



Synthesis and characterization of polypyrrole decorated graphene/ β -cyclodextrin composite for low level electrochemical detection of mercury (II) in water

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ARTICLE INFO

Article history:

Received 15 June 2016

Received in revised form 1 December 2016

Accepted 12 December 2016

Available online 14 December 2016

Keywords:

Screen printed carbon electrode

Graphene

β -cyclodextrin

Polypyrrole

Mercury (II)

Health and environment

ABSTRACT

Mercury (Hg(II)) is considered as one of the most toxic element that directly affects the human health and the environment. Therefore, in this study, we propose a sensitive and disposable electrochemical sensor for the detection of Hg(II) in various water samples using polypyrrole (PPy) decorated graphene/ β -cyclodextrin (GR-CD) composite modified screen-printed carbon electrode (SPCE). The GR-CD/PPy composite was synthesized by chemical oxidation of PPy monomer in GR-CD solution using FeCl_3 . Differential pulse voltammetry (DPV) is used for the detection of Hg(II) and the DPV results reveal that GR-CD/PPy composite modified SPCE has high sensitivity towards Hg(II) than bare, GR, GR-CD and PPy modified SPCEs. The optimization studies such as effect of pH, accumulating time and effect of scanning potential towards the detection of Hg(II) were investigated. The GR-CD/PPy composite modified SPCE could detect the Hg(II) up to $51.56 \mu\text{M L}^{-1}$ with the limit of detection (LOD) of 0.47 nM L^{-1} . The obtained LOD was well below the guideline level of Hg(II) set by the World's Health Organization (WHO) and U.S. Environmental Protection Agency (EPA). In addition, the fabricated GR-CD/PPy composite modified SPCE selectively detected the Hg(II) in the presence of potentially interfering metal cations.

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1. Introduction

The accurate and reliable detection of heavy metal ions have received substantial interest owing to their serious effect in the environment and human health [1,2]. Besides, the most of the environmental pollutions are caused by the heavy metal ions in industrial waste water [3]. Particularly, mercury (Hg(II)) is considered as a most toxic element that could easily accumulate into the human body and environment [4]. The World's

Health Organization (WHO) has stated that a maximum permissible level of Hg(II) is 30 ppb in drinking water [5], while the U.S Food and Drug Administration agency stated that a maximum permissible level of Hg(II) in meat is 1000 nM L^{-1} [6]. The excess level of Hg(II) in water and meat can result in disorders and several diseases, including Hunter-Russell syndrome, pink disease, Minamata disease and severe kidney damage [7–12]. Hence, the monitoring of trace level Hg(II) in pollutant samples has received significant importance in order to secure the health and environment. Different analytical methods have been developed for the reliable detection of Hg(II), including traditional methods such as inductively atomic absorption and emission spectroscopy [13], X-ray fluorescence spectrometry [14], inductively coupled plasma mass spectrometry [15] and capillary electrophoresis [16]. In addition, the different sensing strategies have also been explored for the detection of Hg(II) using photoelectrochemical, surface Plasmon resonance, surface resonance Raman

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scattering, electrochemical, fluorescence and colorimetric methods [14,15]. However, the electrochemical methods are found more significant, simple and straightforward when compared with the available aforementioned traditional and analytical sensing methods [14,16].

To date, different micro and nanomaterials have been utilized on the conventional electrodes to improve the detection ability of Hg(II) such as carbon materials, quantum dots, metal nanoparticles, conducting polymers and molecularly imprinted polymers [17]. Graphene (GR) is a two-dimensional material, has received immense attention in the scientific community due to its high conductivity, excellent mechanical stability and low electrical resistivity [18,19]. The unique properties of GR enable it to use in wide range applications including energy devices, flexible display devices, photocatalysis, transparent conducting electrodes, biomedical applications, biosensors and chemical sensors [20–23]. In addition, GR is widely used for wide range of applications such as ballistic transistors, field emitter, components of integrated circuits, transparent conducting electrodes and field effect transistor sensors. Particularly, GR has been commercially used in touchscreens, liquid crystal displays (LCD) and organic light emitting diodes (OLEDs) due to its high transparency (transmit up to 97.7% of light), high tensile strength, high flexibility, and low electrical resistance [24,25].

