A Highly Sensitive and Selective Electrochemical Mercury(II) Sensor Based on Nanoparticles of Hg(II)-imprinted Polymer and Graphitic Carbon Nitride (g-C₃N₄)

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Using nanoparticles of an ion imprinted polymer an electrochemical sensor was designed for mercury(II) ions. Nanoparticles of the Hg(II)-imprinted polymers were formed using a functional monomer (itaconic acid) through the precipitation polymerization approach. These particles were characterized using FT-IR, TGA and SEM. The particles together with graphitic carbon nitride (g-C₃N₄) were then used to modify a carbon paste electrode (CPE) and the modified electrode was used for the analysis of Hg(II).The analysis method involved a first step of includes accumulating Hg(II) on the modified electrode under open circuit conditions, followed by is a second step of reducing of the mercury(II) ions to Hg under a negative pre-potential, and a final third step of generating the electrochemical signal through a square wave anodic stripping voltammetry (SWASV) routine. The obtained results were compared with those of an unmodified CPE, and it was found that the modified CPE has a higher tendency for Hg(II) ions. The effect of the presence of g-C₃N₄was also evaluated. The modified electrode was found to have a suitable linear response from 0.06 to 25.0 nM, and a lower detection limit (S/N=3) of 18 pM under optimal conditions and its performance was also checked for the analysis of Hg(II) in water samples.

1. INTRODUCTION

The effects heavy metal compounds on humans and the environment is a hot topic. Heavy metals are known as toxic species even at low concentrations. The ionic forms of these elements tend to

accumulate in biological systems and given their nature they are not decomposed over time [1]. Being a heavy metal element, mercury and its compounds have various physical forms chronic exposure to most of which has been associated with different health issues like scrodynia, kidney conditions and memory loss [2, 3]. More specifically, high level exposure to methyl mercury can lead to Minamata and also seriously damage aquatic food chains.

Therefore for the need for designing simple tools and methods for the analysis of mercury in environmental, food, water, and medicinal samples is rather high [4-7].

Accordingly different techniques including classical flame or cold vapor atomic absorption spectrometries [8-10], inductively coupled plasma mass spectrometry or atomic emission spectroscopies (ICP-MS, ICP-AES) [11, 12, 14], spectrofluorimetry [13], X-ray or UV-Vis spectrometry [15-17], gas chromatography [18] and neutron activation analysis [19] were used for trace analysis of Hg(II).

Unfortunately, these listed methods are very costly, relatively difficult to use and required trained and cannot hence be used routinely. Alternatively electrochemical techniques constitute simple, easy to operate, cheap, sensitive selective and stable tools for various analyses [20, 21]. Different materials like mesoporous carbon/self-doped polyaniline nanofibers [22], siliceous mesocellular foam [23], mesoporous NiO [24], Schiff's-bases [25] and ion imprinted polymers [26] are currently used for modifying electrochemical sensors Hg(II). On the other hand biomaterials like enzymes, amino acids, peptides, cells, and nucleic acids are known for their very selective and specific interactions, and are hence considered as important choices for the analysis of heavy metal ions [27].

In the face of all advances, the direct determination of low amounts Hg(II) in the presence of interfering species and matrix effects in aqueous media is still considered a challenge [28]. Therefore, applying pre-concentration steps before the analysis is used. One alternative for this approach is the application of ion-imprinted polymers (IIPs), as a powerful approach, due to the great recognition capability of IIPs [29]. The unique properties of the materials, like the large number of binding sites present on them, their considerable porosity and surface area, selective behavior good mechanical, thermal or chemical robustness and stability [30].

Further, graphitic carbon nitride (g-C_3N_4), being the most stable allotrope of carbon nitride under ambient conditions environment, is very attractive due to its distinctive electronic band structure, considerable thermal/chemical stability, and catalytic characteristics [31]. g-C_3N_4 also has a layered structure with weak interlayer weak van der Waals interaction among the neighboring C-N layers. Consequently, a great deal of research has been performed in the area of preparing and photocatalytic/biosensing applications ofg-C_3N_4normal and ultrathin nanosheets of g-C_3N_4 [32, 33]. The properties originate from the considerable surface area of the 2D g-C_3N_4 nanosheets, which provide higher numbers of surface active sites, increasing the adsorption of target species. A second factor is that the structure of g-C_3N_4 planes formed of highly ordered tris-triazine (C_6N_7) structures provides access to various ideals sites for coordination reactions of the lone pairs of nitrogen atoms and the metal [34, 35]. g-C_3N_4 structures are also are eco-friendly, abundant and low-cost, which changes them to attractive candidates for preparing electrochemical sensors for heavy metal ions [36].

