Schiff Base modified on CPE electrode and PCB gold electrode for selective determination of silver ion

Piyawan Leepheng¹, Songwut Suramitr² and Darinee Phromyothin¹,³,*

¹College of Nanotechnology, King Mongkut’s Institute of Technology Ladkrabang, Chalongkrung Rd., Ladkrabang, Bangkok, Thailand 10520
²Department of Chemical, Faculty of Science, Kasetsart University, Ladyao, Chatuchak, Bangkok, Thailand 10900
³Nanotec-KMITL Center of Excellence on Nanoelectronic Devices, King Mongkut’s Institute of Technology Ladkrabang, Chalongkring Rd., Ladkrabang, Bangkok, Thailand 10520

*E-mail: ksdarine@gmail.com

Abstract. The schiff base was synthesized by 2,5-thiophenedicarboxaldehyde and 1,2,4-thiadiazole-3,5-diamine with condensation method. There was modified on carbon paste electrode (CPE) and Printed circuit board (PCB) gold electrode for determination silver ion. The Schiff base modified electrodes was characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM), respectively. The electrochemical study was reported by cyclic voltammetry method and impedance spectroscopy using modified electrode as working electrode, platinum wire and Ag/AgCl as counter electrode and reference electrode, respectively. The modified electrodes have suitable detection for Ag⁺. The determination of silver ions using the modified electrodes depended linearly on Ag⁺ concentration in the range 1x10⁻¹⁰ M to 1x10⁻⁷ M, with cyclic voltammetry sensitivity were 2.51x10⁻⁸ µAM⁻¹ and 1.88x10⁻⁸ µAM⁻¹ for PCB gold electrode and CPE electrode, respectively, limits of detection were 5.33x10⁻⁹ M and 1.99x10⁻⁸ M for PCB gold electrode and CPE electrode, respectively. The modified electrodes have high accuracy, inexpensive and can applied to detection Ag⁺ in real samples.

1. Introduction
Silver (Ag) is one of heavy metals that have high density and toxic or poisonous even at low concentration. The general of Ag⁺ ions usually forms compound in environment including AgNO₃, AgCl, Ag₂SO₄ and Ag₂O. Human mostly used silver for made jewellery, silver ware, photographs, electronic equipment and dental material [1]. These wastes maybe contaminated in environments that lead to heavy metal pollution. Nowadays, contamination of Ag⁺ ion has become an increasingly serious threat to human health and ecology. Concerning the toxicity, there is an obvious need to their detection and determination at trace level. Several methods by which to determination and monitor low concentration of Ag⁺ ions, such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and fluorescence spectroscopy [2] However, these methods present several shortcomings, expensive equipment, complicated equipment, that usually used by experience person, long time to determination and only used in laboratory. An invention device or methodology to meet the requirements of low cost, simply to use, rapid analyses, accuracy, precision, high sensitivity and can detected low concentration for determining trace Ag⁺ ions is challenging. The development of
selective electrochemical sensor has received widespread attention because of rapid determination, high accuracy, high precision, high sensitivity and low limit of detection (LOD). The carbon pastes electrode (CPE) and the printed circuit board (PCB) gold electrode exhibited interesting to modified selective electrodes. They are used in most materials for the fabrication of electrochemical sensors for analytical purposes. The operation mechanism of modified electrodes depends on the properties of the modifier materials [3].

Schiff base (SB) is an interesting compound that can be used to modify electrodes because it has multi-ligand properties, can designed structure, can be simply synthesized and present good bonding with transition metal [4]. The compound consists of an imine group containing a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group. It can be applied in fields of biochemistry, catalyst chemistry, organometallic chemistry and material chemistry. In this work, the Schiff base ligand was used for modification the Ag⁺ ions selective membrane on CPE and PCB working electrode. The modified electrodes were immobilized membrane with Schiff base ligand by spin coating technique. Cyclic voltammetry in range of -0.6 V. to 0.8 V. with the modified electrodes (SB/PCB and SB/CPE) as working electrode, platinum wire and Ag/AgCl as counter electrode and reference electrode was measured.

