POLYMER MODIFIED CARBON NITRIDE COMPOSITES AS POTENTIAL FLUORESCENCE SENSORS FOR DETECTION OF NITRITE AND NITRATE IONS

NOR SHUHADA BINTI ALIM

UNIVERSITI TEKNOLOGI MALAYSIA

POLYMER MODIFIED CARBON NITRIDE COMPOSITES AS POTENTIAL FLUORESCENCE SENSORS FOR DETECTION OF NITRITE AND NITRATE IONS

NOR SHUHADA ALIM

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy

Faculty of Science
Universiti Teknologi Malaysia

APRIL 2018

Special dedicated to:

To beloved parents,
Alim Maafol and Zaleha Ismail for their love and care, continuous prayer, endless support and encouragement they have provided all these years for me.
My wonderful sibling,
Hazlin, Nizam, Haslin, Azman, Liza, Saiful, Jiha, Aida and Nazirah who supported me on this journey.
My dearest friends, fiancée, and labmates,
For standing by my side when times get hard and always making me happy.
And
Thank you ALLAH for the countless blessing.

ACKNOWLEDGEMENT

Bismillaahirrahmaanirrahim
In the name of Allah, the most Gracious; the most Merciful

First and foremost, all praise to Allah SWT, the Almighty God, for His gracious mercy and bleesing for giving me an opportunity, strength and endurance to complete my master study. There are a number of people behind this journay who deserve to be both acknowledged and thanked here, I would like to express my outmost gratitude and deepest appreciation to my supervisors, Dr. Leny Yuliati, Dr. Hendrik Lintang, and Dr. Hasmerya Maarof for their time, sufficient guidance and continuous commitment throughout this project. It was a great pleasure for me to do my master studied under their supervison and gained a lot of througtful knowledge, advice as well as suggestions which are to the great benefir of this project.

A special gratitude goes to all lecturers, researcher, laboratory officers, and staffs from Ibnu Sina Institute for Scientific and Industrial Research and Postgraduate-Faculty of Science, UTM. I am also greatly indebted to the Ministry of Education Malaysia for financial support through Research University Grant and scholarship provided under MyBrain15 (MyMaster).

A million thanks to my beloved parents and my sibllings for their support, love, encouragement, understanding and continuos pray that makes me stronger each and everyday on completing this study. Not forgetten, a special thanks also to fiancée, all my dearest friends, labmates and group members, whose names are too numerous to mention for their invaluable assistance and support encouragement along this study.

ABSTRACT

The detection of nitrite (NO_2^-) and nitrate (NO_3^-) ions is important since these ions are closely related to environmental remediation and human health. Rapid, sensitive, and yet reusable sensors are of great importance for such applications. In the present study, novel materials were developed as fluorescence sensors for detection of NO_2^- and NO_3^-. Metal-free carbon nitride (CN) was modified with several different polymers, namely polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), polyethylene glycol (PEG) and polyaniline (PANI). The series of polymer(x%)-CN composites (x = 1, 3 and 5 w/w%) were prepared by a simple impregnation method using two types of CN, namely bulk CN (BCN) and mesoporous CN (MCN). X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy results revealed that the chemical structures of the BCN and the MCN did not change with the addition of polymers. In contrast, the specific surface area of the BCN and the MCN decreased with the addition of the polymers, suggesting the presence of the polymers in the composites. Fluorescence spectroscopy of both BCN and the MCN revealed three absorption and excitation peaks, which corresponded to N=C, C=O, and terminal C-N sensing sites. Depending on the type of added polymer, the emission intensities of BCN and MCN were found to either decrease or increase, suggesting the occurrence of interactions between the emission sites and the added polymers. The fluorescence sensor capabilities of the prepared samples were investigated using the quenching test for the detection of NO_2^- and NO_3^- in the range of 5-40 and 3-18 $\times$ 10^3 mol, respectively. All polymer(x%)-CN composites gave almost linear Stern-Volmer plots for quenching of NO_2^- and NO_3^-, suggesting their potential ability as fluorescence sensors for detection of both NO_2^- and NO_3^-. Interestingly, all composites showed superior sensitivity towards NO_2^- than NO_3^-. While specific surface area might not be the direct crucial factor, porosity and larger surface area of MCN than BCN might provide better dispersion of polymers, which in turn resulted in better sensing performance. Among the composites, the PVP(3)-MCN showed the highest sensitivity towards both NO_2^- and NO_3^-. As for the detection of NO_2^-, PVP(3)-MCN gave the highest quenching efficiency with Stern-Volmer quenching constant (K_{SV}) values of 13.5 $\times$ 10^{-3} mol^{-1}, 12.5 $\times$ 10^{-3} mol^{-1}, and 10.5 $\times$ 10^{-3} mol^{-1} at N=C, C=O, and terminal C-N sensing sites, respectively. As for the detection of NO_3^-, PVP(3)-MCN gave the highest K_{SV} values of 21.3 $\times$ 10^{-6} mol^{-1}, 23.9 $\times$ 10^{-6} mol^{-1}, and 24.2 $\times$ 10^{-6} mol^{-1} at N=C, C=O and terminal C-N sensing sites, respectively. Since the K_{SV} value for NO_2^- detection was much higher than that for NO_3^- detection, this study showed that the composite was more sensitive for the detection of NO_2^-. These could be due to the smaller size and higher polarity of NO_2^- compared to NO_3^-. Reproducibility, limit of detection (LOD), reusability, and selectivity studies were carried out on the best sensor (PVP(3)-MCN) for the detection of NO_2^-. It was revealed that PVP(3)-MCN composite showed good reproducibility with LODs of 2.9, 4.6 and 5.2 mol at N=C, C=O and terminal C-N sensing sites, respectively. The reusability test showed that the quenching efficiency of the PVP(3)-MCN did not change much after four cycles of quenching test for NO_2^- detection. PVP(3)-MCN also showed great selectivity for the detection of NO_2^- in the presence of Cl^-, PO_4^{3-} or SO_4^{2-}. These results demonstrated the potential capability of PVP(3)-MCN as a fluorescence sensor for NO_2^-.

