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Construction of a Carbon Paste Electrode Based on Novel Thiolated Ligand Capped Gold Nanoparticles for Determination of Trace Amounts of Mercury(II)

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In the present study, a simple electrochemical sensor for trace determination of Hg(II) ions in aqueous solutions is introduced. The proposed sensor was designed by incorporation of the 4-methyl-piperidine-carbodithioate capped gold nanoparticles (GNPs) into the carbon paste electrode (CPE) that provides a remarkably improved sensitivity for stripping voltammetric determination of Hg(II). Differential pulse voltammetry (DPV) was applied for quantitative determinations. The resulting electrode exhibited a linear relationship towards Hg(II) concentrations ranging from 0.4-100.0 $\mu\text{g l}^{-1}$. The detection limit was found to be 0.2 $\mu\text{g l}^{-1}$ (S/N = 3) that is lower than the permitted value of Hg(II) reported by the Environmental Protection Agency limit for drinkable water. The relative standard deviation (RSD) for 7 successive measurements at different electrodes was also found to be 3.8%. The interference studies showed that the several common metal ions did not interfere with the quantitative mercury determination. The designed sensor was further utilized for the determination of mercury ions in real water samples with satisfactory results.

Keywords: Heavy metals, Gold nanoparticles, Mercury(II), Voltammetry, Carbon paste electrode

INTRODUCTION

Currently, there is an increasing demand to selectively sense heavy metal ions such as Hg(II), Cd(II) and Pb(II) due to their toxic effect on human health [1-3]. Among them, mercury is one of the most widely studied toxicant [4,5]. Even a trace amount of mercury intake can lead to serious central nervous system problems and damage vital human organs [6,7]. Monitoring and measuring mercury in the environment is therefore of great importance. Various methods such as cold vapour atomic fluorescence spectrometry (CV-AFS) [8], inductively coupled plasma optical emission spectrometry (ICP-OES) [9], cold vapour atomic absorption spectrometry (CV-AAS) [10], inductively coupled plasma mass spectrometry (ICP-MS) [11], and different electrochemical methods [12,13] have been successfully reported for the detection of mercury. Electrochemical analysis has attracted significant interest

for mercury detection, due to its excellent sensitivity, low cost, short analysis time and low power consumption [14,15]. The stripping voltammetric techniques including anodic stripping voltammetry (ASV) [16] and adsorptive stripping voltammetry (AdSV) [17], based on the interfacial accumulation and voltammetric determination of metal complexes [18,19], are among the most commonly employed techniques for determination of mercury due to their lower detection limits. In ASV, different types of electrode materials have been used, such as gold [20], glassy carbon [21], carbon paste, [22] and carbon-fiber [23] electrodes. Differential pulse anodic stripping analysis (DPASV) employing modified carbon paste electrode (CPE) is one of the instrumental techniques applicable in the determination of very low concentrations of mercury because of compatibility with various types of modifiers [24]. In the electrochemical mercury analysis, the key parameter is electrode modification that requires an appropriate reagent containing active groups [25].

Nanoscience and nanotechnology are highly developing

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research and application fields in various disciplines. A great number of efforts have been made in order to develop and engineer the surface of nanoparticle by tuning the bulk properties, modify the surface properties including charge density, functionality, reactivity, biocompatibility, stability and dispersibility [26-29]. Recently, gold nanoparticles (GNPs) have revealed to be very convenient for the expansion of modified sensores allowing the fabrication of electrode nanoarrays in one or several dimensions [30,31]. Moreover, the application of GNPs in electro-analytical studies has motivated notable attention because of the GNPs' large surface-to-volume ratio, high stability and conductivity, proper electro-catalysis characteristics, satisfactory biocompatibility, and their interface-dominant properties that significantly differ from those of their bulk counterparts [32]. GNPs based sensors have been designed using glassy carbon [33], ultra-microelectrode arrays [34], metal Au [35] and carbon paste [36] as electrode substrates. In this study, a new mercury electrochemical electrode based on 4-methyl-piperidine-carbodithioate capped GNPs is constructed for trace determination of Hg(II) ions in environmental water samples. The critical factors, linear concentration range, and detection limit of the suggested electrode in the detection of Hg(II) are examined. The prepared electrochemical sensor was employed for voltammetric measuring of mercury ions in different water samples.

EXPERIMENTAL

Materials

Chemicals including tetrachloroauric(III) acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Sodium borohydride (NaBH_4), highly pure graphite powder and high viscosity paraffin oil were purchased from Merck (Darmstadt, Germany). Hg(II) stock solution was prepared by dissolving $\text{Hg}(\text{NO}_3)_2$ with 0.5% HNO_3 . Ultra-pure water (18 $\text{m}\Omega$ resistance) was used throughout the experiments. Electrochemical tests were recorded using a Metrohm electrochemical analyzer Model 757 VA (Herisau, Switzerland) connected to a personal computer. A three-electrode configuration was employed, consisting of a CPE as working electrode, saturated Ag/AgCl as a reference electrode and a platinum wire as an

auxiliary electrode. A Metrohm 827 pH-meter (Herisau, Switzerland) was used to measure the pH.

Preparation of 4-methyl-piperidine-carbodithioate.

