

**SYNTHESIS OF PYRENE-FUNCTIONALIZED SILICA
NANOMATERIAL FOR THE DETECTION OF MERCURY**

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A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMISTRY

MAY 2015

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

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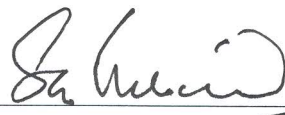


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To the soul of my father in heaven. To my great mother. To my siblings, relatives and all
of my friends

ACKNOWLEDGMENTS

First of all, I would like to thank Allah for everything and ask him to support me and direct me to the right path.

I would like also to thank King Fahd University of Petroleum and Minerals for giving me this opportunity to pursue my study here.

I want to express my deep thanks for Dr. Ahsan Ul-Haq Qurashi for giving me support and time. I appreciate his efforts that are a significant reason behind qualifying me into the academic research.

Special thanks for my committee members; Dr. Safyan Akram Khan and Dr. Nisar Ullah for their help and support.

I would like also to thank Dr. Abdulaziz Al-Assadi the chairman of Chemistry department. My thanks go for all faculty members as well.

Finally, I like to thank my family and my best friends for their sympathy and support.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS	VI
LIST OF TABLES	VIII
LIST OF FIGURES	IX
LIST OF ABBREVIATIONS	XI
ABSTRACT(ENGLISH).....	XIII
ABSTRACT(ARABIC)	XIV
CHAPTER 1 INTRODUCTION.....	15
CHAPTER 2 LITERATURE REVIEW	19
CHAPTER 3 OBJECTIVES AND METHODOLOGY	27
3.1 Objectives	27
3.2 Methodology	28
CHAPTER 4 EXPERIMENTAL PROCEDURE	31
4.1 Synthesis of Silica Nanoparticles	31
4.2 Synthesis of pyrene-attached silica nanoparticles.....	32
4.3 Characterization of the synthesized pyrene-attached silica nanoparticles	35
4.4 Testing the synthesized nanoparticles for the detection of mercury ion	35
CHAPTER 5 RESULTS AND DISCUSSION.....	36

5.1	Characterization of the pyrene-attached silica nanoparticles.....	36
5.1.1	Scanning Electron Microscope (SEM) Imaging	36
5.1.2	Fourier Transfer Infrared Spectroscopy (FT-IR).....	39
5.1.3	Nuclear Magnetic Resonance (NMR) spectra	42
5.1.4	XRD Analysis	45
5.2	Use of the pyrene-functionalized Silica Nanoparticles for the Detection of Mercury	46
5.2.1	Photoluminescence study of the pyrene-attached silica nanoparticles.	46
5.2.2	The effect of mercury ion on the intensities of the nanoparticles within time	65
5.3	Other Applications of the pyrene-functionalized silica nanoparticles.....	75
CHAPTER 6 CONCLUSION.....		76
REFERENCES.....		77
VITAE.....		81

LIST OF TABLES

Table 5-1 The decrease in PL intensities of sensor as Hg^{2+} increases.....	60
Table 5-2 PL intensities of sensing material with Hg^{2+} ions before and after two days...	66

LIST OF FIGURES

Figure 3- 1 Chemical synthesis of pyrene-silane conjugates (4-6).....	29
Figure 4- 1 Formation of the silanol product from the APTES and TEOS precursors....	33
Figure 4- 2 The attachment of pyrene through peptide coupling reaction.....	33
Figure 5- 1 SEM image of silica nanoparticles.....	37
Figure 5- 2 More focused SEM of the silica nanoparticles	38
Figure 5- 3 FT-IR spectra of the silica nanoparticles before the attachment of pyrene....	40
Figure 5- 4 FT-IR spectra of the silica nanoparticles after the attachment of pyrene	41
Figure 5- 5 ^1H NMR of the silica nanoparticles before the attachment of pyrene.....	43
Figure 5- 6 ^1H NMR of the silica nanoparticles after the attachment of pyrene.	44
Figure 5- 7 XRD pattern of the silica nanoparticles	45
Figure 5- 8 PL intensity of the blank sample of sensing material versus wavelength.....	47
Figure 5- 9 Photoluminescence intensity of the sensor in 1 ppb Hg (II)	48
Figure 5- 10 Photoluminescence intensity of the sensor in 3 ppb Hg (II)	49
Figure 5- 11 Photoluminescence intensity of the sensor in 5 ppb Hg (II)	50
Figure 5- 12 Photoluminescence intensity of the sensor in 7 ppb Hg (II)	51
Figure 5- 13 Photoluminescence intensity of the the sensor in 9 ppb Hg (II)	52
Figure 5- 14 Photoluminescence intensity of the the sensor in 11 ppb Hg (II)	53
Figure 5- 15 Photoluminescence intensity of the sensor in 13 ppb Hg (II)	54
Figure 5- 16 Photoluminescence intensity of the sensor in 15 ppb Hg (II)	55
Figure 5- 17 Photoluminescence intensity of the sensor in 17 ppb Hg (II)	56
Figure 5- 18 Photoluminescence intensity of the sensor in 18 ppb Hg (II)	57
Figure 5- 19 Photoluminescence intensity of the sensor in 20 ppb Hg (II)	58
Figure 5- 20 PL intensities of the sensing material versus the concentration of Hg^{2+}	62
Figure 5- 21 Complex formation between mercury and pyrene in sensing material	63
Figure 5- 22 Stern-Volmer equation plot.....	64
Figure 5- 23 The difference in photoluminescence intensities before and after two days	66
Figure 5- 24 intensities of sensing material with 11 ppb of Hg^{2+} before two days.....	67
Figure 5- 25 PL intensities of sensing material with 13 ppb of Hg^{2+} before two days	68
Figure 5- 26 PL intensities of sensing material with 15 ppb of Hg^{2+} before two days	69
Figure 5- 27 PL intensities of sensing material with 17 ppb of Hg^{2+} before two days	70
Figure 5- 28 PL intensities of sensing material with 11 ppb of Hg^{2+} after two days	71
Figure 5- 29 PL intensities of sensing material with 13 ppb of Hg^{2+} after two days	72
Figure 5- 30 PL intensities of sensing material with 15 ppb of Hg^{2+} after two days	73

Figure 5- 31 PL intensities of sensing material with 17 ppb of Hg^{2+} after two days	74
Figure 5-32 Fluorescence of pyrene- attached silica nanoparticles in water and ethanol.	75

LIST OF ABBREVIATIONS

APTES	3-Aminopropyltriethsilane
TEOS	Triethoxysilane
SEM	Scanning electron microscope
NMR	Nuclear magnetic resonance
FT-IR	Fourier transfer infrared spectroscopy
XRD	X-Ray Diffraction
WHO	World Health Organization
Ppb	Parts per billion
DMDES	Dimethoxydiethoxysilane
QDs	Quantum dots
FRET	Fluorescence resonance energy transfer
ECL	Electroluminescence
TMB	Tetramethylbenzidine
MLCT	Metal to ligand charge transfer
UV-vis	Ultraviolet-visible spectroscopy
DLS	Dynamic light scattering

HMDS	Hexamethyl disilazane
PET	Photoinduced electron transfer
ICT	Internal charge-transfer
SiNPs	Silica nanoparticles
CTAB	Cetrimonium bromide
HOBt	Hydroxybenzotriazole
EDCI	1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide
DCM	Dichloromethane
NaOH	Sodium Hydroxide
PL	Photoluminescence

ABSTRACT

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Thesis Title : Synthesis of Pyrene-functionalized Silica Nanomaterial for the detection of mercury

Major Field : Chemistry

Date of Degree : May 2015

A highly sensitive pyrene-attached silica nanoparticles chemosensor has been developed for the purpose of the detection of the mercury ion Hg^{2+} in aqueous solutions. Our chemosensor was synthesized by two steps; in the first step, the silica nanoparticles with (NH_2) endings were synthesized by APTES (3-aminopropyltriethsilane) and TEOS (tetraethoxysilane). However, in the second step pyrene was attached to the synthesized silica nanoparticles through peptide coupling reaction by reacting of the silica nanoparticles with pyrene carboxylic acid. The synthesized silica nanoparticles were characterized by different techniques including: scanning electron microscope (SEM), FT-IR, NMR, EDX and XRD. Afterwards, the pyrene-attached silica nanoparticles were tested as a chemosensor for the detection of Hg^{2+} ions, several samples containing different concentrations Hg^{2+} were added to the sensor and photoluminescence measurements have been done to check its efficiency. Our chemosensor achieved good sensitivity result of 1 ppb of Hg^{2+} ions, which is the WHO value.

ملخص الرسالة

الاسم الكامل: طارق عيسى عبدالله المشرقي

عنوان الرسالة: تحضير دقائق سيليكات نانوية موظفة الباييرين للكشف عن الزئبق

التخصص: الكيمياء

تاريخ الدرجة العلمية: أيار 2015

تم تطوير دقائق سيليكات نانوية موظفة الباييرين ذات حساسية عالية كحساس كيميائي لغرض الكشف عن أيون الزئبق Hg^{2+} في المحاليل المائية. تم تحضير هذا الحساس الكيميائي عن طريق خطوتين. الخطوة الأولى هي تحضير دقائق السيليكات النانوية المنتهية بـ (NH_2) عن طريق مادتين هما: 3-أمينوبروبيل ثلاثي إيثوكسي سايلين (APTES) و رباعي إيثوكسي سايلين (TEOS). وفي الخطوة الثانية تم ربط الباييرين على دقائق السيليكات النانوية عن طريق تفاعل اقتران الببتيد وذلك بمفاعلة دقائق السيليكات النانوية بحمض الباييرين الكربوكسيلي. تم تشخيص دقائق السيليكات النانوية المحضرة بمختلف التقنيات مثل: المجهر الإلكتروني الماسح (SEM)، طيف الأشعة تحت الحمراء (FT-IR)، الرنين النووي المغناطيسي (NMR)، والأشعة السينية المشتتة للطاقة (EDX). بعد ذلك تم اختبار دقائق السيليكات النانوية موظفة الباييرين كحساس كيميائي للكشف عن أيون الزئبق Hg^{2+} . تم إضافة عدة عينات تحتوي على أيون الزئبق بتركيزات مختلفة إلى الحساس ومن ثم قياس اللعان الضوئي لاختبار كفاءته. لقد أحرز هذا الحساس الكيميائي درجة حساسية جيدة لأيون الزئبق وهي واحد بالجزء من البليون (1 ppb) وهي القيمة الواردة في سجلات منظمة الصحة العالمية.

CHAPTER 1

INTRODUCTION

The release of mercury into the environment can have adverse effects on humans and aquatic species, even at very low concentrations. This proposal is an investigation that aims to detect highly toxic mercury pollutants arising from both natural and industrial sources. The development of mercury sensors for aquatic applications poses challenges in terms of deployability in somewhat difficult locations, selectivity, reliability, and robustness in harsh environments.

In the light of these challenges, we will design fluorescent nanoparticles based portable, highly sensitive and selective sensors for the detection of mercury in aquatic environment.

The fluorescence of pyrene is highly sensitive towards mercury. In the proposed work, various derivatives of pyrene, (e.g. carboxylic, amino and/or bromo derivatives), will be chemically attached to different silica precursors (e.g. TEOS, APTS, DMDES). These modified silica precursors will be used to synthesize fluorescent nanoparticles and will be used as opto-chemical sensors for the detection of mercury.

The synthesized fluorescent silica nanoparticles will be exposed to known quantities of mercury and changes in their fluorescent properties will be recorded by Fluorescence Spectrometer. The proposed project will take advantage of synthesized nanomaterials to achieving a high surface area, which will enable greater loading of sensing groups and therefore improved sensitivity in detecting mercury species.

Mercury is a highly toxic element which is widely spread in the atmosphere and water. Release of mercury in environment causes a serious threat to human health. Elemental mercury, ionic mercury, and its organic compounds e.g., methyl or ethyl mercury with different characteristics of solubility, volatility, toxicity and reactivity are naturally present in geologic hydrocarbon including coal, natural gas, gas condensates and crude oil.

Mercury poses extreme risks on human health which included brain and neurological damage (especially among the young), birth deformities, kidney damage and digestive system problems. Victims can suffer memory loss and language impairment alongside many other well-documented effects [1].

The research results, unfortunately, show an increase in the emissions of mercury to the environment, since the beginning of the time of industrial revolution. This led to threat the natural resources [2-4]. Mercury percentages in the atmosphere are 30-60 times higher than the time before the industrial era. Human-related activities release about 4,700 tons of mercury each year into the environment [5].

87% of mercury released in the United States caused by solid waste incineration and fossil fuels combustion [6]. Vast areas of land and water are going to be contaminated by the long atmospheric lifetime of mercury [7]. The problem is going to be worse since bacteria can convert metallic mercury and ionic mercury into methyl mercury, adding this potent neurotoxin to the food chain [8]. Organizations in many countries decided to determine the upper permitted limit of mercury ion Hg (II) in drinking water. For example, the maximum permitted limit of Hg (II) in drinking was determined by The United States Environmental Protection Agency (EPA) is 2 ppb [9] while the European and Chinese limits are 1 ppb [10].

With manifold annual increase of mercury release increase in the environment posing threats and there is a great desire to design new chemical sensors and methods for its fast and low

level detection. There are several methods and techniques are being used to monitor concentration levels of Hg^{2+} such as atomic absorption spectroscopy, inductively coupled plasma-mass spectrometry, plasma-atomic emission spectrometry, gas chromatography and reversed-phase high-performance liquid chromatography [11]. However, their wide utilization is largely limited due to their extremely high cost and non-suitability for remote applications. Therefore, there is a need to develop cost effective and convenient sensor that is capable of detecting the presence of ppb level mercury. Among the various techniques that allow low level detection of mercury, optical methods based on fluorescence are becoming increasingly popular. Such techniques allow on site, real-time qualitative or quantitative detection without requiring any expensive or complicated instrumentation. Our review of literature reveals that most of the sensors are being developed to only target non-organic mercury ion Hg^{2+} . The detection of organic mercury species is rarely present in literature. Furthermore, many reported sensors still have limitation of sensitivity, selectivity and linearity with certain concentration of mercury. On the other hand sensors which utilize precious particles, expensive quantum dots and complicated synthesis receptors are also not commercially attractive. Another problem with most of the reported sensors is that they are tested in liquid dispersed form which is relatively less practical for real life application. Our proposed work is based on readily available fluorescent pyrene in combination with cheap inexpensive sol-gel silica precursors. The use of sol-gel silica precursor gives excellent flexibility in control of the size of sensor nanoparticles for the coating of substrates.

An added advantage of using sol-gel silica precursors is the range of organic functionalities they possess, and their ability to co-condense with different species. Furthermore, sol-gel silica materials offer abundant hydroxyl groups by which to functionalize their surface with receptor ligands for improved organomercury interaction. This makes it possible to tailor the nano-sensor surface to possess more favorable interactions with organic species of mercury,

which pose significant problems in oil-producing countries such as Kingdom of Saudi Arabia.

Based on promising evidence and previous studies in the literature, our proposed sensor system in this proposal is also opto-chemical, as discussed in the following sections.

CHAPTER 2

LITERATURE REVIEW

The development of chemical sensors to monitor environmental pollution is becoming very popular area of sensor research. Mostly common chemical sensors are based on fluorescence signals due to their high sensitivity. Similarly chemical sensors for monitoring ionic mercury by fluorescence quenching are also being explored by researchers. There is a considerable need to synthesize the fluorescent chemosensors that can detect the mercury ions very selectively and sensitively. Among them, use of organic dyes, metallic nanoparticles, and quantum dots are commonly used.

Cho et-al. [12] developed mercury sensor which is based on Au-SiO₂ core/shell nanoparticles having attached red fluorescent porphyrin derivatives which quench on exposure to mercury ions. However, their work was limited to only Hg²⁺ ions. Kumar et-al. [13] reported that linear fluorescence change for the detection of Hg²⁺ between 40 ppb- 2.4 ppm in the presence of variety of interfering metal ions. In their work they used anthroneamine based probes which show highly selective and sensitive reversible colorimetric and fluorescence behavior to Hg²⁺ ions under aqueous conditions.

Pyrene based fluorescence receptors are getting much more attention [14-16]. Pyrene has many advantages, such as large Stokes shift, high quantum yield, and excellent photostability. The phenomenon of quenching or increasing fluorescence due to electron transfer interaction is already well understood in literature [17].

Some potential nanoparticles doped with functional group are also being investigated for the detection of mercury species. It's emphasized by researcher that nanomaterials provide a high potential for better sensitive, rapid, and selective detection of mercury. Several nanomaterial

types have been utilized for the detection of mercury [18]. Gold nanoparticles and gold nanorods functionalized with rhodamine B was also tried for the detection of mercury [19-21]. The advantage of nanoparticles is that they offer high surface area to interact with mercury species.

Koneswaran et-al [22] also reported a unique feature of CdS quantum dots capped with mercaptoacetic acid. The work demonstrates that mercaptoacetic acid capping agent interacts with mercury ions and the fluorescent properties of CdS QDs quenches linearly with increasing concentration. Furthermore, another colorimetric mercury sensor is reported by Shunmugam et-al [23] which is based on binding to terpyridine derivatives. They claim to achieve detection limit of 2 ppb matching the requirement of current EPA-US standard for drinking water. Wang et-al [24] also reported “turn on” fluorescent chemosensor for Hg^{2+} ion based on a new pyrene–thymine dyad. They illustrated that when pyrene is linked to any ligands which can co-ordinate with Hg^{2+} , a strong excimer emission of pyrene was observed. Chao Ma et-al [25] developed a ratiometric sensor for the detection of mercury based on fluorescence resonance energy transfer (FRET). In this work the ratiometric fluorescence signal changes according to the fluorescence response energy transfer process modulated by mercury ions. Cheng-Han Chao et-al [26] designed portable protein-modified gold nanoparticles probes for the detection of mercury ion. The probes enable visual characterization of mercury ion (Hg^{2+}). Liang Ding et-al [27] introduced gold nanoparticles modified glassy carbon electrode for the detection of mercury (II) in chloride media. Results show that the modified electrode is reusable sensor for the detection of mercury (II) with high sensitivity and selectivity. Zhen Zhao et-al [28] developed DNA oligonucleotides and cysteamine modified gold nanoparticles biosensor for the detection of mercury ions. This biosensor was designed based on electroluminescence (ECL) nanoprobe combined with oligonucleotides and cysteamine-gold nanoparticles conjugates and showed high sensitivity

results (a detection limit of 50 pM was achieved). Xiaoyu Wang et-al [29] synthesized chitosan nanoparticles based fluorescence probe for the detection of Hg^{2+} . This sensor could be synthesized by substitution reaction at amino groups of chitosan with dansyl chloride. Fluorescence studies demonstrated the sensitivity and selectivity of this chemosensor toward Hg^{2+} .

Ma Li-Na et-al [30] could successfully design gold nanoparticles-based dynamic light scattering assay for the detection of mercury ion. In the presence of Hg^{2+} ions, the probe DNA molecules have been easily desorbed from gold nanoparticles surface due to the formation of T- Hg^{2+} -T resulting in aggregation of gold nanoparticles which leads to the increase of their average hydrodynamic diameter.

Zahra Mohammadpour et-al [31] reported the development of label-free colorimetric chemosensor of mercury ion using carbon nanodots as enzyme mimics. In this work, carbon nanodots as a new generation of nanozymes were introduced due to their peroxidase mimetic activity to catalyze the oxidation reaction of tetramethylbenzidine (TMB). By oxidation of TMB a blue colored cation radical was generated. Glutathione could decrease in cation radical generation due its radical restoration capability and hence the reduction of the blue color. This fact was utilized in developing label-free chemosensor for the detection of mercury ion because of the strong affinity of thiolated compounds toward mercury.

