

# Comparisons and development of electrochemical sensors using G-PANI composite based on filter paper and transparency film substrate

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## ABSTRACT

Electrochemical sensors based on filter paper and transparency film substrates have been prepared using screen-printing method for the detection of the heavy metals ions including  $Pb^{2+}$ ,  $Cd^{2+}$  and  $Zn^{2+}$ . The electrochemical characteristics of these electrodes were analyzed using cyclic voltammetry (CV) and anodic stripping voltammetry (ASV) while the surface roughness were measured using an optical profilometer. For electrochemical characterization by CV, electrodes on paper give a higher current response for ferri/ferrocyanide than transparency-based electrodes. When using ASV for the detection of heavy metals, the transparency-based device gave higher current response than paper-based device. Moreover, for the surface characterization using optical profilometry, carbon ink penetrated into the porous of filter paper but coated on the transparency film substrate affecting to surface roughness in transparency-based electrodes is higher than electrodes on paper. To improve the sensitivity of these devices, graphene (G) and polyaniline (PANI) nanocomposite was prepared by polymerization of aniline monomer in the presence of G and used for electrode modification. G/PANI nanocomposite-modified electrode was characterized by CV and used for heavy metals detection by ASV. This system will be very useful for portable environmental monitoring.

**Keywords:** Heavy metals detection, Graphene, Nanocomposite, Electrochemical sensors, Paper-based device, Polyailine

## 1 INTRODUCTION

Occupational human exposure to metals including lead (Pb), cadmium (Cd) and zinc (Zn) is a vital concern because of its numerous health effects particularly on respiratory diseases [1–2]. These metal cations are natural components and widespread in the environment. They are highly toxic, non-destroyable, biodegradable and bio-accumulative in human [3]. Therefore, development of the methods for evaluating of heavy metals ion concentration in environmental samples has been commonly concerned. Measurement of these metal ions is an exhaustive cost and resource due to a classical utility of complicated analytical instrument resembling mass spectrometry (MS) [4] and inductively-coupled plasma-mass spectrometry (ICP-MS) [5]. The use of electrochemical biosensors for the detection of trace metal is known for several years [2–3, 6]. Square wave anodic stripping voltammetry procedures commonly use for the detection of these heavy metal ions due to its high sensitivity and low cost [6]. Traditional substrates such as glass, ceramic and polymer were commoly used for sensor applications. One of the most powerful materials for sensor substrate is transparency film polymer due to its low cost and disposability. Recently, cellulose filter paper has become an attractive material for sensor applications due to its high surface area and low cost [7–8] compared to other traditional substrates (*i.e.*, glass, ceramic). The advantage of paper-based sensors are low cost, high abundance, biocompatibility and disposability [9]. In this study, transparency film and filter paper were selected as the substrates for sensor preparation for heavy metal ions detection.

Graphene sheets (G) have attracted much attention in electrochemical sensing areas. The utilization of G also increases the charge transfer in electrochemical sensor. G is a single layer of carbon atoms closely packed into a two-

dimensional honeycomb arrangement. The main advantage of G is its large surface area compared to other carbon allotropes leading to enhanced electrochemical sensitivity of sensors [10]. In the term of applications, nanocomposites of G/conducting polymer have attracted more attention than pure forms of G since the composite forms are more compatible for electrode fabrication and further functionalization [11]. Here, polyaniline (PANI) was chosen along with G for electrode modification since PANI possesses excellent electrochemical property, ease of synthesis, high environmental stability, and low toxicity. Previously, it has been reported that the nanoparticles of PANI can be simply prepared by a reverse dropping method with the assistance of polyvinylpyrrolidone (PVP) [12]. Therefore, PANI was synthesized by reverse dropping method with adding small amount of G to obtain G/PANI nanocomposite and it was used for electrode modification.