In the light of the above, this work was focused on preparing nanoparticles of Hg(II)-imprinted polymerthrough precipitation polymerization, and its subsequent application to modify a CPE for ultra-trace amounts of Hg(II) ions. Given the finding of our former works [26] and due to the significance of

analyzing ultra-trace amounts of Hg(II) we tried to further enhance the analytical properties of the resulting electrochemical sensor. In this work we tested the properties of g-C_3N_4 and used this compound instead of the conventional modifier (MWCNT) [26] resulting in enhanced performance on the part of the developed proposed sensor.

2. EXPERIMENTAL

2.1. Materials and Apparatus

Methylene succinic or itaconic acid (ITA) was obtained from Merck Co. Ethylene glycoldimethacrylate (EGDMA), and 2,2′-azobisisobutyronitrile (AIBN) from Sigma-Aldrich Co. were also used as the functional monomer, cross-linking agent and reaction initiator. Graphite powder and nojul oil from Merck Co., were used to prepare the CPE $HgCl_2$was procured from Merck Co. and used to prepare stock solutions of Hg(II) in double distilled water (DDW). The rest of the chemicals were analytical grade and were obtained from Merck Co. Electrochemical studies were run on a μAutolab type III using GPES software. The electrochemical cell included an Ag/AgCl/KCl reference, a Pt auxiliary and a (modified or bear) CPE as the working electrode.

The modification of CPE was monitored using electrochemical impedance spectroscopy (EIS), on an AutoLab Potentiostat PGSTAT302N (Metrohm AutoLab BV, Utrecht, The Netherlands), using a1.0 mM1:1 solution of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$in 0.1 M KCl in the frequency window of 300 mHz–10^6 Hz, E_{dc} = 0.25 V and ΔE_{ac} =0.1 V. Field emission scanning electron microscopic (SEM) analyses were performed using an XL30 ESEM FEG instrument applying an accelerating voltage of 20 kV. Fourier transform infrared (FT-IR) spectroscopy tests were performed using a Perkin Elmer Spectrum Two instrument. The samples were loaded onto the instrument suing KBr pellets and the experiments were conducted at ambient conditions from 4000 to 400 cm^{-1}. Thermogravimetric analysis (TGA) were conducted using a PerkinElmerSTA-6000 simultaneous thermal analyzer.

2.2. Preparing the IIP nanoparticles

The Hg(II) IIP nanoparticles were formed through a two-step thermal precipitation polymerization approach. The initial step involved adding 2 and 1 mmol of ITA and $HgCl_2$ to 30 mL of acetonitrile under constant stirring and the resulting solution was kept under stirring for 5 h to allow the ingredients from Hg(II)-ITA self-assembly complexes. In the next step Next 8mmolof EGDMA and 0.08 g of 2,2′- azobisisobutyronitrile were added to the reaction mixture and the system was purged with $N_2$for 10 minutes, before it was sealed. The reaction was allowed to continue at 65 °C for 1 day while the system was stirred at 400 rpm using a magnet. The product was polymer then separated and repeatedly washed with methanol and then with a 2M HCl solution for leaching the template. The HCl wash was continued until no Hg(II) was detected in the wash solution based on voltammetric data. The particles were eventually washed with DDW and stored.

2.3. Preparing g-C₃N₄ nano-sheets

Dispersions of g-C$_3$N$_4$in water were prepared as reported elsewhere [37]. To this end, typically bulk C$_3$N$_4$ (b-C$_3$N$_4$) was prepared through heating 5 g of melamine at 550 °C in an sealed alumina crucible for 5 h. Next 1 g of the produced b-C$_3$N$_4$ powder taken and refluxed at 125 °C using 100 mL of a 5 M solution of HNO$_3$ for 12 h. Then the system was cooled to room temperature and the solid product was centrifuged at 10,000 rpm (16,300×g) for half an hour, separated and washed DDW until the pH was neutral. The supernatant was collected and ultrasonically treated for 10 h, and the g-C$_3$N$_4$ nano-sheets were isolated through filtering through a 45 μm water phase microporous membrane filter. The prepared g-C$_3$N$_4$ nano-sheets were kept as 300 μg mL^{-1} dispersions.