Liu and coworkers [32] demonstrated a major achievement in their report of a naked-eye paper sensor for the rapid detection of trace mercury ions in water samples. A mercury-sensing rhodamine B thiolactone was immobilized in silica matrices and impregnated on filter paper. When exposed to a water sample containing mercury, the filter paper's color showed a change from white to purple-red that was visible to the naked eye. This paper-based sensor was able to detect Hg^{2+} at a concentration of 10 nM, the maximum residue level in drinking water recommended by the U.S. EPA. The sensitivity was demonstrated to be as

high as 1.2 nM using a flat-bed scanner. However, the use of filter paper limits continuous monitoring in remote environments such as aquatic.

Many other rhodamine-based mercury sensors have been developed that make use of the Hg^{2+} -induced desulfurization effect [33-36]. The sensing mechanism is not reversible and includes desulfurization of thiocarbonyl groups into oxocarbonyl groups or cyclization products. This leads to simultaneous spiro-ring-opening of rhodamine derivatives with a considerable significant change in color and naked eye detection.

The challenge with all of these sensors is that they only targeted inorganic species of mercury, and experimental results did not demonstrate that these sensors possessed sufficient selectivity, sensitivity, water solubility, and pH independence. Most recently, Tan [37] crafted a rhodamine-based core/shell sensor for Hg^{2+} detection. The outer shell was constructed from a silica molecular sieve with entrapped rhodamine that provided a large surface area and ordered tunnels for the inclusion of the sensing probe, and the acceleration of the adsorption and transportation of the analyte. The inner core consisted of superparamagnetic Fe_3O_4 nanoparticles, making the nanocomposite magnetically removable. The sensing was again limited to Hg^{2+} , and the response time was poor.

Xiaoqian Peng et-al [38] could design di-substituted ferrocene based chemosensor for the detection and separation of mercury ion. This method could achieve high sensitivity (0.01 μM). Ultraviolet spectroscopy, infrared spectroscopy and proton NMR were used to approve the interaction between mercury ion and ferrocene derivatives.

Fanyong Yan et-al [39] introduced carbon dots based chemosensors for highly selectivity and sensitivity detection of mercury ion. Two novel chemosensors have been synthesized and characterized for detection of mercury ion. The carboxyl groups of the carbon dots can catch the mercury ions and therefore an intense quenching of the sensor's fluorescence intensity

has been recorded. Both of the sensors demonstrated high sensitivity toward mercury ion. The detection limits of the sensors were 226nm and 845 nM.

Qing Wang et-al [40] reported unmodified gold nanoparticles based colorimetric method for the detection of mercury ion. This method utilizes the thymine-Hg(II)-thymine { T-Hg²⁺-T } method and can be summarized as : A hairpin with sticky ends was utilized as a probe for the recognition of Hg²⁺ (H₀). When there is no Hg²⁺, the probe can bind to gold nanoparticles that exist in the solution which will prevent any aggregation of these nanoparticles. However, in case of the solution contains mercury ions, the probe will interact with mercury ion through T-Hg²⁺-T interaction. This will leave gold nanoparticles free in the solution, therefore, they will aggregate. As a result of the gold nanoparticles aggregation a color change from red to blue has been remarked. The detection limit of this method was recorded as 30 nM.

Shuyue Fu et-al [41] fabricated a raman probe for the detection of mercury ion. The nanosensor consists of inositol hexaphosphate (IP6) stabilized gold nanoparticles. The particles were modified by crystal violet as a raman signal agent and tri-sodium citrate as a reducing agent. The decrease in band's intensity of the sensing material has been observed as the concentration of the mercury ion increases. This method achieved a new record with a detection limit of 0.5 pM Hg²⁺.

waterXianghong Li et-al [42] demonstrated a reversible colorimetric method for detection of mercury using cycloruthenated complex. According to this method, a noticeable color change from red to yellow has been observed upon the addition of mercury into the sensing material and a significant blue shift at 120 nm of the MLCT absorption band has been also observed. The detection limit of this method was 0.59 μM.

Minghua Wang et-al [43] designed a grapheme nanostructures based DNA sensor for selective detection of mercury ion. The sensor's design consists of multiple layers of nanostructured plasma-polymerized allylamine and grapheme nanosheets which are

conductive. Mercury ion can bind to this biosensor by T-Hg²⁺-T mechanism. Electrochemical measurements show that frequency response of the sensing material decreases as the concentration of mercury ion increases. Minghua Wang' team could achieve detection limit of 0.017 nM.

R.M. Tripathi et-al [44] used gold nanoparticles for sensing of mercury ion Hg (II) purpose. They used non-pathogenic *Trichoderma harzianum* for the synthesis of the gold nanoparticles. These nanoparticles were characterized by many techniques; FTIR, UV-vis spectroscopy, transmission electron spectroscopy (TEM) and dynamic light scattering (DLS).

A dramatic color change could be observed upon the presence of mercury ion.

Zhiyong Guoa et-al [45] presented gamma-polyglutamic acid-graphene-luminol composite and oligonucleotides based electrochemiluminescence biosensor for the detection of mercury ion. The sensor was developed by coating of glassy carbon electrode by gamma-PGA-G-luminol composite. They found that this action will create a strong electrochemiluminescence signal. The system uses T-Hg²⁺-T streptavidin-biotin interaction mechanisms to bind the mercury ions to the sensor. Results show that there is a logarithmic relationship between concentration of mercury ion and electro-chemiluminescence response.

Yongming Guoa et-al [46] developed protein-functionalized gold nanoparticles for colorimetric detection of mercury ion. In this design papain was used to functionalize gold nanoparticles. The prepared gold nanoparticles showed successful simultaneous detection of Hg²⁺, Pb²⁺ and Cu²⁺ and distinguished response for each ion. However, the most observed response in water was for mercury in contrast to copper and lead. The sensitivity of this synthesized sensor was found to be dependent upon the pH of the solution and the size of the gold nanoparticles. The sensitivity increase as the size of gold nanoparticles increases. This system could achieve detection limit of 200 nM.

Haibo Xiao et-al [47] used (TP-PY) dye as a chemosensor for the detection of mercury ion. TP-PY showed responds in fluorescence spectra toward changes in pH of the solution. Results demonstrated that TP-PY shows high sensitivity and selectivity toward mercury ion. The detection limit of this method was found to be 65 nM.

Dong Mei Chen et-al [48] nicking endonuclease signal amplification based electrochemical biosensor for the detection of mercury ion. The probe A has a hairpin shape and contains thiol group at one end and methylene blue tag at the other end. The first step in the recognition process is to immobilize the probe A on Au electrode by Au-S interaction. As mercury ion exists in the solution, probe A and probe B can be connected by mercury ion through T-Hg²⁺-T interaction. Then, probe A fragments will be dissociated. Probe B and Hg²⁺ released can be used again to initiate another cycle, therefore this will free up more electroactive species, as a result, we will end up with remarkable decrease in signal. This method could reach a detection limit of 0.087 nM.

Jianjun Du et-al [49] used gold nanoparticles for developing a colorimetric method for the detection of mercury ion through coordination approach. This method uses the affinity of thymine derivative (N-T) for mercury ion. In the presence of mercury ions, a noticeable colour change from red to blue was observed resulting in fast naked eye colorimetric method for the detection of mercury ion. The detection limit was 0.8 nM.

Azam Bahrami et-al [50] used voltammetric technique to detect mercury ion. This method includes use of carbon ionic paste electrode embedded with Hg²⁺ ion imprinted polymeric nanobeads (IIP) based on dithizone, as a ligand for capture of Hg²⁺ ions. In addition, this method uses differential pulse anodic stripping voltammetry to test the effectiveness of the synthesized sensing material for the detection of mercury ion. Results demonstrate that there is a linear relationship between the concentration of mercury ion and the response of the

modified electrode through the ranges of 0.5 nM–10 nM and 0.08 μ M–2 μ M with a detection limit of 0.01 nM.

Our survey of the literature has shown that most of the sensors are being developed to targets inorganic mercury, and significance of monitoring the organomercury is ignored to some extent. Other than quantum dots based fluorescent sensors being developed, there are successful demonstration of fluorescent dye based sensors especially rhodamine. These rhodamine based sensors cannot be used in aquatic environment as rhodamine is highly soluble in water since it's not chemical attached to the proposed sensors. This clearly indicates there is a need for sensors which can interact with organomercury species having hydrophobic properties to withstand in aquatic environment. Therefore our proposed research strategy will involves use of pyrene which is insoluble in water can be chemically attached to hydrophobic silica surface (as explained in research methodology section). Some newly developed materials based on fluorescent silica nanoparticles have offered great potential for the selective detection of mercury in the presence of other heavy metals. However, few examples of such optical sensors using silica as a solid support to detect Hg^{2+} ions have been reported, and they are limited to certain silica precursors. Their long-term stability, sensitivity, and response time have not been fully investigated and compared with other potential silica precursors, which may have better stability, particularly in water [51]. To date, there have been no systematic studies to fabricate different silica precursors with different pyrene ligand routes; therefore, achieving all of these criteria remains a challenge.

CHAPTER 3

Objectives and Methodology

3.1 Objectives

The overall goal of the proposed work is to fabricate and evaluate opto-chemical nanosensors to monitor mercury pollution. The successful development of these sensors will make it possible to fulfill future legislation challenges related to mercury damage to human health and aquatic ecosystems. In order to achieve the overall goal, this project has the following objectives:

- 1- To investigate synthesis routes systematically and comprehensively for chemical attachment of pyrene with different silica precursor to produce fluorescent nanoparticles which should be stable when exposed to aquatic environment;
- 2- To transform the developed fluorescent nanomaterials into optical based sensor by coating on quartz substrates to measure the changes in optical properties;
- 3- To evaluate the sensitivity and selectivity of optical based constructed sensors for mercury detection up to the ppb level by monitoring the change in fluorescence;

3.2 Methodology

This proposed research will consist of three phases. In the first phase, we will synthesize pyrene-functionalized sol-gel silica precursor molecules. In the second phase, we will use these precursors to synthesize silica nanoparticles with chemically attached pyrene groups by co-condensation with other sol-gel precursors. In the third phase, we will check sensitivity of these fluorescent nanoparticles against different mercury species.

(A) We propose here a systematic study for synthesizing functionalized silica nano-sensors by using different silica precursor's e-g Diethoxydimethylsilane, Tetraethyl orthosilicate 3-Aminopropyltriethoxysilane (APTS) which will have chemically attached fluorescent marker through amino- carboxylic- bromo-pyrene route. The co-condensation of organosilica precursors (such as DMDES or hexamethyl disilazane, HMDS) with TEOS will also be attempted to increase the affinity for the organic mercury species. As an example a possible reaction routes are given in the following scheme for the attachment of pyrene with aminopropyltriethoxysilane precursor. The advantage of using silica precursor is that it allows easy attachment of receptors for interaction with mercury species by the photoinduced electron transfer (PET) or internal charge-transfer (ICT) process.

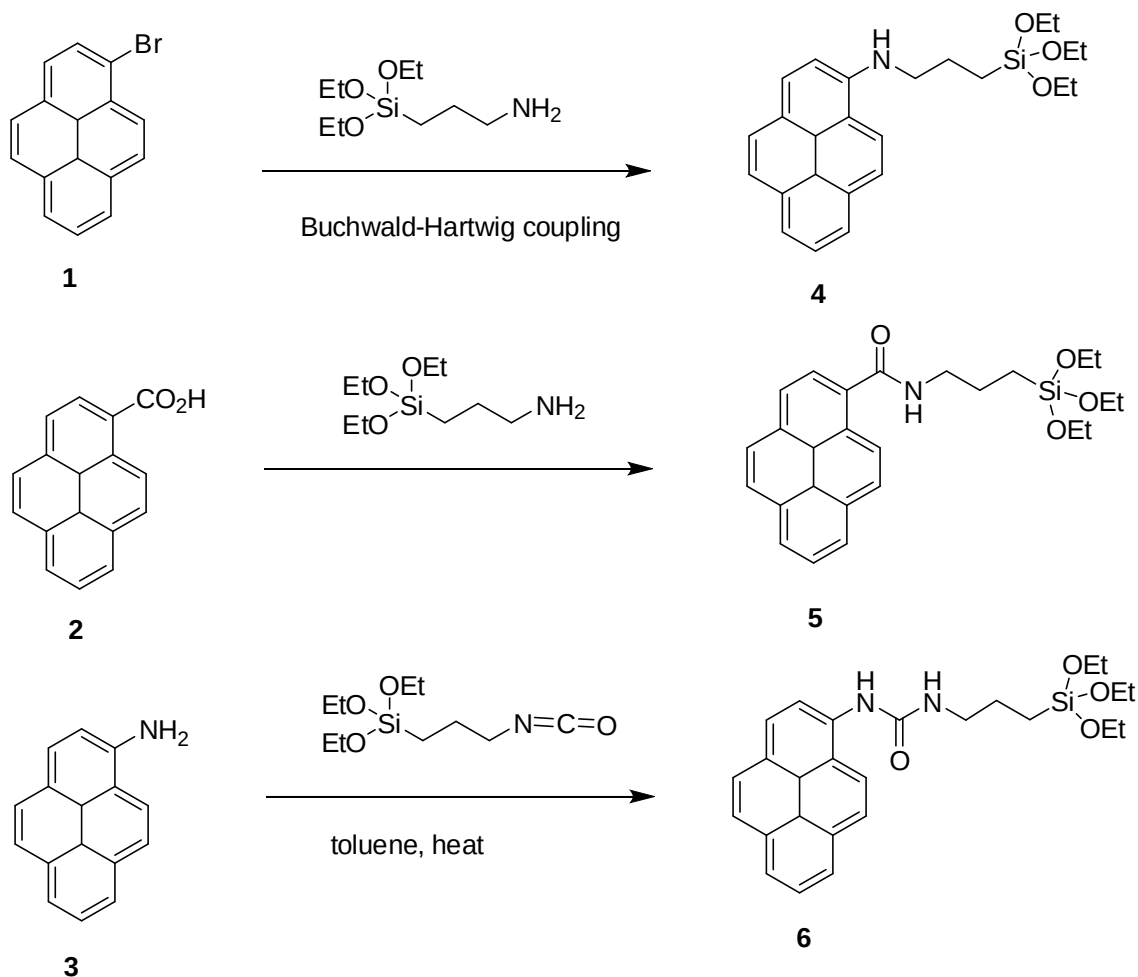


Figure 3- 1 Chemical synthesis of pyrene-silane conjugates (4-6)

The chemical synthesis of pyrene-silane conjugates (**4-6**) will be accomplished as outlined in figure 3-1. Buchwald-Hartwig coupling of 1-bromopyrene (**1**) with aminopropyltriethoxysilane (APTES) would render conjugate (**4**). Likewise reaction of 1-pyrenecarboxylic acid (**2**) with APTES under peptide coupling condition would render amide conjugate (**5**). Finally condensation of 1-aminopyrene (**3**) with triethoxy(3-isocyanatopropyl)silane would give urea conjugate (**6**).

(B) Once conjugates (**4-6**) would be in hands, we next would use them as precursor to synthesize silica nanoparticles (SiNPs).

By exploiting both self-assembly and ligand exchange methodologies the surface of silica nanoparticles can be modified or functionalized with molecular species (amine groups), which can enable them to interact with mercury in their environment. The synthesis of silica particles is well established in literature following Stober process of hydrolysis and condensation reaction. The growth of silica particles will be controlled by adjusting the amount of precursor, catalyst (ammonia solution) and surfactant.

(C) The sensitivity of fabricated sensor will be tested in the laboratory prepared standard water with different mercury species. The concentration of mercury will be varied from minimum advised level by EPA-US up to maximum level where no further quenching or increment of fluorescence emission will be detected.

CHAPTER 4

Experimental Procedure

4.1 Synthesis of Silica Nanoparticles

0.1g of CTAB was added to 5 ml H₂O in a small flask. Then, the components were mixed using a mechanical mixer. They had been mixed for 5 minutes at 3000 rpm. After that, they were transferred into a flask contains 40 ml H₂O and 0.035 g NaOH and the mixture was stirred for 5 minutes, 3 ml of ethyl acetate was then added to the mixture. After 10 minutes, 300 µl of TEOS, the new mixture was left to be stirred for 40 minutes. After that, 200 µl of APTS was added. Then, the new mixture was left stirring overnight. The produced mixture was then centrifuged at 5000 rpm to separate the white produced silica nanoparticles. Then, the produced particles were washed and centrifuged twice with water and once with ethanol. After that, the separated particles were dissolved in a small amount of ethanol. The mixture of silica nanoparticles and ethanol was then poured into a petri dish and left to evaporate ethanol and ending up with the fine powdered silica nanoparticles.

4.2 Synthesis of pyrene-attached silica nanoparticles

0.1 g of the produced silica nanoparticles and 0.15 g of pyrene carboxylic acid were transferred into a dried 50 ml round bottom flask. Then, the flask was immediately closed by nitrogen gas inlet. 0.1095 g of HOBt and 0.1167 g of EDCI were then added to the flask. After that, 10 ml of Dichloromethane (DCM) was poured to the flask. Then, the nitrogen stream was removed and 0.1695 ml of Triethylamine (Et₃N) was injected to the reaction mixture. The reaction mixture was left stirring at 700 rpm at 0 °C by putting the flask over an ice bath. The ice bath was removed after about 20 minutes and the reaction flask was left stirring at room temperature for 24 hours.

Figure 4-1 demonstrates the formation of the silanol product from APTES and TEOS precursors during the synthesis procedure of the silica nanoparticles. The figure shows also that the produced silica nanoparticles end with alkyl amine chain which can be used for the attachment of pyrene through peptide coupling reaction later. Figure 4-2 demonstrates the peptide coupling reaction by which the attachment of the dye (pyrene) was attached to the silica nanoparticles.