Herein, transparency film and paper-based device were prepared and used to compare for the detection of heavy metal ions. The optimized sensor was modified using nanocomposite of G/PANI via coating and electro spraying method. G/PANI-modified electrode was used for the sensitive determination of heavy metal ions using square wave anodic stripping voltammetry (SWASV).

## 2 EXPERIMENTAL

### 2.1 Fabrication of electrochemical sensors

Paper-based sensor was fabricated using wax-printing method according to the previous reports [9, 11] with slight modification. First, Adobe Illustrator software was used to create the patterned paper-based device and then printed onto filter paper (Whatman no. 1) using a wax printer (Xerox Color Qube 8870, Japan). Next, the wax pattern on the paper was melted at 200 °C for 120 s by a hot plate for constructing hydrophobic barriers and hydrophilic channels. For the fabrication of electrochemical system, the three-electrode system was screened onto the transparency film and patterned paper, all electrode including working electrode (WE), counter electrode (CE), and pseudo reference electrode (RE) and conductive pad were screen-printed in-house using carbon ink. Then, the transparency film was placed into oven at 65 °C for 30 min after each screen-printing step [11] to remove the solvent. Finally, the punched of 6 mm diameter hole of packing tape was placed on to TF-based device in the middle of sample reservoir to control the area of electrode, and the back side of paper-based device was covered with clear packing tape.

### 2.2 Preparation of G/ PANI composite

A synthetic process of G/PANI nanocomposite was follows by dissolving 1 g aniline monomers in 1 mL concentrated HCl and added distilled water to obtain a total volume 10 mL (solution I). For the solution II, 0.8 mL concentrated HCl, 1 g ammonium persulfate (APS), and

2.00 g PVP were dissolved in distilled water to obtain a total volume 90 mL. Then, solution II was cooled in an ice-water bath for 30 min. After that, solution I and 15 mg graphene (G) was added into solution II under vigorous stirring and a mixture solution was continuously stirred for 4 h to obtain precipitated powder. Finally, the precipitated powder was filtrated and washed with distilled water and ethanol until the filtrate became colorless and then dried overnight in an oven at 65 °C. To confirm that G-PANI was completely doped with HCl, the dried powder could be re-dispersed in 0.1 M HCl under ultrasonication for 30 min and collected by filtration and drying again [12].

### 2.3 Electrode modification using G/PANI nanocomposite by coating and electro spraying

Firstly, G/PANI nanocomposite was dispersed in PVP solution that prepared by dissolving of 2 mg mL<sup>-1</sup> of PVP in DMF. Then, G/PANI solution was sonicated using probe sonicator for 2 h at room temperature and 0.1% (v/v) PS was added into G/PANI solution. For electrode modification by coating, 1 µL of the dispersed solution of G/PANI was directly dropped onto electrode surface of transparency film and paper based sensors, and allowed it to dry completely at room temperature for 10 min. An electro spraying system consists of syringe pump, high-voltage power supply, ground collector, plastic syringe and stainless-steel needle. During the electro spraying process, the CE and RE were covered with aluminium foil as a masks to prevent the electrode modification. G/PANI nanocomposite solution was mixed thoroughly in a syringe, and a 14 kV of high voltage was applied to the solution. Then, G/PANI solution was sprayed onto the working electrode of sensor attached to a ground collector on a collector. The flow rate was controlled at 3.0 mL h<sup>-1</sup> with 5 cm of the distance between the needle tip and electrode on the collector.

