COPPER SPECIES MODIFIED CARBON NITRIDE AS FLUOROMETRIC DETECTION OF NITRATE AND NITRITE ION AND AS CATALYST FOR REDUCTION OF 4-NITROPHENOL

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DEDICATION

To my beloved family and my lovely fiancé

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ABSTRACT

The presence of N-containing compounds such as nitrate (NO_3^-), nitrite (NO_2^-), and nitrophenol (NP) in industrial wastewater has aroused great interest due to the toxicity of these compounds. Therefore, determination and removal of these compounds are imperative. In this study, copper species modified carbon nitride composites were developed for detection of NO_3^- and NO_2^- ions and reduction of 4-NP. Bulk carbon nitride (BCN) was synthesized using urea as precursor via thermal polymerization process at 823 K for 4 hours, while mesoporous carbon nitride (MCN) was prepared using the same approach as the preparation of BCN with the addition of silica nanoparticles as a hard template. In order to improve the sensing and catalytic performance of the CN, copper acetylacetonate ($Cu(acac)_2$) was added by impregnation method to produce Cu(II)acac(x)/CN composites (x = 0.1, 0.5, 4, 6, 8, 10, 12 mol%). The composites then underwent thermal oxidation to produce CuO(x)/CN and thermal hydrogenation to produce Cu(x)/CN composites. Based on the X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectra, the structure of BCN and MCN did not change after loading of copper species. The diffuse reflectance ultraviolet-visible (DR UV-Vis) spectra of copper species modified CN indicated the ligand-to-metal charge transfer (LMCT) bands at around 277 and 300 nm and d-d transition of Cu^{2+} above 400 nm. BCN and MCN exhibited three excitation peaks at 277, 315, and 369 nm owing to the presence of C=N, C=O, and C-N groups, respectively, while there was only one emission peak observed at 450 nm. The emission intensity decreased with increasing copper species loading, suggesting copper species were deposited on the surface of CN and interact with all active sites of the CN. The performances of BCN, MCN, and their composites as fluorometric detection of NO_3^- and NO_2^- were studied at concentration ranges of 3000-18000 mol and 5-40 mol, respectively. CuO(0.5)/BCN and CuO(0.1)/MCN composites exhibited the highest K_{sv} values for detection of NO_3^- and the NO_2^- which were 22 and 2.3 times higher than that of BCN. The catalytic degradation of 4-NP was carried out in the presence of Cu(II)acaca(x)/BCN composites as catalyst and $NaBH_4$ at room temperature. Cu(II)acac(10)/BCN showed the highest catalytic performance with 97% reduction of 4-NP after 6 minutes. This study demonstrated that the copper species modified CN composite is a promising material for fluorometric detection of NO_3^- and the NO_2^- ions and catalyst for reduction of 4-NP.