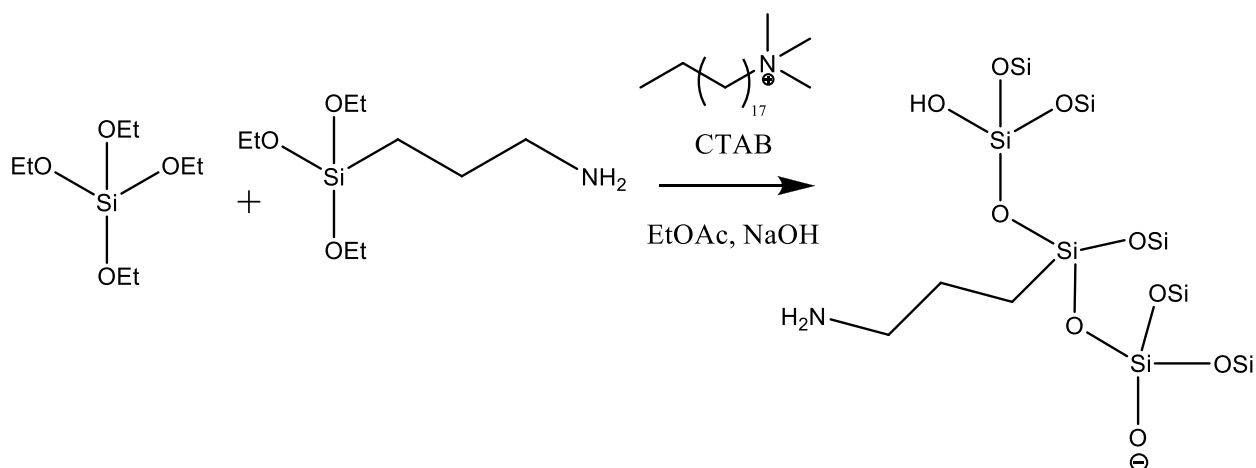


Figure 4- 1 Formation of the silanol product from the APTES and TEOS precursors

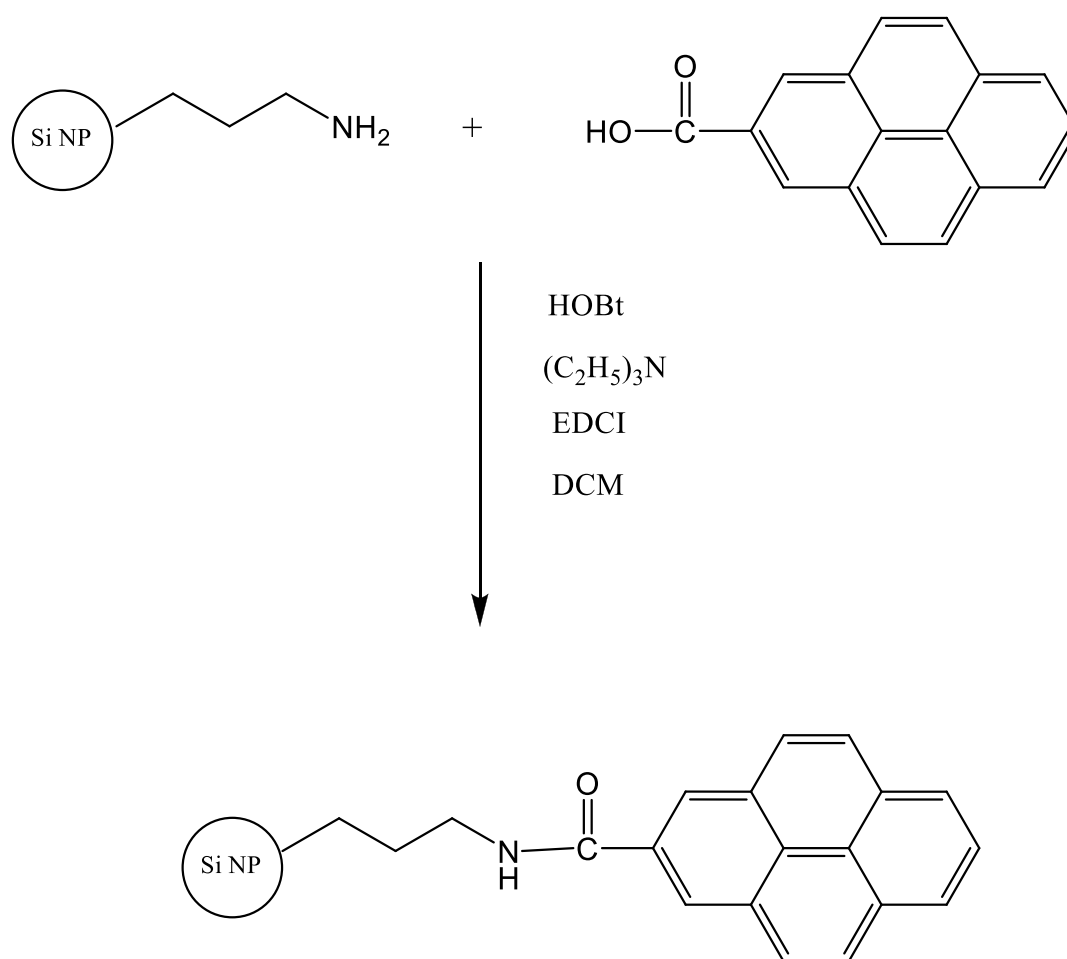


Figure 4- 2 The attachment of pyrene through peptide coupling reaction.

The flask contents were transferred into a clean separatory funnel, and then 10 ml of ethyl acetate was poured into the funnel. The flask was also rinsed by ethyl acetate. Then, 10 ml of 1M NaOH solution was added to the separatory funnel. After this, the ethyl acetate layer (lower layer) was separated. Any excess of pyrene carboxylic acid will remain in the NaOH layer. Sodium sulfate had been then added to the separated ethyl acetate layer as a drying agent for a while, then the ethyl acetate was evaporated using rotatory evaporator and the product kept in fridge.

4.3 Characterization of the synthesized pyrene-attached silica nanoparticles

The synthesized pyrene-attached silica nanoparticles have been characterized using different techniques to approve the formation of the silica nanoparticles and to check the morphology of these nanoparticles. These techniques include; scanning electron microscope (SEM), nuclear magnetic resonance resonance (NMR), Fourier transfer infrared spectroscopy (FT-IR), and XRD.

4.4 Testing the synthesized nanoparticles for the detection of mercury ion

Our sensing nanomaterial has been applied in the detection of mercury ion Hg (II). For this purpose, the changes in photoluminescence intensities for our synthesized sensing material after addition of mercury ion have been recorded. After that, a plot diagram showing the relationship between the changes in in photoluminescence intensity of the sensing material versus the change in the concentration of mercury ion is going to be drawn to demonstrate the effect of the addition of mercury ion on the photoluminescence intensity of the silica nanomaterial.

CHAPTER 5

Results and Discussion

5.1 Characterization of the pyrene-attached silica nanoparticles

Many techniques were used in our work to assure the formation of silica nanoparticles and to approve the attachment of the dye (pyrene) to the surface of the silica nanoparticles as well. The morphology of the produced silica nanoparticles has been taken into consideration. In this chapter we will discuss the results that we got from these techniques and we will use these results to evaluate the performance of our sensing material for the detection of mercury ion.

5.1.1 Scanning Electron Microscope (SEM) Imaging

The figures 5-1 and 5-2 show the scanning electron microscope SEM images of the synthesized silica nanoparticles. SEM images approve the formation of the synthesized silica nanoparticles. These particles were found resemble in morphology as smooth spheres with a mean diameter of about 100 nm. It is obvious that the nanoparticles demonstrate oval and circular shapes with different sizes. This implies that these silica nanoparticles have large surface areas, so they can be used in applications like sensing.

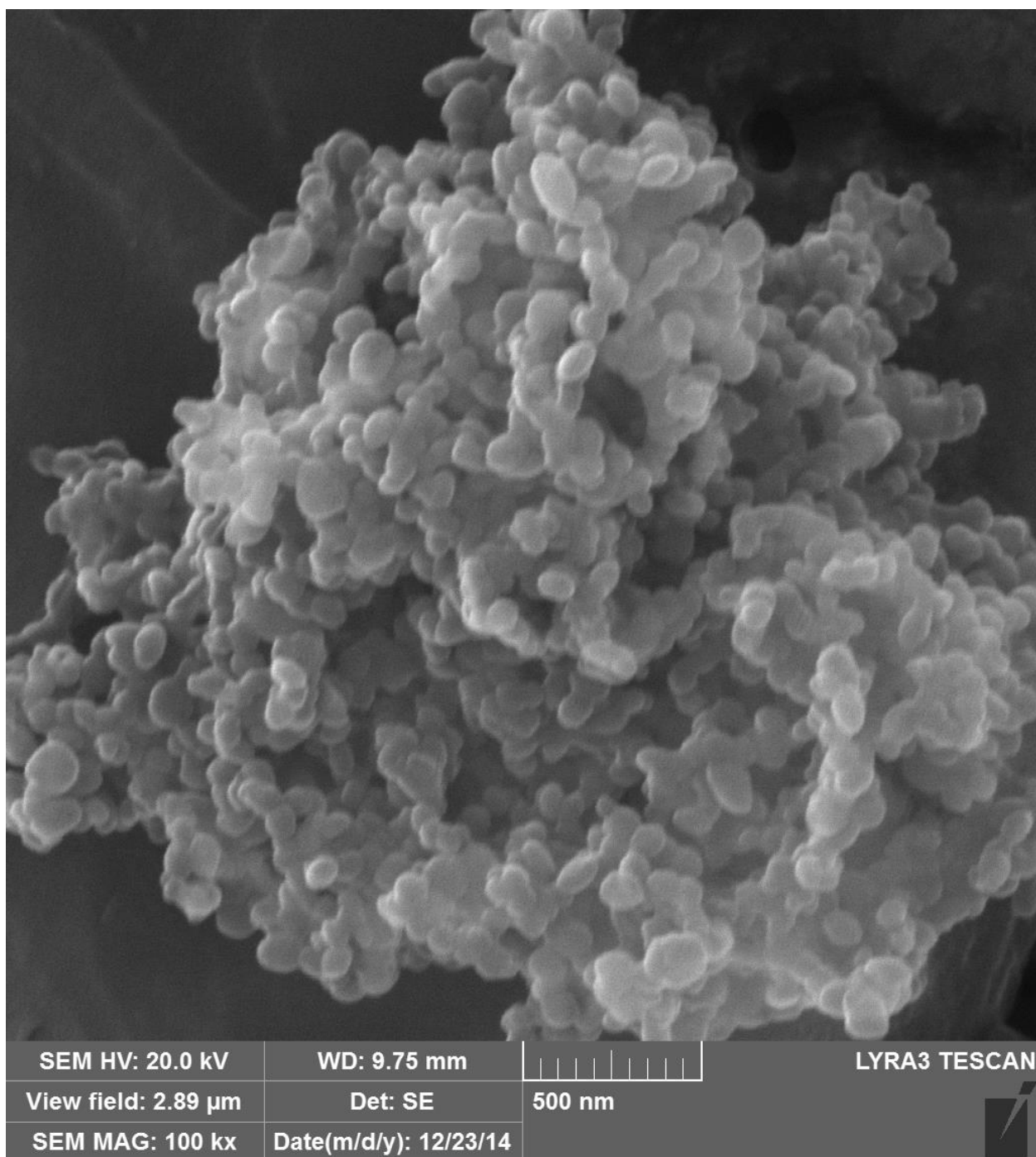


Figure 5- 1 SEM image of silica nanoparticles

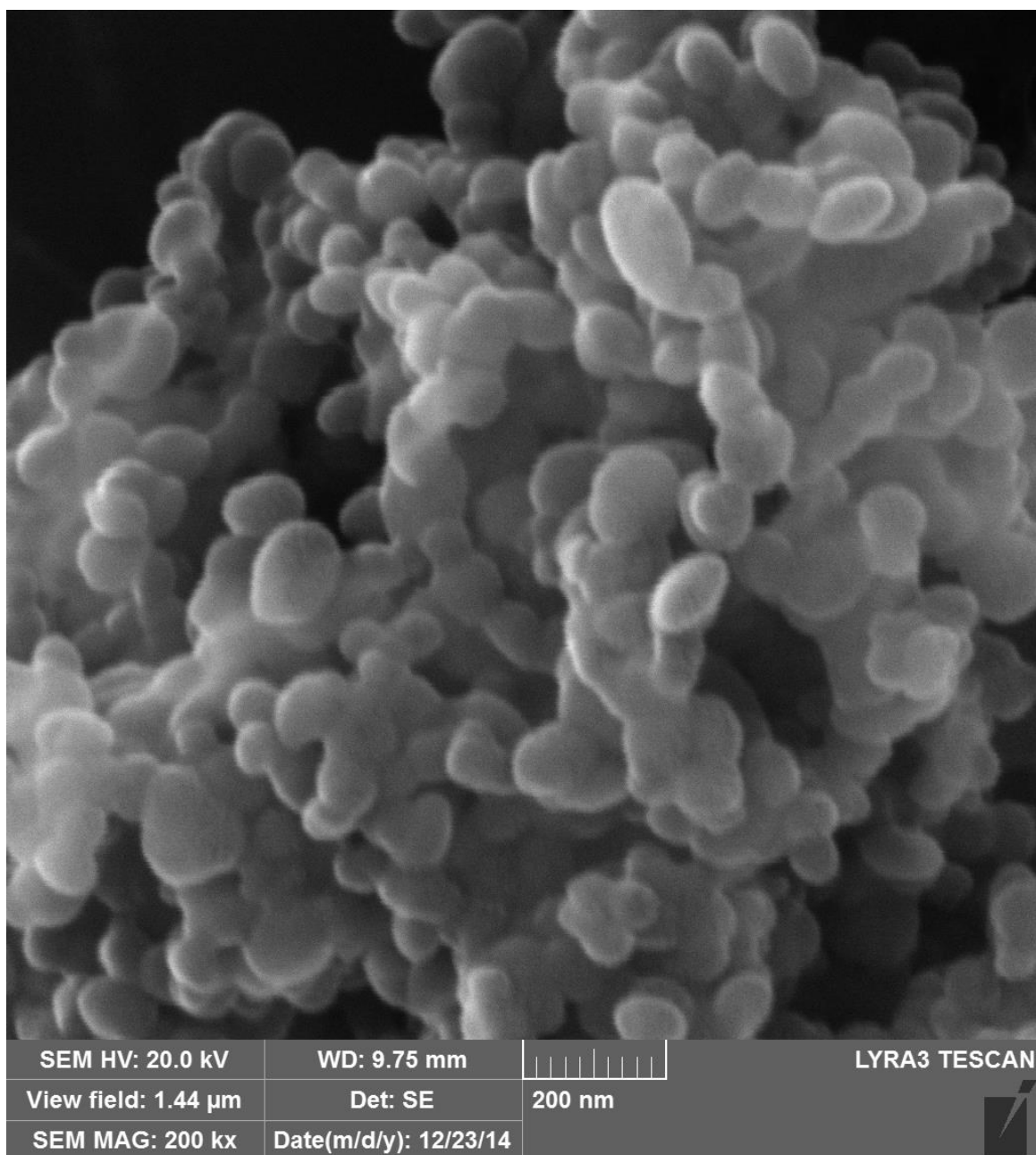


Figure 5- 2 More focused SEM of the silica nanoparticles

5.1.2 Fourier Transfer Infrared Spectroscopy (FT-IR)

The information included in this section can tell about the nature of bonds in the synthesized silica nanoparticles. Figures 5-3 and 5-4 demonstrate the FT-IR spectra of both the synthesized silica nanoparticles before and after the attachment of the dye (pyrene). According to these figures we can see the main bonds in the silica nanoparticles appear in both of the figures. However, the aromatic stretching is absent in figure 5-3 while it appears clearly in figure 5-4, which is a very strong evidence of the attachment of pyrene to the surface of the synthesized silica nanoparticles to get our pyrene-attached silica nanoparticle as a sensing material.

The main peaks in figure 5.3; IR (KBr, cm^{-1}) 3468 (NH_2), 2933 (C-H), (CH_2 bending), 1023 (Si-O).

The main peaks in figure 5.4 are; IR (KBr, cm^{-1}), 3415 (N-H), 3040 (Ar-H), 2926 (aliphatic H), 1774 (overtone), 1642 (C=O), 1569 and 1448 (C=C-Ar), 1383 (C-N), 1092 (Si-O).

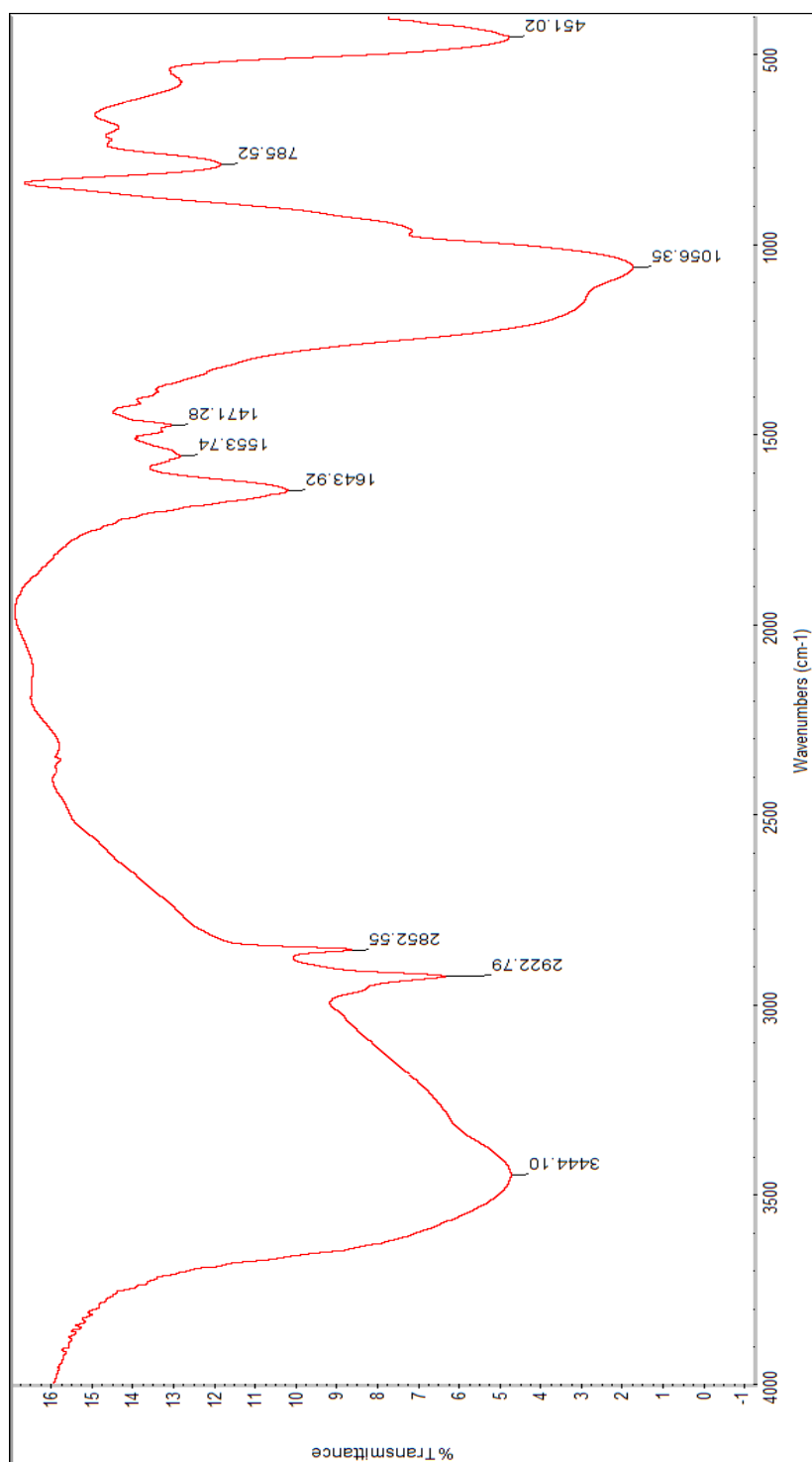


Figure 5- 3 FT-IR spectra of the silica nanoparticles before the attachment of pyrene

