UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF ELECTROCHEMICAL SENSOR BASED ON SILICA AND SILICA/GOLD NANOPARTICLE ELECTRODE FOR DETECTION OF ARSENIC (III)

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ITMA 2019 12

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By

SUHAINIE BINTI ISMAIL

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

November 2017

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

DEVELOPMENT OF ELECTROCHEMICAL SENSOR BASED ON SILICA AND SILICA/GOLD NANOPARTICLE ELECTRODE FOR DETECTION OF ARSENIC (III)

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November 2017

Chair : Nor Azah Yusof, PhD
Faculty : Institute of Advanced Technology

Electrochemical sensor for the detection of arsenic(III) has been successfully developed based on nanoparticles modified screen printed carbon electrode (SPCE). In this research, silica nanoparticles (SiNPs) and gold nanoparticles (AuNPs) were used as a modifier to enhance the performance of disposable screen printed carbon electrode. The electrocatalytic responses of the SiNPs and SiNPs/AuNPs modified electrode for the detection of As(III) were measured using cyclic voltammetry (CV) and linear sweep anodic stripping voltammetry (LSASV). The screen printed carbon electrode was modified by drop casting the nanoparticles onto the working electrode. There are two types of modified electrode were developed for detection and quantification of As(III) ions. Firstly, SiNPs/SPCE electrode was prepared by casting the SiNPs onto the SPCE surface. Meanwhile, AuNPs/SiNPs/SPCE electrode was prepared by casting the SiNPs onto the working electrode, and then layered with 3-mercaptopropionic acid (MPA) followed by attachment of AuNPs. Both modified electrode, SiNPs/SPCE and AuNPs/SiNPs/SPCE were then applied for As(III) detection. Electrochemical studies using LSASV performed with SiNPs/SPCE and AuNPs/SiNPs/SPCE were found to give a better response through the optimization of numerous analytical parameters. The detection of As(III) using SiNPs/SPCE showed a linear response towards different concentration of As(III) and linear calibration curve with R^2 = 0.9702 was obtained. The detection limit of 5.64 μg L^{-1} was achieved by applying deposition potential of -0.5 V and deposition time of 120 s. Meanwhile, the detection of As(III) using AuNPs/SiNPs/SPCE gave a linear response towards different concentration of As(III) and linear calibration curve with R^2 = 0.9975 was obtained. The detection limit of 1.4 μg L^{-1} was achieved by applying deposition potential of -0.4 V and deposition time of 120 s. The modified SPCE was characterized using Field Emission Scanning Electron Microscope (FESEM), Transmission Electron Microscope (TEM), and Energy Dispersive X-ray (EDX) respectively. The proposed methods showed good selectivity of target analyte even in the

presence of some foreign ions. Furthermore, the developed sensors; SiNPs/SPCE and AuNPs/SiNPs/SPCE showed good reproducibility for six measurements where the RSD values of 5.72 % and 4.52 % were obtained, respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PEMBANGUNAN ELECKTROKIMIA SENSOR BERDASARKAN NANOPARTIKEL SILIKA DAN SILIKA/EMAS ELEKTROD UNTUK PENGESANAN ARSENIK(III)