ABSTRAK

Pengesanan ion nitrit (NO_2^-) dan nitrat (NO_3^-) adalah sangat penting kerana ion-ion ini berkaitan rapat dengan pemulihan alam sekitar dan kesihatan manusia. Pengesan yang pantas, sensitif, dan boleh diguna semula adalah sangat penting bagi aplikasi seperti ini. Dalam kajian ini, bahan baharu telah dibangunkan sebagai pengesan pendarfluor untuk pengesanan NO_2^- dan NO_3^-. Karbon nitrida bebas-logam (CN) telah diubahsuai dengan beberapa polimer yang berlainan, iaitu polivinilpirolidon (PVP), polivinil alkohol (PVA), polietilena glikol (PEG) dan polianilin (PANI). Siri komposit polimer(x%)-CN (x = 1, 3 dan 5 w/w%) telah disediakan melalui kaedah pengisitepuan mudah menggunakan dua jenis CN, iaitu CN pukal (BCN) dan CN mesoliang (MCN). Keputusan spektroskopi pembelauan sinar-X (XRD) dan spektroskopi inframerah transformasi Fourier (FTIR) telah mendedahkan bahawa struktur kimia BCN dan MCN tidak berubah dengan penambahan polimer. Sebaliknya, kawasan permukaan tertentu BCN dan MCN berkurangan dengan penambahan polimer, mencadangkan kehadiran polimer di dalam komposit. Spektroskopi pendarfluor bagi kedua-dua BCN dan MCN menunjukkan tiga puncak penyerapan dan pengujaan, yang sepadan dengan tapak pengesan N=C, C=O, dan C-N terminal. Bergantung kepada jenis polimer yang ditambah, keamatan pancaran BCN dan MCN didapati sama ada menurun atau meningkat, mencadangkan berlakunya interaksi antara tapak pancaran dan polimer yang ditambah. Keupayaan pengesan pendarfluor sampel yang disediakan telah dikaji menggunakan ujian pelindapan untuk pengesanan NO_2^- dan NO_3^- masing-masing dalam julat 5-40 dan 3-18 × 10^3 mol. Semua komposit polimer(x%)-CN memberikan plot Stern-Volmer yang hampir lurus untuk pelindapan NO_2^- dan NO_3^-, mencadangkan potensi keupayaan mereka sebagai pengesan pendarfluor untuk mengesan kedua-dua NO_2^- dan NO_3^-. Menariknya, semua komposit menunjukkan kepekaan yang unggul terhadap NO_2^- daripada NO_3^-. Manakala permukaan tertentu mungkin bukan menjadi faktor penting secara langsung, keliangan dan kawasan permukaan MCN yang lebih besar daripada BCN mungkin memberikan penyebaran polimer yang lebih baik, seterusnya menghasilkan prestasi mengesan yang lebih baik. Antara semua komposit, PVP(3)-MCN menunjukkan sensitiviti tertinggi terhadap kedua-dua NO_2^- dan NO_3^-. Bagi pengesanan NO_2^-, PVP(3)-MCN memberikan kecekapan pelindapan tertinggi dengan nilai pemalar pelindapan Stern-Volmer (K_{SV}) masing-masing 13.5 × 10^{-3} mol^{-1}, 12.5 × 10^{-3} mol^{-1}, dan 10.5 × 10^{-3} mol^{-1} pada tapak pengesan N=C, C=O, dan terminal C-N. Bagi pengesanan NO_3^-, PVP(3)-MCN memberikan nilai K_{SV} tertinggi masing-masing 21.3 × 10^{-6} mol^{-1}, 23.9 × 10^{-6} mol^{-1}, dan 24.2 × 10^{-6} mol^{-1} pada tapak pengesan N=C, C=O dan terminal C-N. Oleh kerana nilai K_{SV} untuk pengesanan NO_2^- adalah lebih tinggi daripada pengesanan NO_3^-, kajian ini menunjukkan bahawa komposit adalah lebih sensitif bagi pengesanan NO_2^-. Ini berkemungkinan disebabkan oleh saiz yang lebih kecil dan nilai kekutuban NO_2^- yang lebih tinggi berbanding dengan NO_3^-. Kajian kebolehulangan, had pengesanan (LOD), kebolehgunaan semula, dan kepilihan telah dilakukan ke atas pengesan terbaik (PVP(3)-MCN) untuk pengesanan NO_2^-. Kajian ini mendedahkan bahawa komposit PVP(3)-MCN menunjukkan kebolehulangan yang baik dengan LOD masing-masing 2.9, 4.6 dan 5.2 mol pada tapak pengesan N=C, C=O dan terminal C-N. Ujian kebolehgunaan semula menunjukkan bahawa kecekapan pelindapan PVP(3)-MCN tidak banyak berubah selepas empat kitaran ujian pelindapan bagi pengesanan NO_2^-. PVP(3)-MCN juga menunjukkan kepilihan yang hebat bagi pengesanan NO_2^- dengan kehadiran Cl^-, PO_4^{3-} atau SO_4^{2-}. Hasil ini menunjukkan potensi kemampuan PVP(3)-MCN sebagai pengesan pendarfluor bagi NO_2^-.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

°C	-	Degree Celsius
2D	-	Two dimentional
Å		Armstrong
ADMND	-	2-amino-5,7-dimetyl-1,8-naphthridine
Ag NCs	-	Silver nanoclusters
arb. u.	-	Arbitrary unit
BCN	-	Bulk carbon nitride
BSA	-	Bovine serum bumine
CE	-	Capillary electrophoresis
CN	-	Carbon nitride
CTAB	-	Cetyltrimethylammonium bromide
FTIR	-	Fourier transform infrared spectroscopy
g	-	Gram
h	-	Hour
HPLC	-	High-performance liquid chromatography
K	-	Kelvin
Ksv	-	Stern-Volmer constant
kV	-	Kilo Volt
L	-	Litre
LOD	-	Limit of Detection
M	-	Molarity
MCN	-	Mesoporous carbon nitride
min	-	Minute
mL	-	Mili Liter
mol	-	mole
M_w	-	Molecular weight

nL	-	Nanolitre
nM	-	Nano Molar
nm	-	Nano Metre
NO	-	Nitric acid
NO_2^-	-	Nitrite ions
NO_3^-	-	Nitrate ions
NPYR	-	Nitrosopyrrolidone
NTDs	-	Neural tube defects
P/P_o		Relative pressure
PANI	-	Polyaniline
Pd NCs	-	Pladium nanoclusters
PEG	-	Polyethylene glycol
Ppy	-	Polypyrrole
PVA	-	Polyvinyl alcohol
PVP	-	Polyvinylpyrrolidone
RSD	-	Relative standard deviation
s	-	Second
UV	-	Ultraviolet
w/w%	-	Weight per weight percentage
wt%	-	Weigth percentage
XRD	-	X-ray diffraction
β-CN	-	Beta carbon nitride
μM	-	Micromolar

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

Nitrite (NO_2^-) and nitrate (NO_3^-) ions have been widely used in industrial and agricultural production and are ubiquitous in water and food, thus, they can be easily consumed by human. They have been classified as inorganic nitrogenous compounds that cause disease and hazardous to human health (Kroupova *et al.*, 2008; Li *et al.*, 2013; Wang *et al.*, 2009). Previous studies revealed that the healthy range for NO_2^- and NO_3^- in adult urine is in the range of 0.5 to 4 μM and 300 to 1800 μM, respectively (Tsikas *et al.*, 2007). High level of NO_2^- and NO_3^- in the human urine represents a significant risk to health since it is directly responsible for methemoglobinemia or "blue baby syndrome" (Almeida *et al.*, 2010; Dutt *et al.*, 2002; Hord *et al.*, 2009; Yeh *et al.*, 2012), carcinogenic nitrosamines (Li *et al.*, 2012), gastric cancer (Ensafi 2010; Palanisamy *et al.*, 2014; Yang *et al.*, 2014), spontaneous intrauterine growth restriction (Kyrtopoulos *et al.*, 1989) and neural tube defects (NTDs) (Brender *et al.*, 2004). In the body, NO_3^- can be converted to the NO_2^- that can further oxidize haemoglobin to form methemoglobin, which reduce the capability of the carrying oxygen to the whole body (Ensafi *et al.*, 2004).

Since the excess of the NO_2^- and NO_3^- in human may create health problems, a preventive way by monitoring the content of these ions in human body is very important. One of the established conventional methods is detection of NO_2^- and NO_3^- based on a spectrophotometry technique using a Griess reagent. The Griess reaction is specific for determination of NO_2^- quantification, but it also can be used

for determination of total NO_2^- and NO_3^-. Therefore, when using the Griess reagent, the quantification of NO_3^- has to be determined separately (Thikas *et al.*, 2007). Moreover, the spectrophotometric Griess reaction has numerous meddling factors since they are mostly inaccurate. Besides, the Griess reagent is also difficult to be reused due to the formation of complex compound during reaction with the analyte (Vahid *et al.*, 2012). Therefore, development of a reusable and sensitive sensor to detect the presence of NO_2^- and NO_3^- is still highly required.