ABSTRAK

Kehadiran sebatian yang mengandungi unsur N misalnya nitrat (NO_3^-), nitrit (NO_2^-), dan nitrofenol (NP) di dalam air sisa industri telah membangkitkan minat yang hebat kerana ketoksikan sebatian ini. Oleh itu, penentuan dan penyingkiran sebatian ini adalah penting. Dalam kajian ini, komposit karbon nitrida terubahsuai spesies kuprum telah dibangunkan untuk pengesanan ion NO_3^- dan NO_2^- dan pengurangan 4-NP. Karbon nitrida pukal (BCN) telah disintesis menggunakan urea sebagai bahan pemula melalui proses pempolimeran terma pada 823 K selama 4 jam, manakala karbon nitrida mesoliang (MCN) telah disediakan menggunakan pendekatan yang sama seperti penyediaan BCN dengan penambahan nanopartikel silika sebagai templat keras. Untuk meningkatkan prestasi pengesanan dan pemangkinan CN, kuprum asetilasetanoat ($Cu(acac)_2$) telah ditambah dengan kaedah pengisitepuan untuk menghasilkan komposit Cu(II)acac(x)/CN (x = 0.1, 0.5, 4, 6, 8, 10, 12 mol%). Komposit tersebut kemudiannya menjalani pengoksidaan terma untuk menghasilkan komposit CuO(x)/CN dan penghidrogenan terma untuk menghasilkan komposit Cu(x)/CN. Berdasarkan spektra pembelauan sinar-X (XRD) dan infra-merah transformasi Fourier (FTIR), struktur BCN dan MCN tidak berubah setelah diisi spesies kuprum. Spektra pantulan serakan ultralembayung-cahaya nampak (DR UV-Vis) CN terubahsuai spesies kuprum menunjukkan jalur pemindahan cas ligan-ke-logam (LMCT) pada sekitar 277 dan 300 nm dan peralihan d-d Cu^{2+} di atas 400 nm. BCN dan MCN menunjukkan tiga puncak pengujaan pada 277, 315 dan 369 nm masing-masing disebabkan oleh kehadiran kumpulan C=N, C=O dan C-N, sementara terdapat hanya satu puncak pancaran dilihat pada 450 nm. Keamatan pancaran menurun dengan peningkatan pengisian spesies kuprum, menunjukkan bahawa spesies kuprum telah terenap pada permukaan CN dan berinteraksi dengan semua tapak aktif CN. Prestasi BCN, MCN dan komposit sebagai pengesanan fluorometri NO_3^- dan NO_2^- telah dikaji masing-masing pada julat kepekatan 3000-18000 mol dan 5-40 mol. Komposit CuO(0.5)/BCN dan CuO(0.1)/MCN menunjukkan nilai K_{sv} tertinggi bagi pengesanan NO_3^- dan NO_2^- iaitu 22 dan 2.3 kali ganda lebih tinggi daripada BCN. Degradasi bermangkin 4-NP telah dilakukan dengan kehadiran Cu(II)acac(x)/BCN komposit sebagai mangkin dan $NaBH_4$ pada suhu bilik. Cu(II)acac(10)/BCN menunjukkan prestasi pemangkinan tertinggi dengan pengurangan 97% 4-NP selepas 6 minit. Kajian ini menunjukkan bahawa komposit CN terubahsuai spesies kuprum adalah suatu bahan yang menjanjikan bagi pengesanan fluorometri ion NO_3^- dan NO_2^- dan mangkin bagi pengurangan 4-NP.

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NO_2^-	-	Nitrite ions
NO_3^-	-	Nitrate ions
NTDs	-	Neural tube defects
CN	-	Carbon nitride
nM	-	Nano Molar
PVA	-	Polyvinyl alcohol
PEG	-	Polyethylene glycol
PANI	-	Polyaniline
MCN	-	Bulk carbon nitride
MCN	-	Mesoporous carbon nitride
ADMND	-	2-amino-5,7-dimetyl-1,8-naphthridine
CTAB	-	Cetyltrimethylammonium bromide
nm	-	Nano Metre
XRD	-	X-ray diffraction
FTIR	-	Fourier transform infrared spectroscopy
mol	-	mole
NO	-	Nitric acid
μM	-	Micromolar
HPLC	-	High-performance liquid chromatography
M	-	Molarity
Ppy	-	Polypyrrole
CE	-	Capillary electrophoresis
nL	-	Nanolitre
UV	-	Ultraviolet

s - Second
2D - Two dimentional
L - Litre
Ksv - Stern-Volmer constant
RSD - Relative standard deviation
LOD - Limit of Detection
arb. u. - Arbitrary unit
g - Gram
K - Kelvin
Å Armstrong
P/P_o Relative pressure
wt% - Weigth percentage
w/w% - Weight per weight percentage
M_w - Molecular weight
mL - Mili Liter
min - Minute
h - Hour
kV - Kilo Volt
°C - Degree Celsius
β-CN - Beta carbon nitride
NPYR - Nitrosopyrrolidone
BSA - Bovine serum bumine
Ag NCs - Silver nanoclusters
Pd NCs - Pladium nanoclusters

