

SYNTHESIS AND CHARACTERIZATION OF CARBON NITRIDE
WITH TUNABLE PROPERTIES FOR PHOTOCATALYTIC
DEGRADATION OF PHENOL

MOHD HAYRIE BIN MOHD HATTA

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DEDICATION

Special dedication to my beloved mom and family

“SITI MAIMUNAH ABDUL RAHMAN”

“NURUL AINN MOHD HATTA’

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ABSTRACT

Carbon nitride (CN) has been regarded as a potential visible light photocatalyst due to its light absorption up to *ca.* 450 nm and possesses band gap energy (E_g) of *ca.* 2.7 eV. CN can be prepared by thermal polymerization method using carbon and nitrogen-rich compound as the precursor. However, most of the reported CNs were associated with a defect-rich and less-ordered structure as well as low surface area that could affect their performance. In this study, CNs of high surface area, improved structural order, low E_g and low electron charge transfer resistance (R_{ct}) that are practicable for photocatalytic degradation of phenol under a wide range of sunlight irradiation have been successfully prepared. At the early stage, various salt melts of KCl-LiCl, KCl-NaCl, and KCl-ZnCl₂ were used in order to induce the crystallinity of CN. Despite all the salt melts helped to improve the optical properties as revealed by diffuse reflectance ultraviolet-visible (DR UV-Vis) spectroscopy, only salt melts of KCl-LiCl could form crystalline CN as shown by X-ray diffraction (XRD) patterns with the formation of crystalline poly(triazine imide). The fluorescence and electrochemical impedance (EIS) spectroscopy confirmed that the higher crystallinity has suppressed the electron hole recombination and decreased the values of R_{ct} . Improved photocatalytic degradation of phenol (24%), of *ca.* 2.5 times better than that of amorphous CN (10%), was achieved on crystalline sample of CN-KCl-LiCl. Besides, optimizations of synthesis parameters including amount of precursor, synthesis temperature, synthesis time and amount of salt melt were conducted. Current study revealed that increasing the amount of precursor from 1 g to 3 g led to the decrease in photocatalytic activity from 12% to 5% of phenol degradation. Increasing reaction temperature from 500°C to 550°C increased the photocatalytic activity from 7% to 24%. However, the photocatalytic activity decreased to 20% when the reaction temperature was increased to 600°C. In addition, short synthesis time (2 h) and long synthesis time (6 h) have led to the low photocatalytic activity with 17% and 20% of phenol degradation, respectively. Meanwhile, low (2.5 g) and high (7.5 g) amounts of salt melts showed low photocatalytic activities of 14% and 11%, respectively. The optimized conditions for the synthesis of CN with high crystalline phase were 2 g of precursor, reaction temperature of 550°C, reaction time of 4 h and 5 g of salt melts. By employing the optimized synthesis parameters, both amorphous and crystalline CN were prepared using melamine (Mel) as the precursor. The photocatalytic testing of the crystalline CN-Mel showed an improved activity of *ca.* 1.5 times higher (30%) compared to amorphous CN-Mel (19%). Further modification to increase the surface area was carried out by creating porous structure using Pluronic P123 (P123) surfactant. Increasing the mass ratio of P123 to precursor from 0.02 to 0.05 improved the photocatalytic activity from 20% to 46%, but decreased to 37% at the high mass ratio (0.1). The high photocatalytic activity was due to its high surface area (160 m² g⁻¹) and low R_{ct} values (11.49 kΩ). In order to improve the light absorption, modification of porous crystalline CN with 2,4,6-triaminopyrimidine (TAP) was conducted. Low addition of TAP (0.02 mass ratio) has significantly improved the photocatalytic activity up to 60%. The high activity was mainly due to the combination of high surface area (137 m² g⁻¹), low E_g (2.62 eV) and low R_{ct} (14.52 kΩ) value. However, increasing the mass ratio of TAP from 0.03 to 0.1 decreased the photocatalytic activity from 53% to 19%. Overall, this study has demonstrated that CN with tunable properties improved photocatalytic degradation of phenol that was nearly three times higher than unmodified CN under visible light region.