In this study, metal-free carbon nitride (CN) is proposed for the first time as a potential material for the NO_2^- and NO_3^- detection. The CN is a stable allotrope of graphitic compound under ambient conditions. It is made up of nitrogen and carbon atoms as a building block in the structure to formed tri-*s*-triazine units (Huang e*t al.*, 2014; Lee e*t al.*, 2010; Lee e*t al.*, 2012; Liu e*t al.*, 2011; Sam, e*t al.*, 2014; Xu e*t al.*, 2014). Recently, the CN has attracted a great deal of scientific interest because some investigations have revealed its high photoluminescence (PL) intensity. These unique characteristics make the CN an ideal platform for bioimaging (Zhang e*t al.*, 2013), drug delivery (Lin e*t al.*, 2014) and sensing (Huang e*t al.*, 2014; Lee e*t al.*, 2010; Lee e*t al.*, 2012; Liu e*t al.*, 2011; Sam e*t al.*, 2014; Xu e*t al.*, 2014). The cubic mesoporous-ordered graphitic CN was reported as a selective optical sensor for the detection of trace amount of metal ions, such as copper ions (Lee e*t al.*, 2010). Besides, it was also reported to give high sensitive detection to cyanide with low limit of detection of 80 nM in aqueous solution and yet in human blood serum (Lee e*t al.*, 2012). The CN also showed good interactions with the *N*-nitrosopyrrolidine (Sam e*t al.*, 2014). Therefore, it is expected that the CN can also interact with other nitrogen-containing compounds and the function of the CN as a fluorescence sensor for both NO_2^- and NO_3^- detection is investigated in this study.

Although the CN is expected to be sensitive to NO_2^- and NO_3^- detection, but the modification of CN is still required for further improve its sensing performance. One of the approaches would be by increasing the amount of the active sites that able to improve the interactions between the CN and the NO_2^- and NO_3^- ions. In this study, some polymers, which are polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), polyethylene glycol (PEG) and polyaniline (PANI), were used as the

modifiers for the CN. These polymers can act as modifiers due to the presence of oxygen and nitrogen functional groups on the structure, which is expected to increase the possible sites for interactions with the analytes. Recently, it was reported that PVP solution showed good interaction with the NO_3^- (Tang *et al.,* 2015), while PVA composites were demonstrated as superior polymer matrix materials for photoluminescence due to the presence of OH functional groups in the backbone (Guan *et al.,* 2006). As for PEG, it was reported that PEG could be used as a solid matrix on the surface membrane sensor that enhanced the sensing performance for the detection of copper ions (Zheng *et al.,* 2003). On the other hand, PANI composite was reported to give high sensitivity towards ammonia exposure at room temperature (Wu *et al.* 2013), as well as NO_2 gas due to the conjugated properties of the PANI (Kumar *et al.,* 2010). Since the effect of these polymers as modifiers to improve the sensing cabability of the CN has never been reported yet, it is worthy to investigate the properties and effect of different types of polymers on the polymer-modified CN for NO_2^- and NO_3^- detection in sensing application.

1.2 Statement of Problem

The Griess reagent has been widely used in medical purpose to NO_2^- and NO_3^- detection in human body fluid such as urine, sweat and blood serum. In the Griess reaction, NO_2^- reacts with the sulphanilic acid which made up of aromatic amine in order to form a diazonium salt, which then reacts with tetrahydrobenzoquinoline to produce pink azo dye. Despite that this conventional method is only for single use due to the formation of complex compound between NO_2^- and the Griess reagent, which is difficult to be separated. Therefore, in the point of view of green chemistry, the development of a new reusable sensor material for detection of NO_2^- and NO_3^- would be a great benefit in this study.

In the previous studies, the CN has been reported to exhibit good sensing capability for detection of nitrogen containing compounds such as *N*-nitrosopyrrolidine (Sam e*t al.*, 2014) and cyanide (Lee e*t al.*, 2012). Unfortunately,

no study has been conducted to use the CN as a fluorescence sensor for the detection of NO_2^- and NO_3^-. Besides, the effect of CN properties, such as specific surface area that might affect the efficiency on the sensing performance for the detection of NO_2^- and NO_3^- is still unclear. In this study, since the surface area of the CN can be controlled via generation of mesoporosity (Lee e*t al.*, 2012), both bulk carbon nitride (BCN) and mesoporous carbon nitride (MCN) were investigated in this study to clarify the influence of specific surface area, porosity and functional group on the sensing performance for the detection of NO_2^- and NO_3^-.

Nonetheless, the modification of CN with polymers is one important parameter to further enhance the sensing performance of CN by increasing the sensing sites and promoting better interactions with NO_2^- and NO_3^-. Previous study reported that four types of polymers, which are PVP, PVA, PEG and PANI act as good modifiers for sensing application (Burgess *et al.*, 2008; Du *et al.,* 2007; Huang *et al.,* 2014; Inverson *et al.*, 2013; Mirmohseni *et al.,* 2003; Sidek *et al.,* 2013; Wang *et al.*, 2007; Wu *et al.*, 2013). These polymers have different functional groups that would give different effects on the properties and the sensing performance of the CN, which however, have never been addressed previously. Therefore, this study investigated the effect of different types of polymers on the formation and properties of the polymer-modified CN as fluorescence sensor for the detection of NO_2^- and NO_3^-.

1.3 Objectives

In this study, there are several objectives need to be accomplished in order to investigate the sensing performance of the CN (BCN and MCN) and the polymer-modified CN as sensor materials for the detection of the NO_2^- and NO_3^-. The objectives of this research are:

1) To synthesize the CN and the polymer-modified CN with various loading amounts of different polymers (PVP, PVA, PEG and PANI).

2) To determine the properties of the synthesized CN and polymer-modified CN materials.
3) To investigate the sensitivity, reproducibility, limit of detection (LOD), reusability, and selectivity of the CN and the polymer-modified CN for detection of the NO_2^- and NO_3^-.

1.4 Scope of Study

In this study, the BCN was synthesized only from urea precursor via thermal polymerization approach. The nanocolloidal silica (7 nm) was used as the only hard template for the preparation of the MCN. Meanwhile, four different types of polymers (PVP, PVA, PEG and PANI) were used as modifiers to prepare the series of polymer-modified CN with different loadings of polymers (1, 3 and 5 wt%) by using an impregnation method. The prepared materials were characterized using X-ray diffraction (XRD) diffractometry, Fourier transform infrared (FTIR) spectroscopy, nitrogen adsorption-desorption analysis, and fluorescence spectroscopy.

The comparison study on the sensing performance over BCN and MCN was conducted in order to point out the importance of specific surface area for the detection of NO_2^- and NO_3^-. On the other hand, the performance of the polymer-modified CN was compared to reveal the most suitable polymer as the modifier of the CN. The sensing performance was carried out via quenching tests at room temperature using the fluorescence spectroscopy. The ranges of the NO_2^- and NO_3^- amounts were fixed to 5-40 mol and 3-18$\times10^3$ mol, respectively. The reproducibility and reusability tests were conducted only on the best fluorescence sensor for the detection of NO_2^-. In addition, the effect of interference ions, which were sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), and chloride (Cl^-) were also examined using the best sensor.

REFERENCES

Adejoro, I., Oyeneyin, O. and Obaleye, J. (2013). Characterization of a Novel Polymeric Zinc (II) Complex Containing the Anti-Malarial Quinine as Ligand: A Theoretical Approach (Semi-Empirical and DFT Methods). *American Journal of Science Industrial Research,* 4**,** 111-22.

Aktan, F., 2004. INOS-mediated nitric oxide production and its regulation. *Life Science.* 75, 639.

Albanese, D., Di Matteo, M. and Alessio, C. (2010). Screen Printed Biosensors for Detection of Nitrates in Drinking Water. *Computer Aided Chemical Engineering.* 28**,** 283-288.