2.4. Preparing graphene oxide (GO)

GO was prepared through Tour's method [38]. The conventional procedure involved gradually adding 18 g of potassium permanganate to a mixture of 360 mL H$_2$SO$_4$, 40 mL H$_3$PO$_4$ and 3 g of graphite powder. The resulting mixture was then stirred at 50 °C for 12 hours and then cooled to ambient temperature and then poured onto 500 g of frozen DDW. Next a 30 % H$_2$O$_2$ solution was added to the system until it turned to bright yellow. The solid component was next separated by centrifuging and washed with 5% HCl and then with DDW until the pH turned neutral. This product was then dried for 24 h in a freeze-dryer and stored for further use.

2.5. Modifying the CPE

Various experiments were performed to optimize the Hg(II)-IIP and g-C$_3$N$_4$contents of the electrodes (IIP/C$_3$N$_4$/CPE). Based on the results the best composition of the modified electrode, in terms of the analytical response, was 0.01 g of Hg(II)-IIP, 0.10 g of graphite powder, 0.006 g of the g-C$_3$N$_4$ and 0.015 g of the binder. To prepare the electrodes, the ingredients were thoroughly mixed in a mortar for at least 20 minutes to obtain a uniform paste. This paste was packed into a 2.0 mm (i.d.) glass tube to form a 5.0 mm column of the paste inside the tube. From the other end of the glass tube, a copper wire was pushed into the paste to establish the electrical contact. These electrodes were reused after removing the exterior layer of the paste with soft abrasive paper and obtaining a fresh surface for the electrode.

2.6. Determination Hg(II)

The analyses involved and accumulation step in during which, the modified electrode was inserted in to the test solutions (pH=3) under stirring at 500 rpm and kept under these conditions for a quarter. The electrode was then removed, washed with water, neutral for 10s, and then placed in the electrochemical cell containing 10 mL of 0.5 M HCl. Then a negative pre-potential of −0.5 V (vs. Ag/AgCl) was initially applied for 60 s to reduce Hg(II) ions and then the SWV analysis was started at 100 Hz and a potential amplitude of 200 mV in the potential window of −0.3 to 0.3 V.

3. RESULTS AND DISCUSSION

3.1. Characterization of Hg(II)-IIP nanoparticles

The FT-IR spectra of intact and leached IIP is presented in Figure 1(a). The broad band extending from 3200 to 2900 cm^{-1} (centered at about 3000 cm^{-1}) corresponds to the stretching of O-H groups. The strong signal at 1705 cm^{-1}, on the other hand, reflects the stretching of the C=O group of the carboxylic acid species. The stretching of the C-O species on the carboxylic acid can be seen at 1215 cm^{-1}, that of O-H is noticeable at 1436 cm^{-1} and 911 cm^{-1}.The signal at around 1636 cm^{-1} reflects the stretching of the C=C band. These results indicate that the sample contains a carboxylic acid with conjugated double bonds, which agrees with the structure of IIP. Yet in the presence of Hg(II) the FT-IR spectrum shows distinct changes. In this case the wide band around 3000 cm^{-1} is considerably weakened. Also split bands can be seen at around 3525 and 3585 cm^{-1}. This can be attributed to the stretching of the OH group of the carboxylic acid groups of IIP in the complex with Hg(II). This clear shift in the OH signals as well as their splitting and sharpening is attributed to the elimination of the strong ITA-ITA hydrogen bonds, due to the complexation reaction between ITA and Hg(II). Clearly, the reaction boosts the C=O band, reflecting the involvement of the C=O group in the complexation reaction, since the higher rigidity of the complexation product decreases the vibration of the. The synthesized IIP nanoparticles were also evaluated by TGA and the resulting curves were recorded in an N$_2$ atmosphere from 30 ºC to 300 ºC at a 10 ºC min^{-1} rate (Figure 1(b)). Based on the results, a weight decrease occurred at about 150 °C due to loss of the solvent/moisture.