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Carbon materials have attracted continuous interest due to its unique properties resulted from their tunable surface properties that offers great potential for many different fields of application such as absorption (Hu *et al*., 2019), catalyst (Samad *et al*., 2018), supercapacitors (Cheng *et al*., 2019; Liu *et al*., 2019) and sensor (Lee *et al*., 2018; Su & Zhang, 2017). It was reported that nitrogen containing carbon-based materials improve the properties of the carbon materials as they contain an abundance of functional groups which can extend their fields of application (Straten *et al*., 2018). In recent years, a lot of attentions have been paid on the CN (CN) because of its versatile properties such as porosity (Dong & Zhang, 2012; Kang *et al*., 2018; Wang *et al*., 2019), surface functionalities (Wang *et al*., 2017) and physically and chemically stable (Dong *et al*., 2014; Stagi *et al*., 2016). In addition, CN showed high photoluminescence (PL) intensity, high photostability, and good biocompatibility (Huang *et al*., 2014; Liang *et al*., 2017; Xiong *et al*., 2017). Apart from that, the presence of nitrogen richness and incomplete condensed amino functions in CN gave Lewis basic properties as catalyst by supplying the abundant actives sites for the metal-free catalyst. (Gong *et al*., 2015). These characteristics make

CN an excellent material for catalysis (Gong *et al.*, 2015), photocatalysis (Chai *et al.*, 2012; Cheng *et al.*, 2013), bioimaging, drug delivery and sensing (Wang *et al.*, 2013).

Previously, it has been reported that CN gave low sensitivity towards detection of NO_3^-. This might be due to the low surface area (62 m^2 g^{-1}) of the CN and limited active site in the material for detection of NO_3^- ion (Alim *et al.*, 2015). Thus, these factors are believed might affect the efficiency of sensing performance for detection of NO_3^- ion. In order to overcome these problems, the surface area and the amount of the active sites should be increased for better interactions between the CN and analytes. Moreover, many studies reported that catalytic support such as metal nanoparticle enhanced the catalytic activity of CN for conversion of 4-NP to 4-AMP (Wang *et al.*, 2017; Zhao *et al.*, 2015d). Therefore, modification of the CN has to be carried out to improve the sensitivity towards the targeted analyte. The organic nature of CN itself offers ample choice to design the molecular structure in order to improve its performance. Thus, many strategies such as copolymerization and hybridization with metal atoms and non-metals have been explored to enhance the performance of CN. Besides, the performance of CN could also be improved by fabrication with hard template or soft template approach (Zhang *et al.*, 2014b).

On the other hand, Cu nanoparticles have attracted a great interest as Cu is considered inexpensive in comparison with noble metals such as Au, Pt and Pd (Wang *et al.*, 2015). It has been documented that CuO has high surface-to-volume ratio which makes it is suitable and commonly used as gas sensitive materials and thus shows outstanding performance in gas sensor application (Zhang *et al.,* 2015; Tiong *et al*., 2014; Ahmad *et al.,* 2017; Yan *et al*., 2015). Previously, catalytic oxidation of propargylic alcohol to ynones showed excellent performance with 99% yield in the presence of copper nanoparticle as a catalyst (Han *et al.,* 2011). In a different study, it was claimed that the CN modified copper nanoparticles catalyst showed good yield (85 %) for the oxidation of propargylic alcohol to ynones. In addition, the catalyst could easily be recovered and reused for the next reaction (Lv *et al.,* 2015). Therefore, in this study, copper species including copper complex ($Cu(acac)_2$), copper oxide (CuO) and copper metal (Cu) are selected to be used as modifiers due to their high electrical and thermal conductivities as they exhibited small resistance where the current can flow easily through copper without much loss of energy (Zheng *et al*., 2018), high fluorescence ability and wide usage in sensing and catalysis applications.