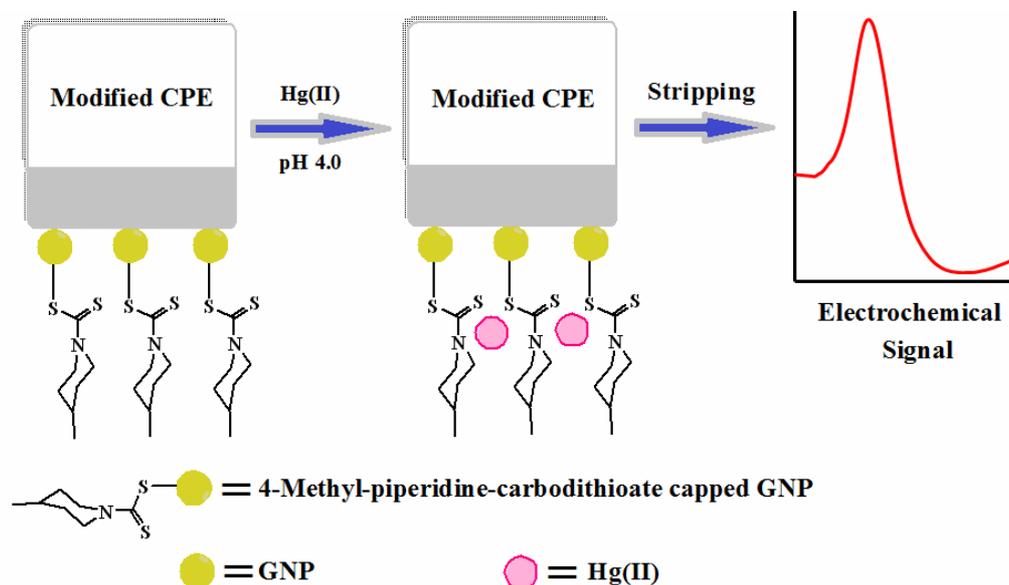
4-Methyl-piperidine-carbodithioate was synthesized and purified in our laboratory according to the following procedure [37]. Briefly, 15.0 ml carbon disulfide was added dropwise to a 24.0 ml ethanolic solution of 4-methyl-piperidine (20 mmol) and potassium hydroxide (20 mmol). The reaction mixture was stirred continuously for 2 h. The resulting product was filtered off, washed with ethanol and dried under reduced pressure.

Preparation of 4-methyl-piperidine-carbodithioate capped GNPs. Firstly, GNPs were synthesized and purified by the reduction of Au(III) ions with NaBH_4 according to the Brust method [38]. Briefly, fresh NaBH_4 (5 ml, 0.072 mg ml^{-1}) was added drop wise to aqueous in 5 ml solution of HAuCl_4 (0.0125 mg ml^{-1}) under vigorous stirring at room temperature. The solution was heated for another 15 min, during which its color was changed from pale yellow to wine red. About 20 min, a vividly red solution was produced. Then, 100.0 μl of 2.0×10^{-4} M of 4-methyl-piperidine-carbodithioate was added to 5.0 ml GNPs under stirring. The capped GNPs were purified by centrifugation and re-dispersed in deionized water twice and finally dried in a vacuum.

Preparation of modified CPE. Carbon pastes were prepared by mixing graphite powder (60-75% (w/w)), capped GNPs (0-15% (w/w)), and paraffin oil (25% (w/w)) and thoroughly hand mixing in a mortar and pestle. The resulting paste was packed into a Teflon tube (2.0 mm inner diameter) and providing it with a copper electrical contact. The external surface of modified CPE was smoothed on a graph paper.

Electrochemical Procedure

Mercury ions were chemically pre-concentrated by immersing the prepared modified CPE in the solution (pH 4.0) containing Hg(II), while stirring at 500 rpm for 20 min in an open circuit. The modified CPE was rinsed by stirring in deionized water for 15 s and then kept in a cell containing 20.0 ml of 0.1 M HCl solution. A negative of -0.6 V was applied to the electrode immediately for 60 s to reduce mercury ions. Subsequently, the differential pulse voltammetry (DPV) measurements were carried out in the



Scheme 1. The working principles of the prepared sensor

potential range of 0.0-0.9 V. The working principles of the prepared sensor are shown in Scheme 1.

RESULT AND DISCUSSION

Characterization

The Fourier transform infrared (FT-IR) spectra for 4-methyl-piperidine-carbodithioate and 4-methyl-piperidine-carbodithioate capped GNPs are shown in Fig. 1. The spectrum of 4-methyl-piperidine-carbodithioate (Fig. 1a) illustrates the presence of S-H (about 2868 cm^{-1} , stretching vibration), C-N (about 1630 cm^{-1} , stretching vibration), and C=S/C-S (about 1034 cm^{-1} , stretching vibration). The FT-IR spectrum of 4-methyl-piperidine-carbodithioate capped GNPs (Fig. 1b) does not show the characteristic of S-H bond at 2868 cm^{-1} . This proves that 4-methyl-piperidine-carbodithioate molecules are linked on the surface of GNPs. The particle sizes of the GNPs were measured by dynamic light scattering (DLS) method. Figure 2 presents the diameter distribution of the GNPs. The average diameter of the prepared GNPs was about 17 nm. The transmission electron microscopy (TEM) images of the 4-methyl-piperidine-carbodithioate capped GNPs before and after additions of mercury ions are shown in Fig. 3. As shown in

Fig. 3b, the 4-methyl-piperidine-carbodithioate capped GNPs are well dispersed with spherical shape in the absence of analyte ions. Upon adding the mercury(II) ions, the TEM image of the 4-methyl-piperidine-carbodithioate capped GNPs (Fig. 3c and Fig. 3d) is exhibited a significant aggregation due to complex formation between ligand and Hg(II) ions.