ABSTRAK

Karbon nitrida (CN) telah dianggap sebagai fotomangkin cahaya nampak yang berpotensi kerana keupayaannya untuk menyerap sehingga *ca.* 450 nm dan mempunyai tenaga luang jalur (E_g) *ca.* 2.7 eV. CN boleh disediakan melalui kaedah pempolimeran terma menggunakan karbon dan sebatian yang kaya dengan nitrogen sebagai pelopor. Walau bagaimanapun, kebanyakan CN yang dilaporkan telah dikaitkan dengan kecacatan yang banyak dan struktur yang kurang tersusun serta luas permukaan yang rendah yang boleh menjejaskan prestasi CN. Dalam kajian ini, CN dengan luas permukaan yang tinggi, susunan struktur yang baik, E_g yang rendah dan rintangan pemindahan cas elektron (R_{ct}) yang rendah yang berguna bagi degradasi fotopemangkinan fenol di bawah penyinaran cahaya matahari berjulat luas telah berjaya disediakan. Pada peringkat awal, pelbagai garam lebur KCl-LiCl, KCl-NaCl dan KCl-ZnCl₂ telah digunakan untuk mengaruh kehabluran CN. Walaupun kesemua garam lebur membantu untuk memperbaiki sifat optik seperti yang didedahkan oleh spektroskopi pantulan serakan ultralembayung-cahaya nampak (DR UV-Vis), hanya garam lebur KCl-LiCl boleh membentuk CN berhablur seperti yang ditunjukkan oleh corak pembelauan sinar-X (XRD) dengan membentuk poli(triazina imida) berhablur. Spektroskopi pendarfluor dan impedans elektrokimia (EIS) mengesahkan bahawa kehabluran yang tinggi telah menindas penggabungan semula lubang elektron dan mengurangkan nilai R_{ct} . Degradasi fotopemangkinan fenol yang baik (24%), iaitu *ca.* 2.5 kali ganda lebih baik daripada CN amorfos (10%), telah dicapai pada sampel CN-KCl-LiCl berhablur. Selain itu, pengoptimuman parameter sintesis termasuk jumlah pelopor, suhu sintesis, masa sintesis dan jumlah garam lebur telah dijalankan. Kajian semasa mendedahkan bahawa meningkatkan jumlah pelopor daripada 1 g kepada 3 g membawa kepada penurunan aktiviti fotopemangkinan daripada 12% kepada 5% degradasi fenol. Meningkatkan suhu tindak balas daripada 500°C kepada 550°C telah meningkatkan aktiviti fotopemangkinan daripada 7% kepada 24%. Walau bagaimanapun, aktiviti fotopemangkinan menurun kepada 20% apabila suhu tindak balas ditingkatkan kepada 600°C. Tambahan lagi, masa sintesis yang pendek (2 j) dan masa sintesis yang panjang (6 j) telah membawa kepada aktiviti fotopemangkinan yang rendah, masing-masing dengan hanya 17% dan 20% degradasi fenol. Sementara itu, jumlah garam lebur yang rendah (2.5 g) dan tinggi (7.5 g) menunjukkan aktiviti fotopemangkinan yang rendah masing-masing dengan hanya 14% dan 11%. Keadaan optimum bagi sintesis CN dengan fasa berhablur yang tinggi ialah 2 g pelopor, suhu tindak balas 550°C, masa tindak balas 4 j dan 5 g garam lebur. Dengan menggunakan parameter sintesis optimum, kedua-dua CN amorfos dan berhablur telah disediakan dengan menggunakan melamina (Mel) sebagai pelopor. Pengujian fotopemangkinan CN-Mel berhablur menunjukkan aktiviti yang lebih baik iaitu *ca.* 1.5 kali ganda lebih tinggi (30%) berbanding amorfos CN-Mel (19%). Pengubahsuaian selanjutnya untuk meningkatkan luas permukaan telah dijalankan dengan membuat struktur liang menggunakan surfaktan Pluronic P123 (P123). Meningkatkan nisbah jisim P123 terhadap pelopor daripada 0.02 kepada 0.05 telah memperbaiki aktiviti fotopemangkinan daripada 20% kepada 46%, tetapi menurun kepada 37% pada nisbah jisim yang tinggi (0.1). Aktiviti fotopemangkinan yang tinggi adalah disebabkan luas permukaannya yang tinggi (160 m² g⁻¹) dan nilai R_{ct} yang rendah (11.49 kΩ). Untuk memperbaiki penyerapan cahaya, pengubahsuaian liang CN berhablur dengan 2,4,6-triaminopirimidina (TAP) telah dijalankan. Penambahan sedikit TAP (nisbah jisim 0.02) telah memperbaiki aktiviti fotopemangkinan sehingga 60%. Aktiviti fotopemangkinan yang tinggi adalah terutamanya disebabkan oleh kombinasi luas permukaan yang tinggi (137 m² g⁻¹), nilai E_g yang rendah (2.62 eV) dan nilai R_{ct} yang rendah (14.52 kΩ). Walau bagaimanapun, meningkatkan nisbah jisim TAP daripada 0.03 kepada 0.1 telah menurunkan aktiviti fotopemangkinan daripada 53% kepada 19%. Keseluruhannya, kajian ini menunjukkan bahawa CN dengan sifat boleh tala telah memperbaiki degradasi fotopemangkinan fenol dengan hampir 3 kali ganda lebih tinggi berbanding CN tidak terubahsuaikan di bawah kawasan cahaya nampak.

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(Poly(triazine imide)) and CN-TAP were obtained in the literature (Jin *et al.*, 2017 and Ho *et al.*, 2015).

LIST OF ABBREVIATIONS

| | | |
|-----------|---|---|
| a.u | - | Arbitrary unit |
| AO | - | Ammonium Oxalate |
| BET | - | Brunauer–Emmett–Teller |
| BJH | - | Barret–Joyner–Halenda |
| BQ | - | 1,4-Benzoquinone |
| CB | - | Conduction Band |
| CN | - | Carbon Nitride |
| CCN | - | Crystalline Carbon Nitride |
| CNT | - | Carbon Nanotube |
| DR UV-Vis | - | Diffuse Reflectance Ultraviolet-Visible |
| EIS | - | Electrochemical Impedance Spectroscopy |
| E_g | - | Band Gap Energy |
| eV | - | Electron Volt |
| FFT | - | Fast Fourier Transform |
| FTIR | - | Fourier Transform Infrared Spectroscopy |
| I | - | Light Intensity |
| k | - | Heterogeneous electron-transfer rate constant |
| HOMO | - | Highest Occupied Molecular Orbital |
| LUMO | - | Lowest Unoccupied Molecular Orbital |
| MCN | - | Mesoporous Carbon Nitride |
| NHE | - | Normal Hydrogen Electrode |
| R_{ct} | - | Charge Transfer Resistance |
| SBA 15 | - | Santa Barbara Amorphous-15 |
| SPE | - | Screen Printed Electrode |
| TBA | - | Terb-butyl Alcohol |
| TEM | - | Transmission Electron Microscope |
| VB | - | Valence Band |
| kV | - | kilovolt |
| ppm | - | Part per million |
| XRD | - | X-ray Powder Diffraction |