Recent years, conducting polymers (CPs) have great potential to wide range of applications including the transistors, sensors and biosensors. In addition, CPs have also been widely used for the removal of heavy metal ions due to their high surface, unique pore structure and ion exchange properties [26]. Despite of high conductivity and cost effectiveness of the CPs, it is being used as an alternative and promising material for heavy metal ions removal from wastewaters replacing available traditional adsorbents (activated carbon based adsorbents) [27]. In particular, polypyrrole (PPy) is a well-known and predominant CP that has been used as a promising material for different applications, such as catalyst support for fuel cells, drug delivery, optical devices, sensors, batteries and supercapacitors [28–33]. Recent studies revealed that the composite of PPy with carbon nanomaterials have high binding affinity to Hg(II), and shown impressive activity towards the selective detection of Hg(II) with improved sensitivity [34,35]. For instance, the PPy combined with graphene oxide (GO) and reduced graphene oxide (RGO) composites are more recently reported for the selective detection of Hg(II). It was reported that the binding affinity of Hg(II) with PPy is due to selective coordination of Hg(II) with the nitrogen of the pyrrole unit [34]. The RGO was used as a support with PPy to provide more active sites and surface area for the enhanced detection of Hg(II) [34]. However, all reported RGO-PPy composites have been prepared using graphene oxide (GO) and pyrrole monomer as a starting material [31,34–36]. The hydrophobic nature and abundant functional groups of GO are often more supportive to prepare RGO and PPy composites, yet the active surface area of the resulting composite is greatly abridged due to the aggregation and strong π – π interaction of RGO [37]. To overcome this problem, we have used pristine graphene (GR) as an alternative material with PPy, and β -cyclodextrin (CD) is used as a dispersing agent for the dispersion of GR in aqueous solution. Since, CD is known for its guest-host interaction ability with hydrophobic materials such graphite, carbon nanotubes and graphene that enable them to disperse in aqueous solutions [38,39]. For the first time, the PPy decorated pristine GR-CD composite (GR-CD/PPy) was synthesized by a simple chemical oxidation of PPy monomer in GR-CD solution and its potential application towards electrochemical sensing of Hg(II) was demonstrated.

2. Experimental

2.1. Materials and method

Graphene (8 nm) flakes were purchased from UniRegion Bio-Tech, Taiwan. Mercury(II) chloride (HgCl_2) and β -cyclodextrin were obtained from Sigma Aldrich. Pyrrole (Azole reagent grade, purity 98%) was obtained from Aldrich and used as received. Screen printed carbon electrodes were purchased from Zensor R&D Co. Ltd, Taiwan. All other chemicals were purchased from Sigma Aldrich and used as received. The stock solutions were prepared using doubly distilled water without any further purification. The supporting electrolyte pH 7.0 was prepared using 0.01 M L^{-1} ammonium acetate and the pH was adjusted using diluted acetic acid or a diluted ammonium hydroxide solution. All electrochemical experiments were carried out in an inert atmosphere at a room temperature. The wastewater and tap water samples were collected from the Taipei Tech campus and used as obtained.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies were performed by a computerized CH750A electrochemical workstation from CH instruments. Surface morphological studies were examined by Hitachi S-3000 H electron microscope. Raman spectrum was recorded using a Raman spectrometer (Dong Woo 500i, Korea). Fourier transform infrared spectroscopy (FT-IR) was performed using JASCO FTIR-6600 spectrometer. The SPCE was used as a working electrode, saturated Ag/AgCl and a platinum wire electrode were used as a reference and auxiliary electrodes, respectively.

2.2. Synthesis of GR-CD/PPy composite and electrode modification

To synthesis GR-CD/PPy composite, first, the GR flakes (5 mg mL^{-1}) were added into 5 mL of CD (5 mg mL^{-1}) aqueous solution and sonicated for 30 min at room temperature. The resulting GR-CD composite was transferred into the magnetic stirrer and stirred for 15 min. Then, 50 mL L^{-1} of pyrrole monomer was added into the as-prepared GR-CD aqueous solution under magnetic stirring at room temperature. Finally, 0.1 M L^{-1} of FeCl_3 solution was added into the GR-CD/pyrrole suspension and the mixture was stirred for 1 h for the polymerization of pyrrole to PPy. The resulting GR-CD/PPy composite was filtered and washed with deionized water and dried in an air oven (50°C) for a day. The unreacted pyrrole monomers in GR-CD/PPy composite was removed by washing the composite with deionized water. The PPy was prepared by the same method using the pyrrole monomer in ethanol solution without GR-CD composite. The CD-PPy was prepared using the pyrrole monomer in CD without GR. The GR-CD/PPy composite and PPy solutions were prepared by dispersing of $0.5 \text{ mg GR-CD/PPy composite}$ and PPy in 1 mL of ethanol, respectively. The GR dispersion was prepared by dispersing of GR flakes (5 mg mL^{-1}) in dimethyl-formamide solution. For electrode fabrication, $8 \mu\text{L}$ of as-prepared GR-CD/PPy composite was dropped on the pre-cleaned SPCE and dried at room temperature. The PPy, GR-CD and GR modified SPCEs were prepared by similar procedure by drop coating of PPy, GR-CD and GR on SPCE. The modified SPCEs were stored at room temperature (27°C) under a dry condition when not in use.