Electrochemical Response of Hg(II) at Modified CPE

The favorable electroanalytical characteristics of the new electrode are revealed in Fig. 4, showing a comparison of DPV voltammograms obtained at the unmodified CPE (curve a) for $25.0 \mu\text{g l}^{-1}$ Hg(II), modified CPE in the absence of Hg(II) ions (curve b), 4-methyl-piperidine-carbodithioate modified CPE (curve c), and 4-methyl-piperidine-carbodithioate capped GNPs modified CPE (curve d) for $25.0 \mu\text{g l}^{-1}$ Hg(II). It can be seen from Fig. 4 that the peak current of mercury at the modified CPE is the highest among different electrodes. As a consequence, the modification of CPE with 4-methyl-piperidine-carbodithioate capped GNPs enhances mercury binding sites of the proposed electrode, providing an advantageous platform for sensing applications.

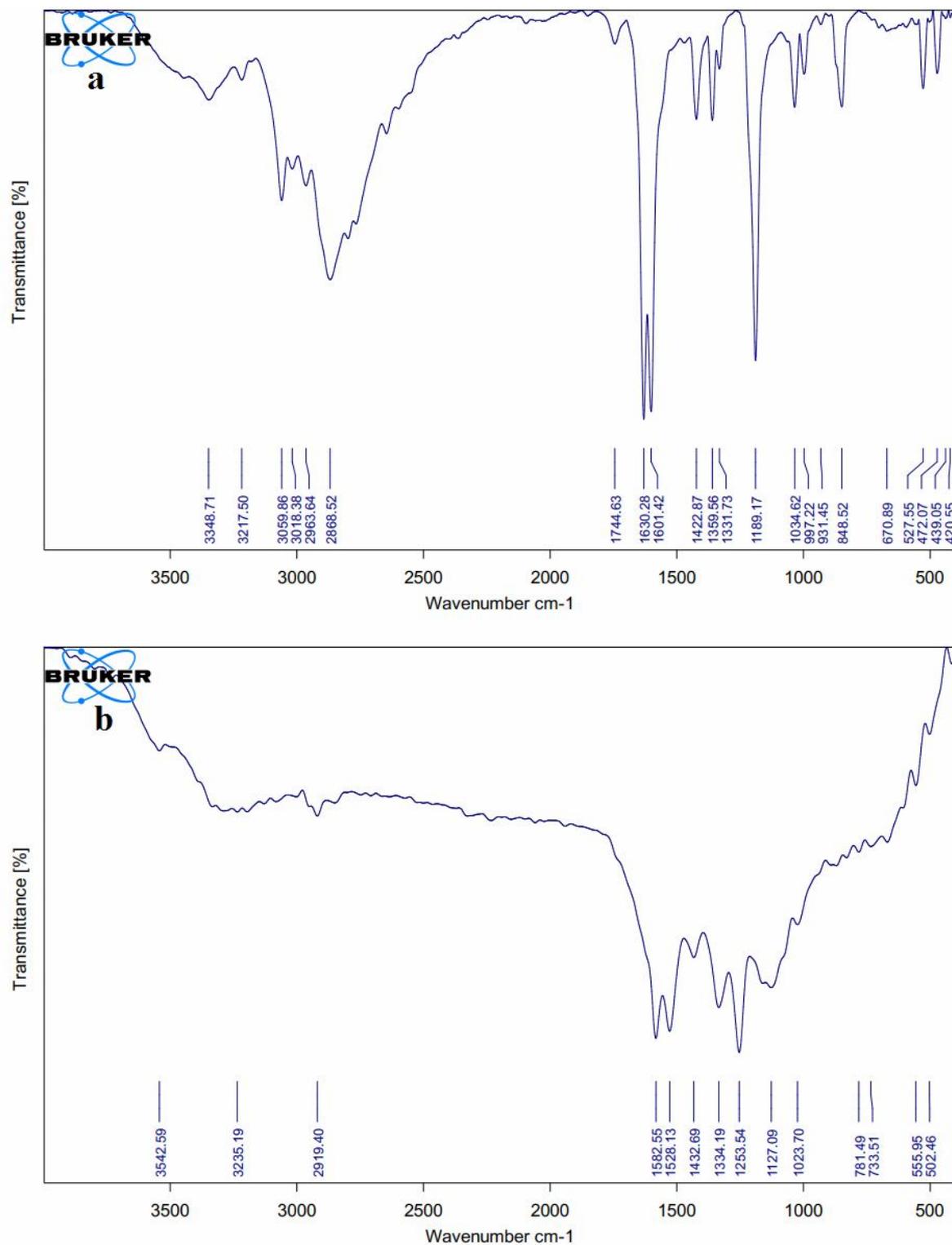


Fig. 1. FT-IR spectra of (a) 4-methyl-piperidine-carbodithioate, and (b) 4-methyl-piperidine-carbodithioate capped GNPs.