| | | |
|---------------------|---|---|
| λ | - | Wavelength |
| 2θ | - | Bragg Angle |
| CuK_α | - | X-ray Diffraction from Copper K_α Energy Levels |
| $\pi\text{-}\pi^*$ | - | Pi Bonding orbital to antibonding Pi Orbital |
| $n\text{-}\pi^*$ | - | Non-bonding orbital to antibonding Pi Orbital |

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CHAPTER 1

INTRODUCTION

1.1. Research Background

Carbon-based materials with a variety of structures and properties have drawn significant attention as they play an important role in heterogeneous catalysis field (Serp and Figueiredo, 2009). Carbon-based material such as carbon nanotube (CNT) (Liu *et al.*, 2013*a*, Liu *et al.*, 2013*b*; Woan *et al.*, 2009) and graphene (Chen *et al.*, 2011; Compton and Nguyen, 2010; Li *et al.*, 2011) have been found to be very attractive and competitive due to the combination of excellent chemical and physical properties such as their tuneable porosity and surface chemistry (Chen *et al.*, 2011; Liu *et al.*, 2013*a*; Liu *et al.*, 2013*b*). The superior mechanical, electronic and the good dispersion properties possessed by these CNT and graphene have also gained a significant attention in both carbon materials for almost three decades (Compton and Nguyen, 2010; Carabineiro *et al.*, 2013; Serp and Figueiredo, 2009). These carbon-based materials have been widely used in the application of photocatalysis as they provide a large surface area and large electron-storage capacity (Carabineiro *et al.*, 2013; Chen *et al.*, 2011; Liu *et al.*, 2013*a*; Liu *et al.*, 2013*b*; Woan *et al.*, 2009; Yu *et al.*, 2011). Owing to these properties, carbon-based materials have been practically and commercially used as supports for various semiconductor photocatalysts such as titanium dioxide (TiO₂) (Woan *et al.*, 2009; Yu *et al.*, 2011), zinc oxide (ZnO) (Lv *et al.*, 2012; Jiang and Gao, 2005), cadmium sulphide (CdS) (Li *et al.*, 2015*b*; Weng *et al.*, 2014) and zinc sulphide (ZnS) (Wu *et al.*, 2008; Zhang *et al.*, 2012*c*). In recent years, it was reported that the substitution of nitrogen with the carbon atom has effectively improved the mechanical, field emission, energy storage properties, conductivity and electrocatalytic performance (Gong *et al.*, 2009; Zhao *et al.*, 2014*a*, Zhao *et al.*, 2014*b*). Therefore, development of such material is considered to be important especially in heterogeneous photocatalysis field in order to move towards sustainable chemistry (Wang *et al.*, 2012*a*; Wang *et al.*, 2012*b*; Woan *et al.*, 2009).

One of the most investigated materials consisting of carbon and nitrogen is carbon nitride (C_3N_4 or abbreviated as CN). To date, five different structures of CN materials have been proposed, specifically hexagonal 3-dimensional α - C_3N_4 , β - C_3N_4 , cubic and pseudocubic phases CN and 2-dimensional graphitic C_3N_4/CN (Bousetta *et al.*, 1994; Liu and Wentzcovitch, 1994; Teter and Hemley, 1996). Among CN allotropic, the graphitic CN or later simplified as CN throughout this study is among the stable CN and has gained much recognition recently due to its unique and excellent properties (Cao *et al.*, 2015; Liang *et al.*, 2008; Thomas *et al.*, 2007; Wang *et al.*, 2012a; Wang *et al.*, 2014b; Zhao *et al.*, 2014a; Zhao *et al.*, 2014a; Zheng *et al.*, 2012; Zheng *et al.*, 2015; Zhu *et al.*, 2014). The CN has abundant surface properties such as basic surface functional, electron-rich properties, and H-bonding motif. Moreover, it also has high thermal and hydrothermal stabilities, which make CN a promising catalyst for wide applications in heterogeneous catalysis (Wang *et al.*, 2012a; Wang *et al.*, 2012b; Zhu *et al.*, 2014). Therefore, the development of CN material has been extensively studied throughout the years (Fettkenhauer *et al.*, 2014; Bhunia *et al.*, 2014; Lee *et al.*, 2012; Schwinghammer *et al.*, 2013; Thomas *et al.*, 2008; Wang *et al.*, 2012a; Wang *et al.*, 2012b; Wirnhier *et al.*, 2011; Zhang *et al.*, 2012a; Zhang *et al.*, 2012b; Zhao *et al.*, 2014a; Zhao *et al.*, 2014b; Zhu *et al.*, 2014).

