PLATINUM NANODENDRITES MODIFIED ELECTRODE FOR LEAD (Pb) DETECTION

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled " Platinum nanodendrites modified electrode for lead (Pb) detection". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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LIST OF SYMBOL

A	Ampere
C	Celsius
g	Gram
Hz	Hertz
L	Litter
M	Molarity
m	Milli
s	Second
V	Voltage
θ	Theta
μ	Micro

LIST OF ABBREVIATION

AAS	Atomic absorption spectroscopy
AC	Alternating current
Ag	Silver
AgNPs	Silver nanoparticles
Al	Aluminium
ASV	Anodic stripping voltammetry
Au	Gold
AuNPs/CNF	Gold nanoparticles carbon nanotubes
AuNPs	Gold nanoparticles
Bi	Bismuth
Cd	Cadmium
Cr	Chromium
CSV	Cathodic stripping voltammetry
CV	Cyclic voltammetry
DPASV	Differential pulse anodic stripping voltammetry
DPV	Differential pulse voltammetry
Fe	Iron
FET	Field effect transistor
GCE	Glassy carbon electrode
Hg	Mercury
HMDE	Hanging mercury drop electrode
ICP/AES	Induced coupled plasma atomic

	emission spectroscopy
ICP/MS	Inductively couple plasma mass spectroscopy
ITO	Indium tin oxide
LOD	Limit of detection
LSV	Linear sweep voltammetry
MFE	Mercury film electrode
MWCNT	Multiwall carbon nanotubes
NFC	Nanofibrillated cellulose
Ni	Nickel
NPV	Normal pulse voltammetry
Pb	Lead
Pt	Platinum
PtNDs	Platinum nanodendrites
rGO	reduced graphene oxide
SEM	Scanning electron microscope
SERS	Surface-enhanced raman scattering
SPCE	Screen printed carbon electrode
SPE	Screen printed electrode
SPR	Surface plasma resonance
SWASV	Square-wave anodic stripping voltammetry
SWV	Square-wave voltammetry
TRGO	Thermally reduced graphene oxide
UV-Vis	Ultraviolet-visible spectroscopy

PENGUBAHSUAIAN ELEKTROD PLATINUM NANODENDRIT UNTUK PENGESANAN PLUMBUM (Pb)

ABSTRAK

Pencemaran logam berat di persekitaran telah menyebabkan pengumpulan logam berat dalam rantai makanan dan mengakibatkan masalah kesihatan yang serius kepada manusia seperti kecederaan otak dan kegagalan buah pinggang. Oleh itu, pengesanan logam berat adalah penting. Dalam penyelidikan ini, platinum nanodendrit (PtNDs) telah disintesis menggunakan kaedah penurunan kimia Sifat-sifat PtNDs telah dikaji dengan menggunakan pembelau sinar-X (XRD), mikroskop transmisi elektron (TEM) dan plasma induksi optik pelepasan spektrometri (ICP-OES). Analisa XRD menunjukkan fasa yang terdapat dalam sampel adalah platinum. Analisis TEM menunjukkan struktur yang dimiliki oleh platinum adalah nanodendrit dengan saiz partikel nano ~35 nm. Analisa dari ICP-OES spektrometer menunjukkan kepekatan koloid Pt ialah 6.77 ppm. PtNDs di letakkan di atas elektrod ITO dengan jumlah lapisan yang berbeza. Nafion seterusnya di letakkan di atas lapisan terakhir elektrod PtNDs/ITO. Elektrod yang diubah suai telah dikaji menggunakan analisa voltametri berkitar (CV) dan voltammetri pelucutan anodik denyut pembezaan (DPASV). Elektrod yang diubah menunjukkan prestasi yang baik dalam pengesanan Pb (II) dengan julat linear 0.1-1 ppm. Nilai had pengesanan (LOD) untuk PtNDs/ITO dan Nafion/PtNDs/ITO ialah 0.877 dan 0.827 ppm dan sensitiviti elektrod ialah 234.11μA / ppm dan 159.89 μA / ppm. Analisis interferens menunjukkan elektrod yang diubah sangat selektif terhadap pengesanan Pb (II). Kebolehgunaan elektrod yang diubah dikaji dalam air laut untuk pengesanan Pb (II) adalah hampir sama dengan analisa menggunakan spektrometer ICP-OES. Hasil kajian mendapati elektrod PtNDs/ITO boleh digunakan sebagai pengesan plumbum.