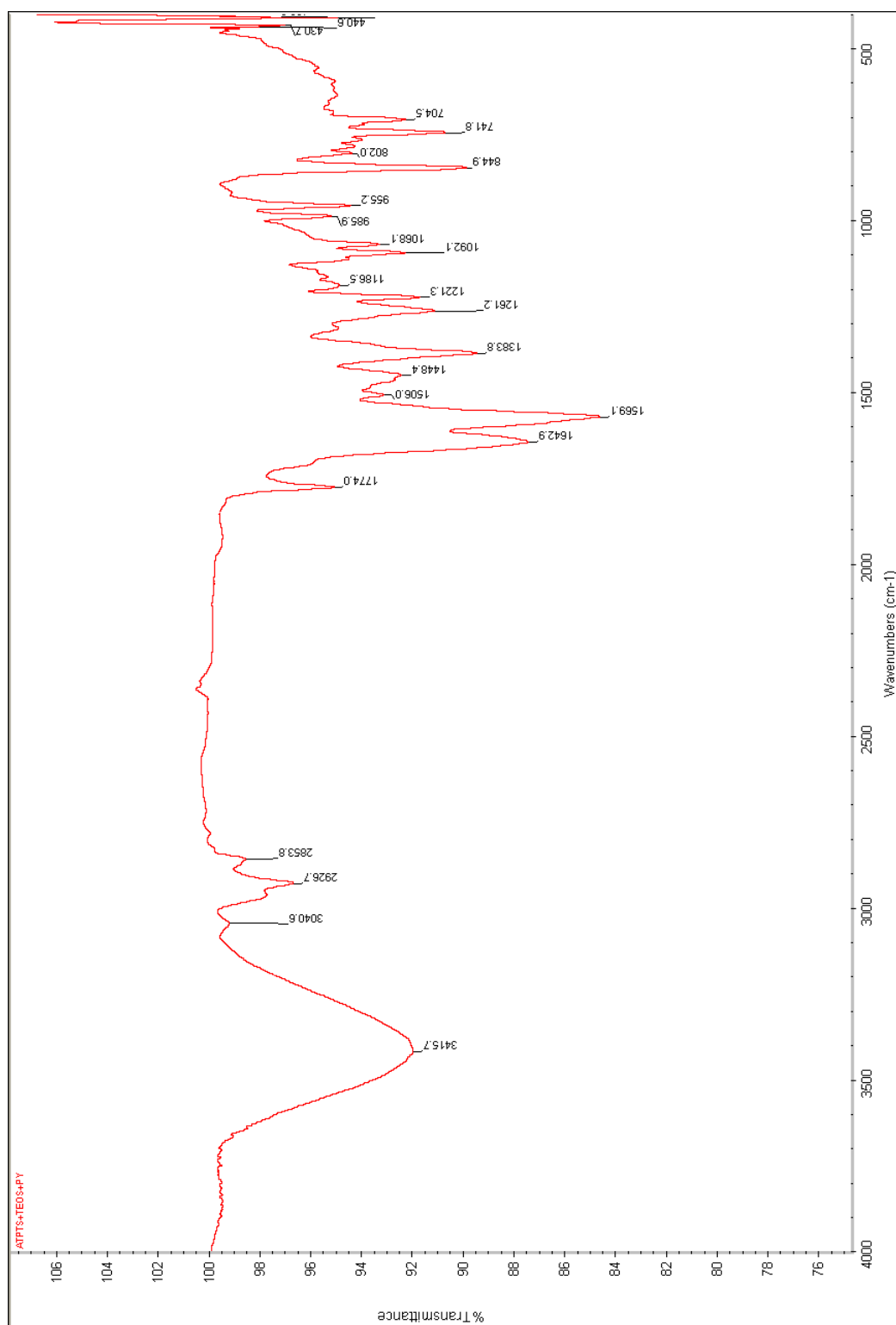


Figure 5- 4 FT-IR spectra of the silica nanoparticles after the attachment of pyrene

5.1.3 Nuclear Magnetic Resonance (NMR) spectra

The nuclear magnetic resonance study was made also to confirm the existence of pyrene dye in the product that we got after the attachment of pyrene reaction. Interestingly the NMR results were found to be consistent with FT-IR results, which emphasize the attachment of pyrene of the surface of the synthesized silica nanoparticles. Figure 5.5 shows ^1H NMR of the synthesized silica nanoparticles before the attachment of pyrene while figure 5-6 shows ^1H NMR of the synthesized silica nanoparticles after the attachment of pyrene. As we can see there are clear peaks in the figure 5-6 that are not exist in figure 5-5 at about 8. This is a very significant proof for the attachment of the pyrene to the silica nanoparticles. The following description demonstrates the main peaks in figure 5.6:

^1H NMR (500MHz, CDCl_3) δ 8.6 (d, 2H, $J=1.00$ Hz, CH_2), 8 (m, 8H, $J=1.94$ Hz, CH), 6.5 (br.s, $J=0.91$ Hz, N-H), 3.8 (t, $J=6.05$, 6H, CH_2), 3.7 (t, 2H, $J=2.17$, CH_2), 1.9 (d, $J=2.07$, 2H, CH_2), 1.2 (t, $J=7.73$, 9H, CH_3), .8 (t, $J=3.52$, 2H, CH_2).

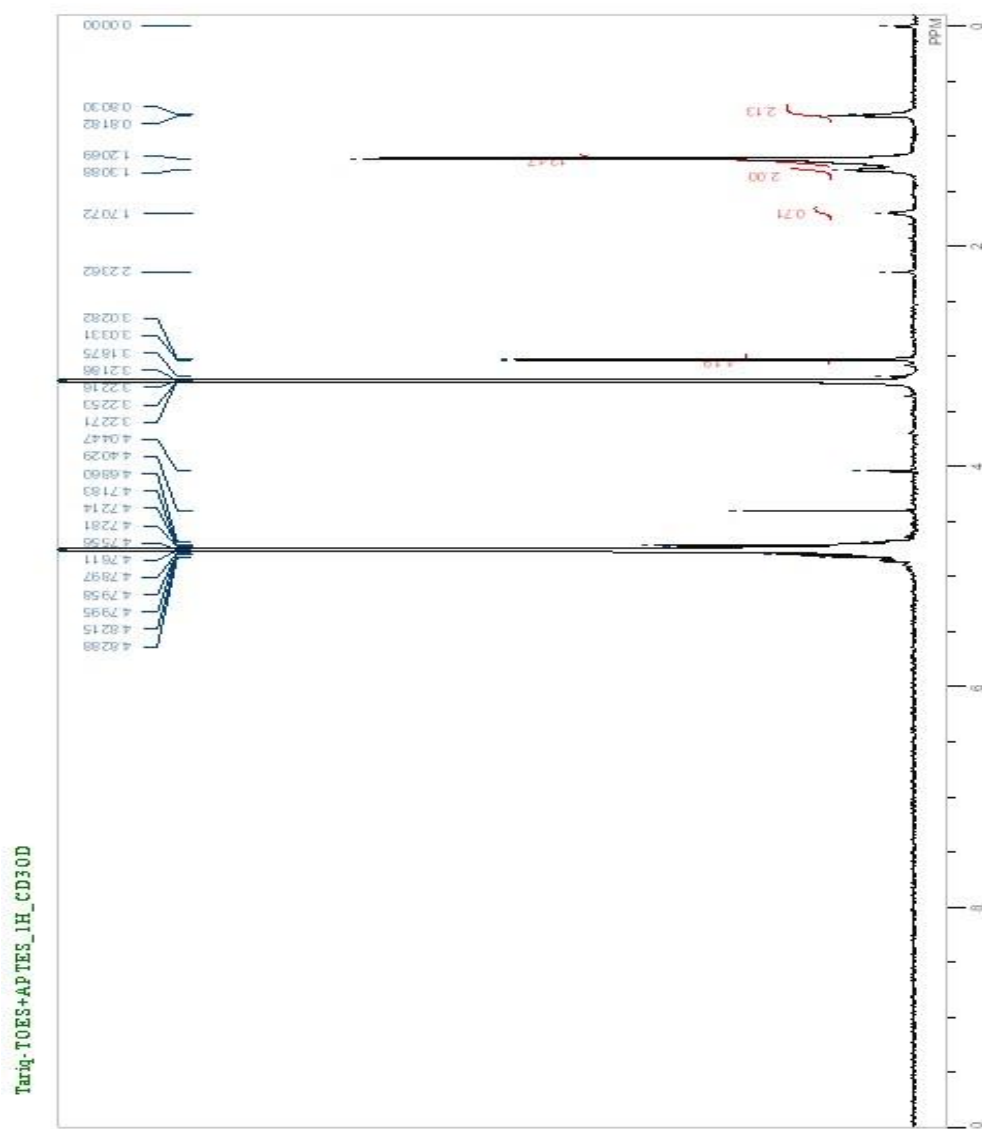


Figure 5- 5 ^1H NMR of the silica nanoparticles before the attachment of pyrene.

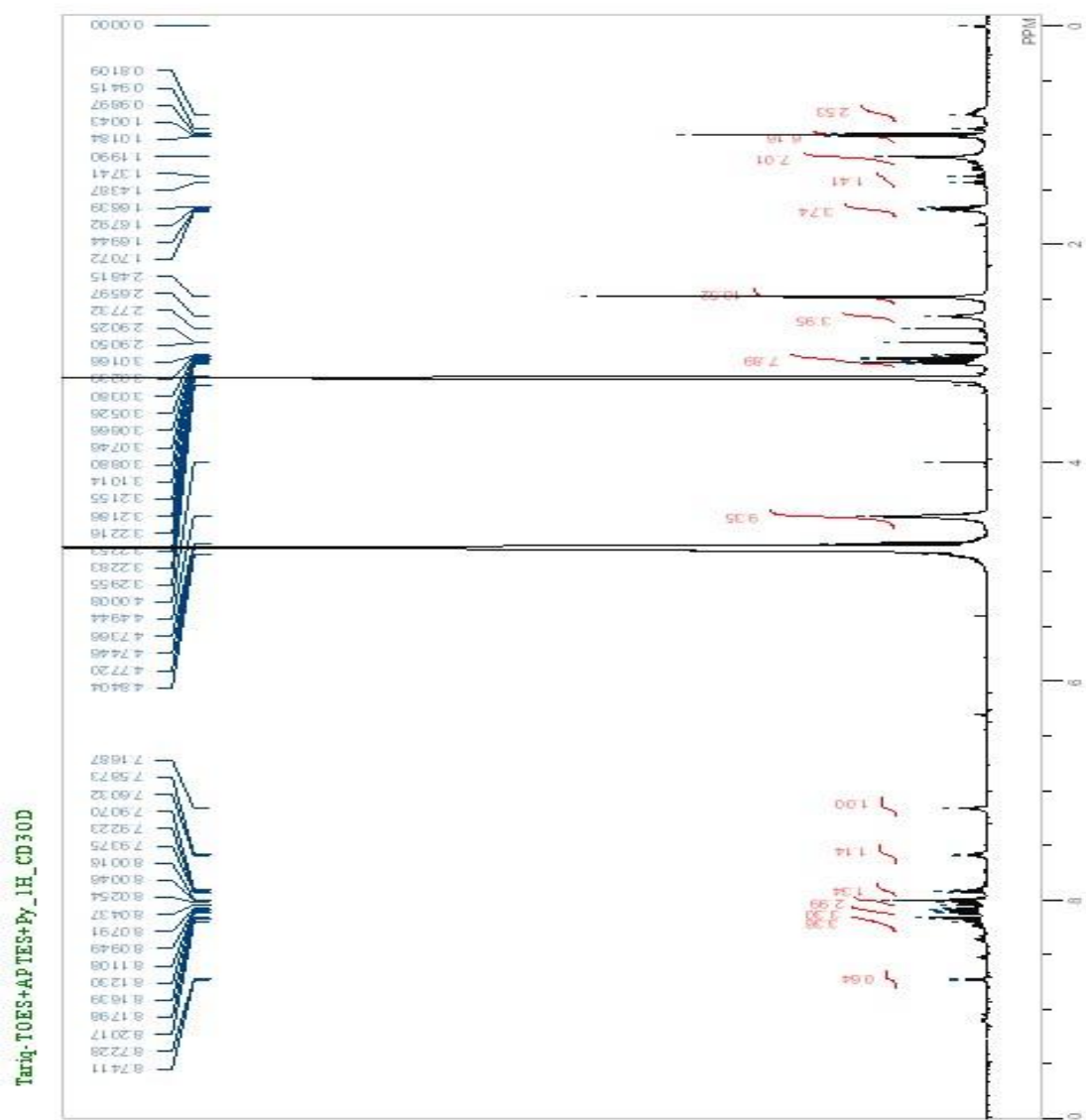


Figure 5- 6 ^1H NMR of the silica nanoparticles after the attachment of pyrene.

5.1.4 XRD Analysis

XRD experiment was used to study the morphology of the produced silica nanoparticles.

Figure 5.8 shows that we have a strong reflection peak at about 24° . This peak is characteristic for silica nanoparticles of alkyl amine chain with uniform pore diameter.

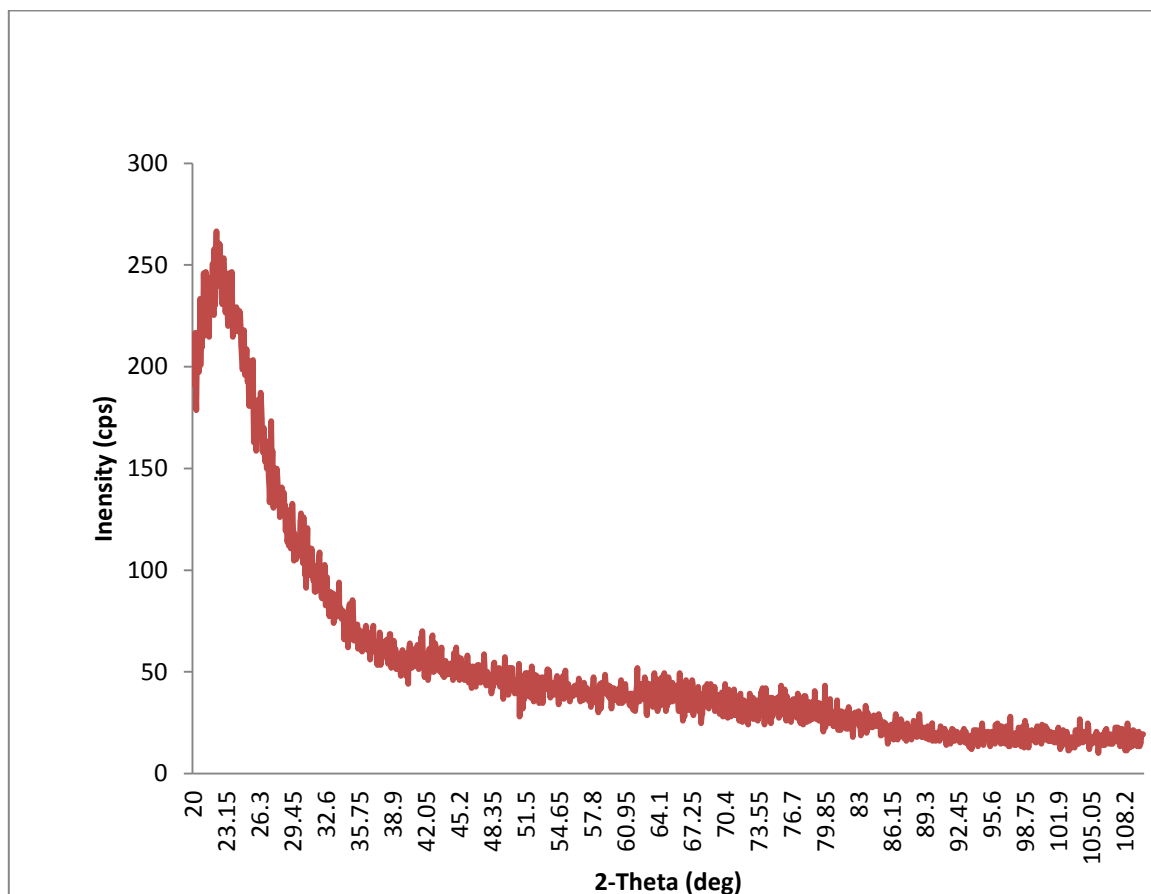


Figure 5- 7 XRD pattern of the silica nanoparticles

5.2 Use of the pyrene-functionalized Silica Nanoparticles for the Detection of Mercury

5.2.1 Photoluminescence study of the pyrene-attached silica nanoparticles.

In order to check the ability of our synthesized nanosensor for detection of mercury ion, a sample of the sensing material was transferred for photoluminescence study. The sensing material exhibits a strong emission peak at the wavelength of about 402 nm. Afterwards, we repeated the same photoluminescence experiment but with initial concentration of mercury ion of 1 ppb. Interestingly, the photoluminescence emission peak was less than for the blank sample that doesn't contain any mercury. Then, we started adding more mercury and checking the photoluminescence measurement for the new Hg (II) concentration. We tested 11 concentration of the mercury ion in the presence of our sensing material. The concentrations are: 1 ppb, 3 ppb, 5 ppb, 7 ppb, 9 ppb, 11 ppb, 13 ppb, 15 ppb, 17 ppb, 18 ppb, and 20 ppb.

The figures from figure 5-9 to 5-19 demonstrate the change in photoluminescence emission versus the change in the concentration of mercury ion.

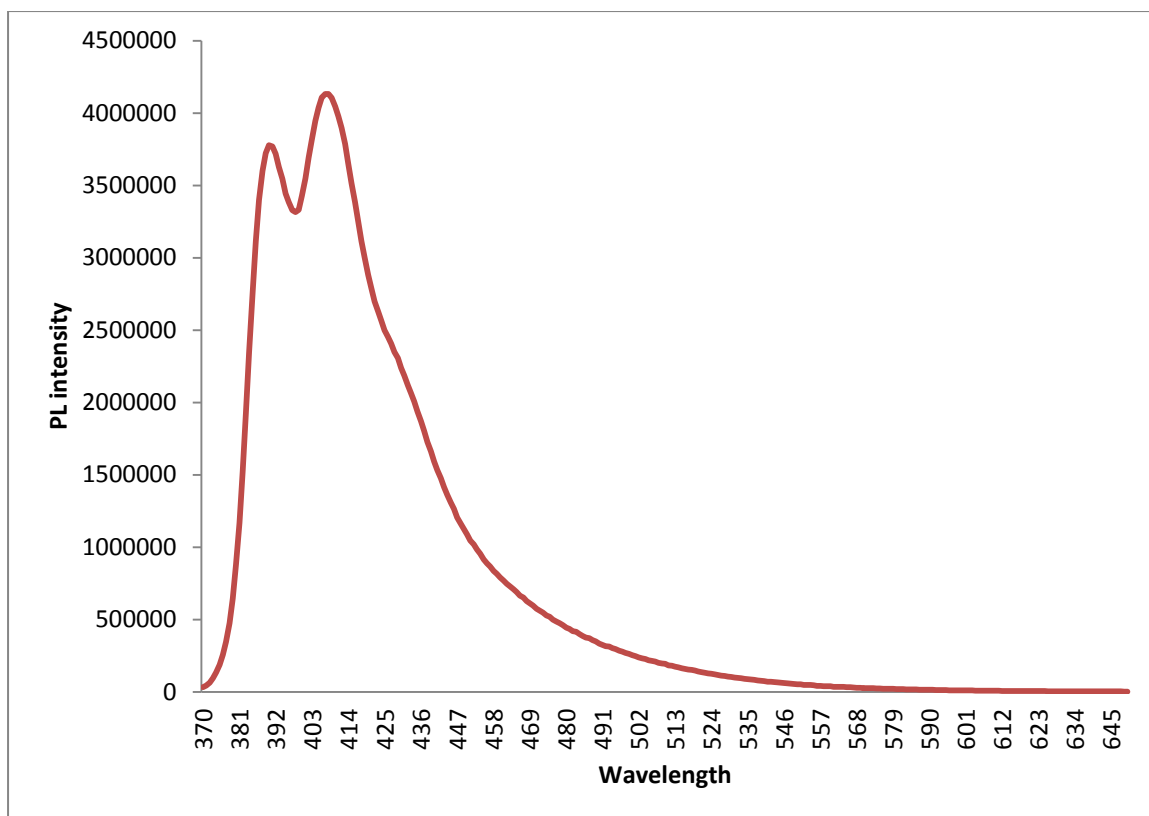


Figure 5- 8 PL intensity of the blank sample of sensing material versus wavelength.