CN possesses an average band gap energy (E_g) of 2.7 eV (Schwinghammer *et al.*, 2013; Wang *et al.*, 2012b; Zheng *et al.*, 2012; Zhang *et al.*, 2012a; Zhu *et al.*, 2014a), which gives typical absorption pattern at about 420 to 470 nm, depending on the packing between layer and the degree of condensation (Fettkenhauer *et al.*, 2014; Wang *et al.*, 2012b; Wirnhier *et al.*, 2011; Zhang *et al.*, 2012a; Zheng *et al.*, 2012; Zhu *et al.*, 2014). As the ability to utilize the larger fragment of the spectrum in natural sunlight is a significant feature in photocatalysis, this characteristic property enables CN to be used as a potential photocatalyst under sunlight irradiation (Fettkenhauer *et al.*, 2014; Lee *et al.*, 2012; Schwinghammer *et al.*, 2013; Wang *et al.*, 2012a; Wang *et al.*, 2012b; Zhang *et al.*, 2012a; Zhao *et al.*, 2014a; Zhao *et al.*, 2014b). Several published literatures have reported the successful removal of organic pollutant and light harvesting via photocatalytic process by using CN materials (Cui

et al., 2012; Lee *et al.*, 2012; Liu *et al.*, 2011; Schwinghammer *et al.*, 2013; Wang *et al.*, 2012b; Xu *et al.*, 2013; Zhang *et al.*, 2012a; Zhang *et al.*, 2012b).

Recently, CN materials have been a fascinating choice in the application of photocatalysis. However, many reported literature showed that the synthesized CN was in amorphous form (Cui *et al.*, 2012; Kouvetakis *et al.*, 1994; Lee *et al.*, 2012; Liu *et al.*, 2011; Khabashesku *et al.*, 2000; Riedel *et al.*, 1998; Xu *et al.*, 2013; Zhang *et al.*, 2012a; Zhang *et al.*, 2012b; ; Zheng *et al.*, 2012; Zhu *et al.*, 2014; Wang *et al.*, 2012a; Wang *et al.*, 2012b; Zhao *et al.*, 2014a; Zhao *et al.*, 2014b). CN with the amorphous phase has been reported to show low photocatalytic performance in the catalytic process (Bhunia *et al.*, 2014). For instance, Bhunia *et al.*, (2014) demonstrated that the photocatalytic performance of hydrogen evolution rate (HER) improved two times higher when using crystalline CN compared to amorphous CN. In photocatalysis, the directional flow of electrons depends on the organization of the molecules in the structure in relation to their crystallinity (Jun *et al.*, 2013a; Jun *et al.*, 2013b; Prins *et al.*, 2001; Seto *et al.*, 1993; Shalom *et al.*, 2013). In addition, the fast rate of electron diffusion in crystalline structure would reduce the trapping and de-trapping effect, thus the rate of electron-hole recombination would be decreased (Celik and Mete, 2012; Gai *et al.*, 2009; Long and English, 2009; Nah *et al.*, 2010; Serpone, 2006). Since the photocatalytic properties are sensitively affected by the crystallinity of the photocatalyst; therefore, constructing a crystalline photocatalyst which is active under natural sunlight is a promising work and highly recommended, but can be a challenging task to be achieved.

Generally, CN with amorphous phase can be synthesized via much a simpler way compared to crystalline CN. For example, a typical amorphous CN with graphene-like structure and layer or widely known as graphitic CN can be prepared by simple pyrolysis of urea or any other reactive precursor which is rich in nitrogen and carbon consisting of pre-bonded C-N structures like dicyandiamide or cyanamide under ambient pressure and calcination temperature of 400–550 °C for 3–4 hours (Cui *et al.*, 2012; Lee *et al.*, 2012; Liu *et al.*, 2011; Thomas *et al.*, 2008; Wang *et al.*, 2012a; Wang *et al.*, 2012b; Xu *et al.*, 2013; Zhang *et al.*, 2010; Zhang *et al.*, 2012a; Zhu *et al.*, 2014). In contrast, several high-end instruments such as pulsed

laser induced reactive quenching at liquid-solid interface, laser-electrical discharge method, chemical vapour deposition, and electrodeposition, are usually required in order to give a better arrangement of CN precursor for aligning the molecules in particular order, which is the important step in preparation of crystalline CN (Chen *et al.*, 1997 α ; Hu and Huo, 2011; Kundoo *et al.*, 2003; Kuo *et al.*, 2001; Lv *et al.*, 2003; Sharma *et al.*, 1996; Teter and Hemley, 1996; Zhang *et al.*, 1996).

To date, several successful preparations of crystalline CN by using the methods mentioned below have been reported. For example, Burdina *et al.* (2000) have successfully prepared the crystalline CN from an amorphous nitrogen-carbon-containing material by using a laser-electrical discharge method at ultrahigh pressure (77 kbar) and high temperature (1200 °C) in the presence of crystalline CN film seeds. On the other hand, Lv *et al.* (2003) have provided a simpler method without the need for high-cost instrument. The crystalline CN was prepared via a solvothermal method using liquid-solid reaction between anhydrous cyanuric chloride (C₃N₃Cl₃) and lithium nitride (Li₃N) in benzene solution at 5-6 MPa and 355 °C for 12 hours. In this process, the benzene acted as a solvent to activate the CN precursors, which favored the crystallization of CN. This method successfully produced the crystalline CN that also consists of pure crystalline α -C₃N₄ and β -C₃N₄, which was very difficult to be synthesized (Kundoo *et al.*, 2003). Although both mentioned methods successfully prepared the crystalline CN, the laser-electrical discharge method caused a high cost of production due to the requirements of vacuum condition and a high amount of energy. On the other hand, the use of benzene as the solvent required it to be in supercritical condition (4.86 MPa).

