

SYNTHESIS OF GRAPHITIC CARBON NITRIDE (g-C₃N₄) POWDER FROM MELAMINE BY PYROLYSIS PROCESS

Daranee Piyachatpanom¹ and Sukasem Watcharamaisakul^{2,*}

Received: January 20, 2020; Revised: March 13, 2020; Accepted: May 26, 2020

Abstract

Graphitic carbon nitride (g-C₃N₄) powders were synthesized by pyrolysis of melamine with various 400-600°C. Phase composition of synthesized powder were confirmed by means of X-ray Diffraction (XRD). Particles morphologies were investigated by means of Field Emission Scanning Electron Microscope (FESEM). The decomposition temperatures analyzed by Thermogravimetric Analysis (TGA) and specific surface areas were measured by The Brunauer Emmett-Teller (BET). As a result, graphitic carbon nitride powder was obtained from pyrolysis at 550-600°C while at the temperature higher than 600°C, graphitic carbon nitride was decomposed.

Keywords: Graphitic carbon nitride, melamine, pyrolysis, synthesis powder, decomposition

Introduction

Graphitic carbon nitride (g-C₃N₄) is a morphological material of carbon nitride compounds and widely used in photocatalytic applications. This material is consisting of carbon atoms (C) and nitrogen (N) arranged in the sheets and stacked as carbon graphite. In each sheet, there are a linking feature of small units which connected to the 2-dimensional

network. It includes of S-triazine or tri-S-triazine which connects to the amino group (Shiraishi *et al.*, 2014; Wang *et al.*, 2017). The connecting various sub-units in the 2-dimensional plane to create a graphitic carbon nitride sheet by a small unit.

The synthesis of graphite carbon nitride powder can be produced in the various

¹ School of Materials Engineering, Suranaree University of Technology 111 University Avenue, Suranaree Sub-District, Muang Nakhon Ratchasima District, Nakhon Ratchasima 30000, Thailand.

² Center of Excellence in Biomechanics Medicine, Suranaree University of Technology 111 University Avenue, Suranaree Sub-District, Muang Nakhon Ratchasima District, Nakhon Ratchasima 30000, Thailand. E-mail: sukasem@sut.ac.th

* Corresponding author

methods such as the chemical vapor deposition process (CVD), the physical vapor deposition process (PVD) and Thermal process (Wang *et al.*, 2009), etc. The precursors for synthesis graphitic carbon nitride powder are widely used such as cyanamide, melamine, urea heat reaction and dicyanamide (Kumar *et al.*, 2014). At present, graphitic carbon nitride material has received a lot of attention due to its possessed high surface area, high chemical and thermal resistance, as a semiconductor with the appropriate energy band gap (2.7 eV) and has a visible light response. Therefore, it possible to be used as a chemical catalyst by optical stimulation, which is a remarkable property than carbon nanotubes and graphene. The applications of graphitic carbon nitride include hydrogen production can be used as a Photocatalyst process. It also can decompose pollutants both organic and inorganic. Using as a gas sensor of various types and can produce hydrogen peroxide (Hu *et al.*, 2015; Rahman *et al.*, 2016).

Therefore, the researchers have focused on the synthesis of graphitic carbon nitride (g-C₃N₄) by using melamine precursors with different temperature heating methods. The melamine was first synthesized by Liebig in 1834. Melamine is a slightly soluble organic substance and appearance is white powder. The chemical formula is C₃H₆N₆. The chemical name of 1, 3, 5-triazine-2, 4, 6-triamine, which is a plastic type of melamine-containing formaldehyde. The melamine is usually used to produce plastics, melamine plates, plastic bags, plastic wrap for food, good quality fire extinguishers, cleaning agents and fertilizers (Edwards *et al.*, 2015). In addition, melamine was used as a precursor of graphitic carbon nitride because the melamine structure has a relatively high nitrogen content of approximately 66.6 percent by mass of carbon nitride.

Materials and Methods

Preparation of g-C₃N₄ Powder

The melamine precursors (C₃H₆N₆) was used in 10 g, then put in the alumina crucible

and heated at a temperature of 400, 450, 500, 550, and 600°C for 2 h in air with the heating rate of 10°C min⁻¹.