Alim, N. S., Hendrik, O. L. and Yuliati, L. (2015). Fabricated Metal-Free Carbon Nitride Characterizations for Fluorescence Chemical Sensor of Nitrate. *Journal Teknologi.* 76(13), 1-5.

Almeida, M. G., Serra, A., Silveira, C. M. and Moura, J. J. G. (2010). Nitrite Biosensing via Selective Enzymes-a Long but Promising Route. *Sensors,* 10, 11530-11555.

Amendola, V., Bergamaschi, G., Buttafava, A., Fabbrizzi, L. and Monzani, E. (2010). Recognition and Sensing of Nucleoside Monophosphates by a Dicopper(II) Cryptate. *Journal of the American Chemical Societ.* 132(1)**,** 147-156.

Ansari, M. B., Min, Byung. H., Mo, Y. H., and Park, S. E. (2011). CO_2 Activation and Protional Effect in the Oxidation of Cyclic Olefins over Mesoporous Carbon Nitride. *Green Chemistry.* 13, 1416-1421.

Ansari, M. O., Khan, M. M., Ansari, S. A. Lee, J. and Cho, M. C. (2014). Enhanced Thermoelectric Behaviour and Visible Light Activity of Ag@TiO_2/polyaniline Nanocomposite Synthesized by Biogenic-chemical Route. *Royal Society of Chemistry Advances.* 4, 23713

Asaad, J., and Salaun, F. (2011). Functionalized Poly(vinyl alcohol) Polymers as Chemodosimeter Material for the Colorimetric Sensing of Cyanide in Pure Water. *Sensors and Actuators B Chemical.* 157(1), 26-33.

Baiya, W., Zhenglong, W., and Weidong, Q. (2017). Polymidoamine Dendrimer-armed Fluorescent Magnetic Nanoparticles for Sensitive and Selective Determination of Nitrite in Beverages. *Sensor and Actuators B: Chemical.* 247, 774-779.

Biagiotti, V., Valentini, F., Tamburri, E., Terranova, M. L., Moscone, D. and Palleschi, G. (2007). Synthesis and Characterization of Polymeric Films and Nanotubule Nets Used to Assemble Selective Sensors for Nitrite Detection in Drinking Water. *Sensor and Actuator B: Chemica.,* 122(1), 236-242.

Bianchi, A., Bowman-James, K. and Garcia-Espana, E. (1996). *Supramolecular Chemistry of Anions*. New York: Wiley-VCH.

Brender, J. D., Olive, J. M., Felkner, M., Suarez, L., Marckwardt, W. and Hendricks., K. A. (2004). Dietary Nitrites and Nitrates, Nitrosatable Drugs, and Neural Tube Defects. *Epidemiology*, 15 (3), 330-336.

Brockmann, T. W. and Tour, J. M. (1995). Synthesis and Properties of Low-Bandgap Zwitterionic and Planar Conjugated Pyrrole-Derived Polymeric Sensors. Reversible Optical Absorption Maxima from the UV to the Near-IR. *Journal of the American Chemical Society,* 117(16), 4437-4447.

Bryan, N. S., Calvert, J. W., Gundewar, S. (2008). Dietary Nitrite Restores NO Homeostasis and is Cardio protective In Endothelial Nitric Oxide Synthase-Deficient Mice. *Free Radical Biology and Medicine.* 45 (4), 468-474.

Bryan, N. S., Grisham, M. B. (2007). Methods to Detect Nitric Oxide and its Metabolites in Biological Samples. *Free Radical Biology and Medicine.* 43 (5), 645-657.

Burgess, I. B., Rochon, P., and Cunningham, N. (2008). Photophysical of Commercial Red Dyes in Polymer Films. *Optical Materials.* 30, 1478-1483.

Can, F., Ozoner, S. K., Ergenekon, P. and Erhan, E. (2012). Amperometric Nitrate Biosensor Based on Carbon Nanotube/Polypyrrole/Nitrate Reductase Biofilm Electrode. *Materials Science and Engineering: C,* 32(1), 18-23.

Chan., T. Y. (1996). Food-borne Nitrates and Nitrites as a Cause of Methemoglobinemia. *The Southeast Asian Journal Tropical Medicine and Public Health.* 27, 189-192.

Chee, P. S., Arsat, R., He, X., Kalantar-zadeh, K., Arsat, M. and Wlodarski, W. (2010). Polivinylpyrrolidone/multiwall Carbon Nanotube Composites 36^{o} YX $LiTaO_3$ Surface Acoustic Wave H_2 Gas Sensor. Abstract Book of Enabling Science and Nanotechnology: 2010 International Conference, Kuala Lumpur, Malaysia.

Cheng, Y. H, Kung, C. W. Chou, L. Y. Vittal, R. and Ho, K. C. (2014). Poly(3,4-ethylenedioxythiophene) (PEDOT) Hollow Microflowers and their Application for Nitrite Sensing. *Sensors and Actuators B*. 192, 762-768.

Cho, H., Yun, C. W., Park, W. K., Kong, J. Y., Kim, K. S., Park, Y. (2004). Modulation of the Activity of Pro-Inflammatory Enzyme, COX_2 and iNOS, by Chrysin Derivatives. *Pharmacological Research*. 49 (1), 37-43.

Choi, K. and Hamilton, A. D. (2003). Rigid Macrocyclic Triamides as Anion Receptors: Anion-Dependent Binding Stoichiometries and 1H Chemical Shift Changes. *Journal of the American Chemical Societ.* 125(34), 10241-10249.

Christopher, B. J., Jennifer, P. M., and Jill, V. B. (2010). Review: Carbon Nanotube Based Electrochemical Sensors for Biomolecules. *Analytica Chimica Acta*. 662(2), 105-127.

Chu, Q., Medvetz, D. A. and Pang, Y. (2007). A Polymeric Colorimetric Sensor with Excited-State Intramolecular Proton Transfer for Anionic Species. *Chemistry of Material.,* 19(26), 6421-6429.

Cuartero, M., Crespo, G. A., and Bakker, E. (2015). Tandem Electrochemical Desalination–Potentiometric Nitrate Sensing for Seawater Analysis. *Analytical Chemistry*. 87 (16), 8084-8089.

Denuault, G. (2009). Eletrochemical Techniques and Sensors for Ocean Research. *Ocean Science*. 5, 697-710.

Du, T., Song, H. and Ilegbusi, O. J. (2007). Sol-gel derived ZnO-PVP nanocomposites thin film for superoxide radical sensor. *Materials Science and Engineering C*. 27, 414-420.

Dutt, J.; Davis, J. (2002). Current strategies in nitrite detection and their application to field analysis. *Journal of Environment Monitoring*. 4, 465-471.

Ensafi, A. A. and Amini, M. (2010). A Highly Selective Optical Sensor for Catalytic Determination of Ultra-trace Amounts of Nitrite in Water and Foods Based on Briliant Cresyl Blue as a Sensing Reagent. *Sensors and Actuators B: Chemistry*. 147, 61-66.

Fahey, J. M. (1990). Pretreatment Effects on Nitrite-induced Methemoglobinemia: Saline and Calcium Channel Anatagonists. *Pharmacology Biochemistry & Behavior*. 37, 457-459.

Fang, H-B., Luo, Y., Zheng, Y-Z., Ma, W., and Tao, Xia. (2016). Facile Large-Scale Synthesis of Urea-Derived Porous Graphitic Carbon Nitride with Extraordinary Visible-Light Spectrum Photodegradation. *Industrial & Engineering Chemistry Research*. 55 (16), 4506-4514.

Fischer, A. (2008). Reactive hard templating: from carbon nitrides to metal nitrides. Doctor Philosophy, Universitat Potsdam, Postdam.