One of the major problems encountered during the preparation of crystalline CN is the kinetic problem such as fast condensation and incomplete condensation. The problem has inhibited a complete reaction and produced an amorphous product (Kroke and Schwarz, 2004; Wirnhier *et al.*, 2011). Therefore, another technique was deployed in order to synthesize and increase the crystallinity of CN with such convenient, promising method and low production cost. The ionothermal method as studied by Antoniette *et al.* (2008) and Bojdys *et al.* (2008) could offer a more appropriate solvent by using salt melts of potassium chloride (KCl) and lithium

chloride (LiCl). Dated back to 1960s, the salt melt of KCl and LiCl with ratio of 45:55 (wt%) and melting point of 352 °C has been reported as a reaction media for electrochemical processes, especially in high-temperature galvanic cells (Laitinen *et al.*, 1960) and more recently as a solvent for salts of lanthanides and actinides (Cassayre *et al.*, 2007). The application of molten salts as a solvent in the organic reaction can be traced back in the 1965 when Sundermeyer *et al.* (1965) demonstrated that several organic chemical reaction could be accomplished in molten salts. They also remarked the good solvating properties of the salt melt of KCl and LiCl with respects to nitrides, carbides, cyanides, cyanates and thiocyanates (Sundermeyer, 1965; Sundermeyer, 1967; Sundermeyer and Anorg, 1961; Verbeek and Sundermeyer, 1967). As the salt melt of KCl-LiCl was recognized as a good solvent due to its stability in high-temperature reaction, non-corrosive properties and its significant melting point under the polycondensation point of *s*-heptazine, various research groups adopted this method in synthesis of crystalline CN (Antonietti *et al.*, 2008; Bhunia *et al.*, 2014; Bojdys *et al.*, 2008; Fettkenhauer *et al.*, 2014; Schwinghammer *et al.*, 2014; Shalom *et al.*, 2013; Wirnhier *et al.*, 2011). According to reported literature aforementioned above, the crystalline CN is composed of poly(triazine imide)-based CN, while amorphous CN is composed of heptazine-based CN or tri-*s*-triazine. In this study, various of salt melts which were the compositions of potassium chloride-lithium chloride (KCl-LiCl), potassium chloride-sodium chloride (KCl-NaCl) and sodium chloride-zinc chloride (KCl-ZnCl₂) as the ionic solvents were used to prepare the crystalline CN and the performances of the various salt melts were investigated and studied. The mixture of KCl-LiCl, KCl-NaCl and KCl-ZnCl₂ have been used due to its high temperature stability, non-corrosive properties, its melting point below the polycondensation of CN. In addition, NaCl has been used due to its non-toxic properties while ZnCl₂ was deployed owing to its ability for tailoring a micro and mesoporosity for the enhanced surface area of the resulting products (Fechler *et al.*, 2013).

In addition to crystallinity, another factor that gave rise to the high photocatalytic activity is the surface area of the photocatalyst. Recent studies showed that crystalline CN possess a specific surface area of *ca.* 90 m² g⁻¹ (Bhunia *et al.*, 2014) and 58 m² g⁻¹ (Fettkenhauer *et al.*, 2014), depending on the type of precursor

and synthesis conditions. Although crystalline CN has better surface area value compared to amorphous CN ($10 \text{ m}^2 \text{ g}^{-1}$) (Bhunja *et al.*, 2014), the value was still considered low. In the perspective of practical applications in catalysis field, the presence of controlled porosity at the nanoscale in CN material is required in order to improve its surface area (Wang *et al.*, 2012a; Wang *et al.*, 2012b; Zhang *et al.*, 2012b; Zhao *et al.*, 2014b. Lee *et al.*, (2012) has successfully synthesized mesoporous CN with increased surface area up $224 \text{ m}^2 \text{ g}^{-1}$ by using nano silica as a hard template. However, this synthesis procedure involved removing the hard template that required a hazardous reagent and multiple-step synthetic procedure. It was also not environmentally friendly and prohibited further functionalization (Antonietti, 2001; Chen *et al.*, 2006; Liang *et al.*, 2008; Yan, 2012). Therefore, preparing porous CN without hard templates would give a great benefit. On the other hand, in the view of physicochemical and thermodynamic basis, preparing materials with porous structure using soft templates approach can be a challenging work (Kosonen *et al.*, 2006; Meng *et al.*, 2006).

Wang *et al.* (2010) have successfully synthesized mesoporous CN using various surfactants, amphiphilic block polymers and ionic liquids as structure directing agents while employing dicyandiamide as an organic precursor. The resulted mesoporous CN material showed an improved surface area up to $90 \text{ m}^2 \text{ g}^{-1}$ when Pluronic P123 was used as soft template compared to only $8 \text{ m}^2 \text{ g}^{-1}$ when prepared without the use of the soft template. Zhao *et al.* (2014b), however, successfully synthesized mesoporous CN having surface area ranging from 505 to $1116 \text{ m}^2 \text{ g}^{-1}$ with a highly ordered structure, depending on the type of template used. The photocatalytic activity of the prepared highly ordered mesoporous CN was reported to achieve high catalytic activity in the dehydrogenation of ethylbenzene to styrene with up to 93.6% selectivity. Even though having the increased ordered in the arrangement of CN, the phase of the prepared mesoporous CN was still an amorphous phase. Thus, in order to improve the surface area of crystalline CN, the introduction of porosity in the crystalline CN was carried out. In this study, Pluronic P123 surfactant as soft templates was used.