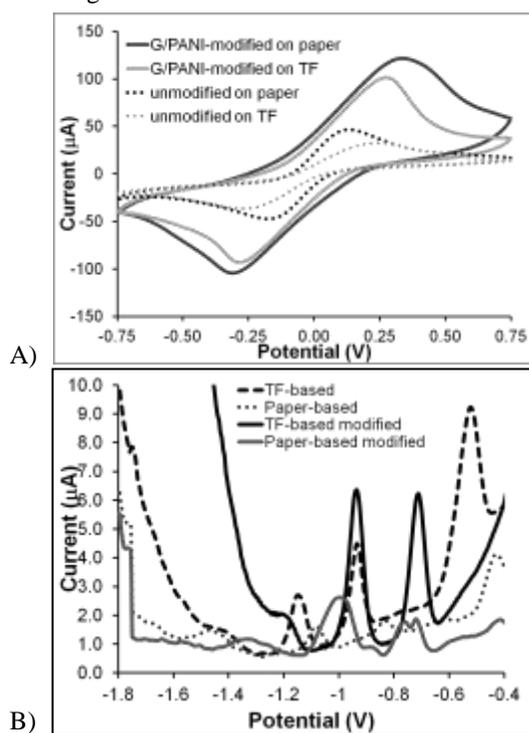
### 2.4 Electrochemical measurement

A three-electrode system fabricated on a transparency film and paper-based sensor was used throughout the experiment. A potentiostat (CHI 660B, CH Instruments, Austin, TX) was used to control all electroanalytical measurements. For the cyclic voltammetric measurements of ferri/ferrocyanide, the potential was scanned from -0.8 V to +0.7 V. SWASV was used for the detection of Pb<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> after dropping 50 µL of standard metals and 2.5 µL of 10 ppm Bi in 0.1 M acetate buffer pH 4.5 onto three electrode system. In the accumulation step, Pb<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> with the concentration range 25–200 ppb was accumulated on electrode surface by applying the deposition potential of -1.6 V for 240 s and 0.5 ppm Bi<sup>3+</sup> in situ. After 5s of equilibration, square-wave voltammograms with a frequency of 10 Hz, a step potential of 5mV, and a pulse amplitude of 25mV were recorded from -1.8 to 0 V.

### 3 RESULTS AND DISCUSSION

#### 3.1 Characterization of TF and paper-based device

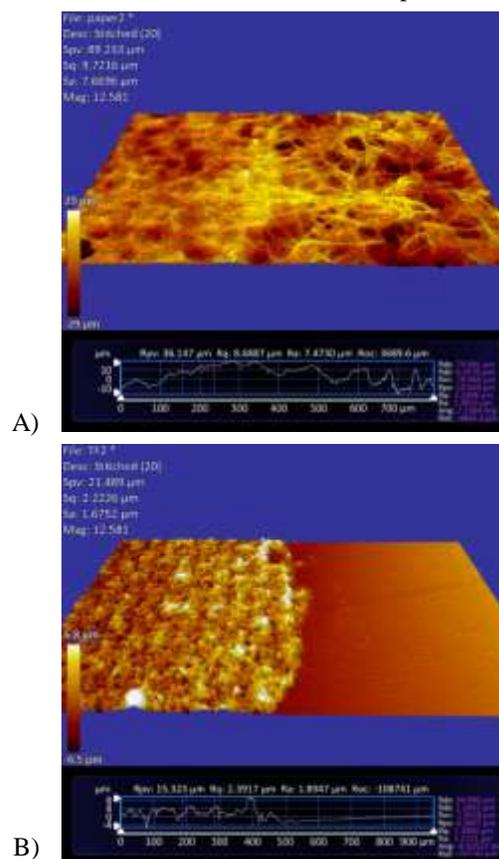
To investigate the electron transfer process of all electrodes, cyclic voltammetric measurements of 2 mM ferri/ferrocyanide were performed on different electrodes including unmodified TF, unmodified paper, G/PANI modified TF and G/PANI modified paper, respectively. The anodic and cathodic peak currents of ferri/ferrocyanide show the well-defined peaks for all electrodes as shown in Fig 1A. For electrochemical characterization by CV, the paper-based device electrodes show a higher current response for ferri/ferrocyanide than transparency-based device electrodes. However, for the detection of metal ions including  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  using SWASV, the transparency-based device electrodes provide the higher current response than paper-based device electrodes as shown in Fig 1B.