Geetha, S. K. Kumari, S. S. P., and Muneera, C. I. (2002). Optical Limiting Behavior Of Congo-red and Crystal-violet Dyes in Solid Matrices for Nanosecond Pulses. *Journal of Materials Science Letters*. 21, 1339-1340.

Goettmann, F., Ficsher, A., Antonietti, M., and Thomas, A. (2006). Chemical Synthesis of Mesoporous Carbon Nitrides using Hard Templates and their use as a Metal-free Catalyst for Friedal-Craft Reaction of Benzene. *Angewandte Chemie International Edition*. 45 (27), 4467-4471.

Guo, Y. X., Zhang, Q. F., Shangguang, X. (2012). Spectrofluorimetric Determination of Trace Nitrite with O-Phenylenediamine Enhanced by Hydroxypropyl-B-Cyclodextrin. *Spectrochimica Acta Part A*. 101, 107-111.

Guo, Y-X., Zhang, Q.-F., hangguang, X., Zhen, G. (2013). Spectrofluorimetric Determination of Trace Nitrite with o-phenylenediamine Enhanced by Hydroxypropyl-β-Cyclodextrin *Spectrochimia Acta Part A: Molecular and Biomolecular Spectroscopy*. 101, 107-111.

Haijun, Z., Keisuke, K., Mitsutaka, O., and Naoki, T. (2014). Colloidal Au single-atom Catalysts Embedded on Pd Nanoclusters. *Journal of Materials Chemistry A*. 33, 13171-13752.

Ham, Y., Maeda, K., Cha, D., Takanabe, K., and Domen, K. (2013). Synthesis and Photocatalytic Activity of Poly (triazine imide). *Chemistry*. 8 (1), 218-224.

Heller, J., Kristeleit, H., Brensing, K. A., Woitas, R. P., Spengler, U., Sauerbruch, T. (1999). Nitrite and Nitrate Levels in Patients with cirrhosis of the Liver: Influence of Kidney Function and Fasting Rate. *Scandinavian Journal of Gastroenterology*. 34 (3), 297-302.

Honikel, K. O. (2008). The use and Control of Nitrate and Nitrite for the Processing of Meat Products. *Meat Sciences*. 78, 68-76.

Hord, N. G., Tang, Y., and Bryan, N. S. (2009). Food Sources of Nitrates and Nitrites: The Physiologic Context for Potential Health Benefits. *American Journal of Clinical Nutrition.* 90, 1-10.

Hossain, M. A., Kang, S. O., Llinares, J. M., Powell, D. and Bowman-James, K. (2003a). Elite New Anion Ligands: Polythioamide Macrocycles. *Inorganic Chemistr.,* 42(17), 5043-5045.

Hossain, M. A., Kang, S. O., Powell, D. and Bowman-James, K. (2003b). Anion Receptors: A New Class of Amide/Quaternized Amine Macrocycles and the Chelate Effect. *Inorganic Chemistr.* 42(5), 1397-1399.

Huang, H., Chen, R., Ma, J., Yan, L., Zhao, Y., Wang, Y., Zhang, W., Fan, J., and Chen, X. (2014). Graphitic Carbon Nitride Solid Nanofilms for Selective and Recyclable sensing of Cu^{2+} and Ag^{+} in Water and Serum. *Chemical Communications*. 50, 15415-15418.

Huang, J. (2006). Syntheses and Applications of Conducting Polymer Polyaniline Nanofibers. *Pure Applied of Chemistry*. 78 (1), 15-27.

Huang, J., Xie, G., Zhou, Y., Xie, T., and Yang, G. (2014). NO_2 Gas Sensor Based on Polyvinylpyrrolidone/Reduced Grapheme Oxide Nanocomposite. IEEE Workshop on Advanced Research and Technology in Industry Application (WARTIA).

Inverson, N. M, Barone, P. W., Shandell, M., Trudel, L. J., Sen, S., Ivanoc, V., Atolia, E., Farias, E., McNicholas, T. P., Reuel, N., Parry, N. M. A., Wogan, G. N., and Strano, M. M. (2013). In Vivo Biosensing via Tissue Localize Near Infrared Fluorescent Single Walled Carbon Nanotube. *National Nanotechnology*, 8 (11), 873-80.

Isaad, J. and El. A. A. (2011). A Novel Glycoconjugated N-acetylamino Aldehyde Hydrazone Azo Dye as Chromogenic Probe for Cyanide Detection in Water. *Analytical Chimica Acta.* 694 (1-2), 120-127.

Işıklan, M., Saeed, M. A., Pramanik, A., Wong, B. M., Fronczek, F. R. and Hossain, M. A. (2011). AC 3 Symmetric Nitrate Complex with a Thiophene-Based Tripodal Receptor. *Crystal Growth Design.* 11(4), 959-963.

Kang, S. O., Begum, R. A. and Bowman-James, K. (2006). Amide-Based Ligands for Anion Coordination. *Angewandte Chemie International Edition.* 45(47), 7882-7894.

Kang, S. O., Llinares, J. M., Powell, D., VanderVelde, D. and Bowman-James, K. (2003). New Polyamide Cryptand for Anion Binding. *Journal of the American Chemical Societ.* 125(34), 10152-10153.

Knobeloch, L. Salna, B., Hogan, A., Postle, J., Anderson, H. (2000). Blue Babies and Nitrate-contaminated Well Water. *Environmental Health Perspectives.* 108 (7), 675-678.

Kong, J., Zhou, C., Michael, G., Peng, S., Kyeongjae, C. and Dai, H. (2000). Nanotube Molecular Wires as Chemical Sensors. *Science.* 287 (5453), 622-625.

Kroupova, H., Machova, J., and Svobodova, Z. (2005). Nitrite Influence on Fish: A Review. *Veterinarni Medacina.* 50, 461-471.

Kumar, R., Singh, S., and Misra, A. K. (2010). Development of NO_2 Gas Sensor Based on Plasma Polymerized Nanostructure Polyaniline Thin Film. *Journal of Minerals & Materials Characterization & Engineering.* 9 (11), 997-1006.

Laith A. M., Koo, S., Kourosh, K. Z., Jodan, D., Seung H. H, Robert, W. K, Richard B. K., Dan L., Xing, L., Gou, Samuel J. and Wojtek W. (2010). Graphene/polyaniline Nanocomposite for Hydrogen Sensing, *Journal Physical Chemistry.* 114, 16168-16173.

Lakowicz, J. R. (2006). Principles of Fluorescence Spectroscopy. Springer, 277-954.

Lawley, P. (1990). N-nitroso Compounds. In Chemical Carcinogenic and Mutagenesis I, Springer, Berlin Heidelberg. 409-469.

Lee, D. H. (1970). Nitrates, Nitrites, and Methemoglobinemia. *Environmental Research.* 3, 484-511.

Lee, E. Z., Jun, Y. S., Hong, W. H., Thomas, A., and Jin, M. M. (2010). Cubic Mesoporous Graphitic Carbon(IV) Nitride: An all-in-one Chemosensor for Selective Optical Sensing of Metal ions. *Angewandte Chemie International Edition.* 49 (50), 9706-9710.

Lee, E. Z., Lee, S.U., Heo, N. S., Stucky, G. D., Jun, Y. S., and Hong, W. H. (2012). A Fluorescent Sensor for Selective Detection of Cyanide Using Mesoporous Graphitic Carbon (IV) Nitride. *Chemistry Communications.* 48, 3942-3944.

Lee, S. C., Lintang, H. O. and Yuliati L. (2012). A urea precursor to Synthesis Carbon Nitride With Mesoporousity for Enhanced Activity in The

Photocatalytic Removal of Phenol. *Chemistry-An Asian Journal*. 7 (9), 2139-2144.