For the main view of application of photocatalysis in water purification of self-sustaining environmental waste (Anku *et al.*, 2017; Wang *et al.*, 2012*a*; Wang *et al.*, 2012*b*), the ability to utilize a large part of the spectrum of natural sunlight is one the significant features for designing photocatalyst (Banerjee, 2011; Ou *et al.*, 2006; Wang *et al.*, 2005; Woan *et al.*, 2009). As CN potentially absorbs light only up to 470 nm (Fettkenhauer *et al.*, 2014; Thomas *et al.*, 2008; Wang *et al.*, 2012*b*; Zhang *et al.*, 2012*a*; Zhang *et al.*, 2012*b*; Zheng *et al.*, 2012; Zhu *et al.*, 2014) and also suffers from fast charge recombination (Cao *et al.*, 2015; Ho *et al.*, 2015; Zheng *et al.*, 2015), modification of highly crystalline CN in order to extend its absorption to longer wavelength and enhance its electrical conductivity as well as suppress charge recombination is required.

The perfect graphitic CN has a layered structure similar to graphite. However, the electrical conductivity of CN was reportedly lower than that of graphene (Zheng *et al.*, 2012). This is due to the symmetrical substitution of high-electronegativity nitrogen atoms for carbon atoms in the carbon ring that leads to an increase in the π -deficiency of the conjugated systems, and thus, decreasing the electron availability of CN compared to graphene and subsequently suppress the charge recombination for CN. Therefore, a practical approach is to reversely and partially replace the nitrogen with carbon atom due to its low electronegativity properties. Substitution of nitrogen with carbon atom is expected to decrease the π -deficiency and increase the π -electron conjugated system and subsequently decrease the band gap energy of CN in order to harvest more visible light in the visible region. Bhunia *et al.* (2014) reported the modification of crystalline CN with 2,4,6-triaminopyrimidine (TAP) and demonstrated that the crystalline CN-TAP improved the photocatalytic hydrogen evolution reaction ten times compared to crystalline CN. However, the surface area and photocatalytic activity decreased with increasing of the amount of TAP. The increasing amount of TAP resulted in extending the absorption of CN up to 700 nm. In addition, the high carbon content of TAP and its structure that parallel with melamine has been a particular interest in this research.

In this study, the synthesized crystalline CN, porous crystalline CN (porous CCN) and modified porous CCN-TAP have been applied in photocatalytic degradation of phenol under solar light irradiation. Phenol is a derivative of benzene and has been regarded as an important raw material that has many applications in industry such as petrochemicals, plastic, oil refineries, paint and pharmaceutical (Dekant *et al.*, 2008; Li *et al.*, 2004; Thomas *et al.*, 2005). It is highly soluble in water and is highly toxic as classified by the Environmental Protection Agency (EPA) (Faweli and Hunt, 1988). The toxic effects due to phenol and its difficulties to be removed from wastewater have increased the concern for public health and environmental quality (Lin and Juang, 2009). Therefore, the total removal of phenol from wastewater is highly required. Among potential solutions, semiconductor-based photocatalysis has been a fascinating choice owing to its economical, renewable, clean and safe technology (Bard, 1980; Hoffmann *et al.*, 1995). Research study on semiconductor photocatalysis was pioneered by Fujishima and Honda in 1972 that focused on TiO₂ water splitting (Fujishima and Honda, 1972). Since then, TiO₂ has always been one of the best materials owing to its excellent photocatalytic properties, non-toxicity and high thermal stability. To date, many kinds of literature have reported the successful enhancement of the photocatalytic properties and optimization of TiO₂ in degradation of various organic pollutants (Cao *et al.*, 2015; Woan *et al.*, 2009). However, as TiO₂ has band gap energy ranging of 3.0–3.2 eV, it needs ultraviolet (UV) light for an electron to be excited with sufficient energy in order to overcome the large band gap. Considering the fact that UV spectrum covers only *ca.* 3–4% (Savoye *et al.*, 2017) of the total solar spectrum, applications of TiO₂ as photocatalyst are restricted since it can only work under UV light that comprises a limited fragment of sunlight. Therefore, in order to fully utilize the sunlight as the largest cost-free energy source in the world, research on the development of visible light-driven photocatalysts such as CN materials has been widely conducted.

1.2 Statements of Problem

Various photocatalysts such as TiO₂, and Zinc Oxide (ZnO) have been reported to give high photocatalytic activity in removal and degradation of organic

pollutant. However, its wide band gap has limited the application of both photocatalysts in visible light region. Therefore, many works have been focusing to visible light-driven photocatalyst such as CN. Nowadays, CN has become an important material due to its good performance, especially as a photocatalyst. In addition, its good photocatalytic activity obtained under visible light irradiation has attracted significant attention as our solar spectrum consists of almost 40% of the visible spectrum compared to UV light (*ca.* 5%). However, various CN photocatalysts that have been reported widely showed the characteristic of the amorphous phase that might limit its activity. In fact, the catalytic activity of amorphous CN was usually low and modification was needed to improve its performance. Since the crystallinity of the photocatalysts influenced the photocatalytic properties, production of a photocatalyst with high crystalline phase is highly recommended, but can be a challenging task. Therefore, in this study, a crystalline CN was synthesized using an ionothermal method in order to improve the photocatalytic performance in the degradation of phenol. A variety of salt melts as the ionic solvent was studied and the properties affected during constructing the crystalline phase were discussed. Although various reports have been made in addressing this method for synthesis of crystalline CN, there is no study on the optimization of the synthesis parameters to obtain a highly crystalline CN photocatalyst. Therefore, in this study, synthesis parameters including the amount of precursor, synthesis temperature, synthesis time and amount of salt melts were performed.