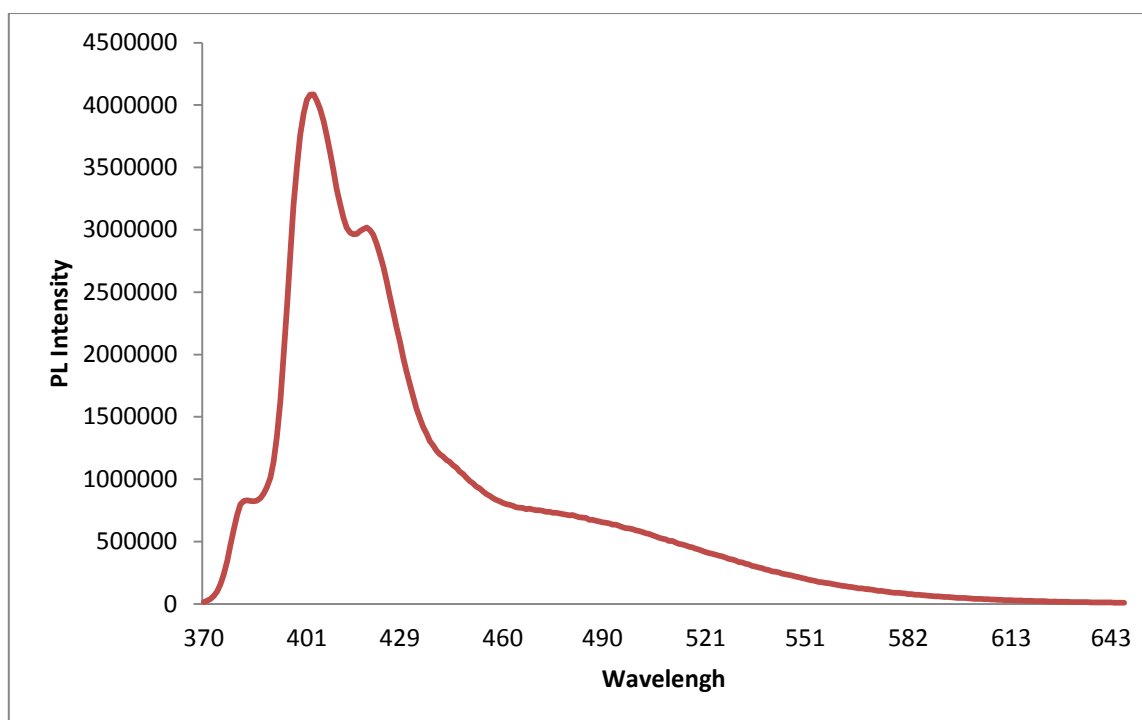


Figure 5- 9 Photoluminescence intensity of the sensor in 1 ppb Hg (II)

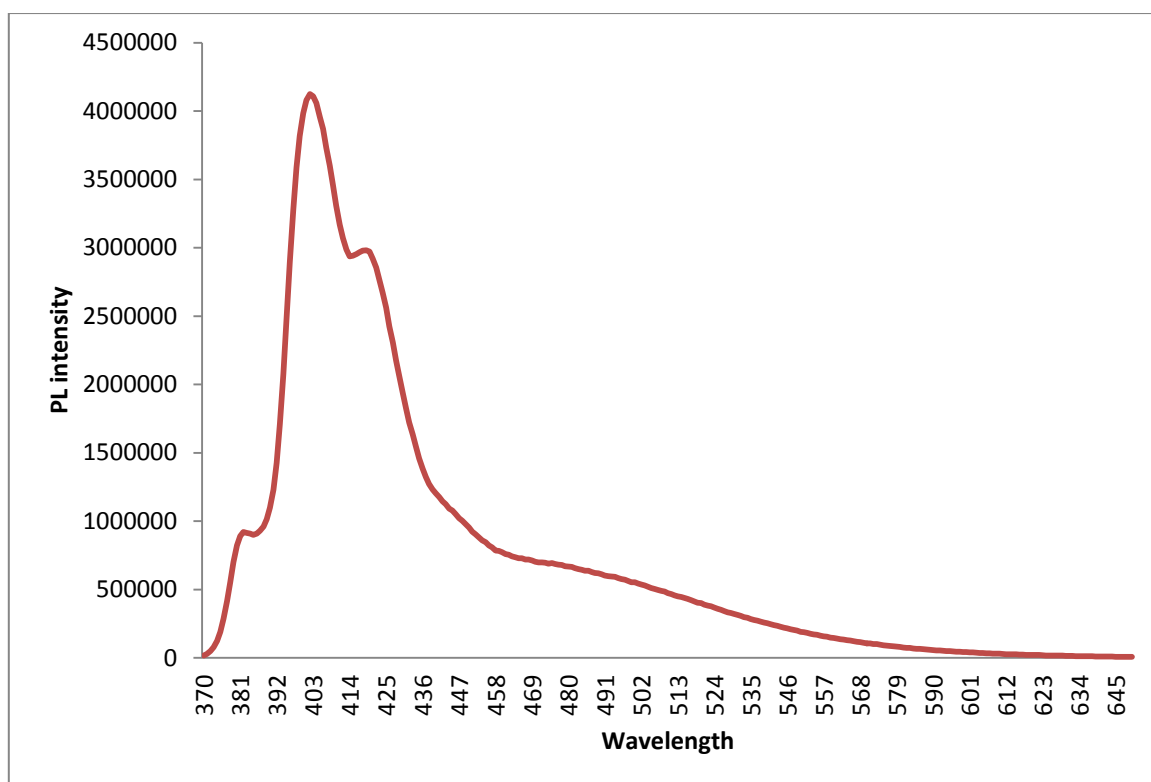


Figure 5- 10 Photoluminescence intensity of the sensor in 3 ppb Hg (II)

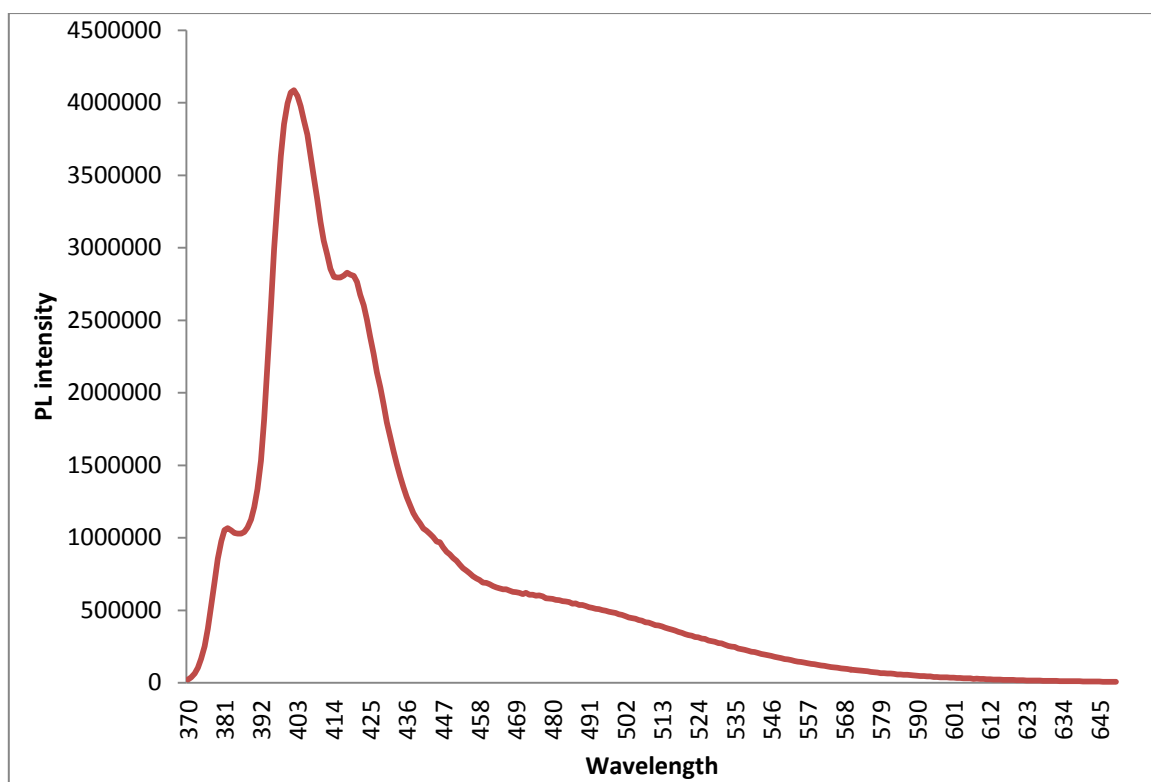


Figure 5- 11 Photoluminescence intensity of the sensor in 5 ppb Hg (II)

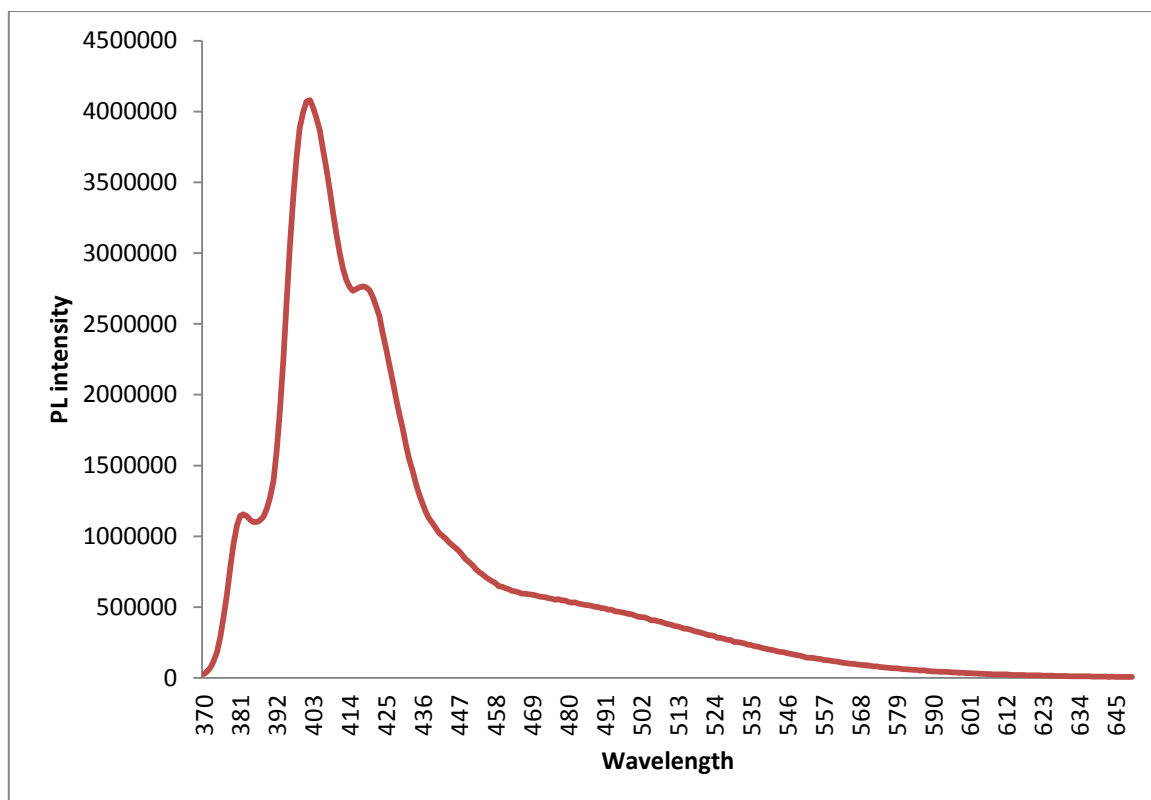


Figure 5- 12 Photoluminescence intensity of the sensor in 7 ppb Hg (II)

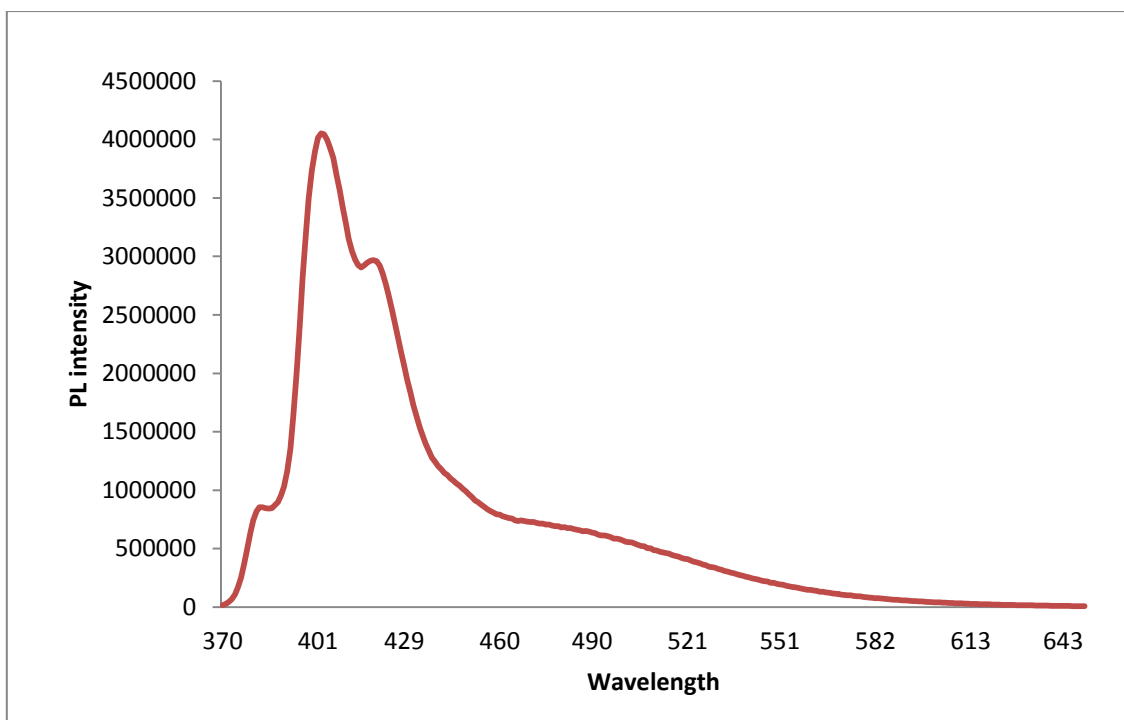


Figure 5- 13 Photoluminescence intensity of the the sensor in 9 ppb Hg (II)

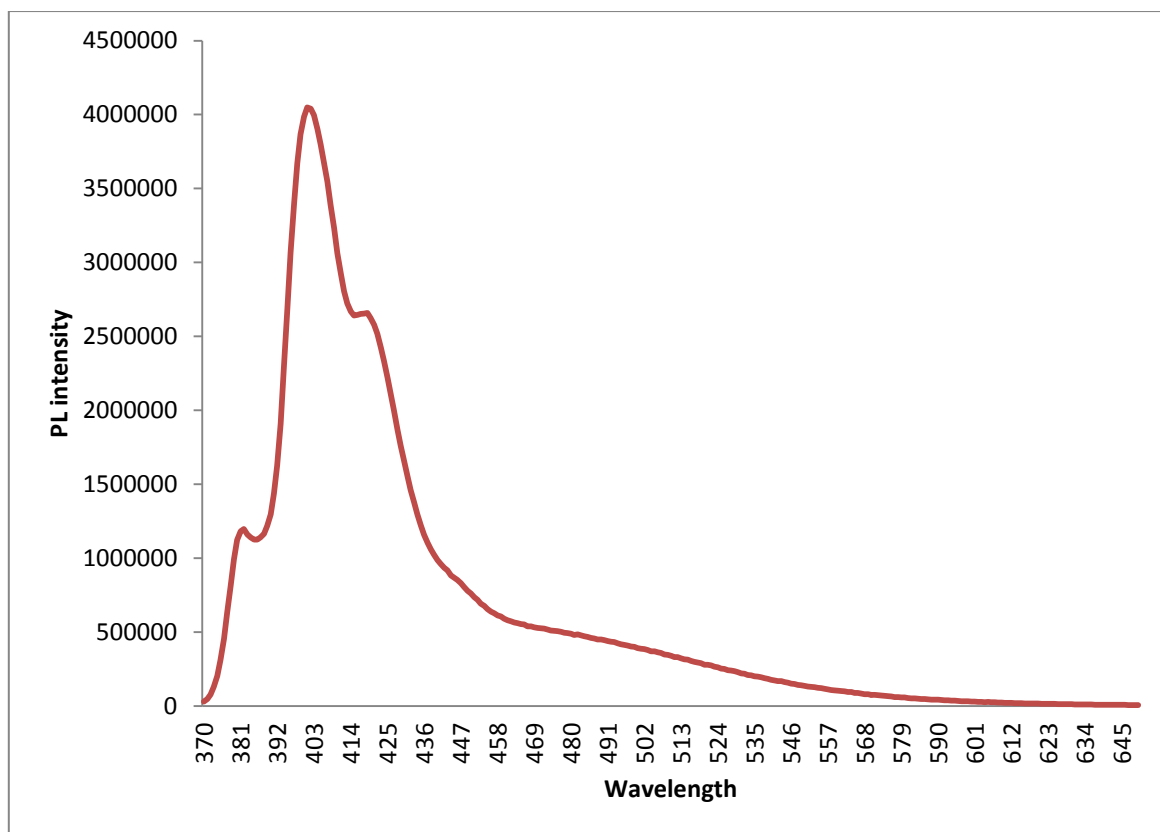


Figure 5- 14 Photoluminescence intensity of the the sensor in 11 ppb Hg (II)

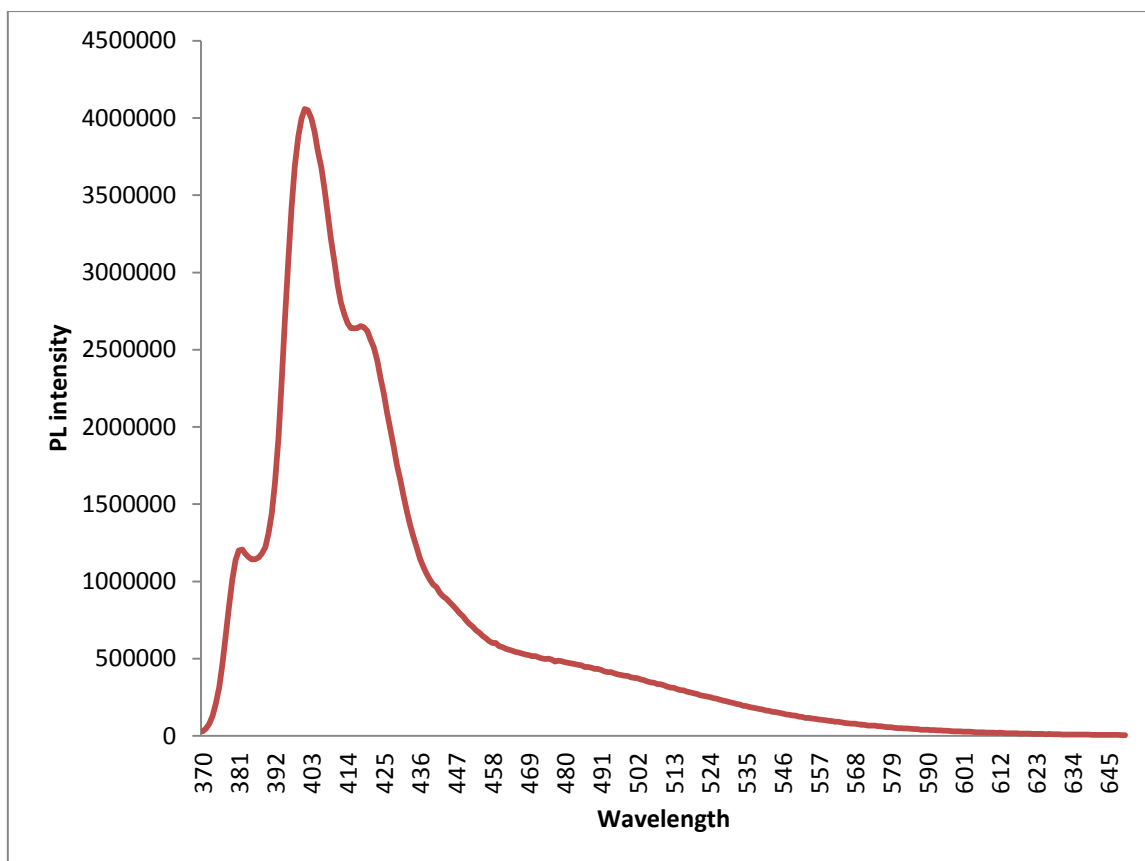


Figure 5- 15 Photoluminescence intensity of the sensor in 13 ppb Hg (II)