Oleh

SUHAINIE BINTI ISMAIL

November 2017

Pengerusi : Nor Azah Yusof, PhD
Fakulti : Institut Teknologi Maju

Sensor elektrokimia untuk pengesanan arsenik(III) telah berjaya dibangunkan berdasarkan modifikasi elektrod karbon skrin bercetak (SPCE) menggunakan nanopartikel . Dalam kajian ini, nanopartikel silika (SiNPs) dan nanopartikel emas (AuNPs) telah digunakan sebagai pengubah untuk meningkatkan prestasi elektrod karbon skrin bercetak (SPCE). Respon elektrokatalik SiNPs dan AuNPs/SiNPs elektrod yang diubahsuai untuk mengesan As(III) diukur menggunakan CV dan LSASV. Elektrod karbon skrin bercetak (SPCE) telah diubahsuai oleh teknik penyalutan acuan menggunakan nanopartikel ke elektrod kerja. Terdapat dua jenis elektrod yang diubahsuai menggunakan nanopartikel untuk pengesanan dan pengukuran ion As(III). Pertama, elektrod SiNPs/SPCE disediakan dengan meletakkan SiNPs ke permukaan elektrod karbon skrin bercetak. Sementara itu, elektrod AuNPs/SiNPs/SPCE disediakan dengan meletakkan SiNPs ke elektrod karbon skrin bercetak kemudian dilapisi dengan asid 3-mercaptopropionic (MPA) diikuti oleh AuNPs. Kedua-dua elektrod diubahsuai, SiNPs/SPCE dan AuNPs/SiNPs/SPCE kemudiannya digunakan untuk pengesanan As(III). Kajian elektrokimia menggunakan teknik LSASV yang dilakukan dengan SiNPs/SPCE dan AuNPs/SiNPs/SPCE didapati memberi tindak balas yang lebih baik melalui pengoptimuman parameter analitikal yang bersesuaian. Pengesanan As(III) menggunakan SiNPs/SPCE menunjukkan tindak balas linear ke arah kepekatan yang berbeza seperti As(III) dan lengkung penentukuran linear dengan R^2 = 0.9702 diperoleh. Had pengesanan 5.64 μg L^{-1} telah dicapai dengan menggunakan potensi pemendapan -0.5 V dan masa pemendapan sebanyak 120 s. Sementara itu, pengesanan As(III) menggunakan AuNPs/SiNPs/SPCE memberikan tindak balas linear ke arah kepekatan yang berbeza dari keluk penentukuran As(III) dan linear dengan R^2 = 0.9975 diperolehi. Had pengesanan 1.4 μg L^{-1} telah dicapai dengan menggunakan potensi pemendapan sebanyak -0.4 V dan masa pemendapan sebanyak 120 s. SPCE yang diubahsuai telah dicirikan menggunakan mikroskop pengimbasan pelepasan medan (FESEM), mikroskop electron transmisi (TEM), dan tenaga dispersif sinar-X (EDX) masing-masing. Kaedah yang dicadangkan menunjukkan pemilihan yang baik bagi penganalisis sasaran walaupun dengan adanya beberapa ion asing. Tambahan pula, sensor yang dibangunkan; SiNPs/SPCE dan AuNPs/ SiNPs/SPCE menunjukkan kebolehulangan yang baik untuk enam ukuran di mana nilai RSD 5.72 % dan 4.52 % diperolehi.

ACKNOWLEDGEMENTS

All praise to Allah S.W.T who has showered me with kindness and affection during my study. His endless grace and love have provided the strength to finish this study.

I would like to express my deepest gratitude to my supervisor, Prof. Dr. Nor Azah Yusof for giving me an opportunity to do my Master and for always gave me continuous support during my Master study and research. I would also like to thank her for her patience, motivation, enthusiasm, and immense knowledge. Her guidance helped me all the time in research and writing of this thesis. Working under her supervision is one of the best experiences in my life. Special thanks to my co-supervisor, Dr. Jaafar Abdullah for his guidance and valuable comments on my Master work. This thesis dedicated to both my parents who have been my source of motivation and strength during moments of despair and discouragement

I also would like to thank all my sisters and my brothers for their supports and assistance in numerous ways, words cannot convey my appreciation.

I would also to thank all my lab mates from Chemistry Department and ITMA for their invaluable assistant during my master. Special thanks to all my colleagues especially Nazifah, Hidayah, Fariza, Norzida, Hayati, Nor Ain, Norhidayat, Norzila, Umi and Zul Adlan for always advise me and make me inspired to finish my journey in this study.

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

APTES	Aminopropyl-triethoxysilane
AuNPs	Gold nanoparticles
ASV	Anodic stripping voltammetry
As(III)	Arsenic(III)
CV	Cyclic voltammetry
CNT	Carbon nanotube
DPV	Differential pulse voltammetry
EDX	Energy dispersive X-Ray
EIS	Electrochemical impedance spectroscopy
GCE	Glassy carbon electrode
ICP-MS	Inductively coupled plasma-mass spectrometry
LSV	Linear sweep voltammetry
LSASV	Linear sweep anodic stripping voltammetry
LOD	Limit of detection
ppb	Part per billion
ppm	Part per million
RSD	Relative standard deviation
SiNPs	Silica nanoparticles
SPCE	Screen printed carbon electrode
SWV	Square wave voltammetry
TEM	Transmission electron microscopy
UV-Vis	Ultraviolet-visible
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1.1 Background of study

Heavy metal pollution has attracted global attention and become the most environmental problems in many parts of the world especially in developed countries (Weerasundara *et al.,* 2017). Asian countries are among the seriously affected countries especially Bangladesh and China and these countries have been reported facing high exposure of heavy metal contamination (Islam *et al.,* 2017; Caravanos *et al.,* 2013; Teh *et al.,* 2016).

Heavy metals can be defined as any metallic element having density more than 5g/cm^3 and atomic weight higher than 63.5 (Saidur *et al.,* 2017). Trace metals such as Cu, Cr, Mn, Zn and Co are essential for biological function in the human body and act as nutrients in plants and microorganism at low concentrations (Paul, 2017; Mahdi Ahmed *et al.,* 2017). However, the excess amount of heavy metals accumulate into human body can be dangerous and hazardous especially at high concentration, resulting in heavy metal poisoning (Chowdhury *et al.,* 2016).