PLATINUM NANODENDRITES MODIFIED ELECTRODE FOR LEAD (Pb) DETECTION

ABSTRACT

Heavy metal pollution in the environment has caused accumulation of heavy metal ions in the food chain and this has led to serious health issues for humans such as brain injury and kidney failure. Thus, the detection of heavy metal is important. In this research, the platinum nanodendrites (PtNDs) were synthesized using chemical reduction method and used for fabrication of Indium Tin Oxide (ITO) modified electrode for heavy metal detection. The properties of PtNDs of was characterized using X-ray diffraction (XRD), transmission electron microscope (TEM) and inductive coupled plasma-optical emission spectroscopy (ICP-OES). XRD analysis revealed the phase present in the sample was platinum. The TEM analysis showed the structure of platinum was nanodendrites with a mean particle size of ~ 35 nm. The ICP-OES spectrometer analysis revealed the concentration of PtNDs solution is 6.77 mg/L. The as-synthesized PtNDs were drop-casted on the ITO electrode with varying number of layers with and without nafion. The modified electrode was subjected to cyclic voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV). The modified electrode showed good performance in detection of Pb(II) with linear range 0.1-1 ppm the limit of detections (LOD) were 0.877 and 0.827 ppm, and sensitivities of 234.11µA/ppm and 159.89 µA/ppm for PtNDs/ITO and Nafion/PtNDs/ITO, respectively. The interference analysis showed the modified electrode was highly selective towards detection of Pb (II). The applicability of modified electrode was studied using seawater sample for Pb (II) detection with reading in good agreement with ICP-OES analysis. The findings revealed the PtNDs/ITO electrode can be used as Pb sensor.

CHAPTER 1
INTRODUCTION

1.1 Introduction

Heavy metal elements are known for toxicity and may cause serious effect to the environment. Examples of heavy metal elements are mercury (Hg), lead (Pb), cadmium (Cd) and arsenic (As). Pb is among the most toxic elements that is harmful to the human health and environment (Pujol et al., 2014). Pb is stated as the second most toxic material by Agency for Toxic Substances and Disease Registry (ATSDR). Pb is non-biodegradable and can persist in the food chain. This can cause serious threat to human health. Heavy metals tend to accumulate inside the human body and cause various diseases such as cancer, kidney failure, brain damage, and organ failure (Koudelkova et al., 2017). Thus, the detection of heavy metal traces is essential. Detection of heavy metal traces are performed through various methods.

Typical conventional methods that have been used for heavy metal detection are Atomic Absorption Spectroscopy (AAS), Induced Coupled Plasma/ Atomic Emission Spectroscopy (ICP/AES), Inductively Coupled Plasma with Mass Spectrometric (ICP/MS) and X-ray fluorescence (Pujol et al., 2014). However, these conventional methods are expensive, high labor cost, and not suitable for on-field applications. The other method that has been used to detect heavy metal is sensor. Types of sensors that have been used to detect heavy metal are optical, electrochemical, and field-effect transistor (FET) sensors. The electrochemical sensor does not need a recognition probe as bare electrode can achieve selectivity towards the specified heavy metal ion because heavy metal has defined redox potential (Li *et al.*, 2013). An electrochemical sensor can be divided into amperometry, conductometry, voltammetry, impedemetry and potentiometry (Li et al., 2013).

An electrochemical sensor by anodic stripping voltammetry (ASV) under voltammetry method is suitable for heavy metal detection (Li *et al.,* 2013). This is because ASV method usually has two steps which are electrochemical deposition or accumulation of heavy metal at a constant potential to pre-concentrate analyte onto the electrode surface and follow by stripping or dissolution of deposited analyte from the electrode surface (Li et al., 2013). ASV is one of the most promising technique as it has high sensitivity and low detection limits (LOD) (Han *et al.*, 2015). The pre-concentration step in ASV allows low detection limits for heavy metal detection (Han *et al.*, 2015). ASV technique consists of differential pulse anodic stripping voltammetry (DPASV) and square wave anodic stripping voltammetry (SWASV). The sensitivity of DPASV was 10 to 20 times higher than normal electrochemical cells (Pujol et al., 2014). Whereas SWASV is the combination of the advantages of other systems and improve the quality of the quantitative information in electrochemical cell (Barón-Jaimez et al., 2013).