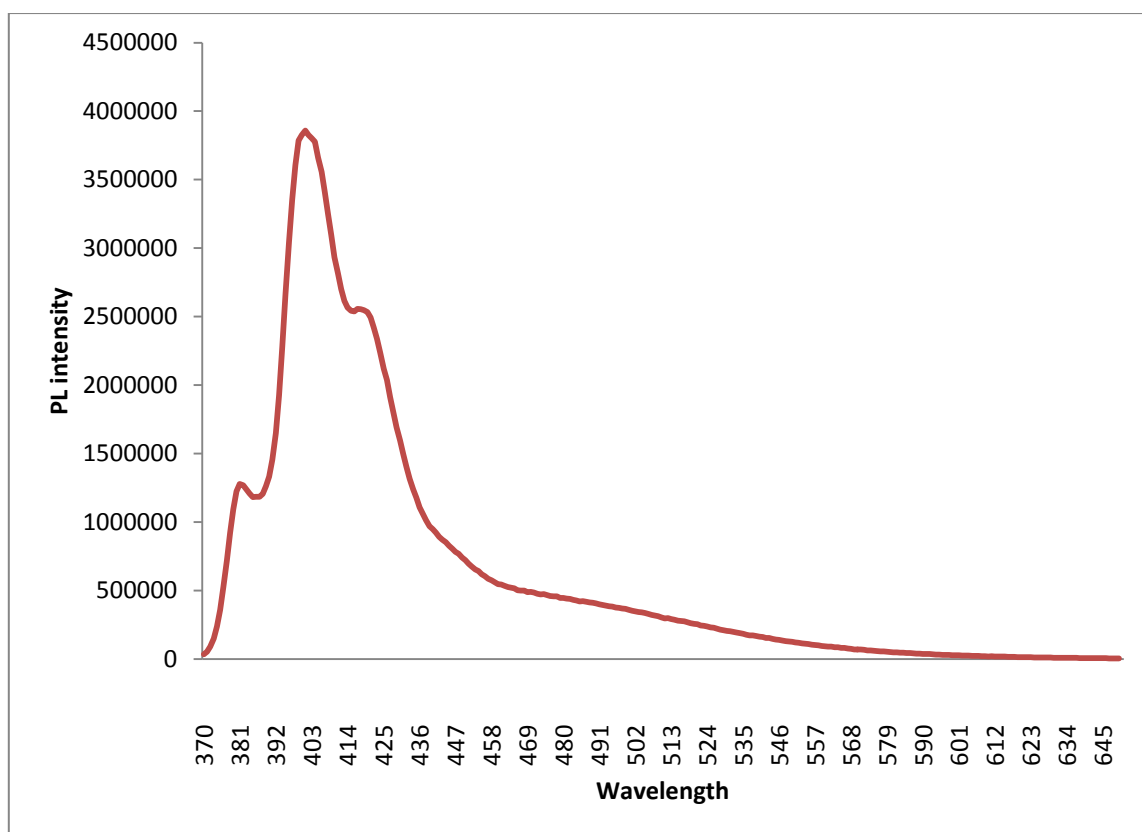


Figure 5- 16 Photoluminescence intensity of the sensor in 15 ppb Hg (II)

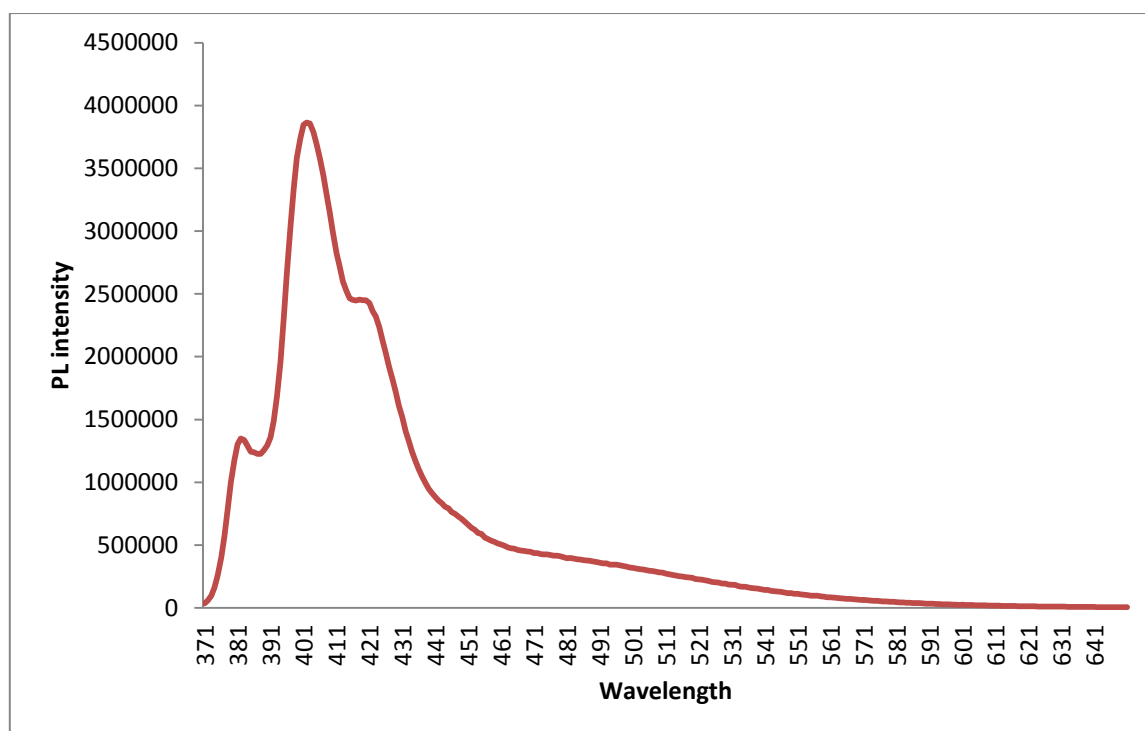


Figure 5- 17 Photoluminescence intensity of the sensor in 17 ppb Hg (II)

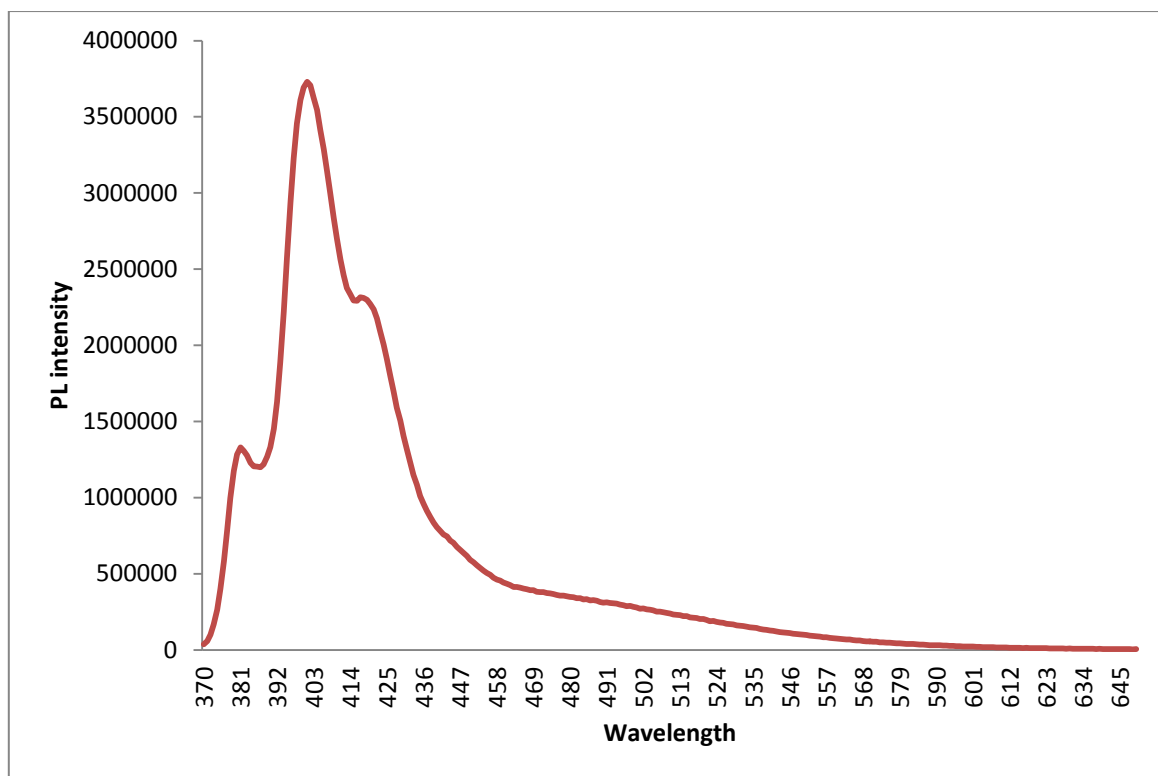


Figure 5- 18 Photoluminescence intensity of the sensor in 18 ppb Hg (II)

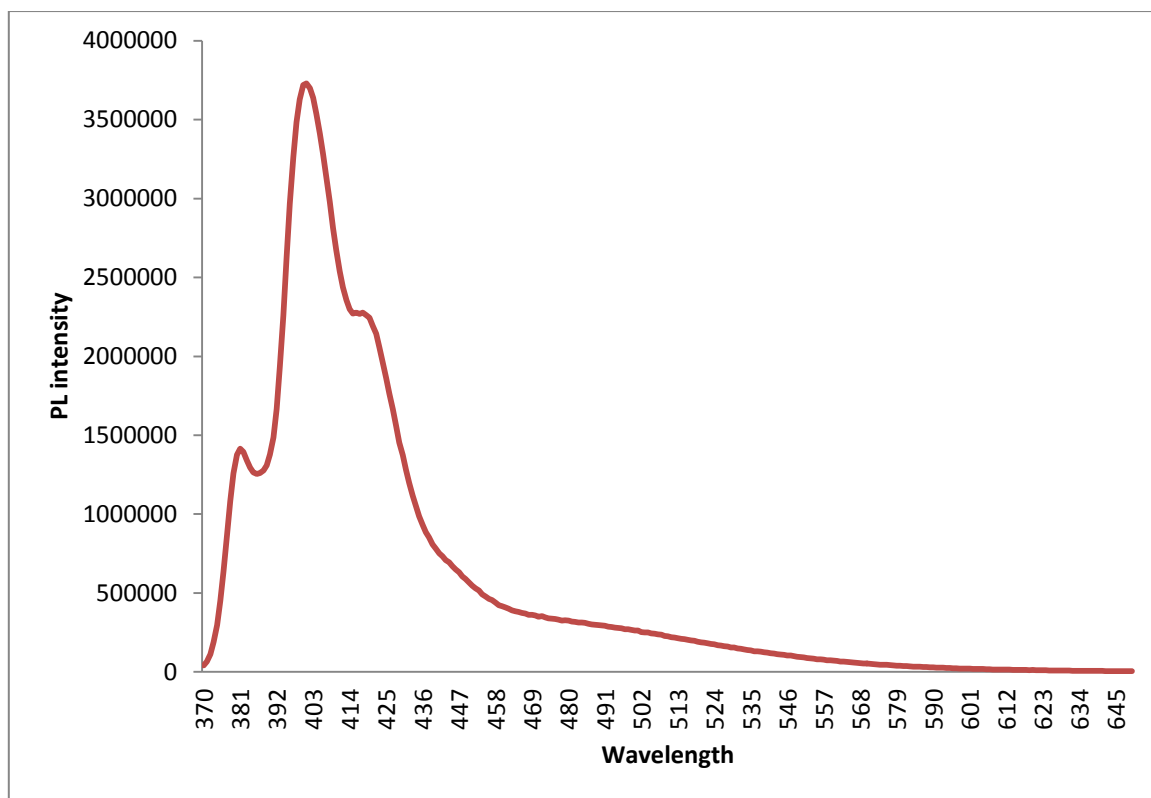


Figure 5- 19 Photoluminescence intensity of the sensor in 20 ppb Hg (II)

As we can see from the previous figures, a noticeable change in the intensities of the sensing material as the concentration of mercury ion increases. The PL intensities of the sensing material decrease as the Hg^{2+} concentrations increase. Table 5-1 demonstrates the PL intensity values of sensing material after each change in the concentration of the mercury ion.

The maximum peak intensities of the sensing material in the presence of mercury ion were found to be at the same wavelength of the black sample (402 nm). This implies that no shift in the maximum intensities of our chemosensor in the presence $\text{Hg}(\text{II})$ was considered during photoluminescence measurement. All photoluminescence intensities for all Hg^{2+} concentrations were at the same wavelength (402 nm).

Table 5-1 The decrease in PL intensities of sensor as Hg²⁺ increases

Hg ²⁺ Concentration (ppb)	PL intensity
Blank	4151730
1	4122376
3	4121100
5	4117272
7	4094299
9	4093623
11	4076432
13	3978304
15	3858976
17	3737238
18	3712416
20	3668321

Figure 5-20 shows that photoluminescence emission of our sensing material was significantly decreased successively with the increment of the concentration of mercury ion Hg^{2+} . This reduction in the intensities of the sensing material can be attributed to the quenching of pyrene in our sensing material (pyrene-functionalized silica nanoparticle) in the presence of mercury ion Hg^{2+} . Our sensing material could detect mercury in very small concentration. The detection limit of our chemosensor was 1 ppb, exactly the same value mentioned in WHO records.

The quenching of the pyrene-attached silica nanoparticles can be attributed to the strong interaction between the mercury ions and the pyrene rings in the sensing material which will lead to form a complex between the pyrene and mercury ions.

Figure 5-20 shows the complex formation between the mercury ions and the sensing material.

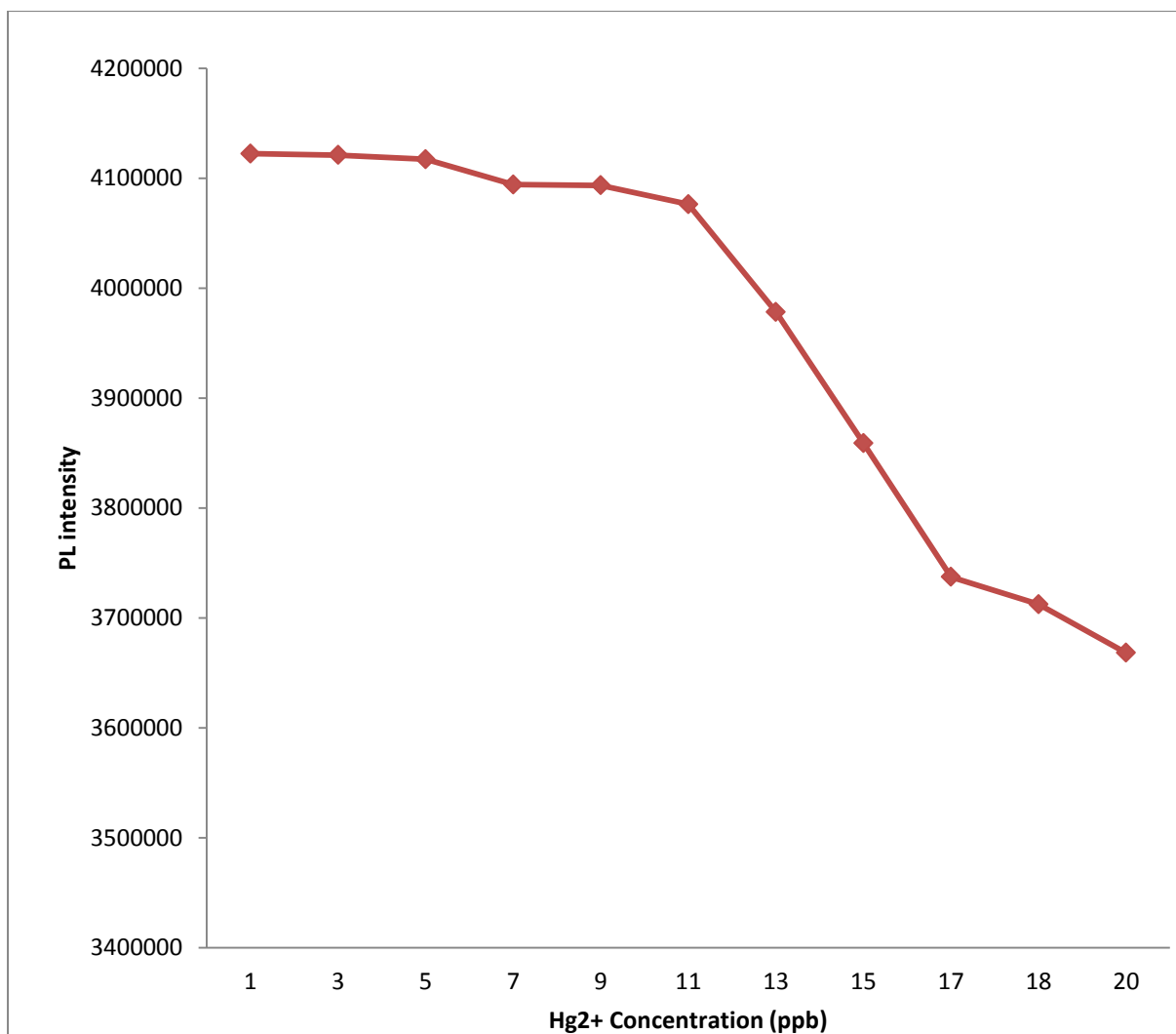


Figure 5- 20 PL intensities of the sensing material versus the concentration of Hg²⁺

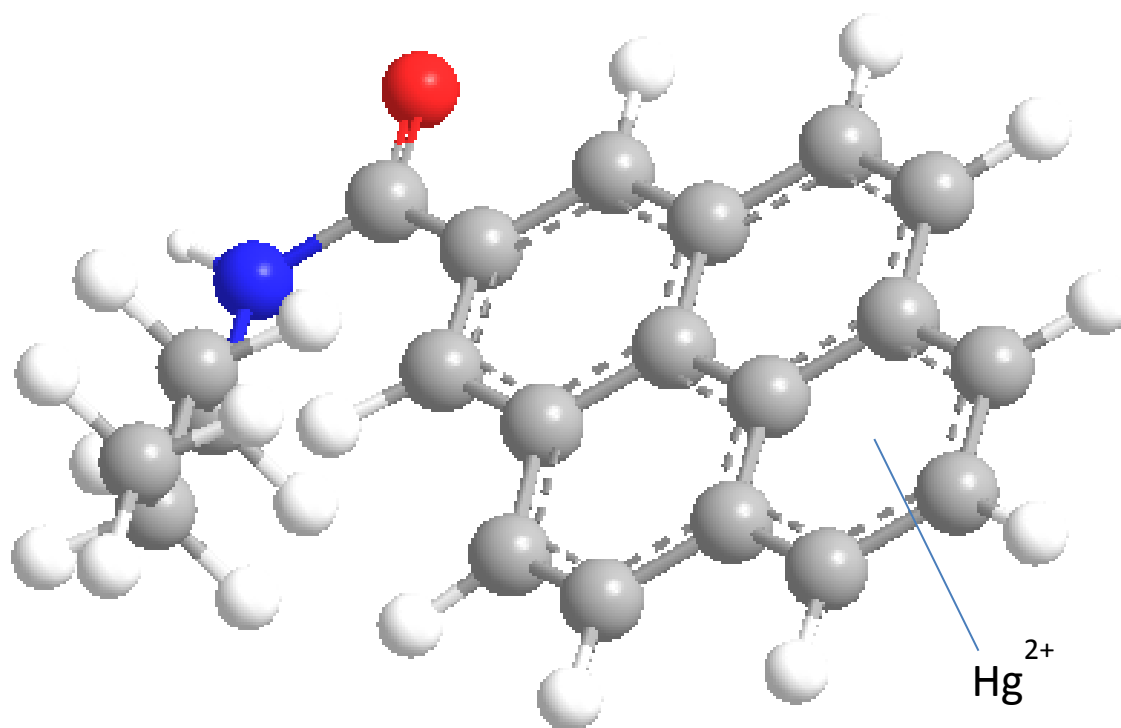


Figure 5- 21 Complex formation between mercury and pyrene in sensing material

We can quantify the quenching of the pyrene-attached silica nanoparticles by applying Stern-Volmer equation:

$$I_0/I = 1 + K_{sv} [Q]$$

I_0 : The maximum intensity of the sensing material without the quencher particles

I : The maximum intensity of the sensing material with the quencher particles

K_{sv} : Stern-Volmer quenching constant

Q : The concentration of the quencher particles in M.