Characterization Techniques

The synthesized g-C₃N₄ powders were analyzed the phase compositions by X-ray diffraction (XRD) using Cu K α radiation = 0.1541 nm. The microstructures were observed by means of field emission scanning electron microscope (FESEM). The morphology and microstructure were observed by means of transmission electron microscope (TEM). The weight loss of receiving heating of powder samples by thermogravimetric analysis (TGA). The specific surface areas were determined by using a BET.

Results and Discussion

Thermogravimetric Analysis

The analysis of thermal properties from the Thermogravimetric analysis of the melamine precursors, in the form of powdered samples, is putted with 9.5 mg in alumina crucible. The temperature measurement with 20-900°C using heating rate 10°C min⁻¹. Figure 1 shows the results of weight loss when receiving melamine precursors. It was found that in the temperature range of 180-450°C, the weight loss was 97.29% and condensation are occurred. The melem (C₆N₉H₆) was formed at the temperature around 300-400°C. In the literature, it is said that melem is formed by the melamine molecule condensation that occurs at temperatures above 300°C (Sattler *et al.*, 2009). When the temperature is about 450-500°C, melem will begin to change the structure to melon. Then, at the higher temperatures of 550-600°C, the g-C₃N₄ structures were formed. However, at 600°C upwards, the g-C₃N₄ become decomposed.

X-ray Diffraction

XRD pattern of melamine, the precursors were heated under different temperatures as shown in Figure 2 The detection of melamine can show the sharp peaks in Figure 2(a) and

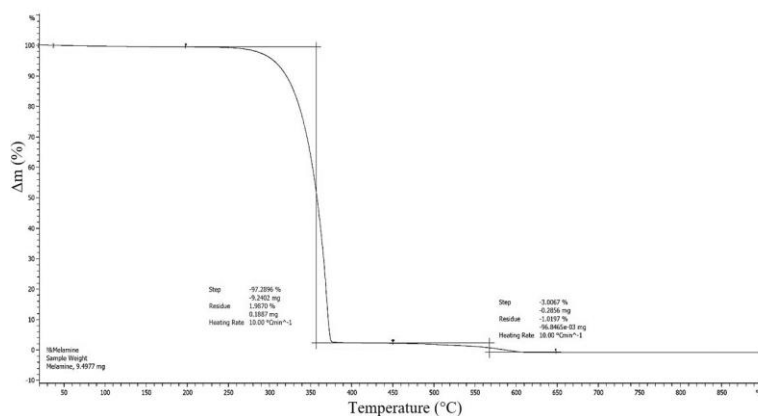


Figure 1. Thermal analysis of melamine precursors

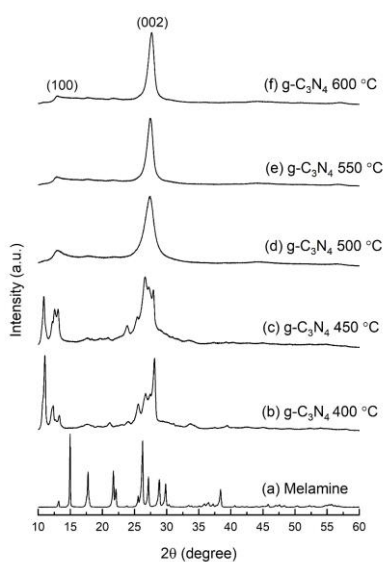
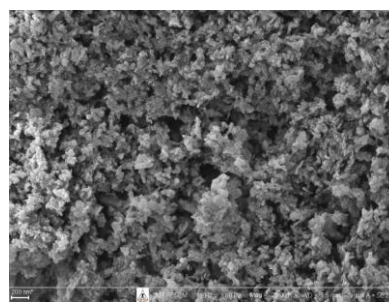
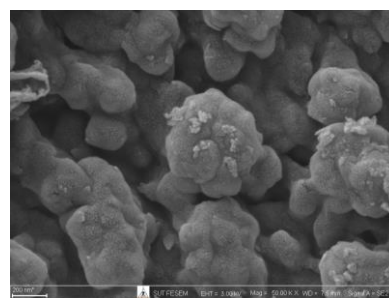