The surface morphology and topography studies were conducted by SEM analyses and the results are presented in Figure 1(c). The size distribution plot shows that the size of the majority of the IIP particles is less than 100 nm.
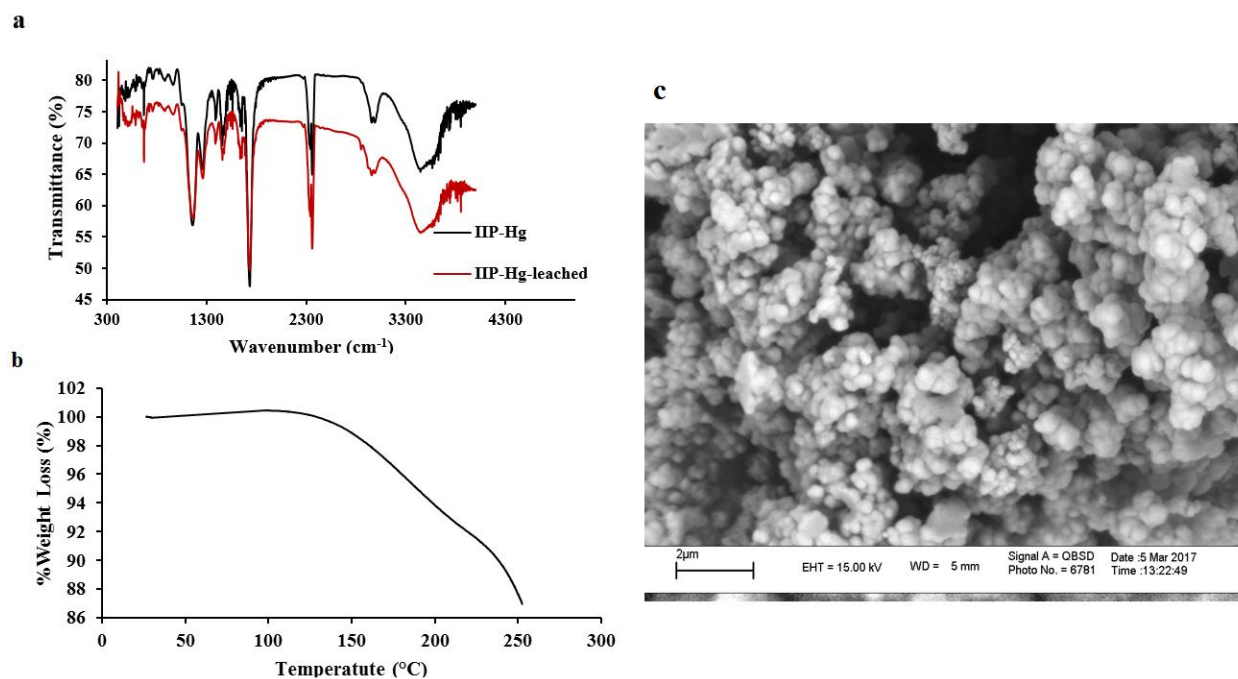

Figure 1. (a) FT-IR spectra of the IIP, and leached IIP-Hg, **(b)** TGA curve obtained for IIP nanoparticles, **(c)** SEM image of the IIP nanoparticles

3.2. Characteristics of g-C_3N_4 and GO

The SEM image of their g-C_3N_4 nano-sheets (Figure 2(a)) indicate the average diameter be 90 nm. The surface morphology of the GO nanosheets was also evaluated by SEM (Fig. 2b), and the surface of the nanosheets was found to be uniform, except for some wrinkles due to random aggregation or crumpled sheets.
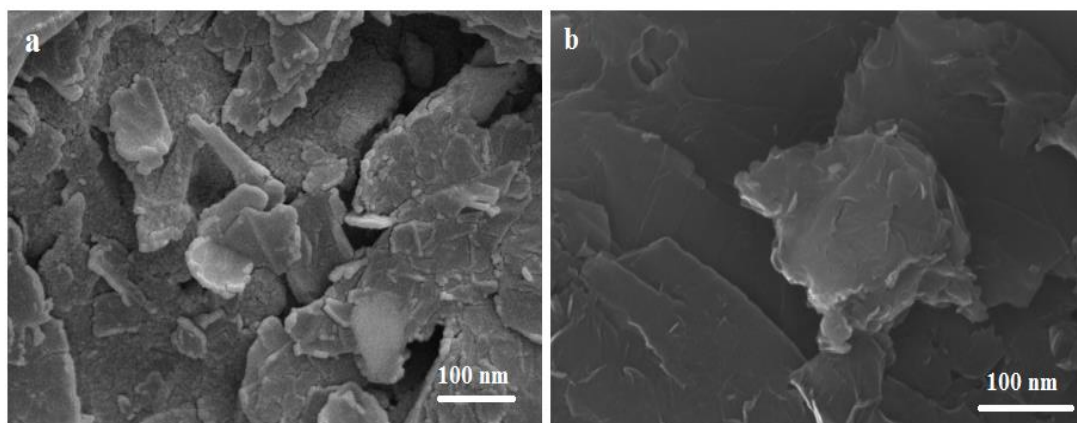