2.3. Electrochemical measurements

The optimized electrochemical experimental conditions were used for DPV measurements. The DPVs were recorded using the pulse amplitude: 50 mV ; pulse period: 0.2 s ; pulse width: 0.05 s ; sampling width: 0.0167 s and quite time: 2 s . The DPV was recorded in the potential scanning from -0.8 to 0.6 V .

3. Results and discussion

3.1. Characterizations

The surface morphological results of as-prepared materials are shown in Fig. 1, and displays the SEM images of PPy (A), GR (B) and GR-CD/PPy composite (C and D). The SEM image of PPy shows well-defined PPy nanoparticles with the average diameter is about 50 ± 5 nm and is consistent with the previous reports [34]. On the other hand, GR-CD/PPy composite shows distinct morphology, where the PPy nanoparticles (white arrow) adsorbed on the crumpled surface of GR (blue arrow) and CD (yellow arrow) composite. The strong interaction between the PPy with GR-CD composite resulted into the formation of GR-CD/PPy composite.

The GR-CD/PPy composite was further confirmed by FT-IR and Raman spectroscopy. Fig. 2 shows the FT-IR spectra of PPy (a), CD (b), GR (c) and GR-CD/PPy composite (d). The FT-IR spectrum of PPy exhibits the sharp bands at 1566, 1361, 1176 and 1055 cm^{-1} , which attributed to the stretching vibration of C–C, stretching vibration of C–N adsorption and C–N in plane deformation vibrations [40]. Furthermore, a broad band was observed at 902 cm^{-1} , which is due to C–N out-plane deformation vibration [41]. On the other hand, the GR-CD/PPy composite shows similar bands for PPy along with three distinct peaks at 3382, 2965 and 1015 cm^{-1} . These three new peaks are associated with the O–H (from water), C–H stretching vibration and C–O–C vibrations of β -CD [42], which are consistent with the bands of CD. While the FT-IR spectrum of GR shows featureless in the fingerprint region. The quality of the utilized GR in GR-CD/PPy and GR/ β -CD composite was confirmed by Raman spectroscopy and the results are shown in Fig. S1. The Raman spectrum of GR-CD composite (red color) shows a weak D bands at 1389 cm^{-1} and strong G band at 1589 cm^{-1} . While, a strong 2D peak was observed at 2723 cm^{-1} , which is corresponding to the typical bands for few layers GR [43]. The GR-CD/PPy composite shows G and 2D bands at 1590 and 2729 cm^{-1} . The 2D/G intensity ratio was found to be 1.08 and 1.14 for GR-CD/PPy and GR/ β -CD composite, respectively, and it reveals that the nature of GR was unchanged in GR-CD/PPy and GR/ β -CD composite.

3.2. Optimizations

Prior to electrochemical detection of Hg(II), the optimization studies such as accumulation time, scanning potential and pH is more vital, and they could affect the performance of the GR-CD/PPy modified electrode towards the detection of Hg(II). Thus, we have optimized the experimental conditions using the CV. Fig. S2A shows the calibration plot for the CV response of GR-CD/PPy composite modified SPCE in different pH (pH 2–9) containing $50\text{ }\mu\text{M L}^{-1}$ Hg(II) at a scan rate of 50 mV/s . The GR-CD/PPy composite modified SPCE exhibited a maximum current response for Hg(II) at pH 7.0 and current response was decreased when the pH was above 7.0. On the other hand, GR-CD/PPy composite modified SPCE shows a diminished response to current when the pH was below 5.0. According to previous reports, the adsorption of Hg(II) is weak at low pH due to the protonation of the lone pair of nitrogen, which hinders the formation of stable complex with Hg(II). If the pH was above 7.0, the hydrolysis of Hg(II) hinders the accumulation on GR-CD/PPy composite modified SPCE [34]. Hence, the lone pair of electrons on nitrogen coordinate with Hg(II) forming a stable complex at pH 7.0. For the above reasons, pH 7.0 was chosen as an optimal value and used for further experiments.

The effect of accumulation time and scanning potential were optimized using CV and the experimental conditions are similar as of in Fig. S2B and C. It can be seen from Fig. S2B that the maximum current response of Hg(II) was observed when the scanning potential at -0.8 V , and the current response was decreased above or below -0.8 V . The result suggests that the maximum partial accumulation of Hg(II) via Hg^{2+} to Hg^0 occurs at -0.8 V on GR-CD/PPy composite modified electrode than that of other potentials. The trace amount of Hg(I) can be neglected because it will be totally reduced during DPV to Hg^0 . Therefore, -0.8 V was chosen as an optimum scanning potential for the detection of Hg(II). On the other hand, the current response of Hg(II) gradually increase with increasing the accumulation time and reaches its threshold at 180 s (Fig. S3C) and it was used throughout the experiments.