Figure 2. XRD patterns of synthesized $\text{g-C}_3\text{N}_4$ obtained powder at different temperatures

from Figures 2(b) and 2(c) and when the temperature increases to 400 and 450 $^{\circ}\text{C}$, then produced the new peaks. It is clearly seen that the peaks are quite wide compared to the previous one as shown in Figure 2(a) but when the temperature rose up to 500, 550, and 600 $^{\circ}\text{C}$, the Figures 2(d), 2(e), and 2(f) shown



(a)



(b)

Figure 3. FESEM images, $\text{g-C}_3\text{N}_4$ powder prepared at 600 $^{\circ}\text{C}$ (a, b)

the peaks value at $2\theta = 12.9^{\circ}$ and 27.2° respectively and $\text{g-C}_3\text{N}_4$ had been occurred. At 600 $^{\circ}\text{C}$, $\text{g-C}_3\text{N}_4$ had completely formed, which can confirm that all diffraction peaks that occur consistent with the details of the X-ray patterns of $\text{g-C}_3\text{N}_4$ (Chen and Zhang., 2014; Yang *et al.*, 2017).

Field Emission Scanning Electron Microscope

Analysis of microstructure from Field Emission Scanning Electron Microscope (FESEM) of g-C₃N₄, the sample is yellow powder in 1 g as shown in Figures 3(a) and 3(b) FESEM of g-C₃N₄ prepared at 600°C. The g-C₃N₄ has a clearly layered structure that is similar to the graphite structure. The particles of g-C₃N₄ have an irregular shape with average particle size of 500 nm. And was observed in FESEM shows the large agglomerate morphology which contains many g-C₃N₄ crystals. In addition, elemental analysis EDS is used to confirm the composition of g-C₃N₄ from the FESEM image as shown in Figure 4, which found carbon, nitrogen, and oxygen atoms of the sample g-C₃N₄.

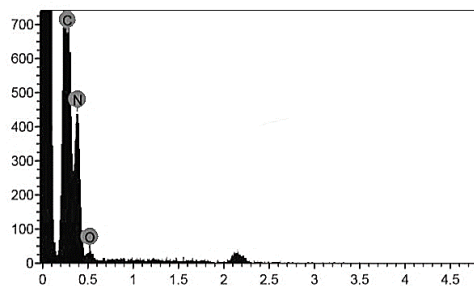


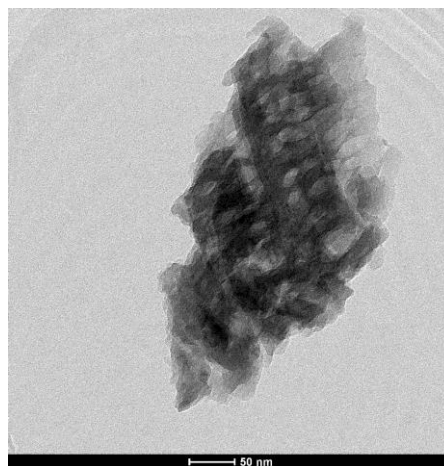
Figure 4. EDS peak of synthesized g-C₃N₄ powder

Specific Surface Area

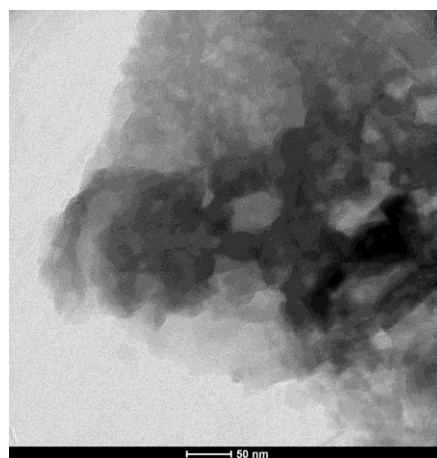
BET specific surface area was calculated from the adsorption of nitrogen at 77K temperature obtained result g-C₃N₄, approximately 2.36 m²/g. Nevertheless, with the higher specific surface area of samples the higher reactivity is obtained.