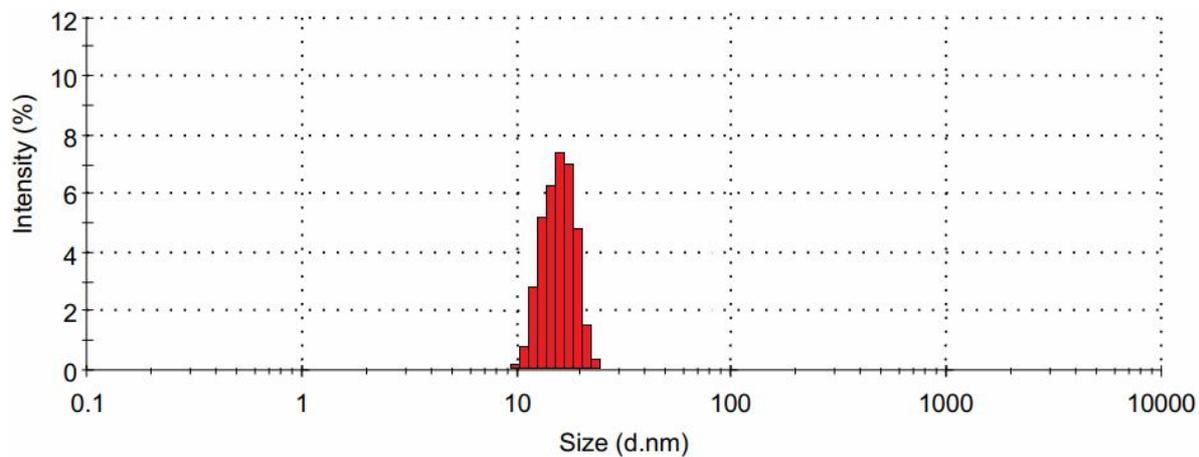


Fig. 2. Size distribution of GNPs measured by the DLS technique.

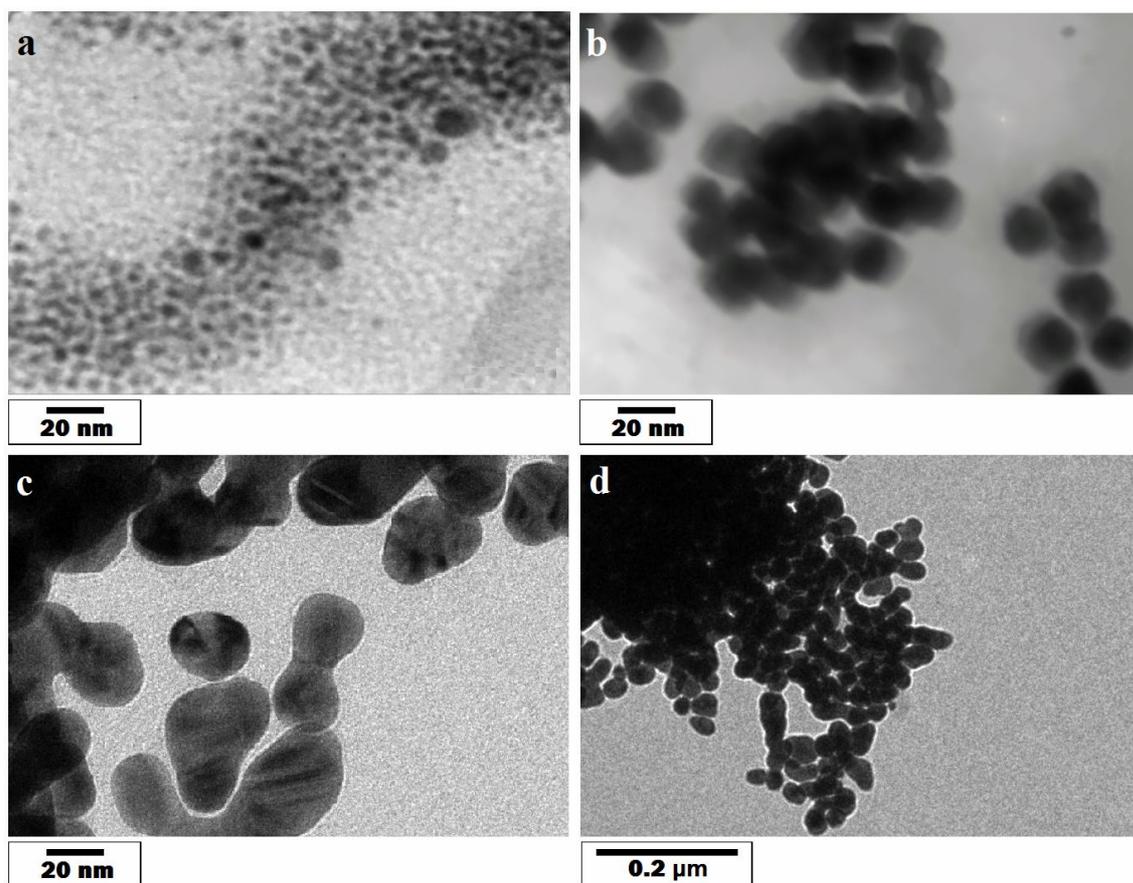


Fig. 3. Typical TEM images of (a) GNPs, (b) 4-methyl-piperidine-carbodithioate capped GNPs, and (c,d) 4-methyl-piperidine-carbodithioate capped GNPs in the presence of 0.1 mM Hg(II) ions.