Li, S. J., Zhao, G. Y., Zhang, R. X., Hou, Y. L., Liu, L., Pang, H. (2013). A sensitive and Selective Nitrite Sensor Based on a Glassy Carbon Electrode Modified with Gold Nanoparticles and Sulfonated Graphene. *Microchimica Acta*, 180, 821-827.

Lin, C. Y., Vasantha, V. S., and Hoa, K. C. (2009). Detection of Nitrite using Poly (3,4-ethylenedioxythiophene) modified SPCEs. *Sensors and Actuators B*. 140, 51-57.

Lin, L-S., Cong, Z-X., Li., J., Ke, K-M., Guo, S-S., Yang, H-H., and Chen, G-N. (2014)Graphitic-phase C_3N_4 Nanosheets as Efficient Photosensitizers and pH-Responsive Drug Nanocarriers for Cancer Imaging and Therapy. *Journal of Materials Chemistry B*. 2, 1031-1037.

Liu, H., Yang, G., Abdel-Halim, E., and Zhu, J. J. (2013). Highly Selective and Ultrasensitive Detection of Nitrite Based on Fluorescent Gold Nanoclusters. *Talanta*. 104, 135-139.

Liu, J., Zhang, T., Wang, Z., Dawson, G., and Chen, W. (2011). Simple Pyrolysis of Urea Into Graphitic Carbon Nitride With Recyclable Adsorption and Photocatalytic Activity. *Journal of Materials Chemistry*. 21, 14398-14401.

Long, W. Y., Li, M. S., Liu, Y. X., Siu, K. L., and Wang, J. M. (2003). Synthesis of Beta Carbon Nitride Nanosized Crystal Trough Mechanochemical Reaction. *Journal of Physics: Condensed Matter*. 15, 309-314.

Madasamy, T., Pandiaraj, M., Balamurugan, M., Bhargava, K., Sethy, N. K. and Karunakaran, C. (2014). Copper, Zinc Superoxide Dismutase and Nitrate Reductase Coimmobilized Bienzymatic Biosensor for the Simultaneous Determination of Nitrite and Nitrate. *Biosensors and Bioelectronics.* 52**,** 209-215.

Mansor, A., Mei, Y. T., Kamyar, S., Mohd, Z. H., and Jenn, J. L. (2011). Green Synthesis and Characterization of Silver/Chitosan/Polyethylene Glycol Nanocomposites without any Reducing Agent. *International Journal of Melecular Sciences.* 12, 4872-4884.

Marcone A. L., Gláucia S. T., Mara C. G., and Fernando A. S. V. (2012). Optimization of an Alternative Methodology for Simultaneous Analysis of Nitrite and Nitrate in Water From Urban Stream by Capillary

Electrophoresis Under Direct UV Detection. *American Journal of Analytical Chemistry*. 3, 484-490.

Martinez-Máñez, R., Sancenón, F., Belén Descalzo, A. and Rurack, K. (2009). *Supramolecular Hybrid Materials- Integrating Functionality with Sensing. Macromolecules Containing Metal and Metal-Like Elements*. Germany: John Wiley & Sons, Inc.

McQuade, D. T., Hegedus, A. H. and Swager, T. M. (2000a). Signal Amplification of a "Turn-On" Sensor: Harvesting the Light Captured by a Conjugated Polymer. *Journal of the American Chemical Society*. 122(49), 12389-12390.

McQuade, D. T., Pullen, A. E. and Swager, T. M. (2000b). Conjugated Polymer-Based Chemical Sensors. *Chemical Reviews*. 100(7), 2537-2574.

Mesquita, R. B. R., Ferreira, M. T. S. O. B., Segundo, R. L. A., Teixeira, C. F. C. P., Bordalo, A. A., Rangel, A. O. S. S. (2009). Development of a Sequential Injection System for the Determination of Nitrite and Nitrate in Waters with Different Salinity: Application to Estuaries in NW Portugal. *Analytical Methods*. 1, 195-202.

Miranda, K. M., Espey, M. G. Wink, D. A. (2001). A Rapid, Simple Spectrophotometric Method for Simultaneous Detection of Nitrate and Nitrite. *Nitric oxide*. 5, 62-71.

Mirmohseni, A and Oladegaragoze, A. (2003). Construction of Sensor for Determination of Ammonia and Aliphatic Amine using Polyvinylpyrrolidone Coated Quartz Crystal Microbalance. *Sensors and Actuators B: Chemical*. 89, 164-172.

Miyado, T., Tanaka, Y., Nagai, H., Takeda, S., Saito, K., Fukushi, K., Yoshida, Y., Wakida, S. and Niki, E. (2004). Simultaneous Determination of Nitrate and Nitrite in Biological Fluids by Capillary Electrophoresis and Preliminary Study on Their Determination by Microchip Capillary Electrophoresis, *Journal of Chromatography A*. 1051, 185-191.

Moldovan, Z. (2010). Kinetic Spectrophotometric Determination of Nitrite with Tropaeolin Bromate System. *Analytical Letters*. 43, 1344-1354.

Moorcroft, M. J., Davis, J. and Compton, R. G. (2001). Detection and Determination of Nitrate and Nitrite: A Review. *Talanta*. 54(5), 785-803.

Namasivayam, C. and Sageetha, D. (2005). Removal and Recovery of Nitrate from Water by $ZnCl_2$ Activated Carbon from Coconut Coir Pith, and Agricultural Solid Waste. *Indian Journal of Chemical Technology*. 12, 513-521.

Palanisamy, S. Karuppiah, C. Chen, S. M. and Periakaruppan, P. (2014). Highly Sensitive and Selective Amperometric Nitrite Sensor Based on Electrochemically Activated Graphite Modified Screen Printed Carbon Electrode. *Journal of Electroanalytical Chemistry*. 727, 34-38.

Pietrzak, M. and Meyerhoff, M. E. (2009). Nitrite-selective Liquid Membrane Elctrode. *Analytical Chemistry*, 81 (9), 3637-3644.

Plumeré, N. (2013). Interferences from Oxygen Reduction Reactions in Bioelectroanalytical Measurements: The Case Study of Nitrate and Nitrite Biosensors. *Analytical and Bioanalytical Chemistry*. 405(11), 3731-3738.

Prasad, G. K., Takei, T., Yonesaki, Y., Kumada, N., Kinomuran N. (2006). Hybrid Nanocomposite Based on $NbWO_6$ Nanosheets and Poly-aniline. *Materials Letters*. 60, 3727–3730.

Qi, S., Zhang, X., Yang, X., Chen, K., Zhang, L., Yand, G., Liang, X., and Tian, T. (2007). Adsorption Characteristic and Limiting Effect of Congo Red Doped PVA film. *Optical Materials*. 29, 1348-1351.

Quan, D., Shim, J. H., Kim, J. D., Park, H. S., Cha, G. S. and Nam, H. (2005). Electrochemical Determination of Nitrate with Nitrate Reductase-Immobilized Electrodes Under Ambient Air. *Analytical chemistry*. 77(14), 4467-4473.

Rastogi, P. K., Ganesan, V. and Krishnamoorthi, S. (2014). A Promising Electrochemical Sensing Platform Based on a Silver Nanoparticles Decorated Copolymer for Sensitive Nitrite Determination. *Journal of Materials Chemistry A*, 2, 933-943.

Ricciardi, R.; Auriemma, F.; De Rosa, C.; Lauprêtre, F. (2004). X-ray Diffraction Analysis of Poly(vinyl alcohol) Hydrogels, Obtained by Freezing and Thawing Techniques. *Macromolecules*. 37, 1921-1927.