Figure 2. (a) SEM images of g-C_3N_4 nano-sheets **(b)** SEM images of GO nano-sheets
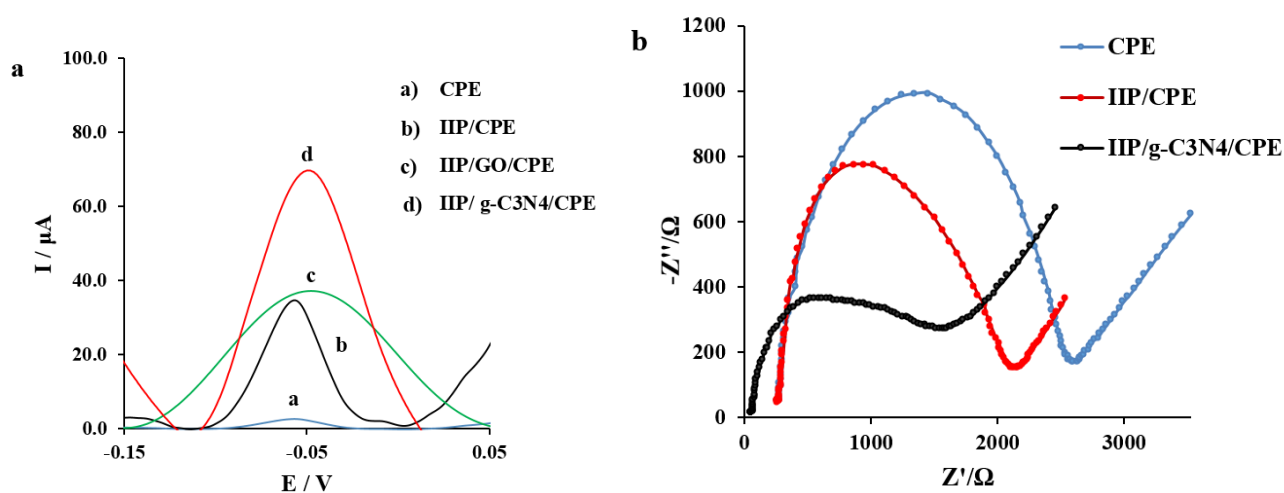
3.3. The Hg(II)-IIP sensor

Figure 3. (a) Square wave voltammograms of CPE, IIP/CPE, IIP/GO/CPE and IIP/g-C_3N_4/CPE in a15 nmol L^{-1} solution of Hg^{2+} [extraction conditions: extraction time = 15 min, extraction pH =3, stripping conditions: HCl solution concentration = 0.5 mol L^{-1}, SW frequency = 100 Hz, SW amplitude = 0.2 V, conditioning potential: -0.5V vs Ag/AgCl, conditioning time = 60s]. **(b)** Nyquist plots of bare CPE, IIP/CPE, and IIP/g-C_3N_4/CPE [recording conditions: 1.0 mM $[Fe(CN)_6]^{3-/4-}$ (1:1) solution in 0.1 M KCl, frequencyrange of 0.3–10^6 Hz, E_{ac} = 0.1Vand E_{dc} = 0.25V].

The responses of bare CPE, and those modified with IIP, GO, and g-C$_3$N$_4$ in voltammetric analyses are presented in Figure 3(a). Evidently the a unmodified CPE showed a weak response to Hg(II) at -0.05 V (vs. Ag/AgCl). Yet, comparing the response of the bare and IIP modified CPEs (voltammograms a and b) clearly shows the effect of modification on the response of the CPE. The enhanced sensitivity on the part of the modified CPE rises from the high affinity of Hg(II) sites present on the Hg-IP/CPE. The effects of incorporating GO and g-C$_3$N$_4$ in the CPE were also studied (Figure 3c and d). According to Figure 3(a), the increase in the signal due to the presence of g-C$_3$N$_4$ is much more than in the case of GO.