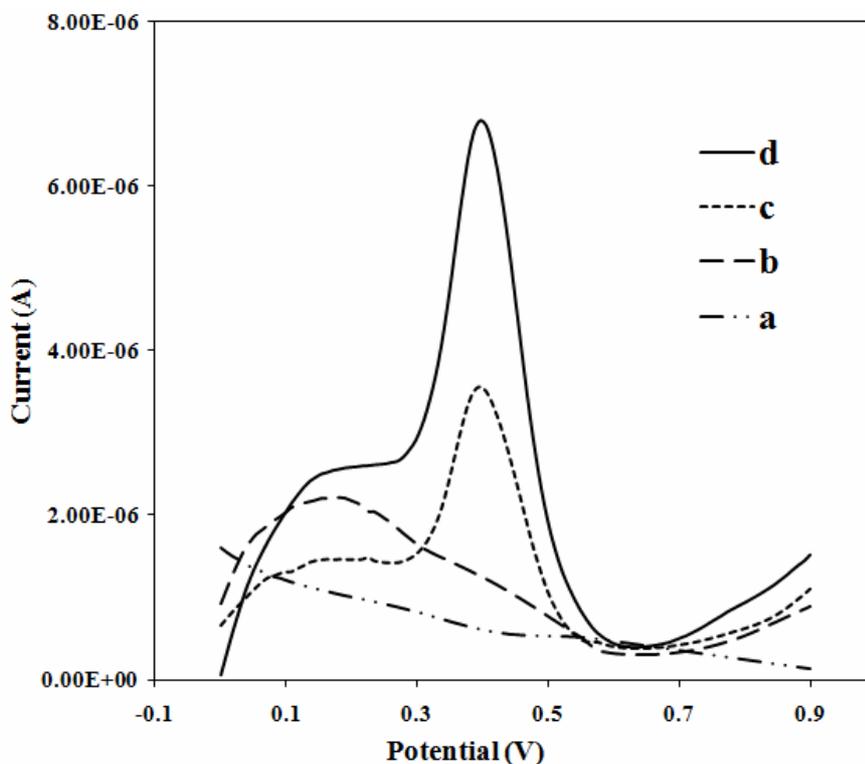


Fig. 4. Differential pulse voltammograms of (a) unmodified CPE in the presence of $25 \mu\text{g l}^{-1}$ Hg(II), (b) 4-methyl-piperidine-carbodithioate capped GNPs modified CPE in the absence of Hg(II) ions, (c) 4-methyl-piperidine-carbodithioate modified CPE, and (d) 4-methyl-piperidine-carbodithioate capped GNPs modified CPE with Hg(II) concentration of $25 \mu\text{g l}^{-1}$.

Optimization of Experimental Condition

To evaluate the amount of modifier, the DPV studies were carried out for different amount of 4-methyl-piperidine-carbodithioate capped GNPs in the range of 5-15% (w/w) in a $25.0 \mu\text{g l}^{-1}$ Hg(II) solution. It can be seen from Fig. 5a that the sensor response firstly enhances with increasing the modifier in carbon paste up to 10%, and then the conductivity of the modified CPE will drop when the amount of 4-methyl-piperidine-carbodithioate capped GNPs was over 10%. In this study, the optimal paste used in next experiments had the following composition in weight: 10% 4-methyl-piperidine-carbodithioate capped GNPs, 65% graphite and 25% paraffin oil.

An appropriate pH is not only important for the extraction of the metal ions but also important for the selectivity behavior. The effect of pH on the

electrochemical performance of the prepared modified CPE was tested in the range of pH 2.0-8.0. As shown in Fig. 5b, the maximum peak current was appeared at pH 4.0 and 5.0. The decreased response in more acidic solutions can be attributed to the protonation of heteroatoms of 4-methyl-piperidine-carbodithioate present in the modifier that can obviously decrease the complexing capability of the modifier sites for Hg(II) ions. Also, above pH 5.0 the signal of the proposed sensor toward mercury ions decreased, probably due to hydrolysis of the Hg(II) ions. To improve the selectivity of the proposed method, pH 4.0 was used as optimum value for the further experiments.

Figure 5c shows the effect of extraction time of $25.0 \mu\text{g l}^{-1}$ Hg(II) on the DPV peaks. The peak current was increased with extraction time and a relatively constant value was observed after around 20 min. However, good