2. Experimental

2.1. Synthesis Schiff base method and determination selectivity of Schiff base ligand
The Schiff base ligand was synthesized from 2,5-thiadiazolecarboxaldehyde and 1,2,4-thiadiazole-3,5-diamine with the ratio of 1:1 in ethanol, under reflux for 3-5 h at 50 °C. After the reaction completed, solvent was eliminated by evaporation process and then purified with ethanol and stored in vacuum desiccator. The Schiff base ligand was fine shining yellow powder and was characterized a new functional of imine using IR spectroscopy. The selectivity of Schiff base ligand was measured by the cyclic voltammetry method. In this manner, 1.0 mM ligand in acetone and 1 mM metal ions (Ag⁺, Hg²⁺, Cd²⁺, Pb²⁺ and Zn²⁺) in water were studied the selectivity of Schiff base ligand. The cyclic voltammetry with the potential in range of -1 to +1 V using Au electrode as working electrode, Ag/AgCl as reference electrode and Pt as counter electrode was performed.

2.2. Preparation of modified electrode
The PCB or CPE electrode was cleaned by sonication in water, acetone and water each step 10 min, respectively. The surface area was fixed and immersed in piranha solution (30%H₂O₂;H₂SO₄; 1:3 v/v) for 3 min and then rinsed with water. Afterwards the cleanliness of electrode surface was electrochemically cleaned by cycling the potential between -0.3 V. to 0.8 V. using Ag/AgCl as reference electrode and Pt wire as counter electrode in 0.05 M K₃Fe(CN)₆ solution. 3.0 mM of Schiff base ligand was immobilized on the surface of the electrode by spin coating with 1000 rpm at 10 sec.

2.3. Determination Ag⁺ ions
1x10⁻¹⁰ M to 1x10⁻⁵ M of Ag⁺ ions solution in 0.1 M phosphate buffer pH 7.0 was prepared for testing. Electrochemical analysis, cyclic voltammetry method and impedance spectroscopy was measured. The modified electrode potential continuously cycled from -0.6 V to 0.8 V with the scan rate of 50 mV/s in 0.05 M K₃Fe(CN)₆ solution containing 0.1 M phosphate buffer solution.

3. Results and Discussion

3.1. IR spectra of Schiff base and Selectivity of Schiff base
Schiff base ligand is organic compound called imine which presents signification of imine group as C=N bonding. This characterization ensures that imine group is existed at 1653 cm⁻¹.

The selectivity of a membrane is one of the most important for detection. The cyclic voltammetry method was determined the selectivity of schiff base ligand with Ag⁺, Hg²⁺, Cd²⁺, Pb²⁺ and Zn²⁺ ions. As the result, Ag⁺ ions presented higher current than other metals because the electrons transfer between schiff base molecule to Ag⁺ ions in which other metals are not shown this behaviour.
3.2. Morphology Characterization

The morphology of SB/PCB electrode was tested by the scanning electron microscope (SEM) and the atomic force microscope (AFM). The electrochemical response was related to the physical morphology of surface such as surface area and roughness of film. The surface morphological analysis of bare PCB electrode and SB/PCB electrode was confirmed by SEM as shown in Figure 1(a) and Figure 1(b). As can be seen, cluster of the schiff base makes a distinct appearance on the SEM image of SB/PCB electrode while there is smooth and unbroken surface on bare PCB electrode. It is indicated that the cluster of Schiff base is greatly immobilized. The SEM images of bare CPE electrode and bare SB/CPE electrode is shown in Figure 1(c) and Figure 1(d). The SB/CPE electrode appeared cluster of Schiff base on the surface area while the bare SB/CPE electrode is not shown cluster of Schiff base. They have smooth surface than the modified electrode, indicated the cluster of Schiff base greatly immobilized on the surface are of SB/CPE electrode. Atomic force microscopy is used to measure topography and properties of surfaces. The 3-dimension AFM images compared between bare electrode in Figure 2(a) and SB/PCB electrode Figure 2(b) the result found the surface of electrodes have difference textures, on the modified electrode has cluster of Schiff base immobilized on electrode while is not shown on bare electrode. So, maybe confirmed Schiff base can immobilized on modified electrode.