Electrochemical impedance spectroscopy (EIS) was also used to evaluate the developed electrode. Nyquist plots obtained for unmodified CPE, IIP/CPE, and IIP/g-C$_3$N$_4$/CPE (Figure 3(b)) reveal that incorporating IIP in the CPE composition lowers the charge transfer resistance, which might seem unusual due to the non-conducting nature of many polymeric materials. Yet the increase in the surface polarity of the electrode due to the presence of the ITA-based polymer particles, facilitates the access of [Fe(CN)$_6$]$^{3-/4-}$ couple to the surface of the electrode. The presence of g-C$_3$N$_4$ further decreases the charge transfer resistance, due to the electronic properties of g-C$_3$N$_4$.

3.4. Optimal parameters

The most significant parameters influencing the response of the IIP/g-C$_3$N$_4$/CPE to Hg(II) are(i) amount of the IIP, (ii) pH and extraction time, (iii) concentration of the solution (HCl concentration), (iv) SW potential frequency and amplitude,(v) conditioning potential and time. The best response was observed at 7.5% of IIP, respective extraction time and pH values of 15 min and 3.0, HCl concentration of 0.5 mol L^{-1},respective ASW frequency and amplitude values of 100 Hz and 0.2 V, and respective conditioning potential and time of −0.5 V and 60s.

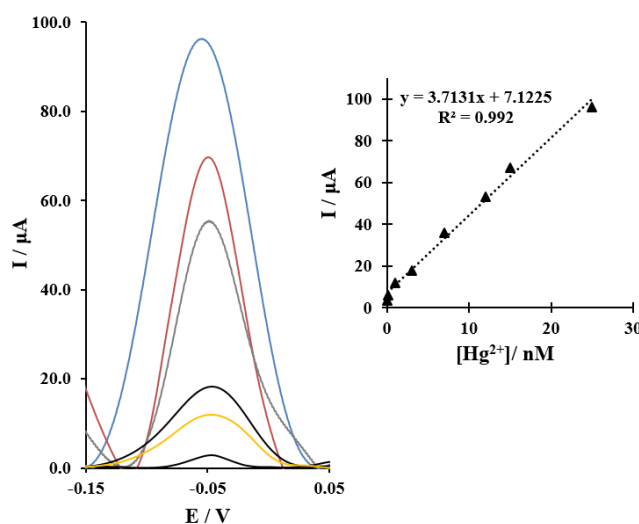## 3.5. Analytical application of the modified CPE

Figure 4. Square wave voltammetric responses of the IIP/g-C$_3$N$_4$/CPE in different concentrations of Hg(II),recorded in the optimized conditions, Inset: the plot of peak currents as functions of the concentration of Hg(II) in the range 0.06–25.0 nmol L^{-1}.

The SWV calibration graph of the developed sensor under optimal conditions (Figure 4) was linear in the concentration window of 0.06×10^{-9} to 25×10^{-9} mol L^{-1} and a detection limit of 1.8×10^{-11} mol L^{-1} (S/N = 3) was determined for the method.

3.6. Analysis

Table 1. Determination of Hg^{2+} in some real samples by the proposed electrode

sample	Added (nmol l^{-1})	Found (nmol l^{-1})	RSD (n=3) (%)	Recovery (%)
Tap water	0.0	ND	3.88	----
	5.0	5.23	4.05	104.6
	10.0	10.16	4.12	101.6
Sea water	0.0	ND	3.74	----
	2.5	2.46	3.94	98.4
	15.0	15.22	4.21	101.4

ND: not detected

Real tap and seawater samples were analyzed before manually adding Hg(II) using the developed sensor under optimal conditions and they were found to be Hg(II) free. Next the standard addition method was performed through spiking 25 mL of the real water samples with various amounts of Hg(II), followed by the analysis of the samples. The results (Table 1), indicated that the developed sensor could successfully determine ultra trace levels of Hg(II), with the need for any pretreatment steps.