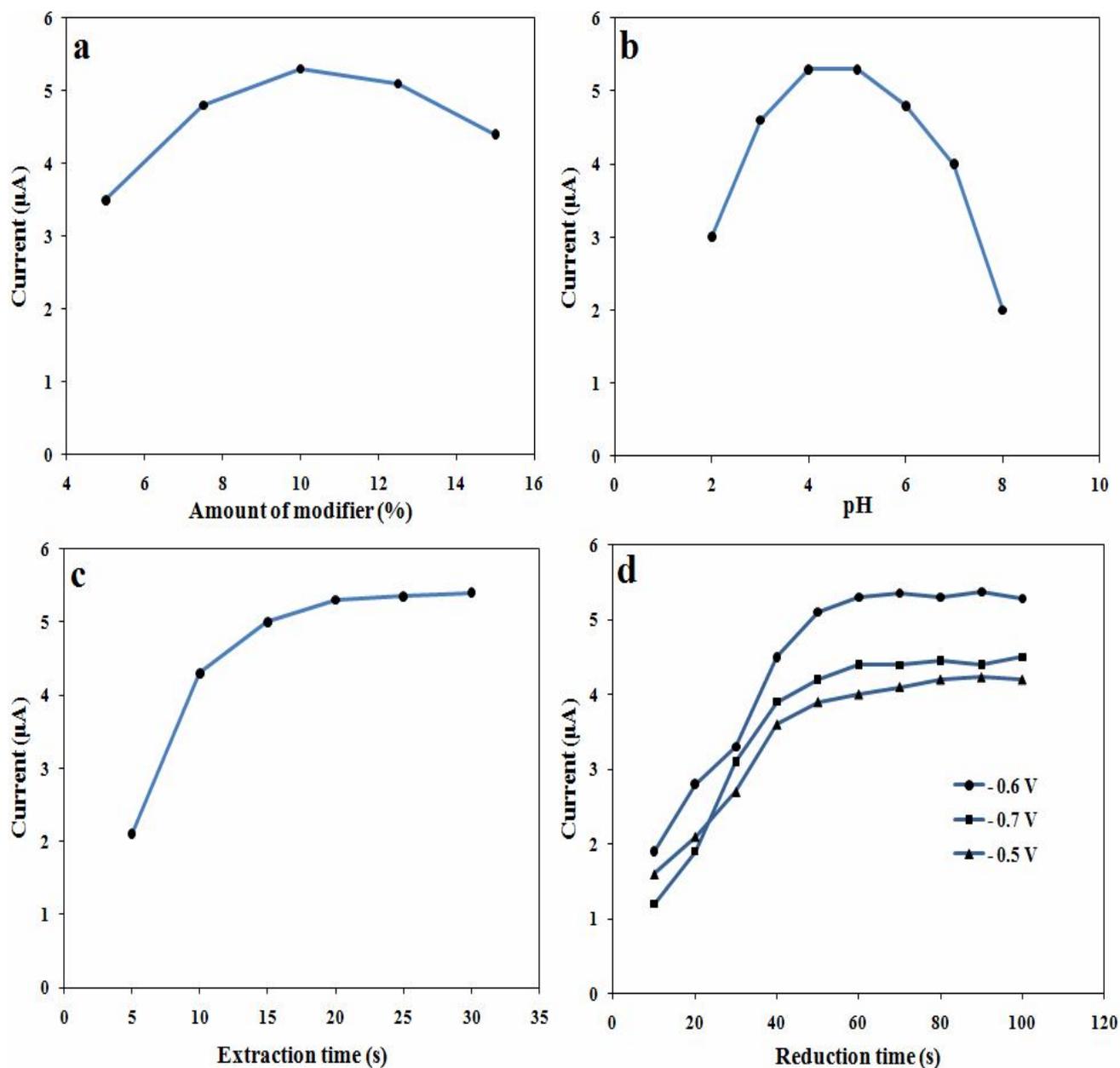


Fig. 5. (a) The DPV peak current as a function of the modifier percentage, (b) DPV peak current as a function of mercury solution pH, (c) DPV peak current as a function of extraction time, and (d) DPV peak current as the function of reduction potential and time in modified CPE for $25 \mu\text{g l}^{-1}$ Hg(II) solution.

sensitivity could be used for lower concentrations by increasing the extraction time. In order to decrease the analyzing time, as much as possible, the time of 20 min was selected for further studies.

Figure 5d illustrates the effect of the reduction potential and time on the peak height of Hg(II). The DPV signals for all tested potentials enhanced with increasing the time up to 60 s and then remained nearly constant. Hence, the

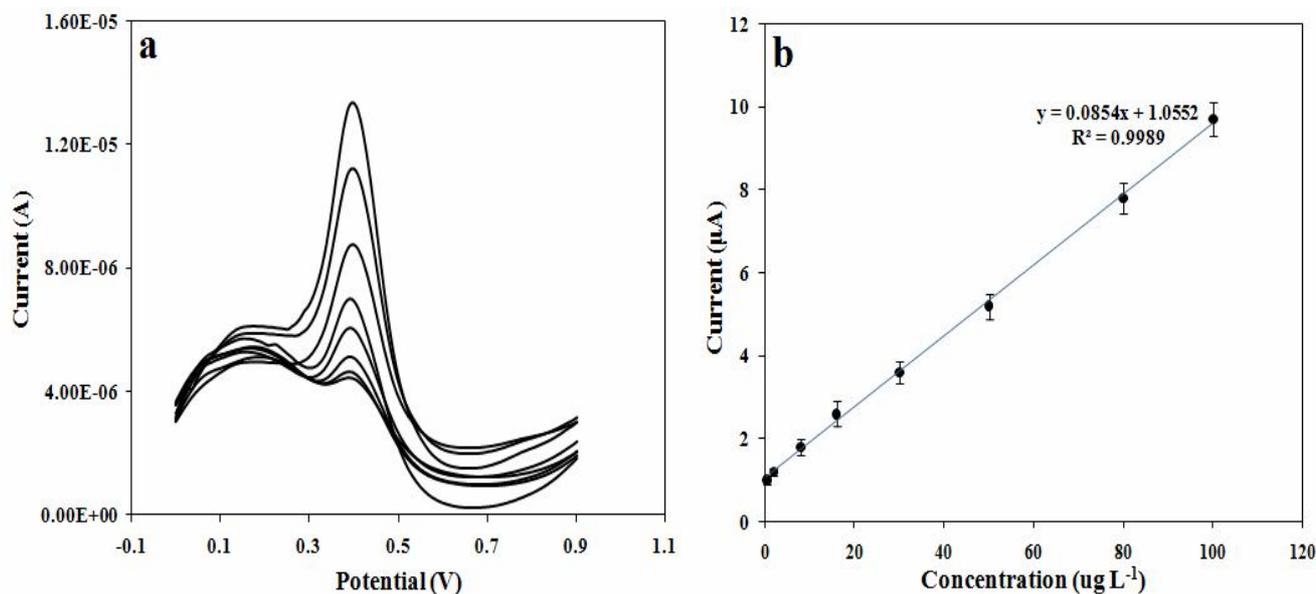


Fig. 6. (a) Differential pulse voltammograms with different concentrations of Hg(II), and (b).