Typically, electrochemical sensors for heavy metal detection consists of three electrodes: working electrode, reference electrode and counter electrode. Sensitivity and specificity of electrochemical sensors are highly dependent on a working electrode. Previously, mercury-based electrodes have been used as the working electrode in electrochemical detection of heavy metal owing to their high sensitivity and good for heavy metal detection (Li et al., 2013). Examples of mercury-based electrodes are hanging mercury drop electrode (HMDE), mercury film electrode (MFE) and dropping mercury electrode (DME/SMDE) (Ariño *et al.*, 2017). However, mercury is highly toxic, thus, other electrodes with less toxic becomes of interest. Several works reported used of bismuth film electrode (Hutton *et al.*, 2006) and gold film electrodes for electrochemical sensors (Sun *et al.*, 1997). However, bulk electrode did not satisfy the sensitivity required for heavy metals detection. Thus, to enhance the electrode performance, the surface modification using nanoparticles on the electrode surface becomes of interest. There are several types of substrate electrodes have been used for modification which are glassy carbon electrode (GCE) (Yang *et al.*, 2014a), screen-printed carbon electrode (SPCE) (Wang and Yue, 2017) and indium-tin-oxide (ITO) electrode (Tang and Cheng, 2013). The method used for nanomaterial synthesis can affect the properties of nanomaterials modified electrodes. Several methods have been used in nanomaterials modified electrodes such as direct electrochemical deposition method (Xing *et al.*, 2011), *in-situ* synthesis method (Sang *et al.*, 2017), and *ex-situ* synthesis method such as hydrothermal method (Hoa *et al.*, 2015) and chemical reduction method (Ting *et al.*, 2015). Synthesis method produces specific properties of nanomaterials (Khan *et al.*, 2019). Among all the synthesis method, chemical reduction method is one of the most promising method to synthesis colloidal metal nanoparticles owing to convenient operation and simple equipment (Martínez-Abad, 2011).

There are various nanoparticles that have been used in modifying working electrodes. The advantages of using nanomaterials to modify electrode are high surface area, low solution resistance and can enhance electron transfer (Li et al., 2013). Hence, sensitivity and specificity of heavy metal detection can be enhanced. Examples of nanomaterials used in modification of working electrode are bismuth (Bi) (Sahoo *et al.*, 2013; Yang *et al.*, 2014b), carbon (C) (Wang and Yue, 2017), silver (Ag) (Xing *et al.*, 2011; Sang *et al.*, 2017) and platinum (Pt) (Nguyen *et al.*, 2019a). Nanomaterials modified electrodes possess strong potential and may improve the sensitivity and selectivity of the electrochemical sensors (Abdel-Karim *et al.*, 2020).

The properties of nanomaterials are dependent on their size, structure, and distribution. Different morphologies of nanomaterials have been used for electrode modification; nanoparticles (Han *et al.*, 2015), nanoflower (Nguyen *et al.*, 2019b), nanotubes (Jeromiyas *et al.*, 2019) and nanostar (Dutta *et al.*, 2019). The size and structure of nanomaterials used for electrode modification affect the number of adsorption sites and surface to volume ratio possess by the nanostructure (Tonelli et al., 2019). Higher surface to volume ratio and large number of adsorption sites can enhance the electrode properties such as sensitivity, selectivity, and efficiency in electrochemical analysis (Tonelli et al., 2019). The modified electrode performance also can be improved with the addition of nafion. Nafion is well known as ionomer membrane that has hydrophobic poly(tetrafluorothylene) component (Xing *et al.*, 2011). The ionomer membrane is a proton-conductive polymer film that allows only protons to cross-over the membrane (Yusoff, 2018). The advantages of nafion is it is chemically and mechanically stable and can prevent nanoparticles leaching from the electrodes surface (Szoke *et al.*, 2019). Most reported work used nafion for electrochemical sensors for glucose detection (Kang *et al.*, 2019), However, limited works can be found on using nafion for heavy metal detection.

1.2 Problem statement

Heavy metal that accumulate in the environment and food chain causes exposure to the living organism. The high exposure to heavy metal may lead to serious health effect (Koudelkova *et al.*, 2017). Thus, the detection of heavy metal that accumulated in the environment such as seawater, river and groundwater need to be done. The spectroscopy techniques such as AAS, ICP-MS and ICP-OES have been used in detection of the heavy metal (Li *et al.*, 2013). However, these spectroscopy techniques require high labour cost and not suitable for on field applications (Han *et al.*, 2015). Thus, for detection of heavy metal, sensors are favourable as alternative as it is simple, low-cost, and suitable for field used (Li *et al.*, 2013). The electrochemical sensor is one of the best ways for heavy metal detection.