In this current work, both bulk CN (BCN) and mesoporous CN (MCN) are investigated for potential application as fluorescence sensor for detection of the NO_3^- and the NO_2^- and as catalyst for reduction of 4-NP to 4-AMP. Both the BCN and the MCN were modified by copper(II) acetylacetonate ($Cu(acac)_2$), copper(II) oxide, and copper metal. It would be very interesting to study the effect of different copper species modified CN as fluorescence sensor for detection of NO_3^- and NO_2^- and as catalyst for reduction of 4-NP to 4-AMP. From the literature survey, there is no study on the use of such copper species modified CN composites for detection of NO_3^-

and NO_2^- by using fluorescence spectroscopy and as catalyst for reduction of 4-NP to 4-AMP.

Nitrogen is a colourless inert neutral gas which exists 78% of earth atmosphere and appear as important element of all living things. Nitrogen presents in different form such as nitrogen gas, ammonia nitrogen, nitrates, nitrites and organic compounds in the environment (Michalski & Kurzyca, 2006; Moo *et al.*, 2016). In wastewater management, nitrogen level is set as the measurement standards in the determination of water quality as it is easily dissolved in water and can produce miscellaneous effects on the environment (Abdel-Raouf *et al.,* 2012; Moo *et al.*, 2016). It was stated that the main contributors to the eutrophication are from the treated and untreated nitrogen in domestic wastewater (Abdel-Raouf *et al.,* 2012; Liu & Wang, 2017). Usually, the source of nitrogen mainly originates from urban sewage and manufacturing waste (Moo *et al.,* 2016).

Nitrate (NO_3^-) and nitrite (NO_2^-) ions are naturally occurring inorganic compounds. These ions exist in the environment and food product which can cause hazards to human health. The NO_3^- and NO_2^- are mainly found as food preservatives and fertilizing agents, in which their wastewaters from anthropogenic activities, such as agriculture and industry, are causing contamination of the water resource for human consumption (Guadagnini & Tonelli, 2013). In human body, especially in stomach, the NO_2^- reacts with secondary amines and amides to form carcinogenic N-nitrosamine in the gastrointestinal tract, hence causing stomach cancer (Ensafi & Amini, 2010; Palanisamy *et al.*, 2014; Yang *et al.*, 2014; Quek *et al.*, 2015).

Meanwhile, the NO_3^- can produce the same effect due to its reduction to NO_2^- through bacterial or microbial reduction. The NO_2^- is more toxic than the NO_3^- because the NO_2^- can interact with blood pigments to produce methemoglobinemia or baby blue syndrome which can cause blood disorder and breathing difficulties in human (Kazemzadeh & Daghighi, 2005; Quek *et al.*, 2015; Zhang & Angelidaki, 2012). The World Health Organization (WHO) has set the maximum concentration level of the NO_2^- and NO_3^- in drinking water of 3 mg/L and 10 mg/L, respectively (Zhang *et al.*, 2005). Moreover, it has been reported that the NO_2^- and the NO_3^- in urine of healthy adults should range 0.5 to 4 µM and 300 to 1800 µM, respectively. Therefore, removal and determination of NO_2^- and NO_3^- are significant from the health and environmental point of view.

4-nitrophenol (4-NP) is one of the nitrogen-containing pollutants listed as the most priority pollutants in the U.S.A Environmental Protection Agency (EPA) due to its persistence and toxicity (Li *et al.*, 2012; Luo *et al.*, 2015). The 4-NP is deliberated as organic wastewater produced from the production of pesticides, pharmaceuticals, dyes, explosives and petrochemicals and it is harmful to the water environment and human health even at low concentrations in natural environment (Chen *et al.*, 2017; Lin *et al.*, 2017; Wiench *et al.*, 2017). The nitro and phenol functionalities in 4-NP can cause strong intense stimulation on the skin and eyes (Qu *et al.*, 2017). Besides, EPA has also reported that 4-NP has major adverse effects on the blood, liver, central nervous system and hypoxia which are very harmful to wildlife and humans (Revathy *et* *al*., 2018). To keep the ecosystem safe, therefore, there is urgent need for efficient techniques to remove 4-NP from aqueous systems.