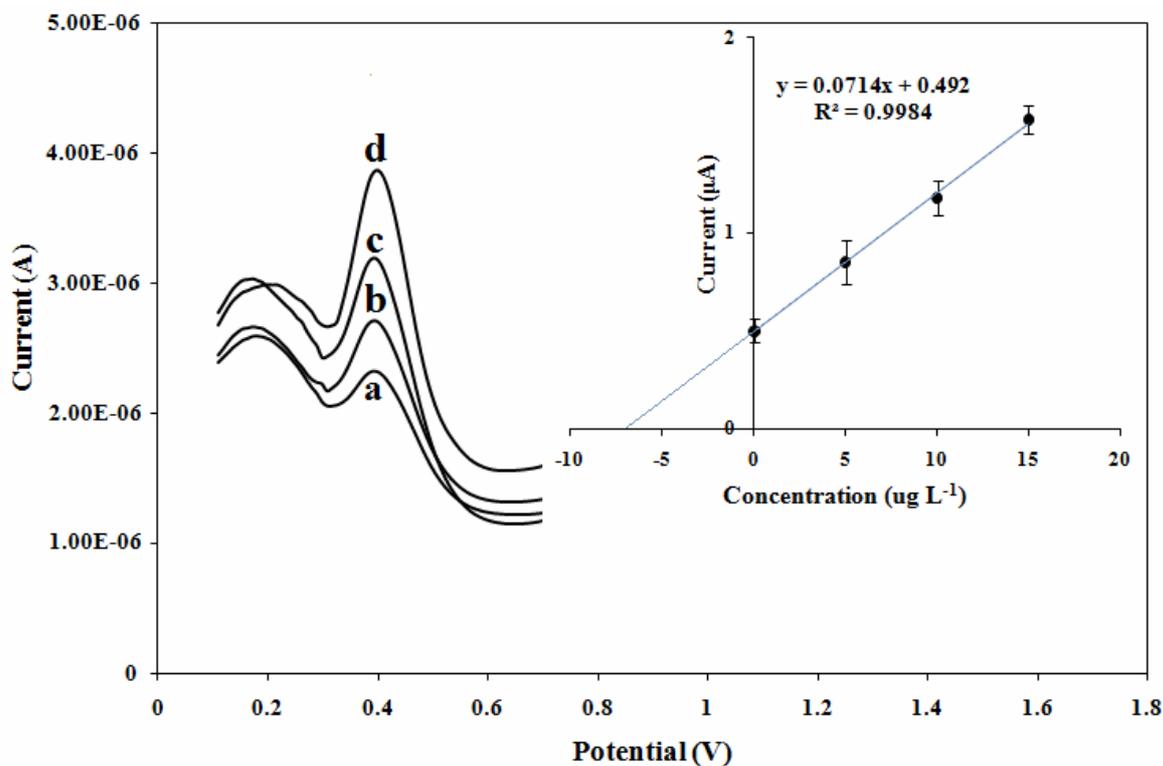


Fig. 7. Differential pulse voltammograms of (a) modified electrode in the presence of wastewater, (b-d) in the presence of wastewater and different concentrations of Hg(II) (5-15 µg l⁻¹).

reduction time of 60 s was applied to reduce analysis time. The influence of reduction potential on the stripping signal of Hg(II) ions was also studied by varying the potential from -0.5 to -0.7 V *vs.* Ag/AgCl reference electrode. As it is seen, the peak current of Hg(II) increased as the reduction potential became more negative, and reached its maximum value at -0.6 V due to more completely reduction of Hg(II) ions at this potential. However, more negative potential (-0.7 V) resulted in decreased peak current due to hydrogen evolution. Therefore, a potential of -0.6 V *vs.* Ag/AgCl was used as an optimum potential for all subsequent measurements.

Study of Interferences

To check the selectivity of the proposed stripping voltammetric sensor for the mercury ions, the effect of various potentially interfering ions including Cu(II), Co(II), Cd(II), Zn(II), Ni(II), Pb(II), Mn(II), Al(III), Fe(III), Cr(III) and Ag(I) were examined. The tolerance level was described as the maximum amount of the interfering ions that can produce an error of $\pm 5\%$ on the Hg(II) peak current. It is shown that a 50-fold excess of Cr(III), Fe(III), Mn(II), Al(III), Ni(II), 40-fold excess of Co(II), Zn(II), Cd(II), 30-fold excess of Pb(II), Cu(II) and 20-fold excess of Ag(I) did not affect the DPV signal of $25.0 \mu\text{g l}^{-1}$ Hg(II). Based on these results, it is concluded that the proposed electrode is suitable for the determination of Hg(II) from various matrices without significant interference by common interfering species.

