal reaction forming $g\text{-C}_3\text{N}_4$ from $\text{C}_3\text{N}_3\text{Cl}_3$ and NaNH_2 is a step-by-step process through reactions (2)–(4). However, the formation of Na_3N in formula (3) is questionable, since it is very unstable and has been synthesized only under extreme conditions such as ultrahigh vacuum [46] and high pressure [47]. In fact, Khabashesku et al. [36] detected a significant amount of hydrogen by FT-IR in the solid-solid reaction product of $\text{C}_3\text{N}_3\text{Cl}_3$ and Li_3N , an analogue alkali-metal mononitride of Na_3N , at 380°C under N_2 atmosphere. Furthermore, Guo and his colleagues [19] also identified the presence of hydrogen in the product obtained by the solvothermal reaction between $\text{C}_3\text{N}_3\text{Cl}_3$ and NaN_3 . These results suggest a strong chemical affinity between alkali-metal nitrides such as Li_3N and NaN_3

TABLE 3: The observed Raman peak positions (cm^{-1}) of our product together with those of melem, melon, and melamine as references. The abbreviations in the assignment column are as follows, b.: bending; t.: twisting; bre.: breathing; def.: deformation; str.: stretching; w.: wagging.

This study	Melem ^a	Melon ^a	Melamine ^b	Assignment
462	462	478		Unassigned
542	549	549	580	b. (NCN) + t. (NH ₂) [34]
635		595		Unassigned
691	688	705	675	bre. (ring) [34]
747	748	754		b. (ring) [14]
983	983	985	982	b. (CNC) + b. (NCN) [34]
			1029	
1156	1157	1157	1189	def. (ring) + def. (NH ₂) [34]
		1243		Unassigned
1307			1302	b. (NH) [34]
1407	1408	1427		b. (CH) [37]
	1456	1471	1442	
1527	1537		1554	str. (CN) + b. (NH ₂) [34]
1605	1587	1572		
	1657		1657	b. (NH ₂) [34]

^aRef. [14]; ^bRef. [34]

FIGURE 5: The variation of the main XRD peaks at around 27° of the products obtained at various heating durations. ((a) and (b)) d-value and FWHM of the three deconvoluted peaks; diamond: s-triazine ring alignment of structural framework of cyanuric chloride 310 peak, square: s-triazine ring interlayer plane 002 peak, and triangle: heptazine ring interlayer plane 002 peak. (c) Intensity ratio of each 002 peak from the interlayer planes of s-triazine ring and heptazine ring ($I_{\text{tri002}}/I_{\text{hep002}}$).

and hydrogen (mostly from moisture) to form N-H bonds in the reaction. The result of the present study demonstrates that the reaction between NaNH_2 and $\text{C}_3\text{N}_3\text{Cl}_3$ proceeds by substituting the Cl groups of the latter by NH_2 and NH groups of the former to form $\text{C}_3\text{N}_5\text{H}_3$ compound. Taking into account the presence of NH groups, the decomposition of NaNH_2 to Na_2NH may have partly occurred. Such Na_2NH and NaNH_2 may directly react with $\text{C}_3\text{N}_3\text{Cl}_3$, and thus the true process is expressed as follows:

The fact that the chemical compositions of our products synthesized at various heating durations are almost identical

(Figure 1) suggests that the reaction completes within 6 hours of heating and further heating only promotes the construction of the layered structure composed of s-triazine ring units.

4. Conclusion

The present study clearly demonstrates that “graphitic” carbon nitride synthesized by the solvothermal reaction (Guo et al.’s recipe) contains a large amount of hydrogen at a molar ratio of C:H = 1:1. The structure of the product ($\text{C}_3\text{N}_5\text{H}_3$) is mainly built up of stacked layers of s-triazine ring units with low degree of polymerization similar to melamine oligomer with dangling bonds terminated by N-H and O-H molecules. This means that pure graphitic carbon nitride

(C_3N_4) cannot be obtained by the reported solvothermal method due to the strong chemical affinity between hydrogen and nitrogen/carbon. This can explain why our attempt to synthesize a dense cubic carbon nitride under high pressure and high temperature failed and the products were always hydrogen-containing forms such as $C_2N_2(NH)$ [7].

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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