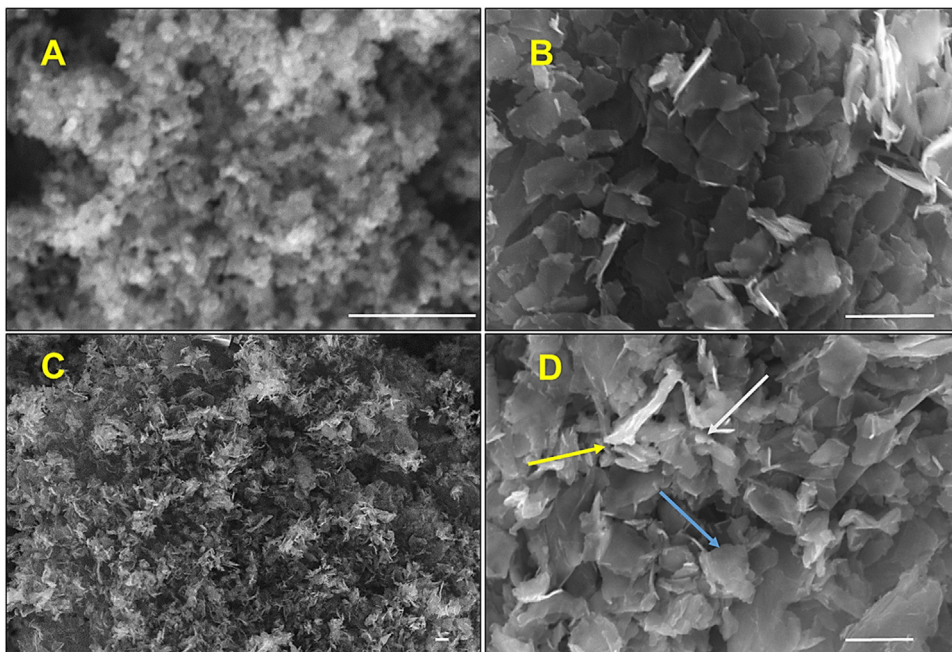


Fig. 1. SEM images of PPy (A), GR (B) and GR-CD/PPy composite in lower (C) and higher magnification (D). Scale bar = $5\text{ }\mu\text{m}$.

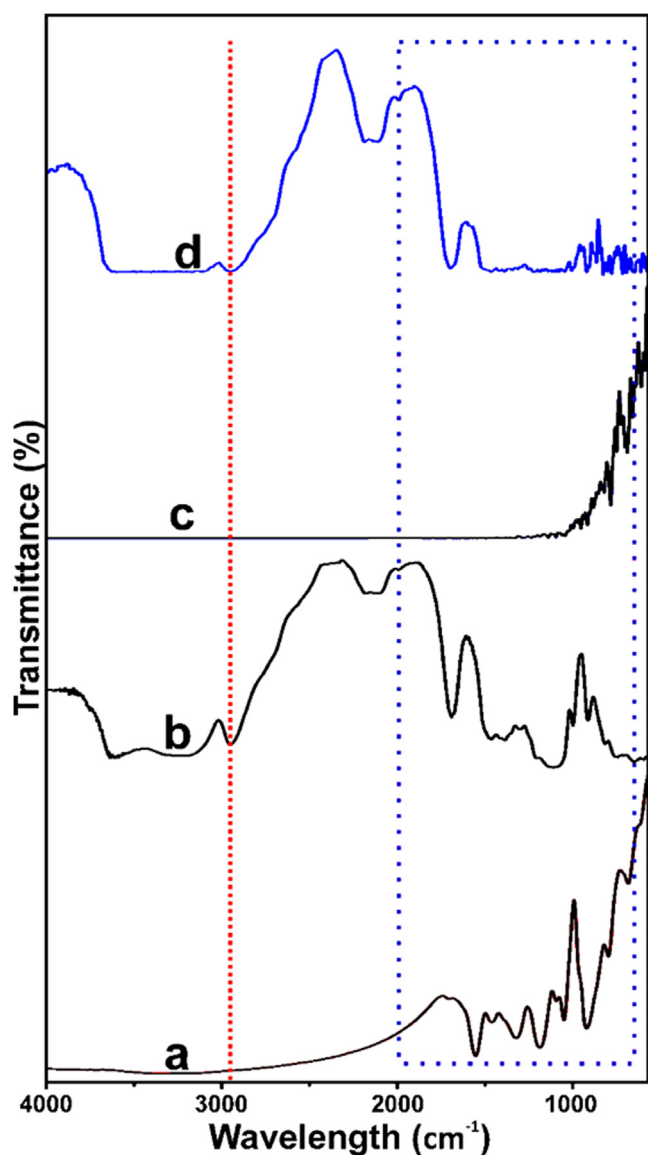


Fig. 2. FT-IR spectra of PPY (a), CD (b), GR (c) and GR-CD/PPy composite (d).