![Figure 1](image1.png)

**Figure 1** SEM images the surface of modified electrodes (a) bare PCB electrode, (b) SB/PCB electrode, (c) bare CPE electrode and (d) SB/CPE electrode

![Figure 2](image2.png)

**Figure 2** 3-Dimension of AFM images the surface of modified electrode (a) bare electrode and (b) SB/PCB electrode.

3.3. Electrochemical analysis

The cyclic voltammograms of SB/PCB electrode present the decrease of reduction current peaks when rising concentration of Ag⁺ ions at -0.18 V. Ag⁺ ions detection linearly depended on concentration from 1.0x10⁻¹⁰ M to 1.0x10⁻⁷ M, with amperometric sensitivity of 2.51x10⁸ µA M⁻¹ as shown in Figure 3(a). The linear graph is \( y = 4.37x10^7x + 5.86 \) (y; peak current (µA) and x; logarithm concentration of Ag⁺ ions) presented in Figure 3(b). The limit of detection (LOD) was calculated using \( LOD = 3\text{S.D.}_b/m \), where S.D.ₘ is a standard deviation of the blank, it estimated by five of the blank signals; m is slope of calibration graph [5] Value of LOD was found to be 5.33x10⁻⁹ M for Ag⁺ ions. In part of SB/CPE electrode the results shown in Figure 4(a), the oxidation current peak decreased with rising concentration of Ag⁺ ions at 0.56 V. Ag⁺ ions detection linearly depended on concentration from
1.0x10^{-10} \text{ M} \text{ to } 1.0x10^{-7} \text{ M}, \text{ with ampetometric sensitivity of } 1.88x10^{8} \text{ µA M}^{-1}. \text{ The linear graph is } y = 1.11x10^{7}x + 2.72 \text{ as presented in Figure 4(b). The value of LOD was found to be } 1.99x10^{-8} \text{ M for Ag}^{+} \text{ ions. The SB/PCB electrode has sensitivity higher than SB/CPE electrode and it has value of LOD lower than SB/CPE electrode, indicated the SB/PCB electrode better determination Ag}^{+} \text{ ions than SB/CPE electrode.}

![Figure 3](image)

**Figure 3** Determination Ag$^{+}$ ions by SB/PCB electrode (a) CV curves of Ag$^{+}$ ions and (b) Calibration curve of Ag$^{+}$ ions; varied range of Ag$^{+}$ ions concentration 1x10^{-10} \text{ M} \text{ to } 1x10^{-5} \text{ M}

![Figure 4](image)

**Figure 4** Determination Ag$^{+}$ ions by SB/CPE electrode (a) CV curves of Ag$^{+}$ ions and (b) Calibration curve of Ag$^{+}$ ions; varied range of Ag$^{+}$ ions concentration 1x10^{-10} \text{ M} \text{ to } 1x10^{-5} \text{ M}

![Figure 5](image)

**Figure 5** Nyquist Plots of electrochemical impedance measurements with varied range of Ag$^{+}$ ions concentration on SB/PCB electrode

The characterization electrochemical property of SB/PCB electrode for determination Ag$^{+}$ ions by impedance spectroscopy was shown in Figure 5. The nyquist plot of SB/PCB electrode presented resistance of modified electrode when determination Ag$^{+}$ ions, the results found when concentration of...
Ag⁺ ions increased lead to higher resistance on modified electrode. That may be indicated Ag⁺ ions can be blocked charge-transfer on surface area of SB/PCB electrode and this result has relation with the reduction current in CV curves. The cyclic voltammogram of SB/PCB electrode presented the decreased reduction current when increased amount of Ag⁺ ions for determination, which maybe because of Ag⁺ ions blocking charge-transfer.

4. Conclusions
Schiff base ligand was synthesized and used as selective electrode for Ag⁺ ions detection. The modified electrode was characterized the morphology by SEM and AFM. The electrochemical properties were studied using cyclic voltammetry and electrochemical impedance spectroscopy. The limit of detection for Ag⁺ for SB/PCB and SB/CPE electrode are 5.33x10⁻⁹ M and 1.99x10⁻⁸ M, which the sensitivity are 2.51x10⁸ µAM⁻¹ and 1.88x10⁸ µAM⁻¹, respectively. The SB/PCB electrode presented higher sensitivity and lower limit of detection than that SB/CPE electrode. The proposed SB/PCB electrode is selectivity, simple, low cost. The determination of time is about 5 min and can applied to portable device for determination Ag⁺ ion in river or real sample.

5. References
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