Heavy metals such as Hg, Pb, Cd, Cr and As are among various heavy metals that have been reported as most hazardous heavy metals and very toxic to living organism even in trace concentration (Nagajyoti *et al.,* 2010). The toxicity of heavy metals depends on several factors such as dose, path of exposure and chemical species (Omole *et al.,* 2006). Heavy metals can be found naturally on earth's crust. Nevertheless, most of the heavy metal contamination are not only exist from naturally occurring elements, it is also can be resulted from anthropogenic activities, natural phenomena and industrial sources (He *et al.,* 2008; Gupta *et al.,* 2008; Liu *et al.,* 2011; Liu *et al.,* 2012).

Heavy metals are not biodegradable, can cause environmental problems and very harmful to living things. Heavy metals can be found mostly in water and soil, and only a small amount in atmosphere. Agriculture, industrial and natural activity are different sources of heavy metal contamination. Figure 1.1 shows the pathways and sources of heavy metals that accumulate into the environment.

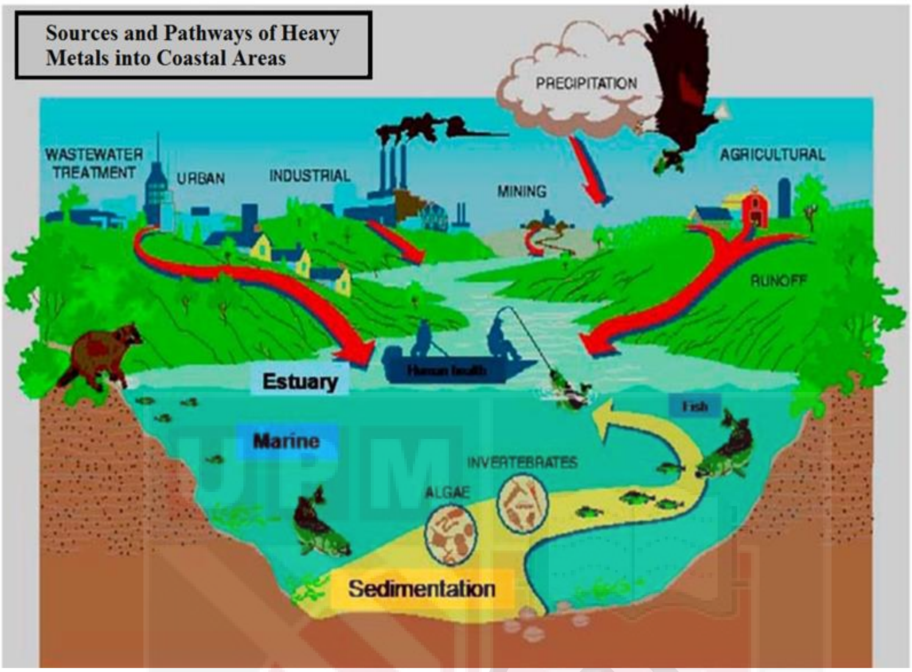

Figure 1.1: Sources of Heavy Metal Pollution to Aqueous System (Cheng, 2003)

Heavy metals such as Al, Zn, Pb and Hg are emitted in high levels from volcanic eruptions and also from the wind-blown dust. Mining and smelting activities are the mainly industrial sources that contributed to heavy metal pollution. Heavy metals such as lead can be emitted from the mining and smelting activities (Nagajyoti *et al.,* 2010). Heavy metals are also dispersed in the environment through industrial effluents, organic waste, refuse burning, transport and power regeneration (Agarwal *et al.,* 2009). These activities cause toxicity and accumulation in the environment and living organism. Heavy metals pollution become an environmental issue since it causes variety of environmental problems and can risk to human health.

Thus, exposure to heavy metals which can be passes through skin, respiratory and gastrointestinal tissues cause serious health problems and can damage human system (H.Yang *et al.,* 2007). Arsenic exposure can damage nervous, cardiovascular, respiratory, and dermatologic systems while lead, cadmium and manganese can effects kidney, hematopoietic cells, nervous system, and bones (Adal and Chief, 2015).

Electrochemical techniques have been used extensively owing to its sensitivity, low cost, fast analytical time and portable, which is very suitable for on-site analysis and for the determination of low concentrations of trace elements

(Gumpu *et al.,* 2015; Reverte *et al.,* 2016; Deshmukh *et al.,* 2017). This electroanalytical technique includes cyclic voltammetry (CV) (Brusciotti and Duby, 2007), differential pulse voltammetry (DPV) (Saha and Sarkar, 2016), square wave voltammetry (SWV) (Robles *et al.,* 2016), linear sweep voltammetry (LSV) (Gu *et al.,* 2013) and anodic stripping voltammetry (ASV) (Song and Swain, 2007).

