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ORIGINAL PAPER

Highly sensitive and selective voltammetric detection of mercury(II) using an ITO electrode modified with 5-methyl-2-thiouracil, graphene oxide and gold nanoparticles

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Abstract We have developed an electrochemical sensor for highly selective and sensitive determination of Hg(II). It is based on the specific binding of 5-methyl-2-thiouracil (MTU) and Hg(II) to the surface of an indium tin oxide (ITO) electrode modified with a composite made from graphene oxide (GO) and gold nanoparticles (AuNPs). This leads to a largely enhanced differential pulse voltammetric response for Hg(II). Following optimization of the method, a good linear relationship (R=0.9920) is found between peak current and the concentration of Hg(II) in the 5.0–110.0 nM range. The limit of detection (LOD) is 0.78 nM at a signal-to-noise ratio of 3. A study on the interference by several metal ions revealed no interferences. The feasibility of this method was demonstrated by the analyses of real water samples. The LODs are 6.9, 1.0 and 1.9 nM for tap water, bottled water and lake water samples, respectively, and recoveries for the water samples spiked with 8.0, 50.0 and 100.0 nM were 83.9–96.8 %, with relative standard deviations ranging from 3.3 % to 5.2 %.

Keywords Mercury ion · 5-Methyl-2-thiouracil · Graphene oxide · Gold nanoparticle

Introduction

Mercury ion, Hg(II), has attracted extensive attention due to its highly toxic and bioaccumulative properties, possibly causing brain damage and other chronic diseases [1–3]. Therefore, it is urgently required to monitor and determine trace Hg(II) timely and accurately by developing highly sensitive and selective methods. Various available methods for Hg(II) include atomic absorption/emission spectrometry [4, 5], inductively coupled plasma mass spectrometry [6], electrochemistry [7], spectrometry [8–10], chromatography [11], etc. Compared with the above other ones, electrochemical methods simultaneously possess many advantages such as convenient and simple operation, rapid completion, low consumption, high sensitivity and selectivity, as well as possible application in field tests and on-site monitoring [12, 13]. As reported, anodic stripping voltammetry is mostly employed for heavy metal ions [13, 14], while single voltammetry is rarely used [15], which often requires some specific interactions but without electro-deposition to adsorb targeted ions compared to the former.

Nanomaterials, of various shapes, sizes, and compositions, have been widely used for construction of electrochemical sensors, since they often exhibit unique electronic conductivity and large specific surface area [16, 17]. Amongst them, graphene oxide (GO) and gold nanoparticles (AuNPs) are now increasingly utilized in fabrication of novel electrodes and have showed drastically increased sensitivity [18–21]. GO is a monolayer of 2-dimensional carbon-based materials containing multi-functional groups such as carboxyl, epoxy, ketone and hydroxyl groups in its basal and edge planes [22], which will not only facilitate surface modification but also enhance adsorption capability for metal ions and thereby improve detection sensitivity. GO has shown great application potentials because of its excellent water-dispersibility, high mechanical strength, and versatile surface modification, and has become a research hotspot [19, 20, 23, 24]. On the other hand, electrochemical sensors based on AuNPs have been massively fabricated and have showed good stability, high catalytic properties and excellent sensitivity [25, 26]. Their unique enrichment

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capacity towards heavy metals makes AuNPs attain wide applications in electrochemical sensing for heavy metal detection [27, 28]. More importantly, it is extremely attractive to develop GO-AuNPs hybrids that will reveal highly enhanced electron conductive nanostructured membrane and large electroactive surface area based on synergistic effects, although little has been done to explore GO combined AuNPs in electrochemistry [29].

Meanwhile, as is well known, thymine (T) bases in DNA sequences have often been used as ligand for Hg(II) because they can form stable T–Hg(II)–T complexes while other heavy metal ions do not show any evident interaction with T [30]. The special T–Hg(II)–T interaction has been widely utilized for Hg(II) determination, such as colorimetric detection [31], fluorescence analysis [32, 33] and electrochemical sensing [34].