3.3. Electrochemical behavior of Hg(II) at different modified electrodes

The electrochemical behavior of Hg(II) at different modified SPCEs was investigated by DPV. The DPVs were performed in the potential scanning from -0.8 to 0.6 with an accumulation time of 180 s. Fig. 3 shows the DPV response of PPY (a), GR (b), GR-CD (c) and GR-CD/PPy (d) modified SPCEs in $1 \mu\text{M L}^{-1}$ of Hg(II) containing pH 7. The GR-CD and PPY modified SPCEs exhibit a sharp anodic peak at 0.22 and 0.24 V, which is due to the oxidation of adsorbed Hg(0) to Hg(II) [34]. While, the GR modified electrode shows the anodic peak at 0.244 V, and the observed current response for Hg(II) was lower than those observed at GR-CD and PPY modified SPCEs. On the other hand, GR-CD/PPy modified SPCE shows a sharp and well-defined DPV response for Hg(II) and the anodic peak was observed at 0.22 V. Furthermore, the observed current response was two and one folds higher than those observed at GR, GR-CD and PPY modified SPCEs. The main adsorption sites for Hg(II) are the nitrogen atoms in the macromolecular chain of PPY because the nitrogen atom has a lone pair of electrons that can efficiently bind with Hg(II) metal ions and forms a stable metal complex. Besides, GR-CD could

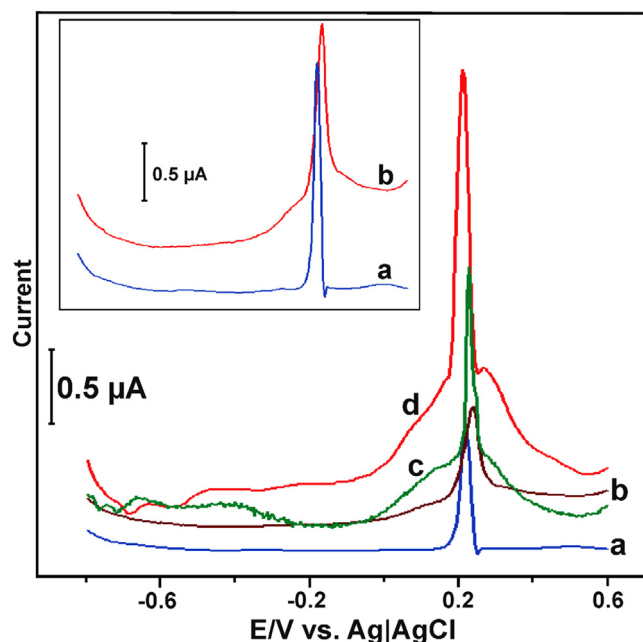


Fig. 3. DPV response obtained at PPY (a), GR (b), GR-CD (c) and GR-CD/PPy composite (d) modified SPCEs for $1 \mu\text{M L}^{-1}$ of Hg(II) containing pH 7.0. Inset shows the DPV response of PPY (a) and CD-PPy (b) modified SPCEs for $1 \mu\text{M L}^{-1}$ of Hg(II) containing pH 7.0. DPV parameters are: pulse amplitude: 50 mV; pulse period: 0.2 s; pulse width: 0.05 s; sampling width: 0.0167 s; quiet time: 2 s.

provide more active surface area and more number of active sites for accumulation of more Hg(II) on the electrode surface. The aforementioned unique properties of PPY and GR-CD in the composite resulted into the fast electron transfer and enhanced sensitivity for the detection of Hg(II). We have also tested the response of CD-PPy modified electrode (curve b) by DPV and the obtained results were compared with the response of PPY (Fig. 3 inset). The comparison results clearly show that the enhancement in the sensitivity of Hg(II) is due to the presence of PPY and GR, not due to CD. Therefore, the high sensitivity of the developed sensor is due to the high adsorption ability of PPY and high surface area of GR. The obtained results confirmed that as-prepared GR-CD/PPy composite modified SPCE can be used for the sensitive detection of Hg(II) than other modified SPCEs.