3.7. Interference effects

The selectivity of the developed modified CPE was evaluated under optimal conditions. To this end the effect of some commonly occurring species on the response of the sensor were studied. Given that in the case of the present sensor, the pre-concentration of Hg(II) is performed through it adsorption at the open circuit potential, a great deal of interferences are eliminated. Yet the competitive adsorption of metallic species onto the binding sites of the IIP might case interferences and hence various 5×10^{-9} mol L^{-1} solutions of Hg(II), also containing various concentrations of different ionic species were prepared. Considering the tolerance limit as the highest concentration of the interfering species leading to a relative error of 5% in the signal of the target species the test were performed and the results are presented in Table 2. It is clear that as the presence of As^{3+}, Ag^{+}, Pb^{2+}, Cr^{3+}, Ni^{2+} and Zn^{2+} did not influence the response of the sensor. This behavior can be due to the selectivity of the IIP sites to Hg(II).

Table 2. Interference levels for some ions in the determination of Hg(II) by the proposed electrode

Species	Interference level
As^{3+}, Ag^+, Pb^{2+}, Cr^{3+}, Zn^{2+}, Ni^{2+}, Co^{2+}	No interference
Fe^{2+}	>200
Cd^{2+}, Cu^{2+}	>400

No interference: no interfering effect was found even at 500-fold molar excess of the tested foreign species

3.8. Comparison of the sensor

To show the applicability f he proposed sensor, it was compared with several similar works. Table 3 illustrates the results obtained using the Hg IIP/g-C₃N₄/CPE, as well as, those of other previously reported Hg(II) sensors. The working electrode was a carbon paste or a glassy carbon electrodes which modified with Hg(II)-imprinted polymers alone [40, 42] or with some carbonic nanomaterials [26, 39, 45]. Also in two reports, microporous poly(2-mercaptobenzothiazole) films [41] and polypyrrole/sulphur containing carboxy methyl ion imprinted polymer [43] were utilized on the surface of a glassy carbon electrode for Hg(II) sensing. Clearly, the developed sensor has a wider linear range, and a lower detection limit in comparison with previously reported counterparts. Furthermore, Cu(II) and Cd(II) are general interferences for Hg(II) measurements, thus, these ions have been considered as interfering species. As it can be seen, in case of [39,43,44], the interferences are rather significant while in [42] is certainly negligible. In case of the presented sensor and [26, 40] and even [41,45], the interference can be almost insignificant.

Table 3. Comparison of the efficiencies of some electrochemical methods in the determination of Hg(II)

Electrode	Modifier	Linear range (nmol L^{-1})	LOD (nmol L^{-1})	Interference level		[Ref]
				Cu^{2+}	Cd^{2+}	
CPE	MWCNTs and Hg(II) -imprinted polymer nanoparticles	0.1–20	0.029	>300	>400	[26]
GCE	Graphene-based ion imprinted polymer	0.35–400	0.1	>40	>40	[39]
CPE	Mercury ion imprinted polymer	2.5–500	0.52	>400	>200	[40]
GCE	Microporous poly(2-mercaptobenzothiazole) films	1–160	0.1	>100	>100	[41]
CPE	Ion imprinted polymer	1–8000	0.19	>850	>850	[42]
GCE	polypyrrole/Sulphur containing carboxy methyl ion imprinted polymer	100–800	0.5	>10	>10	[43]
CPE	ion imprinted polymeric nanobeads	0.5-10 and 80-200	0.1	>45	>45	[44]
GCE	Hg(II) ion imprinted polymeric nanobeads and MWCNTs	10-7×10^5	5.0	>100	>100	[45]
CPE	g-C₃N₄ and Hg(II) -imprinted polymer nanoparticles	0.06–25	0.018	>400	>400	This work

4. CONCLUSION

The application of nanoparticles of an Hg(II)-imprinted polymer and g-C₃N₄ to modify a CPE as found to lead to the development of a voltammetric sensor for the ultra-trace analyses of Hg(II). The

Hg(II)-IIP nanoparticles, give rise to the selective absorption of Hg(II) within a pre-concentration step, followed by the analysis of the sample. It was also found that incorporating g-C$_3$N$_4$ in the CPE composition improves the charge transfer rate and hence the Hg(II). The developed sensor had excellent affinity to Hg(II)in the presence of relatively high amounts of interfering species, and comparing it with formerly reported electrodes indicated that it enjoys some distinct advantages over them.

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