When we plot I_0/I of our data versus Q which is the concentration of the mercury ions we get the following curve in figure 5-22.

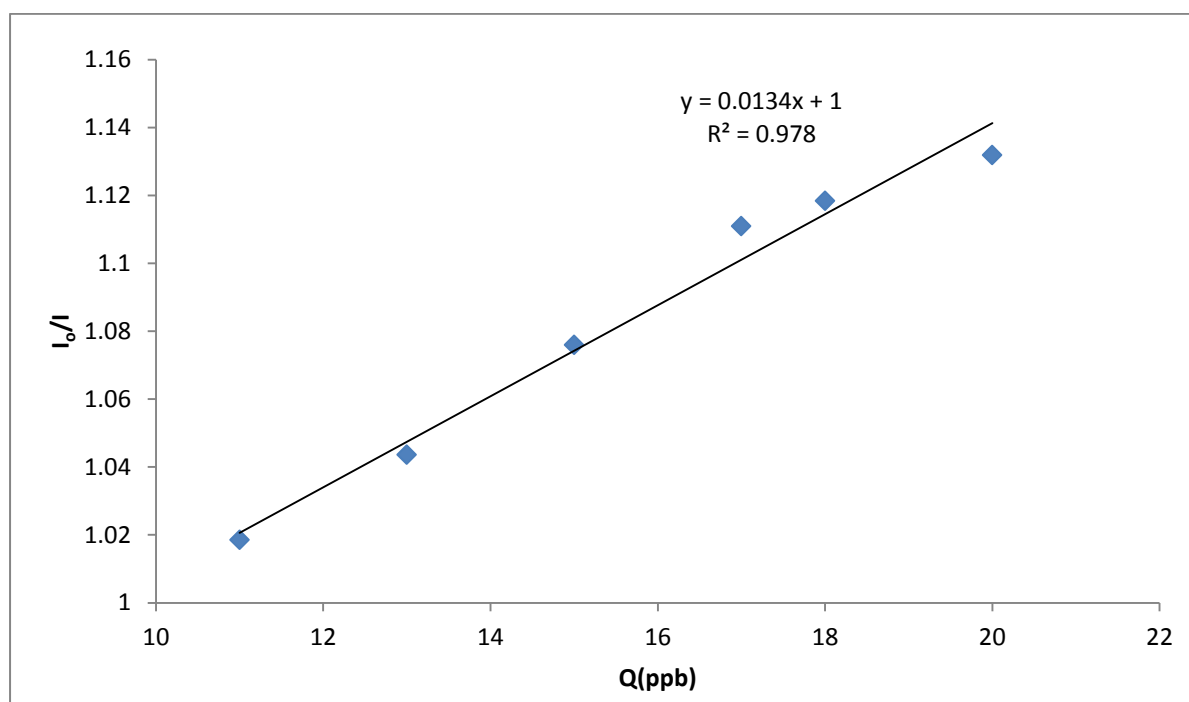


Figure 5- 22 Stern-Volmer equation plot

We got a slope of 0.0134 ppb^{-1} , so we need to convert it into M^{-1} . Since 1 ppb of mercury = $4.985 \times 10^{-9} \text{ M}$, we get Stern-Volmer quenching constant ($K_{sv} = 2.7 \times 10^6 \text{ M}^{-1}$).

5.2.2 The effect of mercury ion on the intensities of the nanoparticles within time

To study the effect of time of incubation of mercury ion with pyrene-functionalized silica nanoparticles, four samples of the sensing material contain four different concentrations of the mercury ion were prepared to measure their photoluminescence intensities. These samples were incubated for two days under room temperature and measured again to see if there is any change in their photoluminescence values. Surprisingly, there was a significant decrease in the photoluminescence intensities of our sensing material in comparison with the photoluminescence intensities that we got before two days. This will lead us to conclude that quenching of our sensing material in the presence of mercury ion keeps going even after two days of incubation. This reflects the high reproducibility of our material as a chemosensor.

Table 5-2 shows the photoluminescence intensities of the sensing material before and after two days of incubation with the mercury ion.

Figure 5-23 exhibits the difference in photoluminescence intensities of the sensing material in the presence of mercury ion before and after two days of incubation at room temperature.

Figures from figure 5-24 to figure 5-31 show the PL intensities of the sensing material before and after two days of incubation with Hg^{2+} ions.

Table 5-2 PL intensities of sensing material with Hg^{2+} ions before and after two days

Hg^{2+} Concentrations (ppb)	PL intensities before 2 days	PL intensities after 2 days
11	4057288	4027935
13	3916832	3851744
15	3858976	3724653
17	3748865	3628616

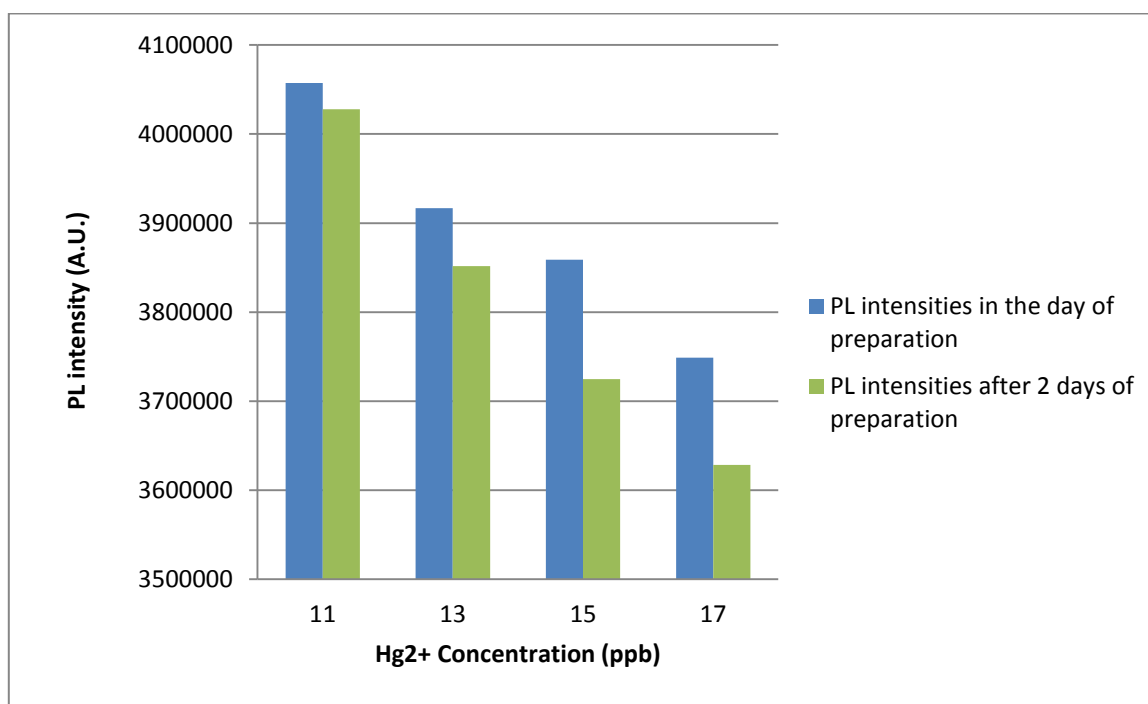


Figure 5- 23 The difference in photoluminescence intensities before and after two days

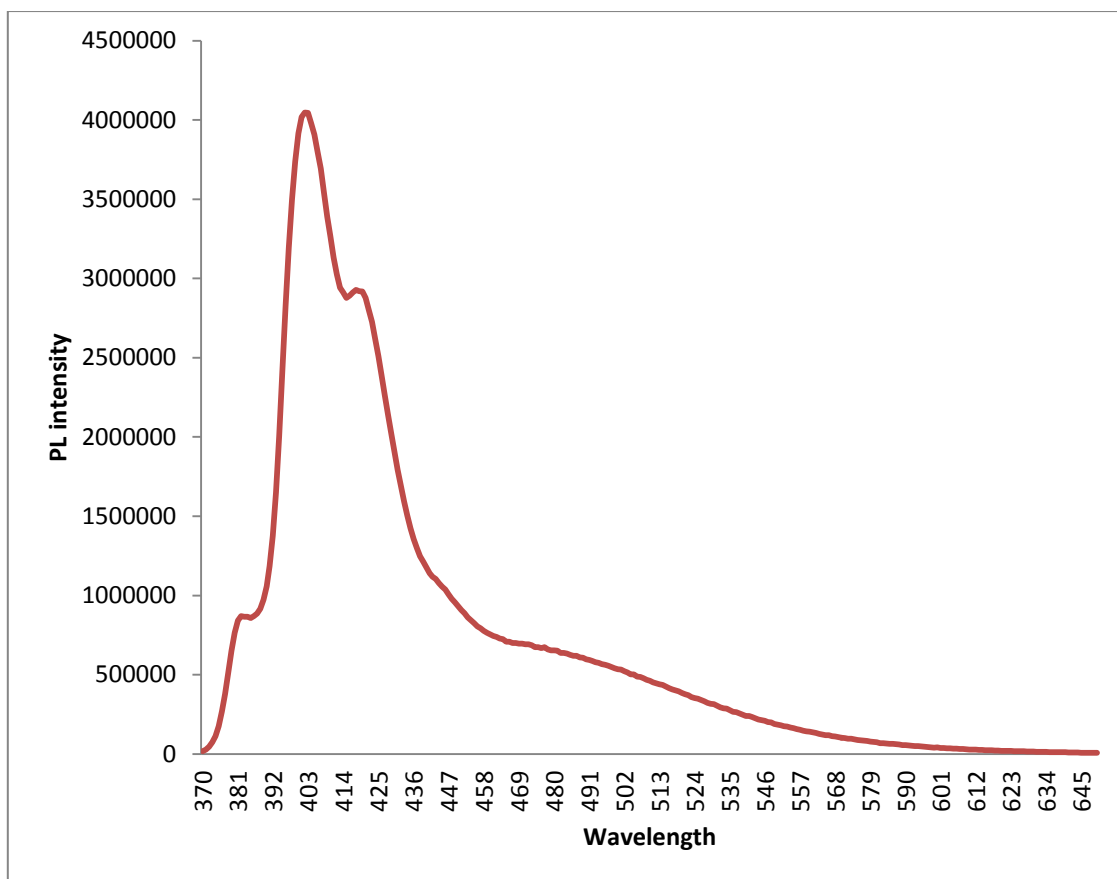


Figure 5- 24 intensities of sensing material with 11 ppb of Hg^{2+} before two days

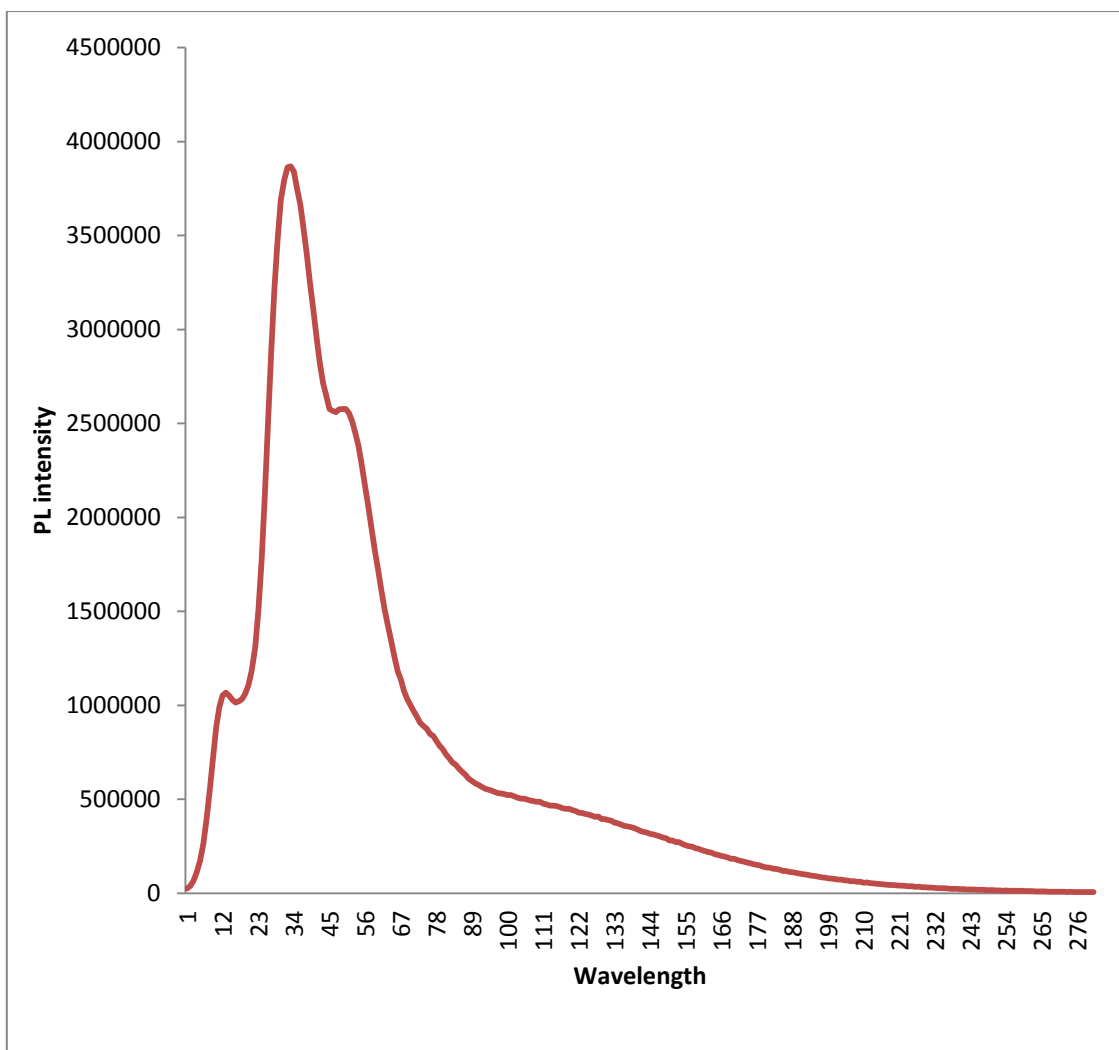


Figure 5- 25 PL intensities of sensing material with 13 ppb of Hg^{2+} before two days

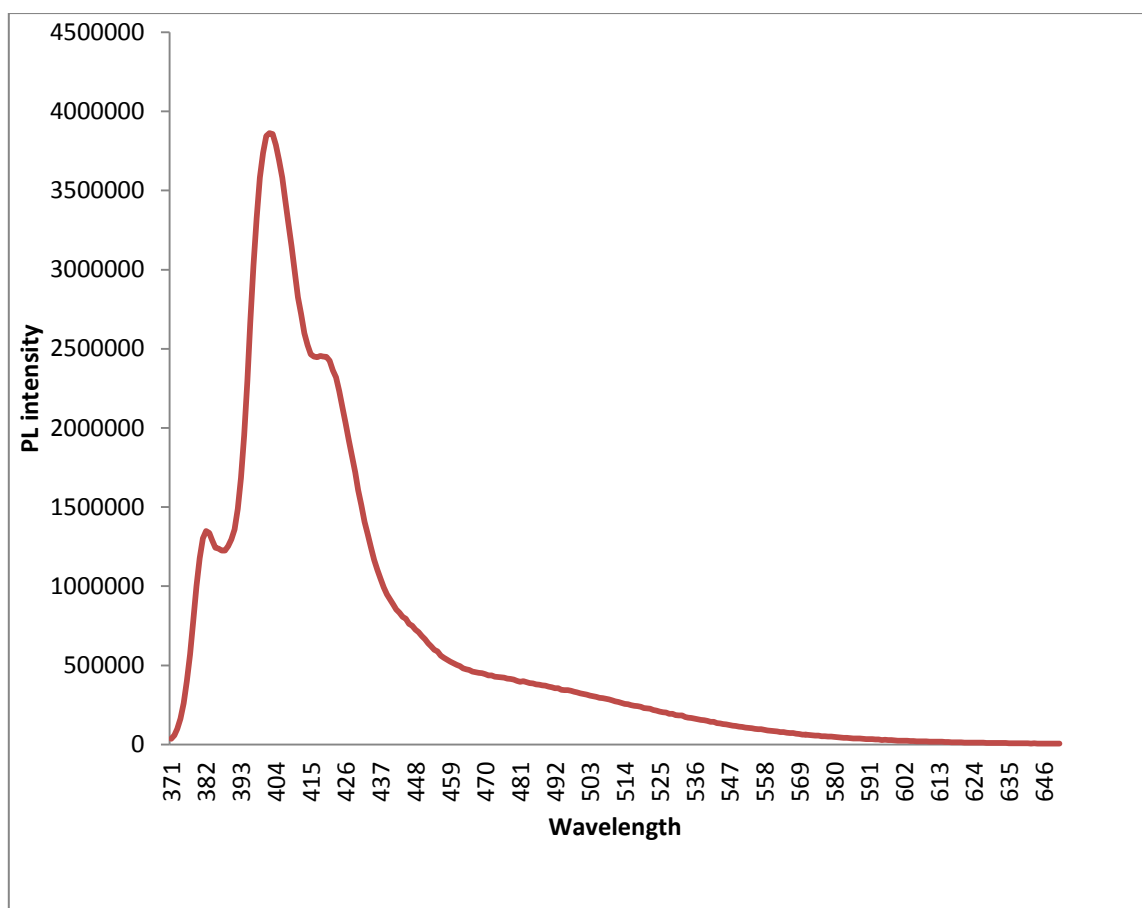


Figure 5- 26 PL intensities of sensing material with 15 ppb of Hg^{2+} before two days

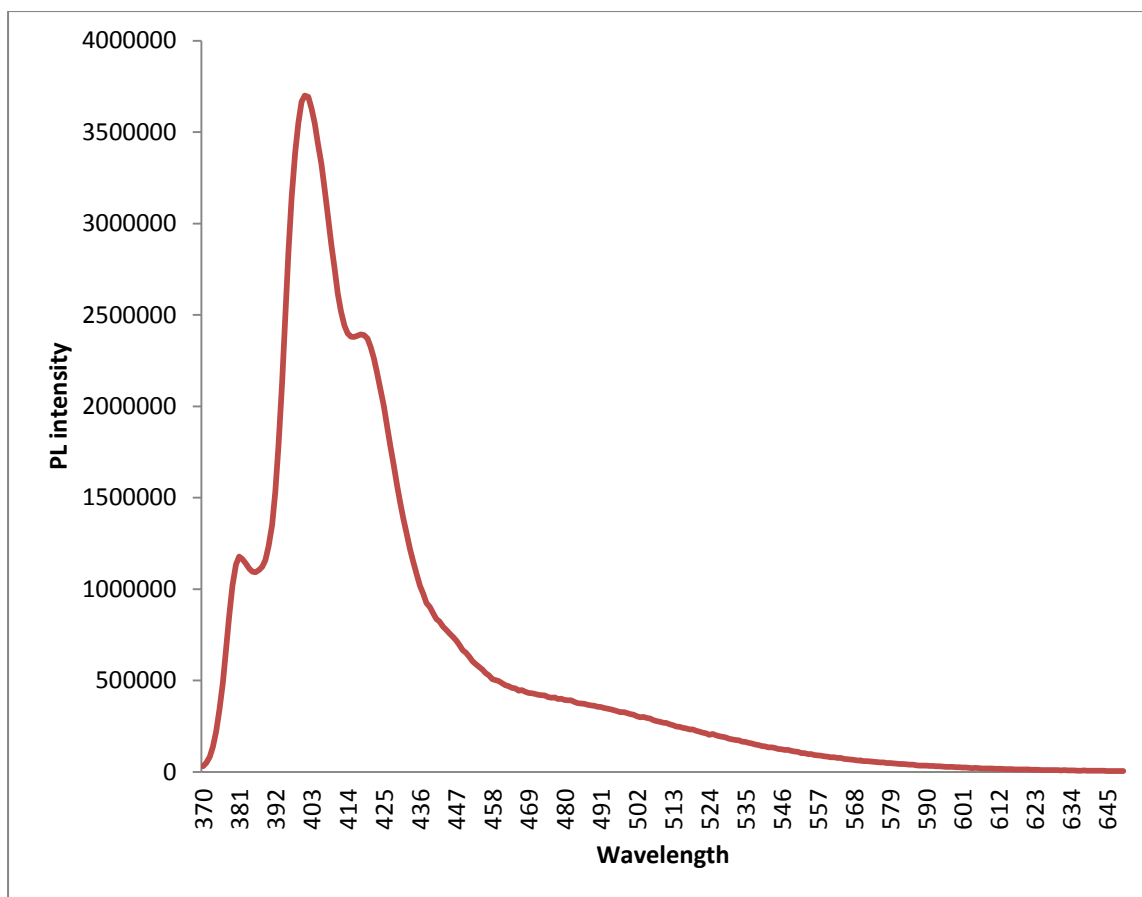


Figure 5- 27 PL intensities of sensing material with 17 ppb of Hg^{2+} before two days