Besides high crystallinity, the large specific surface area also plays a significant role in increasing the performance of the photocatalyst. The high surface density of active sites that exposed on the surface of photocatalyst and the facile accessibility by simple diffusion resulted from the high surface area and large pore volume have effectively enhanced the photocatalytic performance. While some studies showed that the photocatalytic activity was improved on the crystalline CN or highly ordered amorphous mesoporous CN, there is still no report at this point on the successful synthesis of highly crystalline porous CN. Therefore, there is no clear understanding about the effect of both crystallinity and mesoporous structures in the photocatalytic activity. The highly crystalline phase and improved surface area might

help to provide better efficiency of charge transfer process that could improve the performance of CN. In addition, large surface area could harvest more light in the visible region. Therefore, in this study, highly crystalline porous CN was synthesized by the ionothermal method using salt melts of KCl-LiCl as the solvent and Pluronic P123 surfactant as a soft template. The effect of the soft template in constructing the porosity of the crystalline CN was studied and investigated.

It has been reported that photocatalysts having ability to absorb light in longer wavelength resulted in higher photocatalytic activity when utilizing visible light as the light source. As CN material was only able to absorb up to *ca.* 470 nm, modification of CN to enable its light absorption at a wider range of the visible spectrum is highly suggested. In this study, the modification of crystalline porous CN with TAP was investigated in order to improve the light absorption to the longer wavelength in visible region. TAP was chosen as it has high carbon content and its structural features parallel to those of melamine, which was the intermediate to produce the CN. Although it was reported that modification of crystalline CN with TAP resulted in high hydrogen production rate, there is still no report whether the same enhancement can be observed in the photocatalytic oxidation of phenol.

Phenolic compounds can be easily found in our environments due to their high usage in research and industrial purpose. As phenol has been categorized as a hazardous compound, the method to degrade phenol that would give high percentage degradation is required. Although degradation of phenol using TiO₂ photocatalyst has been widely used, it can only work excellently under UV irradiation. Since the solar spectrum consists of about 40% of solar light compared to 5% of UV light, the application of photocatalyst that can work in visible light is highly required nowadays. Therefore, in this study, all the CN series comprised of amorphous CN and crystalline CN, porous CCN and porous CCN-TAP series were employed as active visible light-driven photocatalysts. The effect of crystallinity, porosity and dopant in photocatalytic degradation of phenol by CN were studied and investigated.

1.3 Objectives of Studies

In order to obtain photocatalysts that are highly active in longer visible wavelength for removal of phenol, several objectives need to be accomplished as shown below:

1. To synthesize crystalline CN and porous crystalline CN by an ionothermal method and soft template technique.
2. To modify porous crystalline CN with TAP in order to extend the absorption to a longer wavelength.
3. To study and investigate the structural, optical, textural, morphological and electrochemical properties of prepared CN photocatalysts.
4. To investigate the photocatalytic performance of the synthesized photocatalysts in photocatalytic degradation of phenol.

1.4 Scope of Studies

The scope of this research can be divided into five parts which were development of crystalline CN, optimization on the synthesis parameters, preparation of crystalline CN from melamine precursor and preparation of porous CCN as well as porous CCN-TAP materials. The photocatalytic performance of synthesized CN materials were evaluated for the degradation of phenol under solar light simulator irradiation.

In the first part of works, the effectiveness of salt melts in inducing the formation of crystalline CN was investigated using KCl-LiCl, KCl-NaCl and KCl-ZnCl₂. Urea, an abundant, easily accessible, inexpensive and less toxic was deployed as the precursor for the synthesis of crystalline CN in this part. Various spectroscopy instrumentations and analytical methods such as X-ray diffraction (XRD) spectroscopy, diffuse reflectance ultraviolet-visible (DR UV-Vis) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and nitrogen (N₂) adsorption-

desorption analysis for Brunauer-Emmett-Teller (BET) specific surface area and Barret-Joyner-Halenda (BJH) pore size distribution were deployed to study and investigate the properties of the prepared samples. The photocatalytic performances of prepared photocatalysts were evaluated for photocatalytic degradation of phenol. The remaining concentration of phenol at the end of the reaction was analysed using high performance liquid chromatography (HPLC) with a ultraviolet (UV) detector at a wavelength of 283 nm. As KCl-LiCl gave better crystallinity and photocatalytic activity than other salt melts, the KCl-LiCl was chosen for optimization of synthesis condition. Prior to the optimization studies, the physical and chemical properties of crystalline CN were also compared with amorphous CN. Transmission electron microscopy (TEM) was deployed to investigate the morphological of amorphous and crystalline CN while fluoroscence spectroscopy (PL) was employed to study the recombination of electron-holes. In addition, the charge transfer resistance (R_{ct}) and heterogeneous electron-transfer rate constant (k) were studied by electrochemical impedance (EIS) spectroscopy.