Inspired by these studies, we developed a novel electrochemical sensor for enhanced voltammetric detection of Hg(II) based on GO-AuNPs hybrids, by virtue of the synergistic and amplifying effects of nanocomposites as well as the specific binding of 5-methyl-2-thiouracil (MTU) and Hg(II) forming similar interaction to T–Hg(II)–T. Excellent selectivity of this sensor can be expected by the specific identification between MTU and Hg(II). Experimental conditions and analytical performances were systematically investigated. The developed sensor was also successfully applied for the detection of trace Hg(II) in tap water, bottled water and lake water with satisfactory results.

Experimental

Chemicals and reagents

GO was purchased from Nanjing XFNano Materials Technology Company (Nanjing, China. http://www.xfnano.com/). MTU was obtained from Sigma (Shanghai, China. http://www.sigmaaldrich.com/china-mainland.html). Chitosan, gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), sodium borohydride ($NaBH_4$), hydrochloric acid (HCl), $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$ and other affiliated chemicals were all obtained from Sinopharm Chemical Reagent (Shanghai, China. http://www.sinoreagent.com.cn/).

Instruments

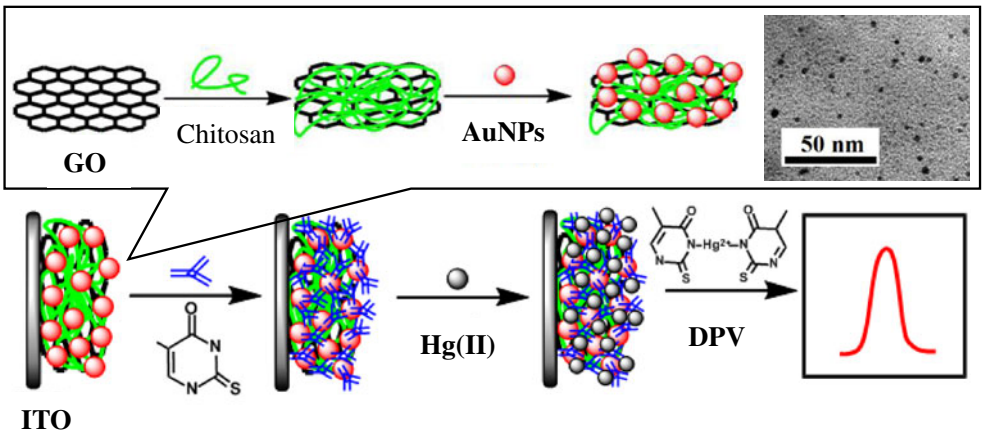
Electrochemical studies were performed with a CHI 660C instrument (Chenhua Instruments, Shanghai, China). An indium tin oxide (ITO) electrode (1 cm×5 cm) served as a working electrode, an Ag/AgCl (saturated KCl solution) was used as a reference electrode, and a Pt wire was employed as an auxiliary electrode. Transmission electron microscope (TEM) analysis was performed on a JEM-1230 electron microscope (JEOL Ltd., Japan) operating at 100 kV.

Synthesis of GO-AuNPs nanocomposites

GO-AuNPs nanocomposites were synthesized according to the reported method [35] with necessary modification. Briefly, the chitosan-protected GO nanocomposites were prepared firstly. Subsequently, the GO-chitosan-AuNPs hybrids were constructed using the $NaBH_4$ reduction method. TEM test was performed immediately for morphological evaluation. As seen the TEM image in Scheme 1, the homogeneously structured nanocomposites were formed.