To confirm the electrochemical behavior of Hg(II) at GR-CD/PPy composite modified SPCE, the effect of scan rate was studied using CV. Fig. S3 shows the CV response of GR-CD/PPy composite modified SPCE in $1 \mu\text{M L}^{-1}$ of Hg(II) containing pH 7.0 at different scan rates from 20 to 200 mV/s. It can be seen that the anodic and cathodic peak current of Hg(II) increases with increasing the scan rate from 20 to 200 mV/s. In addition, the log scan rate was linearly proportional to the log anodic current (inset), and the slope value was found 0.57 with the correlation coefficient of 0.998 . The result suggests that the electrochemical behavior of Hg(II) was controlled by a mixed kinetic process, where the Hg(II) was first adsorbed and then diffused on the electrode surface. The similar phenomenon has been reported earlier for Hg(II) on carbon nanomaterials modified electrodes [5]. The possible mechanism for the detection of Hg(II) on GR-CD/PPy composite is shown in Fig. 4. The Hg(II) binds with the lone pair of electrons on nitrogen atoms of PPY in $1:4$ complexation mode and forms a stable metal complex on the electrode surface. In addition, PPY was attached strongly to GR-CD via hydrogen bonding and enables the fast electron transfer towards the electrode surface.

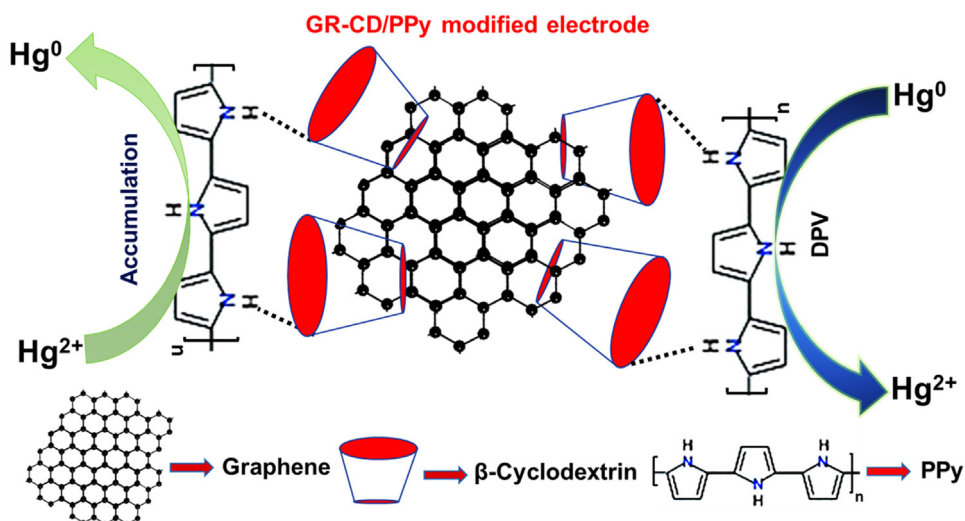


Fig. 4. The possible electrochemical mechanism for detection of mercury at GR-CD/PPy composite.

3.4. Electrochemical determination $\text{Hg}(\text{II})$

The GR-CD/PPy composite modified SPCE was further used for electrochemical detection of $\text{Hg}(\text{II})$ by DPV. The DPVs of GR-CD/PPy composite modified SPCE for quantification of $\text{Hg}(\text{II})$ were investigated in the potential scanning from -0.8 to 0.6 with an accumulation time of 180 s. Fig. 5A shows the DPV response of GR-CD/PPy composite modified SPCE for the lower concentration additions of $\text{Hg}(\text{II})$ (1 nM L^{-1} to $1.055 \text{ } \mu\text{M L}^{-1}$) into the pH 7.0 . It can be seen that a sharp anodic peak was observed for the addition of $1, 5, 50, 100$ and 300 nM L^{-1} of $\text{Hg}(\text{II})$ into the pH 7 (Fig. 5A), and response current increases with increasing the addition of $\text{Hg}(\text{II})$ concentration. The DPV response current increases with the addition of $\text{Hg}(\text{II})$ from 1 nM L^{-1} to $51.557 \text{ } \mu\text{M L}^{-1}$ into the pH 7.0 (Fig. 5A inset). As shown in Fig. 5B, the DPV response of the sensor was linear over the $\text{Hg}(\text{II})$ concentration ranging from 1 nM to $51.56 \text{ } \mu\text{M L}^{-1}$. The detection limit (LOD) was estimated as 0.47 nM L^{-1} based on $3 \times$