The determination of NO_3^- and NO_2^- has been a great challenge in the field of analytical chemistry. Numerous approaches have been explored for the determination of NO_3^- and NO_2^-, such as spectroscopic (Gajaraj *et al.,* 2013), electrochemical (Manea *et al*., 2010; Yilong *et al.,* 2015) and chromatographic (Zhao *et al.,* 2015a) methods. However, all of the methods aforementioned have tedious experimental procedures and are usually time consuming. The NO_2^- is also recognized to be chemically unstable, thus, a fast detection process is preferable particularly for on-site analysis (Kumar & Anthony, 2014). The spectroscopic method for the NO_3^- and the NO_2^- detection is commonly originated from the classic Griess reaction. Typically, griess reaction is the reaction between NO_2^-, sulfanilamide and N-(1-naphtyl)ethylenediamine to form colored azo dye (Ridnour *et al*., 2000; Bhakta *et al*., 2014; Kumar & Anthony, 2014). The diazoniation of nitrous acid and aromatic amines produced a highly colored azo dye (Correa-Duarte *et al.,* 2015). However, it has several disadvantages including usage of high concentration of hazardous reagents and its inability to detect NO_3^- (Miranda *et al.,* 2001). Moreover, due to the formation of coloured azo dye after reaction, the method is difficult to be reused. Therefore, development of a reusable and sensitive sensor for detection of NO_3^- and NO_2^- is highly required.

The conventional methods like chemical oxidation and biodegradation are usually used for the treatment of 4-NP but they not efficient and time consuming. From the literature, it was noted that the chemical treatments such as advanced oxidation, membrane filtration, and electrochemical methods are highly efficient but expensive (Dhorabe *et al.,* 2016). Various techniques such as membrane filtration (Ivančev-Tumbas *et al.,* 2008), photo-degradation (Sun *et al.,* 2011; Umabala, 2015), adsorption (Mehrizad *et al.,* 2012; Ahmed & Theydan, 2014) and chemical reduction have been reported (Gangula *et al.,* 2011; Chi *et al*., 2014) to remove nitrophenol from contaminated water consequently. To date, among many other methods, catalytic conversion of 4-NP to 4-aminophenol (4-AMP) using excess sodium borohydrate ($NaBH_4$) reductant has been considered as an efficient and environmentally friendly way (Wang *et al.,* 2017, Zhang *et al.,* 2011). 4-AMP as a potent intermediate has been applied to manufacturing of many analgesic and antipyretic drugs, such as paracetamol and phenacetin (Som *et al*., 2000; Zhang *et al.,* 2011).

The objective of this research is to investigate a dual function material which can be used as fluorescence sensor for NO_3^- and NO_2^- determination and as catalyst for reduction of 4-NP to 4-AMP. For this purpose, CN is proposed as a potential material to be implemented as fluorescence sensor for detection of NO_3^- and the NO_2^- and reduction of 4-NP to 4-AMP. Herein, this study focuses on the synthesis of BCN, MCN, and their modified composites with $Cu(acac)_2$ (metal complex), CuO (metal oxide) and Cu (metal). All the synthesized materials were characterized by X-ray diffractometer (XRD), Fourier transform infrared (FTIR) spectroscopy, N_2 adsorption-desorption analysis, diffuse reflectance UV-Visible (DR UV-Vis) spectroscopy, and fluorescence spectroscopy and inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. In addition, the chemical interaction between the copper species and the CN were confirmed by using computational study calculated via Avogadro Software. Lastly, all the synthesized materials were applied as fluorescence sensor for detection of NO_3^- and the NO_2^- ions and catalyst for reduction of 4-NP and 4-AMP.