**Figure 1.** A) cyclic voltammograms of 2.0 mM ferri/ferrocyanide in 0.1 M KCl measured on different working electrodes with a scan rate of  $100 \text{ mV s}^{-1}$  and B) SWASV of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  on different working electrodes with  $-1.6 \text{ V}$  of deposition potential for 240 s in 0.1 M acetate buffer at a pH of 5.0.

Moreover, for the surface characterization by optical profilometry, carbon ink used as a working electrode penetrates into the porous of filter paper (Fig.2A) but it coats on the transparency film substrate (Fig. 2B) This phenomena make the surface roughness of transparency based electrodes higher than the paper based electrodes.

These results indicate that paper-based device was inappropriate for the detection of heavy metals by ASV because the metal ions are difficult to accumulate on the electrode surface in an accumulation step.

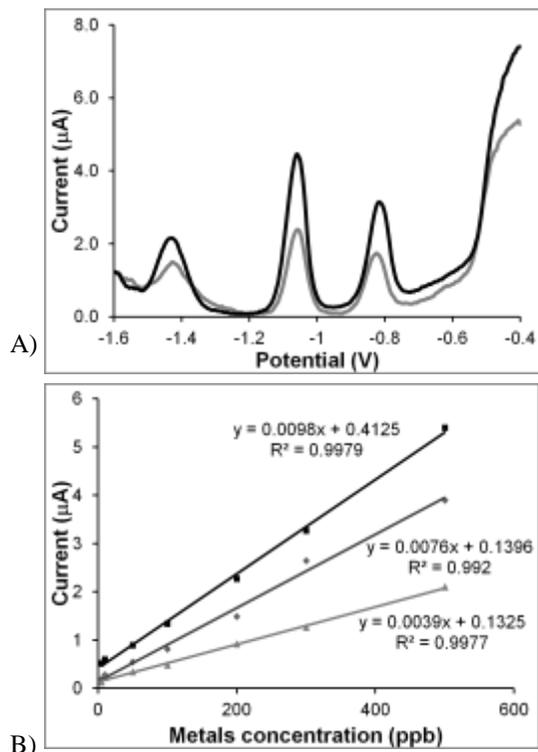


**Figure 2.** Profilogram of carbon working electrode on paper (A) and TF (B) substrates.

#### 3.2 Detection of heavy metal ions by SWASV

For monitoring the extremely low levels of heavy metal ions including  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ , SWASV was performed for trace metals analysis on G/PANI-modified TF used for the highly sensitive detection of heavy metal ions in the presence of Bi. Bi have been commonly applied for improving the performance of heavy metal ions detection by SWASV due to it can be enhance the preconcentration capacity to form metal-Bi alloy at the electrode surface. Moreover, it has lower toxicity than mercury-modified electrode [3]. In the SWASV procedure, there are two steps including accumulation step and stripping step. For the accumulation step, the ionized  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  were cumulatively deposited at  $-1.6 \text{ V}$  to form zero-valent metal or metal-alloy on the surface of electrode for 240 s. Then, for stripping step, the potential of working electrode was scanned toward positive direction from  $-1.8$  to  $0.0 \text{ V}$ , the zero-valent metal or metal-alloy was then oxidized to offer the oxidative peaks of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ . Under the optimum conditions, the anodic peak currents were

proportional to  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  levels in the range of 25–200 ppb and  $\text{Zn}^{2+}$  levels in the range of 50–200 ppb with the limit of detection of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  is 25 ppb and  $\text{Zn}^{2+}$  is 50 ppb when using G/PANI-modified TF by coating method.



**Figure 3.** A) SWASV of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  on G/PANI-modified electrode by — coating and — electro spraying and B) calibration curve between metal and anodic current of —  $\text{Pb}^{2+}$ , —  $\text{Cd}^{2+}$  and —  $\text{Zn}^{2+}$ .