Sd of the blank response/slope of the calibration plot. The sensitivity of the sensor was calculated as $13.49 \text{ } \mu\text{A } \mu\text{M}^{-1} \text{ L}^{-2} \text{ cm}^{-2}$ from the slope of the calibration plot/electrochemically active surface area of the electrode (0.127 cm^2). To further verify the novelty of the developed sensor, a comparison was made with the previously reported $\text{Hg}(\text{II})$ sensors. The LOD of the sensor (0.47 nM L^{-1}) is lower than hydroxyapatite nanoparticles (141 nM L^{-1}) [42], gold nanoparticles (1 nM L^{-1}) [43], RGO-PPy (6 nM L^{-1}) [44] and nitrogen doped GR (50 nM L^{-1}) [45] and graphene/gold nanoparticles (6 nM L^{-1}) [46] modified electrodes for the determination of $\text{Hg}(\text{II})$. In addition, the response range of the sensor is more comparable with aforementioned $\text{Hg}(\text{II})$ sensors [42–46]. The result clearly reveals that the developed GR-CD/PPy composite modified SPCE has an appropriate analytical performance towards the detection of $\text{Hg}(\text{II})$. It is worthy to note that the LOD of the sensor (0.47 nM L^{-1}) is much lower than the value recommended by the WHO and U.S. Environmen-

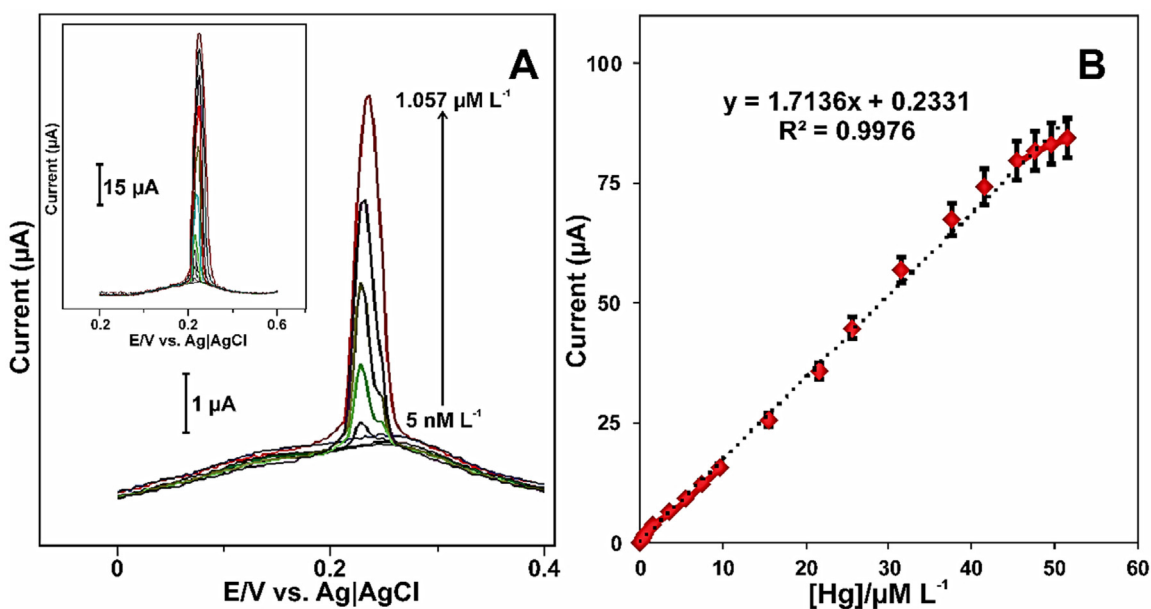


Fig. 5. (A) DPV response of GR-CD/PPy composite modified SPCE for successive addition of different concentrations (1 nM L^{-1} to $1.055 \text{ } \mu\text{M L}^{-1}$) of $\text{Hg}(\text{II})$ into the pH 7.0 . Inset shows the DPV response of GR-CD/PPy composite modified SPCE for the addition of $\text{Hg}(\text{II})$ from 1 nM L^{-1} to $51.557 \text{ } \mu\text{M L}^{-1}$ into the pH 7.0 . (B) Linear plot for current response vs. $[\text{Hg}(\text{II})]$.

Table 1

Determination of Hg(II) in different water samples using GR-CD/PPy composite modified SPCE by DPV.

| Sample labeled | Spiked (nM L ⁻¹) | Detected (nM L ⁻¹) | Recovery (%) | RSD ^a |
|----------------|------------------------------|--------------------------------|--------------|------------------|
| Waste water | ND ^b | ND | | |
| | 10 | 9.2 | 97.0 | 4.6 |
| | 30 | 29.0 | 96.6 | 4.8 |
| | 300 | 296.3 | 98.8 | 4.2 |
| Tap water | ND | ND | | |
| | 10 | 9.8 | 98.0 | 3.4 |
| | 30 | 29.4 | 98.0 | 3.3 |
| | 300 | 298.6 | 99.5 | 2.9 |
| Drinking water | ND | ND | | |
| | 10 | 9.9 | 99.0 | 2.6 |
| | 30 | 29.6 | 98.7 | 2.9 |
| | 300 | 299.1 | 99.7 | 2.4 |

^a RSD – Relative standard deviation for 3 measurements.