Electrochemical sensor can be constructed using nanomaterials and transducer system. Nanomaterials have been used widely to develop electrochemical sensor and have been received much interests among researches compared to conventional materials because of their unique electronic, chemical, thermal and mechanical properties (Aragay *et al.,* 2011). Different types of nanomaterials have been explored in the construction of electrochemical sensor including gold nanoparticles (A. De Barros *et al.,* 2016), quantum dots (Gong *et al.,* 2016), carbon nanotubes (Hassan *et al.,* 2017) and graphene (Cinti and Arduini, 2017).

1.2 Problem Statement

Heavy metals are hazardous pollutants that possess a serious threat to organisms and human health because of their toxicity and accumulation in the environment. One of the most devastated heavy metals that are highly present in environment is arsenic. Arsenic is very harmful and was reported four times more poisonous than mercury. Arsenic toxicity is mostly found in drinking and ground water and its contamination affects more than 140 million people in 70 different countries (Luong *et al.,* 2014).

Arsenic exists in four oxidation states; -3, 0, +3, +5 and can be found in nature as organic and inorganic arsenic. Inorganic arsenic, As(V) and As(III) was categorized as the most dominant forms of arsenic contamination in ground water. Among those forms, up to 80 % toxicity of total arsenic was contributed by As(III). Vega and co-workers were reported that the toxicity of As(III) was 50 times higher than As(V) due to the reaction with enzymes in human respiratory system (Vega *et al.,* 2001).

Previously, numerous techniques have been carried out to design accurate detection and quantification of As(III) such as AAS, AFS and ICP-MS. However, those techniques could not detect individual arsenic species and must be used together with an upstream separation scheme. In addition, these techniques also possess limitations such as expensive, long analysis time, low selectivity and sensitivity, and can only be handled by a trained operator. Thus, it becomes necessarily important to develop a simple, economic, fast, selective and precise detection method for trace level determination of heavy metal. Electrochemical methods with the advent of screen printed carbon electrode (SPCE) satisfy many requirements such as inexpensive, portable, and simple to operate.

Nanomaterials have been widely used in many applications for electrochemical sensors and biosensors. These nanomaterials can improve the sensing devices due to their unique chemical, physical and electronic properties. Metal nanoparticles such Au, Pt and Pd have been the most extensively used to enhance the electrode performance and increase the sensitivity of the sensing system. Their extraordinary properties such as excellent conductivity and high catalytic properties have received great attention in metal-based nanomaterials for the detection of heavy metal ions. This developed nanomaterials based electrochemical devices can provide high sensitivity and low detection limit.

In this study, the fabrication of SiNPs/SPCE and AuNPs/SiNPs/SPCE modified electrode were presented as a new strategy to improve the electrochemical detection of As(III) ion using linear sweep anodic stripping voltammetry (LSASV) technique. The utilizing of SiNPs with AuNPs on electrode surface can improve the sensing device and show a good electrocatalytic performance. Besides, these nanomaterials also possess high surface to volume ratio, high chemical stability, high catalytic activity and fast electron transfer rate. To date, the utilization of SiNPs and combinantion of SiNPs and AuNPs as modifier in the electrochemical sensor for As(III) detection has not been reported. The electrochemical method based on SiNPs and AuNPs was used in this research as it offers high sensitivity and selectivity, low cost, portability and short analytical time measurement of As(III).

1.3 Objectives of the study

The goal of this study is to develop novel, simple and portable electrochemical sensor based on SiNPs/SPCE and AuNPs/SiNPs/SPCE for detection of heavy metal ion As(III). The following specific objectives were designed to achieve this goal;

1. To synthesize and characterize SiNPs, AuNPs, SiNPs/SPCE and AuNPs/SiNPs/SPCE for electrochemical detection of As(III).
2. To optimize and evaluate the analytical performance of the develop sensor SiNPs/SPCE and AuNPs/SiNPs/SPCE for electrochemical detection of As(III) using linear sweep anodic stripping voltammetry (LSASV).
3. To test the sensing ability of the fabricate sensor on a real water sample.

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LIST OF PUBLICATIONS

Publication

S. Ismail, N. A. Yusof, J. Abdullah, S. Fatimah, and A. Rahman, "Development of electrochemical sensor based on silica / gold nanoparticles modified electrode for detection of arsenite," *IEEE Sens. J.*, vol. PP, no. c, p. 1, 2019.

Conference

1. International Symposium on Applied Engineering and Sciences, the 4th Universiti Putra Malaysia- Kyushu Institute of Technology, Japan (17th-18th November 2016)

Workshops

1. Workshop on Basic Electrochemistry and Application in Sensor and Development (3rd - 4th April 2014)

2. Workshop on advance Materials and Nanotechnology, UPM (4th- 5th November 2015)

3. The Fundamental Science Congress (12th-13th November 2015)

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