1.2 Problem Statement

In medical purposes, Griess reagent has been widely used for the determination of NO_3^- and NO_2^- in human fluid such as urine and blood. This method requires reduction of NO_3^- to NO_2^- and followed by detection of NO_2^- by using Griess reaction. Briefly, NO_2^- reacted with sulfanilamide to produce diazonium ion. Next, N-(1-napthyl)ethylenediamine was added into the mixture which resulted an azo dye with an absorption at 540 nm (Bryan & Grisham, 2007; Flower *et al*., 2006; Hetrick & Schoenfisch, 2009). Even though, the Griess reaction offers a fast and simple procedure step, its utility showed indirect estimation of NO_3^- via the measurement of NO_2^- (Ridnour *et al.*, 2000). In addition, this conventional method is a single used technique as the azo dye product formed from the Griess reaction cannot be reused in the next reaction. Therefore, it is important to develop a reusable sensor for detection of NO_3^- and NO_2^- in order to sustain the environment stability. Recently, carbon nitride has been reported to exhibit sensing capability for detection of nitrogen containing compounds such as N-nitrosopyrrolidine (NPYR)

(Sam *et al.,* 2014), cyanide (Lee *et al.,* 2012) and NO_3^- (Alim *et al.*, 2015). Unfortunately, bare carbon nitride still gave low sensitivity towards the detection of NO_3^- (Alim *et al.*, 2015). Thus, modification of carbon nitride for high detection of NO_3^- and NO_2^- is still highly required.

Apart from its sensing capabilities, CN has also been applied in many catalytic areas. Several studies have been carried out for the reduction of 4-NP to 4-AMP includes metal/acid reduction, electrocatalytic reduction and catalytic hydrogenation. Among all previous mentioned methods, catalytic hydrogenation of 4-NP is considered an environmentally friendly and most efficient method as it could achieve high reduction of 4-NP without producing acid effluent (Sun *et al*., 2014). In addition, the formation of 4-AMP is very useful in pharmaceutical application as an intermediate for the manufacture of analgesic antipyretic drug (Abhilash & Singh, 2009). Besides, 4-AMP exhibited strong reducing agent for photographic developers (Lunar *et al*., 2000). This compound was also used as corrosion inhibitor in paints and anticorrosion-lubricant agent in fuels (Vaidya *et al*., 2003; Meng *et al*., 2015; Lang and Yu, 2017). Many previous studies have reported on the use of metal-based catalyst such as Pd (Park *et al.,* 2017; Zhao *et al.,* 2015d), Au (Corma *et al*., 2007; Gangula *et al*., 2011), Ag (Geng & Du, 2014; Kastner & Thunemann, 2016), Pt (Pandey & Mishra, 2014; Chang *et al*., 2012) for the reduction of 4-NP to 4-AMP. However, these metal-based catalysts were expensive for industrial application. To overcome this problem, many researchers turn to discover the usage of low-cost material as alternative catalyst.

1.3 Objectives

In this study, several objectives have been underlined in order to explored the dual functions of CN based materials as fluorescence sensor for the detection of NO_3^- and NO_2^- as well as catalyst for reduction of 4-NP to 4-AMP. The objectives of this study are listed as below:

1) To synthesize BCN, MCN, copper species modified BCN, and copper species modified MCN.
2) To investigate the properties of BCN, MCN, copper species modified BCN, and copper species modified MCN.
3) To evaluate the performance of BCN, MCN, copper species modified BCN, and copper species modified MCN as fluorescence sensors for the detection of NO_3^- and NO_2^-.
4) To determine the catalytic performance of BCN, MCN, copper species modified BCN, and copper species modified MCN for reduction of 4-NP to 4-AMP.

1.4 Scope of Study

This study was divided into four parts, which involved synthesis of BCN, MCN and copper species modified CN, characterization of the synthesized materials, application as fluorescence sensor for the determination of NO_3^- and NO_2^-, and lastly investigation on the catalytic performance of the composites for the reduction of 4-NP to 4-AMP.