Calibration Plot

Figure 6a shows the typical DPV voltammograms obtained at the modified CPE containing different concentrations of Hg(II) ions. The relationship of the peak current and the concentration of Hg(II) can be described by the following equation:

$$I(\mu\text{A}) = 0.0854 C (\mu\text{g l}^{-1}) + 1.0552$$

Moreover, the peak current of the suggested sensor toward mercury ions increased linearly in the range of 0.4-100.0 $\mu\text{g l}^{-1}$ with $R^2 = 0.9989$ (Fig. 6b). The detection limit of the sensor, defined as 3σ /sensitivity, was calculated to be $0.2 \mu\text{g l}^{-1}$ that is comparable or lower than some reported

mercury sensors [23,39-45] (Table 1). Moreover, our detection limit is enough to meet the requirements of the U.S. Environmental Protection Agency regulations for acceptable Hg(II) levels in drinking water ($2 \mu\text{g l}^{-1}$). Furthermore, the proposed sensor is characterized by a rapid surface renewal, easy preparation, and high selectivity for the detection of mercury. The repeatability of the response of $25.0 \mu\text{g l}^{-1}$ Hg(II) was evaluated with seven replicates on the same modified CPE. The relative standard deviation was 2.6%. The reproducibility was performed by analysing $25.0 \mu\text{g l}^{-1}$ Hg(II) independently on seven different electrodes. The relative standard deviation was 3.8%. It should be pointed out that the proposed sensor indicated good stability and could be applied for at least two weeks.

Practical Application

In order to study the performance of the sensor in a practical analytical situation, the present method was used to determine traces of mercury in water samples. The standard addition method was applied for the calculation of recoveries in the spiking of mercury ions to the water samples. Typical DPV voltammograms of the modified electrode in wastewater sample and different concentration of Hg(II) in wastewater real sample (standard addition protocol) are shown in Fig. 7. The concentration of Hg(II) in this real water sample is about $6.9 \mu\text{g l}^{-1}$. Also, it can be seen that the average recoveries of Hg(II) in real water samples are 95.8-102.0% (Table 2). These results evinced the practicability of the proposed sensor toward Hg(II) detection in water samples.

CONCLUSIONS

In this work, a new electrochemical voltammetric sensor based on a CPE modified by 4-methyl-piperidine-carbodithioate capped GNPs was used for the detection of trace Hg(II) ions. The electrochemical properties of the proposed sensor for Hg(II) in aqueous solution were discussed. Using this voltammetric sensor, mercury ion could be detected with a detection limit of $0.2 \mu\text{g l}^{-1}$ by DPV. The analytical performances of the proposed sensor were comparable with the previous results. The modified CPE exhibits acceptable selectivity and excellent reproducibility. In addition, this sensor validates the

Table 1. Comparison of the Proposed Method with other Reported Electrochemical Methods for Detection of Mercury

Electrode	Analysis method	Modifier	Detection limit ($\mu\text{g l}^{-1}$)	Linear range ($\mu\text{g l}^{-1}$)	Ref.
CFME	ASV	Thiophenolate	NR	1-2000	[23]
MCPE	DPV	HNTs-Fe ₃ O ₄ -MnO ₂	0.2	0.5-150	[39]
SPGE	SWASV	-	1.1	5-30	[40]
CPE	SWASV	Magnetic nickel zinc ferrite nanocomposite	8.0	40-2005	[41]
GCE	DPV	DNA grafted graphene	1.0	1.6-20	[42]
GCE	DPV	IIP-MWCNTs	1.0	2-1403	[43]
CCCE	SWASV	Poly(vinylsulfonic acid)	3	10-10025	[44]
CPE	SV	Bi-GNPs	0.28	5-200	[45]
MCPE	DPV	4-Methyl-piperidine-carbodithioate capped GNPs	0.2	0.4-100	This work

Abbreviation; MCPE: Magnetic carbon paste electrode, CPE: carbon paste electrode, HNTs: halloysite nanotubes, SWASV: Square wave anodic stripping voltammetry, SPGE: Screen-printed gold electrode, GCE: Glassy carbon electrode, DPV: Differential pulse voltammetry, CFME: Cylindrical carbon fiber microelectrode, ASV: Anodic stripping voltammetry, NR: not reported, IIP: ion imprinted polymer, CCCE: Ceramic-carbon composite electrode, SV: Stripping voltammetry, Bi-GNPs: Bismuth and gold nanoparticles.

Table 2. Determination of Mercury in Water and Synthetic Samples (n = 3)

Sample	Added ($\mu\text{g l}^{-1}$)	Found ($\mu\text{g l}^{-1}$)	Recovery (%) \pm RSD
Tap water	-	N.D. ^a	-
	10.0	9.8	98.0 \pm 4.0
	20.0	19.6	97.5 \pm 3.8
Aqueduct water	-	N.D. ^a	-
	10.0	10.2	102.0 \pm 3.9
	20.00	19.8	99.0 \pm 4.3
Wastewater	-	6.9	-
	10.0	16.2	95.8 \pm 4.5
	20.0	26.1	97.0 \pm 4.2
Synthetic sample	-	19.7	98.5 \pm 3.9
Composition (Mn: 50.0, Ag: 20.0, Ca: 30.0, Mg: 40.0, Ni: 20.0, Pb: 15.0, Co: 25.0, Zn: 30.0, Al: 20.0, Hg: 20.0 $\mu\text{g l}^{-1}$)			

^aNot detected.

practicability towards the determination of Hg(II) in real water sample.

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