In the electrochemical sensor, the modification of the working electrode is crucial as it affects the sensitivity and selectivity of the electrochemical sensor. The mercury-based electrode has been used as it has high sensitivity but highly toxic. The mercury-based electrode is then replaced with a bismuth electrode that is more environmentally friendly. However, the bulk electrode cannot satisfy the need for high sensitivity detection limit for heavy metal traces. Problem arises from using a bulk electrode is large overpotential during analyte deposition (Li *et al.*, 2013). This problem can be minimized by using nanomaterials modified electrode that requires lower potential for analytes deposition compared to bare electrodes (Abraham *et al.*, 2020).

Modification of the electrode surface with nanomaterials can enhance the sensitivity and selectivity of the electrode in heavy metal detection (Li *et al.*, 2013).

Nanomaterials are known for its advantages of enhancing the surface area and can improve the electron transfer rate (Ward Jones and Compton, 2008). Various metallic nanomaterials have been used for Pb detection such as mercury (Hg) nanomaterial (Nagles *et al.*, 2012), bismuth (Bi) nanomaterial (Yang *et al.*, 2014a), silver (Ag) nanomaterial (Pérez-Ràfols *et al.*, 2017), gold (Au) nanomaterials (Wan *et al.*, 2015) and platinum (Pt) nanomaterials (Nguyen *et al.*, 2019b). However, Hg and Ag nanomaterials are toxic compared to Pt (Asharani *et al.*, 2011). Bi nanomaterials also suffer from instability due to its natural oxidization, thus, Pt is more stable compare to Bi nanomaterials (Li *et al.*, 2013). Pt has better electrocatalytic properties compared to Au (Han *et al.*, 2015).

Various Pt nanomaterials have been used for electrode modification such as Pt nanoparticles (Dai and Compton, 2006), Pt nanoflower (Nguyen *et al.*, 2019b), and Pt nanotubes (Xu *et al.*, 2008). The properties of nanoparticles are dependent on the nanostructures of the nanomaterials. To enhance the properties of Pt nanomaterial modified electrode for Pb detection, Pt nanodendrites is used. Furthermore, there is no reported work on Pt nanodendrites modified electrode performance.

Nafion is known as sulfonated tetrafluoroethylene-based fluoropolymer-copolymer with conductive properties (Yusoff, 2018). Nafion can improve the electrode stability as it has excellent ability in film forming and only enables cations conduction to pass through the membrane and reach the electrode surface thus makes the electrode more selective (Yusoff, 2018). Thus, to improve the selectivity and stability of the modified electrode, nafion is used for the electrode modification.

In this work, the Pt nanodendrites was synthesized using chemical reduction method. The PtNDs was characterized with TEM, XRD and ICP-OES spectrometer. The modification of ITO electrode with PtNDs was performed using drop-cast technique. 1% of nafion was used in fabrication of the PtNDs/ITO electrode. The performance of PtNDs/ITO electrode was measured with cyclic voltammetry (CV) and for Pb detection, differential pulse anodic stripping voltammetry (DPASV). The specificity of the modified electrode was analyzed using multi-element solution and the applicability of the produced electrode was tested in the real sample water.

1.3 Objectives

The main objectives of this research are:

1. To synthesize and investigate the properties of platinum nanodendrites
2. To study the physical properties of platinum nanodendrites modified electrodes
3. To study the electrochemical properties of platinum nanodendrites in heavy metal detection of Pb^2

1.4 Scope of study

This study focuses on the synthesis and characterization of PtNDs. PtNDs were synthesized by using chemical reduction method and were characterized by X-ray Diffraction (XRD) for phase identification. Transmission Electron Microscope (TEM) was used to observe the morphology and size of the Inductive Couple Plasma-Optical Emission Spectroscopy (ICP-OES) was used to determine the concentration of the PtNDs solution. The fabrication of modified electrode was performed by drop-cast technique. The number of PtNDs layer was varied; 1-layer, 2-layer, 3-layer, 4-layer, 5-layer, and 6-layer, on the ITO electrode. The physical properties of the modified ITO electrode PtNDs were determined using contact angle