For the synthesis part, urea was used as precursor for the preparation of BCN through thermal polymerization approach. While for the preparation of the MCN, silica was introduced as a hard template using the same approach for the preparation of the BCN. In order to improve the performance of the CNs, the BCN and the MCN were modified with different mole loadings of metal complex, which was copper-acetylacetonate ($Cu(acac)_2$) via an impregnation method with certain amount of $Cu(acac)_2$ in mol% loading to produce Cu(II)acac(x)/BCN and Cu(II)acac (x)/MCN composites. The Cu(II)acac (x)/BCN and the Cu(II)acac (x)/MCN composites were oxidized via thermal oxidation approach to produce CuO(x)/BCN and CuO(x)/MCN composites. Lastly, Cu(II)acac (x)/BCN and the Cu(II)acac (x)/MCN composites were reduced using hydrogenation method to produce Cu(x)/BCN and the Cu(x)/MCN composites.

The properties of the synthesized materials were characterized using X-ray diffractometer (XRD), Fourier transform infrared (FTIR) spectroscopy, N_2 adsorption-desorption analysis, diffuse reflectance UV-Visible (DR UV-Vis) spectroscopy, fluorescence spectroscopy and inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. The chemical interaction between the copper species and CN was evaluated by using Avogadro Software.

The dual function of the copper species modified CN was investigated as fluorescence sensors for the detection of NO_3^- and NO_2^- and as catalyst for the reduction of 4-NP to 4-AMP. For fluorescence sensor, the prepared materials were introduced with the NO_3^- and the NO_2^- ions by using quenching test in the range of 3×10^3 to 18×10^3 mol and 5 to 40 mol, respectively, using fluorescence spectroscopy. The best sensor was further investigated for its reproducibility, stability and selectivity as sensor. Meanwhile, the synthesized materials were also tested as catalyst for the conversion of 4-NP to 4-AMP with the addition of sodium borohydrate ($NaBH_4$) as reducing agent. The optimization of the catalytic reaction by investigating the effect of 4-NP concentration, molar ratio of $NaBH_4$ and the amount of catalyst was carried out.

1.5 Significance of Study

Many studies have been carried out in order to find the suitable material and method for the determination and removal or reduction of hazardous compounds to less hazardous compound. In this study, BCN and MCN were tested as bifunctional material for detection of NO_3^- and NO_2^- ions and as catalyst for reduction of 4-NP to 4-AMP. Both BCN and MCN were novel materials for such applications. CN exhibited strong fluorescence property and high surface area which were the ideal characteristics to be utilized as fluorescence sensor and catalyst for sensing and reduction of nitrogen-containing pollutants. Rather than using different material for different application, this work explores the bifunctionalities of CN as fluorescence sensor for detection of NO_3^- and NO_2^- and as catalyst for reduction of 4-NP to 4-AMP.

The modification of copper species toward CN such as copper complex, copper oxide and copper species modified CN were successfully synthesized via simple approach. Copper species modified CN composites would result in a novel series of materials and it is very important in the development of material science. Besides, the functionalization of CN by copper species enhanced the quenching rate of NO_3^- and NO_2^- and improved the catalytic performance for the reduction of 4-NP to 4-AMP. This research finding would contribute to the knowledge in fluorescence sensor science and catalysis. Other than that, this work can also be the stepping stone for other researchers to explore the use of copper species modified CN composites for different applications.

In addition, the early detection of nitrogen-containing pollutants as well as reduction of the pollutants to the less harmful compounds is significant in protecting our ecosystem and also human health. By applying the copper species modified CN composites for detection and reduction of nitrogen-containing pollutants it would be great advantage to be applied in the environmental management. The reduction of 4-NP to 4-AMP is very beneficial in pharmaceutical industry, thus minimizing the harmful effects towards human being.

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