Transmission Electron Microscope

The analysis of morphology and microstructures of g-C₃N₄ with the TEM as shown in Figure 5 TEM of g-C₃N₄ sample at 600°C. From Figure 5(a) it is shown the g-C₃N₄ has a large block of layers which can be clearly seen and has an interlayer stack structure. Furthermore, the g-C₃N₄ powder caused agglomeration, the Figure 5(b) and the average particle size of about 50 nm.



(a)



(b)

Figure 5. TEM images of synthesized g-C₃N₄ powder at 600°C (a, b)

Conclusions

The g-C₃N₄ was synthesized by pyrolysis of melamine with various temperatures of 400, 450, 500, 550, and 600°C for 2 h. As the result, the phase composition of synthesized g-C₃N₄ were found the presence of g-C₃N₄ with the samples calcined at 550-600°C for 2 h. Nevertheless, at higher temperature than 600°C, g-C₃N₄ was decomposed as confirmed by TGA.

Acknowledgement

The authors would like to acknowledge Center of Excellence in Biomechanics Medicine, Suranaree University of Technology for supporting research fund.

References

- Chen, L.Y. and Zhang, W.D. (2014). $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$ composite photocatalysts with enhanced visible light driven activity. *Appl. Surface Sci.*, 301:428-435.
- Edwards, J.K., Freakley, S.J., Lewis, R.J., Pritchard, J.C., and Hutchings, G.J. (2015). Advances in the direct synthesis of hydrogen peroxide from hydrogen and oxygen. *Catalysis Today*, 248:3-9.
- Hu, S., Li, F., Fan, Z., Wang, F., Zhao, Y., and Lv, Z. (2015). Band gap-tunable potassium doped graphitic carbon nitride with enhanced mineralization ability. *Da. Trans.*, 44(3):084-1,092.
- Kumar, S., Surendar, T., Kumar, B., Baruah, A., and Shanker, V. (2014). Synthesis of highly efficient and recyclable visible-light responsive mesoporous $\text{g-C}_3\text{N}_4$ photocatalyst via facile template-free sonochemical route. *RSC. Advances*, 4(16):8,132-8,137.
- Rahman, M.Z., Ran, J., Tang, Y., Jaroniec, M., and Qiao, S.Z. (2016). Surface activated carbon nitride nanosheets with optimized electro-optical properties for highly efficient photocatalytic hydrogen production. *J. Mat. Chem. A.*, 4(7):2,445-2,452.
- Sattler, A., Pagano, S., Zeuner, M., Zurawski, A., Gunzelmann, D., Senker, J., and Schnick, W. (2009). Melamine-melem adduct phases: investigating the thermal condensation of melamine. *Chem. EU. J.*, 15:13,161-13,170.
- Shiraishi, Y., Kanazawa, S., Sugano, Y., Tsukamoto, D., Sakamoto, H., Ichikawa, S., and Hirai, T. (2014). Highly selective production of hydrogen peroxide on graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) photocatalyst activated by visible light. *ACS. Catalysis*, 4(3):774-780.
- Wang, A., Wang, C., Fu, L., Wong-Ng, W., and Lan, Y. (2017). Recent advances of graphitic carbon nitride-based structures and applications in catalyst, sensing, imaging, and LEDs. *Nano-micro Lett.*, 9(4):47.
- Wang, X., Maeda, K., Thomas, A., Takanabe, K., Xin, G., Carlsson, J.M., and Antonietti, M. (2009). A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nature Mat.*, 8(1):76.
- Yang, X., Qian, F., Wang, Y., Li, M., Lu, J., Li, Y., and Bao, M. (2017). Constructing a novel ternary composite ($\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}$) $4\text{W}_{10}\text{O}_{32}/\text{g-C}_3\text{N}_4/\text{RGO}$ with enhanced visible-light-driven photocatalytic activity for degradation of dyes and phenol. *Appl. Catalysis B. Env.*, 200:283-296.