The second part covered the studies on the optimization of synthesis conditions including amount of precursor (2 g, 3 g and 4 g), synthesis temperature (500 °C, 550 °C and 600 °C), synthesis time (2, 4 and 6 hours) and amount of salt melts (2.5 g, 5 g, 7.5 g). The physical and chemical properties were also studied and investigated by XRD, DR UV-vis, FTIR, and N₂ adsorption-desorption analyses. The photocatalytic performances of prepared photocatalysts were evaluated in the photocatalytic degradation of phenol under solar light irradiation for 6 hours. The final concentration of phenol at the end of the reaction was determined using HPLC with the UV detector at the wavelength of 283 nm.

Following the successful preparation of crystalline CN using urea as organic nitrogen-rich precursor, in the third parts of the works, the crystalline CN was also prepared by using melamine as the precursor. The properties of the prepared crystalline CN was also compared with amorphous CN and both CN photocatalysts were denoted as amorphous CN-Mel and crystalline CN-Mel. The properties of prepared photocatalysts were characterized by XRD, DR UV-Vis, FTIR, TEM, N₂ adsorption-desorption analyses, TEM, PL spectroscopy and EIS. The prepared

amorphous CN-Mel and crystalline CN-Mel were subjected to photocatalytic degradation of phenol under solar light irradiation for 6 hours in order to evaluate their photocatalytic performance. The concentration of phenol after the reaction was determined using HPLC with the UV detector at the wavelength of 283 nm.

Fourth parts of the works included the introduction of porosity in the crystalline CN. Throughout this study, a Pluronic P123 surfactant was used as soft template for the preparation of porous CCN series. In this part, urea was first used as precursor but since urea was unable to provide a high surface area, melamine was chosen for the replacement of urea. Parameter like mass ratio of Pluronic P123 to precursor (0.02, 0.03, 0.04, 0.05 and 0.1) was studied. The prepared photocatalysts were characterized by XRD, DR UV-vis, FTIR, EIS spectroscopy, N₂ adsorption-desorption analyses, elemental analysis and TEM for selected samples (CCN-0.02P123). The photocatalytic performances of porous CCN-*x*P123 (*x* = 0.02, 0.03, 0.04, 0.05 and 0.1) series were assessed in the photocatalytic degradation of phenol under solar light irradiation for 6 hours. The final concentration of phenol at the end of the reaction was determined using HPLC with the UV detector at the wavelength of 283 nm. The radical scavengers studies were carried out to propose the mechanism on sample porous CCN-0.05P123. The *tert*-butyl alcohol (TBA), 1,4-benzoquinone (BQ), silver nitrate (AgNO₃) and ammonium oxalate (AO) were used as radical scavengers for hydroxyl radical ($\bullet\text{OH}$), superoxide (O₂ \bullet^-), photogenerated electrons (e⁻), and photogenerated holes (h⁺), respectively.

In the final part, the porous CCN-0.05P123 which possesses high surface area with best photocatalytic activity was modified with TAP in order to increase its absorption to a longer wavelength. Different mass ratio of TAP into melamine (0.02, 0.03, 0.04, 0.05 and 0.1) was carried out and prepared samples were denoted as porous CCN-*x*TAP which *x* refer to 0.02, 0.03, 0.04, 0.05 and 0.1. The properties of prepared modified porous CCN-*x*TAP photocatalysts were characterized using XRD, DR UV-vis, FTIR, EIS spectroscopy, N₂ adsorption-desorption analyses for BET surface area and BJH pore size distribution as well as pore volume, TEM and elemental analysis. The photocatalytic performance of prepared porous CCN-*x*TAP series were evaluated in the degradation of phenol under solar light irradiation for 6

hours. The remaining concentration of phenol at end of the photocatalytic reaction was determined using HPLC with the UV detector at the wavelength of 283 nm. Radical scavengers studies were performed on porous CCN-0.02TAP in order to propose its reaction mechanism. Radical scavengers used in these studies for scavenging $\cdot\text{OH}$, $\text{O}_2\cdot^-$, e^- , and h^+ were TBA, BQ, AgNO_3 and AO, respectively.

1.5 Significance of Studies

The primary focus of this study is to increase the productivity of CN by constructing a crystalline CN having a porous structure. To the best of our knowledge, although several successful research works have demonstrated the successful preparation of crystalline CN and highly ordered mesoporous amorphous CN, there is still no report on the successful synthesis of crystalline CN with the presence of the porous structure. Therefore, this study is very important for advancement in material science, since this study could provide good knowledge and understanding of how to prepare the materials. Furthermore, the use of salt melts as an ionic solvent in the reaction is the key factor in the crystallization process, thus, this study also highlighted the effect of different concentrations and types of salt melts in the crystallization process and the photocatalytic properties as well. On the other hand, the use of TAP as a modifier to improve the visible light absorption of prepared materials to extended wavelength in visible region was able to fully optimize the utilization of the solar energy that is the largest free and renewable energy source. The combination of high surface area and wide absorption in the visible light region gave high photocatalytic activity in photocatalytic degradation of phenol. Hence, this study also gives a great contribution to the knowledge of photocatalysis science.

As the phenol compound is very hazardous and toxic to human and environment, the study on the degradation of phenol would give a positive contribution to reduce the environmental problem. At the end of this study, a reaction mechanism on the modified porous CCN-TAP was also proposed. Therefore, this

study provided us the important knowledge, especially in the mechanism of photocatalytic phenol degradation. Moreover, the use of photocatalytic reaction for the conversion of hazardous organic compounds to harmless compounds such as carbon dioxide and water should be among the best approaches to deliver an environmentally friendly process to progress the green technology. This work would also provide an important contribution to the sustainability of our nature.

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