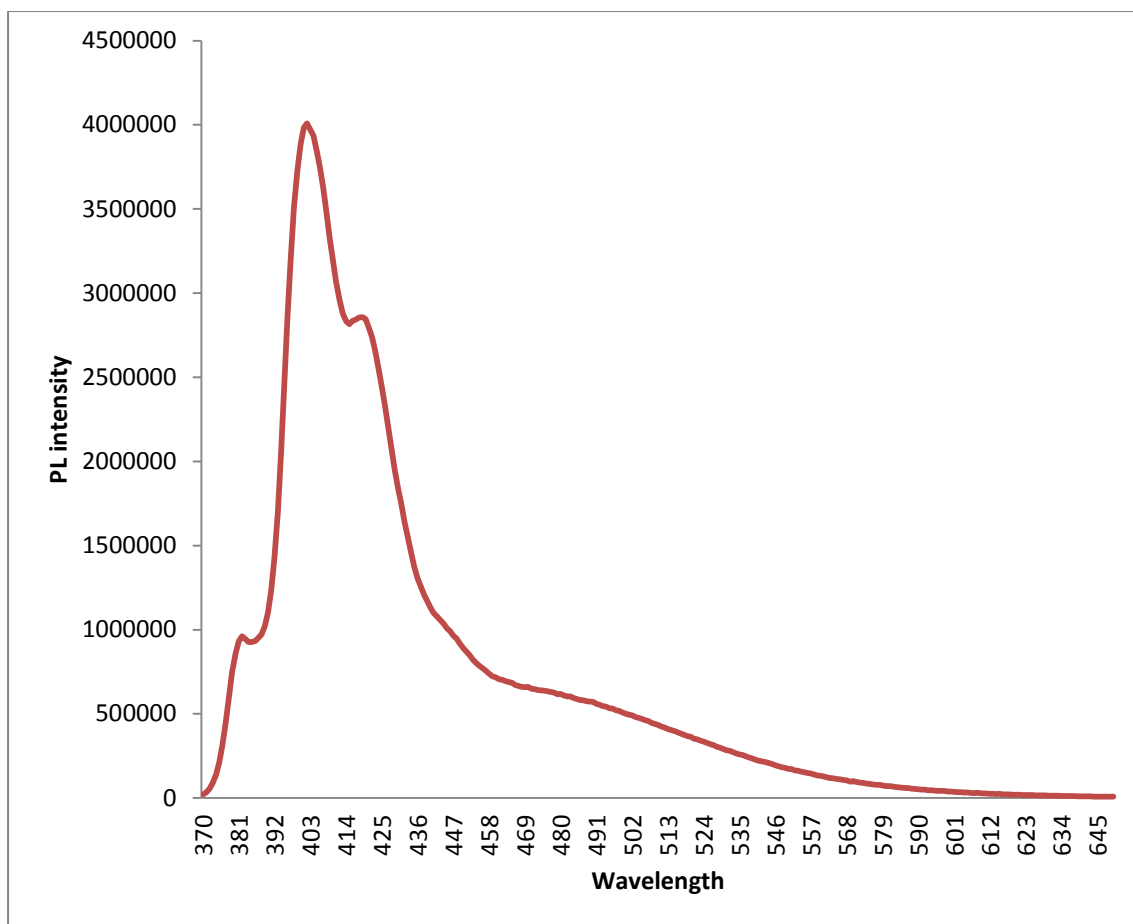


Figure 5- 28 PL intensities of sensing material with 11 ppb of Hg^{2+} after two days

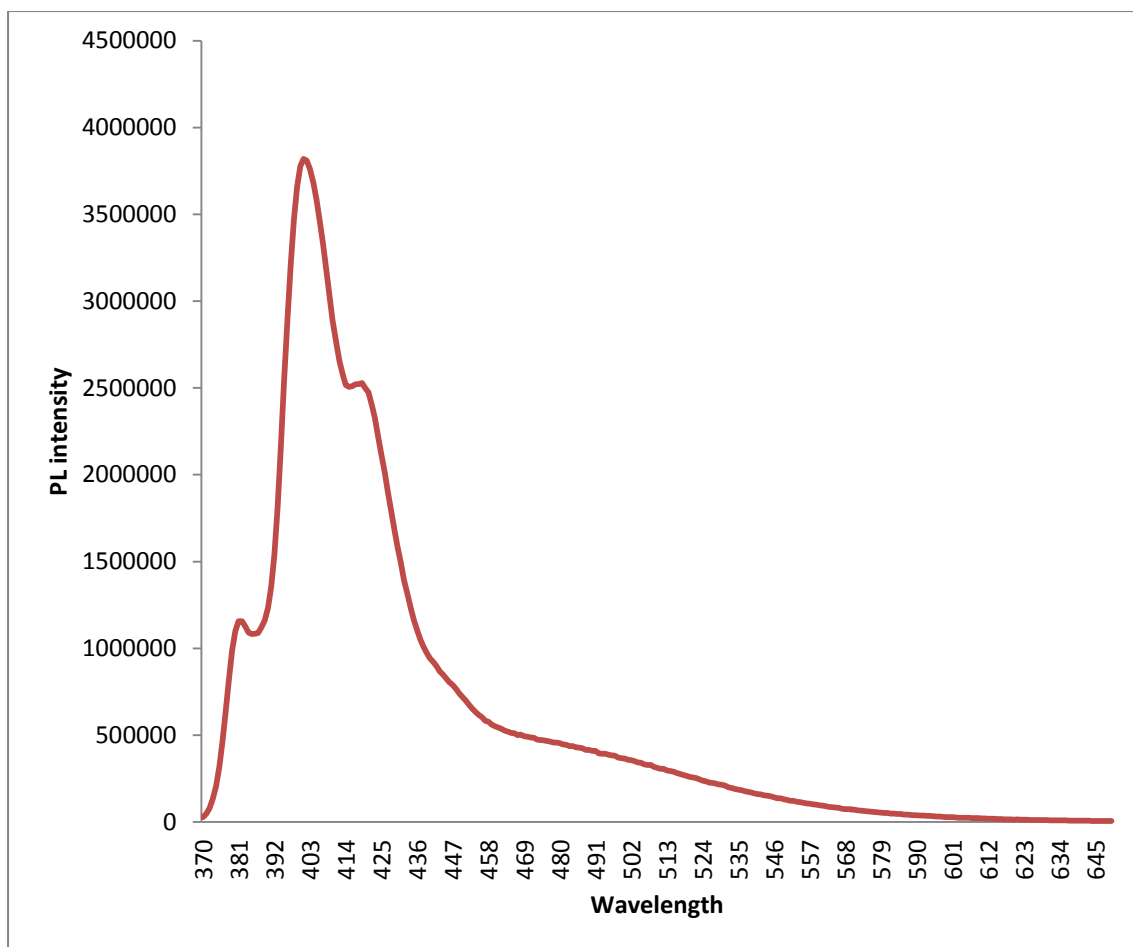


Figure 5- 29 PL intensities of sensing material with 13 ppb of Hg^{2+} after two days

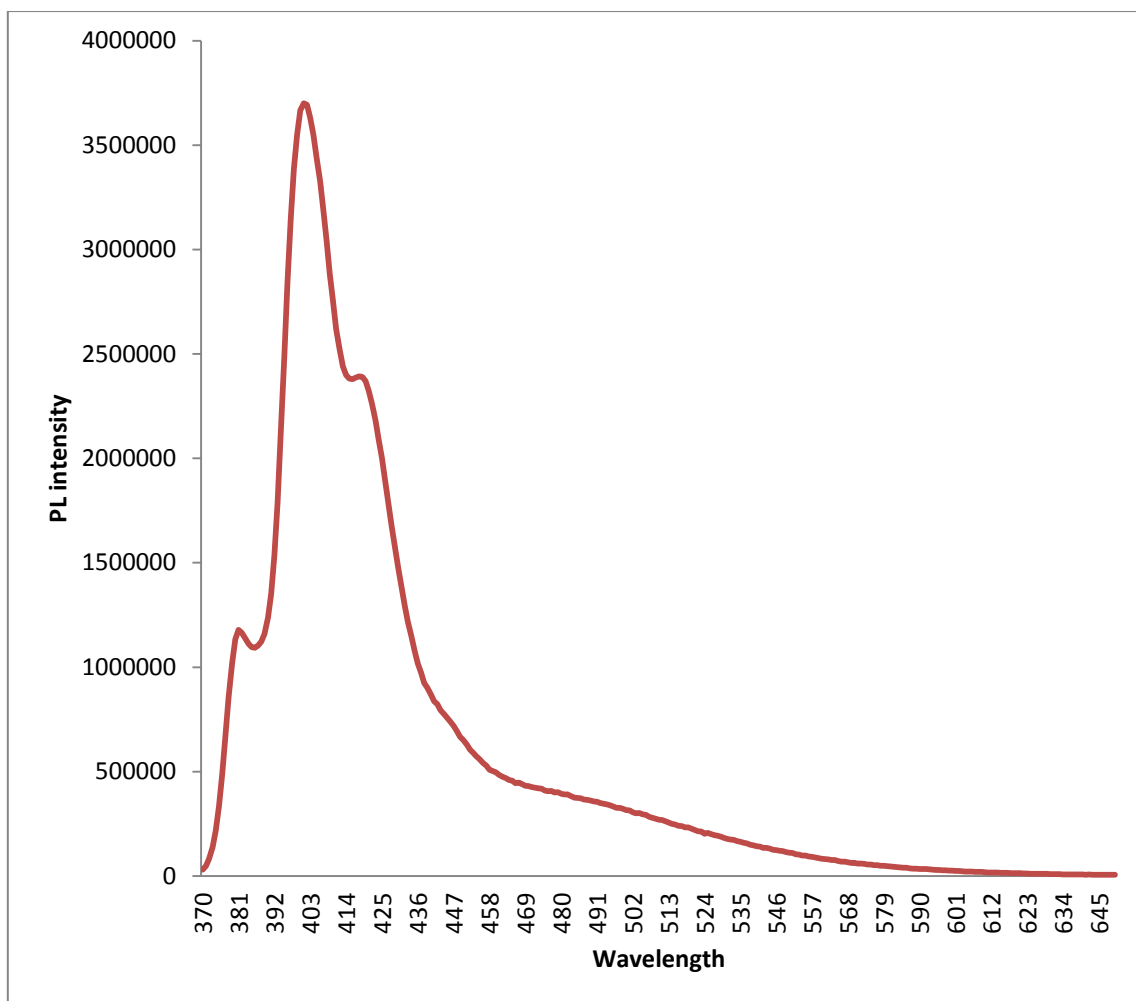


Figure 5- 30 PL intensities of sensing material with 15 ppb of Hg^{2+} after two days

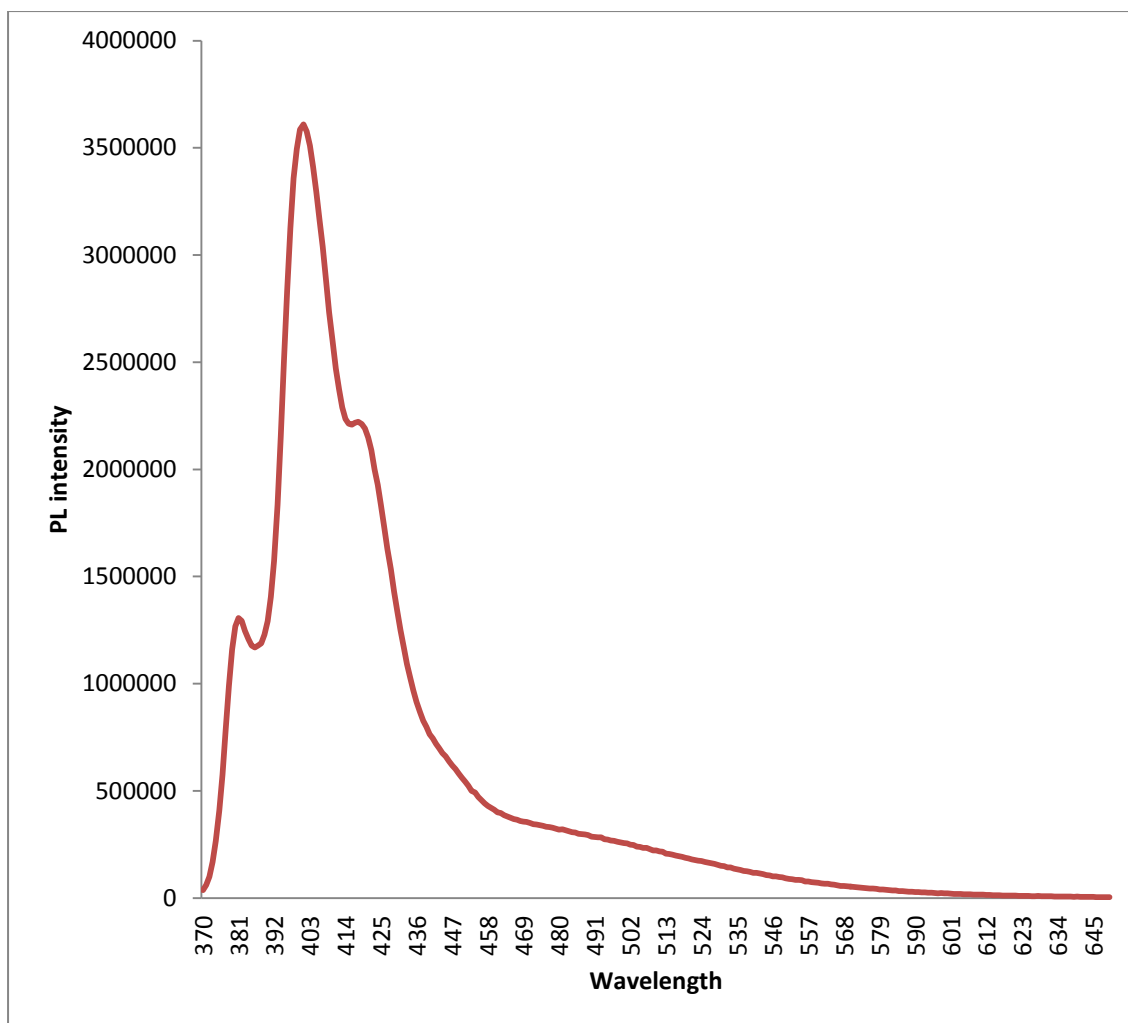


Figure 5- 31 PL intensities of sensing material with 17 ppb of Hg^{2+} after two days

5.3 Other Applications of the pyrene-functionalized silica nanoparticles

Our sensing material appeared fluorescent when it was dissolved in ethanol. As a result, our synthesized pyrene-attached silica nanoparticles can be successfully applied in the detection of ethanol or even other alcohols.

Figure 5-32 shows our sensing material fluorescent in when it is dispersed in water and ethanol.

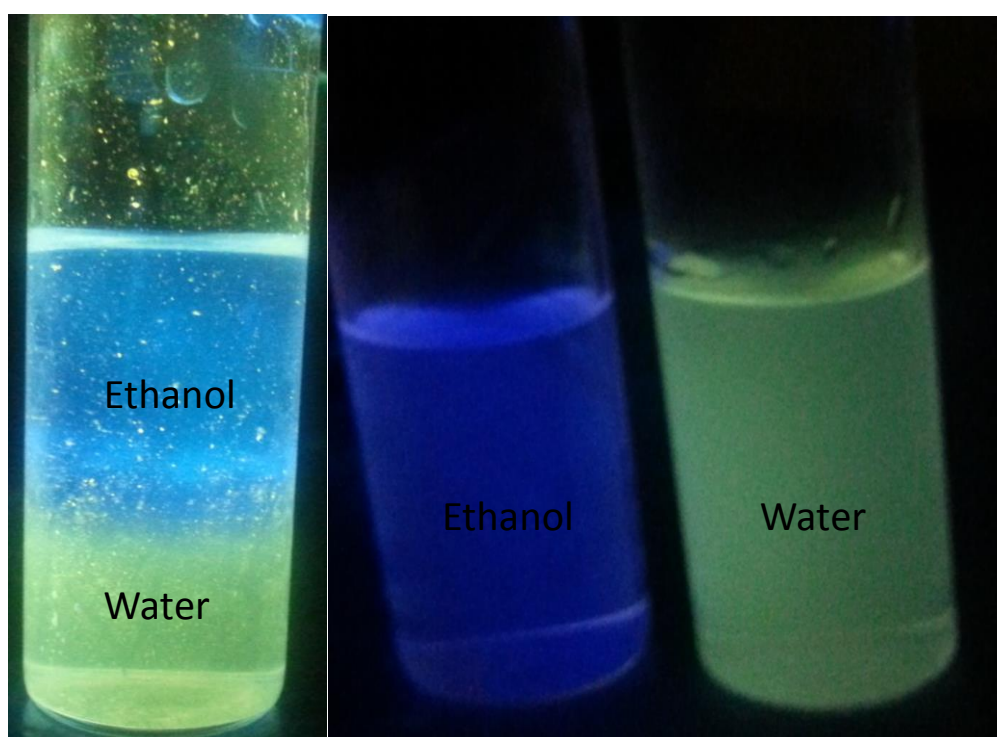


Figure 5-32 Fluorescence of pyrene- attached silica nanoparticles in water and ethanol.

CHAPTER 6

CONCLUSION

Our sensing material (pyrene-functionalized silica nanoparticles) exhibited high sensitivity toward the detection of mercury ion in aqueous media. The detection limit is 1 ppb, which is a very good result, since it is the highest permitted values of mercury ions in drinking water mentioned in WHO records. Our sensing material was developed through simple process by cheap silica precursors as well. The attachment of pyrene was also achieved by a well-known peptide coupling reaction. Our method does not include any complicate process or any expensive material. As a result, our work can provide a new method for developing an efficient portable silica nanoparticles-based chemosensor for the detection of mercury ion. The pyrene-attached silica nanoparticles demonstrate also fluorescence properties in the ethanol which gives us a hint that this sensor can be used for the detection of ethanol as well. In future, our synthesized pyrene-attached silica nanoparticles could be further studied for the detection of other metals. This chemosensor may be modified so it may be used for removal of mercury not only detection of mercury. Our sensor can be also further studied to check its ability to detect other alcohols. The pyrene-attached silica nanoparticles can be synthesized of different size shape and morphologies with high surface area to interact with mercury ions and other possible pollutants as well.

The silica nanoparticles can be synthesized from hydrophobic silanes to develop sensors work with organomercury species as well as in hydrophobic elements.

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