To improve the specific surface area and sensitivity of these devices using G/PANI, electro spraying technique was selected for electrode modification. Compared to thin-film or coating modified electrodes, G/PANI-modified electrodes by electro spraying shows a higher surface area, which leads to enhanced sensitivity of the sensors. In this study, an electrochemical sensor based on a G/PANI electro sprayed-modified electrode was used for the sensitive detection of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  using SWASV. The SWASV of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ , measured on the G/PANI-modified electrode prepared by coating compared to electro spraying are illustrated in Fig. 3A. The anodic current signal of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  on G/PANI-modified TF-based sensor by electro spraying increased about 2 times when compared to G/PANI-modified TF-based sensor by coating verifying that electro spraying technique will be a very useful tool for portable environmental monitoring. The calibration plot was linearly proportional to the concentration of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  over the range of 5 ppb to 500 ppb with a correlation coefficient more than 0.99 with the limit of detection (LOD) for  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  is 5 ppb as shown in Fig. 3B.

## 4 CONCLUSIONS

Electrochemical sensors based on TF and filter paper substrates have been prepared and used for the simultaneous detection of the heavy metal ions including  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ . A TF-based sensor shows higher surface roughness and sensitivity for the detection of heavy metal ions than paper-based sensor. In addition, a novel G/PANI nanocomposite can be used for electrode modification to improve the electrochemical sensitivity and surface area for the detection of heavy metal ions. Coating and electro spraying were selected as the fabrication methods for electrode modification. The highest conductivity and large surface area of the G/PANI-modified electrode obtained from electro spraying significantly improve the electrochemical sensitivity for the detection of heavy metal ions. Under optimum conditions, a high-sensitivity, wide linear range and low LOD are achieved for heavy metal ions using G/PANI-modified TF-based sensors fabricated by electro spraying. This novel and sensitive system might be a very useful tool for portable environmental monitoring.

## REFERENCES

- [1] Y. Sameenoi, K. Koehler, J. Shapiro, K. Boonsong, Y. Sun, J. Collett, J. Volckens, and C. S. Henry, *J. Am. Chem. Soc.* 134, 10562–10568, 2012.
- [2] R. Ouyang, Z. Zhu, C. E. Tatum, J. Q. Chambers, and Z.-L. Xue, *J. Electroanal. Chem.* 656, 78–84, 2011.
- [3] G.-J. Lee, C.K. Kim, M.K. Lee, and C.K. Rhe, *Electroanalysis*, 22, 530–535, 2010.
- [4] E. Furia, D. Aiello, L. D. Donna, F. Mazzotti, A. Tagarelli, H. Thangavel, A. Napoli and G. Sindona, *Dalton Trans.*, 43, 1055–1062, 2014.
- [5] J.V. Maciel, C.L. Knorr, E.M.M. Flores, E.I. Müller, M.F. Meskoc, E.G. Primel, and F.A. Duarte, *Food Chem.*, 145, 927–931, 2014.
- [6] U. Injang, P. Noyrod, W. Siangproh, W. Dungchai, S. Motomizu, and O. Chailapakul, *Anal. Chimica. Acta*, 668, 54–60, 2010.
- [7] W. Dungchai, O. Chailapakul, and C.S. Henry, *Anal. Chem.* 81, 5821–5826, 2009.
- [8] A. Apilux, W. Dungchai, w. Siangproh, N. Praphairaksit, C.S. Henry, and O. Chailapakul, *Anal. Chem.* 82, 1727–1732, 2010.
- [9] M.M. Mentele, J. Cunningham, K. Koehler, J. Volckens, and C.S. Henry, *Anal. Chem.* 84, 4474–4480, 2012.
- [10] A.K. Geim and K.S. Novoselov, *Nature Mat.*, 6, 183–191, 2007.
- [11] N. Ruecha, R. Rangkupan, N. Rodthongkum, and O. Chailapakul, *Biosens. Bioelectron.* 52, 13–19, 2014.
- [12] P. Zhang, X. Han, L. Kang, R. Qiang, W. Liu, and Y. Du, *RSC Adv.*, 3, 12694–12701, 2013.