Rider, B., Mellon, M. (1946). Calorimetric Determination of Nitrites. *Industrial and Engineering Chemistry Analytical Edition*. 18, 96-99.

Rochat, S. and Swager, T. M. (2013). Conjugated Amplifying Polymers for Optical Sensing Applications. *American Chemical Society Applied Materials & Interfaces*. 5(11), 4488-4502.

Rong, M., Lin, L., Song, X., Wang, Y., Zhong, Y., Yan, J., Feng, Y., Zeng, X. and Chen, X. (2015). Fluorescence Sensing of Chromium(VI) and Ascorbic Acid using Graphitic Carbon Nitride Nanosheets as a Fluorescent "Switch". *Biosensors and Bioelectronics*. 68, 210-217.

Rostami, A. and Taylor, M. S. (2012). Polymers for Anion Recognition and Sensing. *Macromolecular Rapid Communications*. 33(1), 21-34.

Saini, P., Bhandari, H., Choundary, V., and Dhawan, K. (2008). Thermal, Spectroscopic and Electrical Transport Properties of Processable Poly(Aniline-Co-Alkylaniline) Copolymers. *Indian Journal of Engineering & Materials Sciences*. 15, 497-504.

Sakamoto, M., Tachikawa, T., Kim, S. S., Fujitsuka, M., and Majima, T. (2007). Fabrication of Chromophore-Functionalized Gold Nanoparticles-Poly(Vinyl Alcohol) Thin Film Nanocomposite: New Coordination Method using the Ni(II)-nitrilotriacetic Acid Complex Formation. *Chemical Physics and Physical Chemistry*. 8, 1701-1706.

Saleem, M., Abdullah, R., Hong, I. S., and Lee, K. H. (2013). Turn-On Type Fluorogenic and Chromogenic Probe for the Detection of Trace Amount of Nitrite Ion in Water. *Bulletin of the Korean Chemical Society*. 34 (2013) 389-398.

Sam, M. S., Lintang, H. O., Sanagi, M. M., Lee, S. L., and Yuliati, L. (2014) Mesopore Carbon Nitride for Adsorption and Fluorescence Sensor of N-nitrosopyrollidone. *Spectrochimia Acta Part A: Molecular and Biomolecular Spectroscopy*. 124, 357-364.

Sesha, V. and Tamer, U. (2014). Fluorescence from Graphene Oxide and the Influence of Ionic, p-p Interactions and Heterointerfaces: Electron or Energy Transfer Dynamics. *Physical Chemistry Chemical Physics*. 16, 21183-21203.

Sharma, B. K., Gupta, A. K., Kharea, N., Dhawan, S. K., and Gupta, H. C. (2006) Synthesis and Characterization of Polyaniline–ZnO Composite and its Dielectric Behavior. *Synthetic Metals*. 159, 391-395

Shen, W., Ren, L., Zhou, H., Zhang, S., and Fan, W. (2011). Facile One-Pot Synthesis Of Biomodal Mesoporous Carbon Nitride and Its Function as a Lipase Immobilization Support. *Journal of Materials Chemistry*. 21 (11), 3890-3894.

Sheng, W., Chen, Q., Yang, P., and Chen, C. (2015). Synthesis, Characterization, and Enhanced Properties of Novel Graphite-Like Carbon Nitride/Polyimide Composite Films. *High Performance Polymer*. 27 (8), 950-960.

Shi, L., Liang, L., Wang, F., Ma, J., and Sun, J. (2014). Polycondensation of Guanidine Hydrochloride Into a Graphitic Carbon Nitride Semiconductor with a Large Surface Area aAs a Visible Light Photocatalyst. *Catalysis Science & Technology*. 4, 3235-3245.

Sidek, A., Arsat, R., He, X., Zadeh, K. K. and Wlodarski, W. (2013). Polyvinlspyrrolidone/polyaniline Composite Based 36^{o} YX $LiTaO_3$ Surface Acoustic Wave H_2 Gas Sensor. *Sains Malaysiana*. 42 (2), 213-217.

Singh, A. S. and Sun, S.-S. (2012). Recognition, Encapsulation, and Selective Fluorescence Sensing of Nitrate Anion by Neutral C3-Symmetric Tripodal Podands Bearing Amide Functionality. *The Journal of Organic Chemistry*. 77(4), 1880-1890.

Sisson, A. L., Clare, J. P., Taylor, L. H., Charmant, J. P. H. and Davis, A. P. (2003). Perturbing the Hofmeister Series: A Steroid-Based Anion Receptor with Preorganised Quaternary Ammonium and H-Bond Donor Groups. *Chemical Communications*. 17, 2246-2247.

Spadavecchia, J, Movia, D., Moore, C., Manus, M. C., Moustaoui, H., Casale, S., Volkov, Y., Prina-Mello, A. (2016). Targeted Polyethylene Glycol Gold Nanoparticles for the Tretment of Pancreatic Cancer: from Synthesis to Proof-of-concept in Vitro Studies. *International Journal of Nanomedicine*. 11, 791-822.

Stamenov, P., Madathil R., Coey, J. M. D. (2012). Dynamic Response Of Ammonia Sensors Constructed from Polyaniline Nanofibre Films with Varying Morphology. *Sensors and Actuators B: Chemical*. 161, 989-999.

Stetter, J. R. Stetter, Penrose, W. R. and Yao, S. (2003). Sensors, Chemical Sensors, Electrochemical Sensors, and ecs. *Journal of the Electrochemical Society*. 150(2), 11-16.

Strianese, M., Milione, S., Bertolasi, V. and Pellecchia, C. (2013). Iron and Manganese Pyridoxal-Based Complexes as Fluorescent Probes for Nitrite and Nitrate Anions in Aqueous Solution. *Inorganic Chemistry*. 52(20), 11778-11786.

Suzuki, H., Iijima, K., Moriya, A., McElroy, K., Scobie, G., Fyfe, V., McColl, K. (2003). Conditions for Acid Catalysed Luminal Nitrosation are Maximal at the Gastric Cardia. *Gut*. 52, 1095-1101.

Tămăşan, M and Simon, V. (2011). Thermal Structural, Characterization of Polyvinyl Alcohol-kaoline Nanocomposites. *Digest Journal of Nanomaterials and Biostructures*. 6 (3), 1311-1316

Tang, C. M., Tian, Y. H., and Hsu, S. H. (2015). Poly(vinyl alcohol) Nanocomposites Reinforced with Bamboo Charcoal Nanoparticles: Mineralization Behavior and Characterization. *Materials*. *8*, 4895-4911

Tang, I. H., Hendrik, O. L. and Yuliati, L. (2016). Detection of Nitrite and Nitrate Ions in Water by Graphene Oxide as a Potential Fluorescence Sensor. *IOP Conference Series: Materials Science and Engineering*. 8-9 September, Solo, Indonesia, 012027.

Tang, I. H., Sundari, R., Lintang, H. O., and Yuliati, L. (2015). Polyvinylpyrrolidone as a New Fluorescent Sensor for Nitrate Ions. Book of Abstract 27th Regional Symposium of Malaysia Analytical Sciences.

Tannous, M., Amin, R., Popoff, M. R., Fiorentini, C., Kowluru, A. (2001). Positive Modulation by Ras of Interleukin-1b-Mediated Nitric Oxide Generation in Insulin-Secreting Clonal B (HIT-T15) Cells. *Biochemical Pharmacology*. 62 (11), 1459-1468.

Thomas, A., Fischer, A, Goettmann, F., and Antonietti, M. (2012). Graphitic Carbon Nitride Materials: Variation of Structure and Morphology and Their Use as Metal-Free Catalysts. *Journal of Materials Chemistry*. 18, 4893-4908.