^b ND – Not detected.

tal Protection Agency. Hence, the GR-CD/PPy composite modified SPCE could be used for sensitive and low level detection of Hg(II).

3.5. Selectivity of the sensor

In order to evaluate the selectivity, the GR-CD/PPy composite modified SPCE was evaluated by DPV for detection of 1 $\mu\text{M L}^{-1}$ Hg(II) in the presence of 10 folds (10 $\mu\text{M L}^{-1}$) addition of different metal ions and the DPV working parameters are similar as of in Fig. 5A. The selectivity results of the fabricated GR-CD/PPy composite modified SPCE is shown in Fig. S4A. It can be seen that the metal ions such as Zn^{2+} , Cd^{2+} , Cu^{2+} , Co^{3+} , Fe^{2+} and Ni^{2+} have less effect (2%) with the current response of Hg(II). While, Pb had little more effect on the current response of Hg(II) when compared to the effect of other metal ions. However, the GR-CD/PPy composite modified SPCE has acceptable selectivity for the detection of Hg(II) even in the presence of 10 $\mu\text{M L}^{-1}$ common metal ions. The result authenticates that the proposed GR-CD/PPy composite modified SPCE could be used for the selective detection of Hg(II).

3.6. Practicality and reproducibility of the sensor

The practical ability of the GR-CD/PPy composite modified SPCE was tested in Hg(II) containing different water samples using DPV. The standard addition method was used for the calculation of the Hg(II) recovery [5]. In order to verify the usefulness of the sensor, DPV was performed using the GR-CD/PPy composite modified SPCE in Hg(II) containing different water samples. The water samples were used without any additional treatment or purification (except filtration of waste water). The DPV experiments were performed in the potential scanning from -0.8 to 0.6 with an accumulation time of 180 s. Other DPV working conditions are similar to Fig. 5. All the water samples were tested for Hg(II) free before the addition of Hg(II) with optimized conditions. The pH of the waste water, tap water and drinking water samples was 8.1, 7.8 and 7.3, and the pH of real sample solutions was adjusted to 7.0 before the electrochemical experiments. The DPV response of GR-CD/PPy composite modified SPCE towards the addition of different concentration (10, 30 and 300 nM L^{-1}) of Hg(II) containing water samples were recorded and its corresponding recovery of Hg(II) in different water samples was summarized in Table 1. It is evident from Table 1 that the GR-CD/PPy composite modified SPCE has an appropriate recovery of Hg(II) in different water samples, and the recoveries were 97.5%, 98.5% and 99.1% in waste water, tap water and drinking water samples, respectively. The result shows that GR-CD/PPy

composite modified SPCE can be used for the real-time sensing of Hg(II) in the investigated water samples.

It is significant to test the sensor for reproducibility and therefore, five different GR-CD/PPy composite modified SPCEs were tested for the detection of 50 $\mu\text{M L}^{-1}$ Hg(II) by CV at a scan rate of 50 mV/s. The obtained reproducibility results of the five different GR-CD/PPy composite modified SPCEs are shown in Fig. S4B. The relative standard deviation (RSD) for five modified electrodes was calculated as 3.9% for the detection of 50 $\mu\text{M L}^{-1}$ Hg(II). The result validates that the as-fabricated GR-CD/PPy composite modified SPCE is highly reproducible and could be used for precise detection of Hg(II).

4. Conclusions

A reliable Hg(II) sensor using the GR-CD/PPy composite modified SPCE was developed. The physicochemical characterizations confirmed the formation of GR-CD/PPy composite. The as-prepared GR-CD/PPy composite modified SPCE showed an enhanced sensitivity for the detection of Hg(II) than other modified electrodes such as PPy, PPy-CD, GR, GR-CD and CD-PPy. In addition, the GR-CD/PPy composite modified SPCE showed good analytical performance towards the detection of Hg(II), including high sensitivity, low LOD with a wider linear response range. The as-prepared sensor exhibited appropriate selectivity for the detection of Hg(II) in the presence of potentially active metal ions. The appropriate reproducibility and practicality of the GR-CD/PPy composite modified SPCE further revealed that it can be used for the detection of Hg(II) in the investigated water samples with high precision.

Acknowledgements

The authors extend their appreciation to the International Scientific Partnership Program ISPP at King Saud University for funding this research work through ISPP#6. In addition, this work was supported by the Ministry of science and technology of Taiwan (Republic of China).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2016.12.068>.

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