Tian. J., Liu, Q., Asiri, A. M., Al Youbi, A. O., and Sun, X. (2013). Ultrathin Graphitic Carbon Nitride Nanosheet: a Highly Efficiency Fluorescence for Rapid, Ultrasensitive Detection of Cu^{2+}. *Analytical Chemistry*. 85 (11), 5595-5599.

Tsikas, D. (2007). Analysis of Nitrate and Nitrite in Biological Fluids by Assays Based on The Griess Reaction: Appraisal of The Griess Reaction in The L-Arginine/Nitric Oxide Area of Research. *Journal of Chromatography B*. 851, 51-70.

Vahid, S., Dashti-Khavidaki, S., Ahmadi, F., Amini, M., Salehi Surmaghi, M. H. (2012). Effect of Herbal Medicine Achillea Millefolium on Plasma Nitrite

and Nitrate Levels in Patients with Chronic Kidney Disease: A Preliminary Study. *Iran Journal of Kidney Diseases.* 6, 350-354.

Wang, B., Guan, X., Hu, Y., Su, Z. (2007). Preparation and Fluorescent Properties of Poly (Vinyl Alcohol) Beating Coumarin. *Polymer Advanced Technology.* 18, 529-533.

Wang, L., Li, B., Zhang, L., Zhang, and Zhao, L. (2012). Fabrication and Characterization of a Fluorescent Sensor Based Rh 6G-Functionlized Silica Nanoparticles for Nitrite Ion Detection. *Sensors and Actuators B: Chemistry*. 171, 946-953.

Wang, X., Adams, E., Van Schepdael, A. (2012). A Fast and Sensitive Method for the Determination of Nitrite in Human Plasma by Capillary Electrophoresis with Fluorescence Detection. *Talanta.* 97, 142-144.

Wang, Y., Wang, X., and Antonietti, M. (2011). Polymeric Graphitic Carbon Nitride for Heterogeneous Photocatalysis. *American Chemical Society Catalysis.* 2 (8), 1596-1606.

Wanning, Y., Hong, Z., Junxin, L., Xinyi, P., Yuping, H., Wei, G., and Ling, Ye. (2018). Carbon Dots with Red-shifted Photoluminescence by Fluorine Doping for Optical Bio-imaging. *Carbon.* 128, 78-85.

Whittington, C. L., Maza, W. A., Woodcock, H. L. and Larsen, R. W. (2012). Understanding Ion Sensing in Zn(II) Porphyrins: Spectroscopic and Computational Studies of Nitrite/Nitrate Binding. *Inorganic Chemistry,* 51(8), 4756-4762.

Wu, K., Shi, L., Zhang, W., An, Y., Zhang, X., Li, Z. and Zhu, X. (2006b). Thermoresponsiveness of Hybrid Micelles from Poly(Ethylene Glycol)-Block-Poly (4-Vinylpyridium) Cations and SO_4^{2-} Anions in Aqueous Solutions. *Langmuir.* 22(4), 1474-1477.

Wu, K., Shi, L., Zhang, W., An, Y., Zhu, X.-X., Zhang, X. and Li, Z. (2005). Formation of Hybrid Micelles between Poly(Ethylene Glycol)-Block-Poly(4-Vinylpyridinium) Cations and Sulfate Anions in an Aqueous Milieu. *Soft Matter.* 1(6), 455-459.

Wu, Z., (2013). Enhanced Sensitivity of Ammonia Sensor Using Grapheme/Polyaniline Nanocomposite. *Sensors and Actuators B.* 178, 485-493.

Xu, H., Yan, J., and Xu, Y. G. (2013). Novel Visible-Light-Driven AgX/graphite-like C_4N_3 (X = Br, I) Hybrids Materials with Synergistic Photocatalytic Activity. *Applied Catalysis B*. 129, 182-193.

Xu, L., Xia, J., Wang, L., Ji, H., Qian, J., Xu, H., Wang, K. and Li, H. (2014), Graphitic Carbon Nitride Nanorods for Photoelectrochemical Sensing of Sensing Trace Copper (II) ions. *European Journal of Inorganic Chemistry*, 3665-3673.

Yamaguchi, S., Jin, R.-Z. and Tamao, K. (1998). Modification of the Electronic Structure of Silole by the Substituents on the Ring Silicon. *Journal of Organometallic Chemistry*. 559(1), 73-80.

Yan, S. C., Li, Z. S., and Zou, Z. G. (2009). Photodegradation Performance of g-C_4N_3 Fabricated by Directly Heating Melamine. *Langmuir*, 25 (17), 10397-10401.

Yang, S. and Meyerhoff, M. E. (2013). Study of Cobalt(III) Corrole As The Neutral Ionophore For Nitrite And Nitrate Detection Via Polymeric Membrane Electrodes. *Electroanalysis*. 25, 2579-2585.

Yang, S. Wo, Y. and Meyerhoff, M. E. (2014). Polymeric Optical Sensors for Selective and Sensitive Nitrite Detection using Cobalt(III) Corrole and Rhodium(III) Porphyrin as Ionophores. *Analytica Chimica Acta*. 843, 89-96.

Yanke, C. and Ling, Z. (2009). Enhanced fluorescence sensing of amine vapor based ultrathin nanofibers. Chemistry *Communication*. 5106-5108.

Yeh, T. S., Liao, S. F., Kuo, C. Y. and Hwang, W. I. (2012). Investigation of the Nitrate and Nitrite Contents in Milk and Milk Powder in Taiwan. *Journal of Food and Drug Analysis*. 21 (1), 73-79.

Yuri, B. (2006). Probing the Interaction of Poly (vinylpyrrolidone) with Platinum Nanocrystals by UV-Raman and FTIR. *Journal of Physical Chemistry B*. 110, 23052-23059.

Zhang, S., Han, G., Xiang, Z., Zhang, S and Zhang, X. (2014). Multiplex DNA Assay Based on Nanoparticle Probes by Single Particle Inductively Coupled Plasma Mass Spectroscopy. *Analytical Chemistry*. 86 (7), 3541-3547.

Zhang, W., Zhang, Q., Dong, F., and Zhao, Z. (2013). The Multiple Effects of Precursors on The Properties of Polymeric Carbon Nitride. *International Journal of Photoenergy*. Article ID: 685038. 1-9.

Zhang, X, Ji, L., Zhang, S., and Yang, W. (2007). Synthesis a Novel Polyaniline-intercalated Layered Manganese Oxide Nanocomposites as Electrode Materials for Electrochemisal Capacitor. *Journal of Power Source.* 1017-1023.

Zhang, Y., Liu, J., Wu, G. and Chen, W. (2012). Porous Graphitic Carbon Nitride Synthesized *Via* Direct Polymerization of Urea For Efficient Sunlight-Driven Photocatalytic Hydrogen Production. *Nanoscale.* 4, 5300-5303.

Zhou, H. H, Li, T., Li, C. Y, Xia, Z. Y., Duan, Y-Y. (2015). Polyurethane/poly(vinyl alcohol) Hydrogel Coating Improves the Cytocompatibility of Neural Electrodes. *Neutral Regeration Research.* 10 (12),

Zhou, S. L, Mo, S. S, Zou, W. J., Jiang, F. P., Zhou, T. X., and Yuan, D. S. (2011). Preparation of Polyaniline/2-Dimensional Hexagonal Mesoporous Carbon Composite for Supercapacitor. *Synthetic Metals.* 161 (15-16), 1623-1628.

Zhou, S., Xie, M., Yuan, X., Zeng, F., Zou, W., and Yuan, D. (2012). Polyaniline/AgCl Hybrid Materials for Selective Determination of Dopamine by Electrochemical Methods. *American Journal of Analytical Chemistry.* 3(5), 19443-19450.