Electrochemical procedures

The obtained GO-AuNPs nanocomposite solution of 30 μL was dripped onto the surface of the ITO electrode and naturally dried in the air to form GO-AuNPs modified ITO electrode. Then, 30 μL of MTU at 5 mM was dripped onto the electrode surface, resulting in GO-AuNPs/MTU modified ITO electrode via strong sulfur–gold (S–Au) interactions. And then, it was rinsed with double deionized water (DDW) (18.2 MΩ) to remove physically adsorbed species before use. Cyclic voltammetry (CV) was performed to characterize the different modified electrodes in 1.0 mM $K_3[Fe(CN)_6]$/$K_4[Fe(CN)_6]$ (1:1) solution containing 0.1 mol.L^{-1} KCl at a



Scheme 1 Schematic illustration of the enhanced electrochemical detection strategy for Hg(II) via specific interaction of MTU and Hg(II) based on GO-AuNPs composites modified on the ITO electrode; TEM image of GO-AuNPs composites with the aid of chitosan.

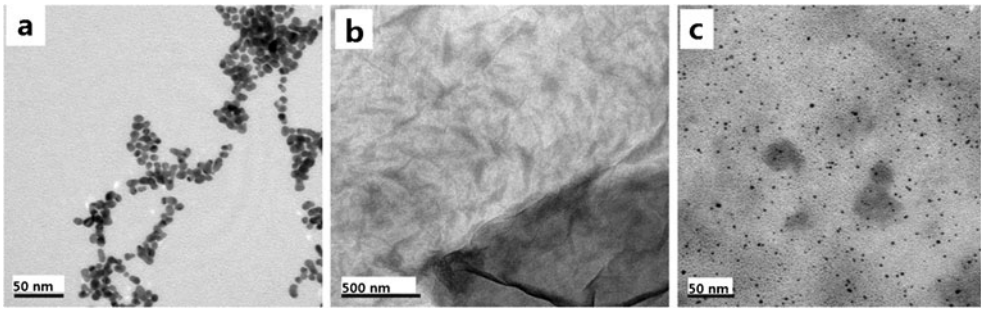


Fig. 1 TEM morphologies of (**a**) AuNPs, (**b**) GO and (**c**) GO-AuNPs nanocomposites with the aid of chitosan

scan rate of 100 mV.s^{-1}. Finally, the modified electrode was immersed into a 0.2 M PBS solution containing the different concentrations of Hg(II) for 5 min. Following the adsorption step, the differential pulse voltammetry (DPV) signals were recorded in the range from 0 to +1.0 V.

Real water sample preparation

Tap water was obtained in the laboratory when needed, and was collected after flowing for about 5 min. Bottled purified water, a well-known brand, was purchased from a local supermarket. Lake water was obtained from Sanyuanhu Lake in Yantai University (Yantai, China). Before use, the water samples were firstly filtered through a 0.45 μm nuclepore filter for removing the silt soil and sand grain.

Results and discussion

Possible sensing mechanism

The sensing strategy for Hg(II) is illustrated in Scheme 1. Chitosan, with excellent biological compatibility, film forming ability and electrochemical inertness, was introduced to protect GO and combine AuNPs, which could significantly improve the ability of GO-AuNPs composites and thereby the sensor. MTU was easily coupled to the surface of AuNPs through the strong Au–S bond, and thereby the GO-AuNPs/MTU coating was formed. Herein, ITO was employed as a working electrode, simultaneously possessing many

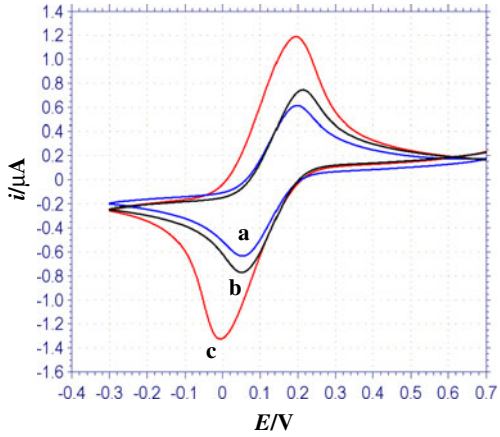


Fig. 2 Cyclic voltammograms acquired at different modified electrodes: **a** bare ITO electrode, **b** AuNPs/ITO and (**c**) AuNPs-GO/ITO in 1 mM of $[Fe(CN)_6]^{3-/4-}$ containing 0.1 M KCl solution

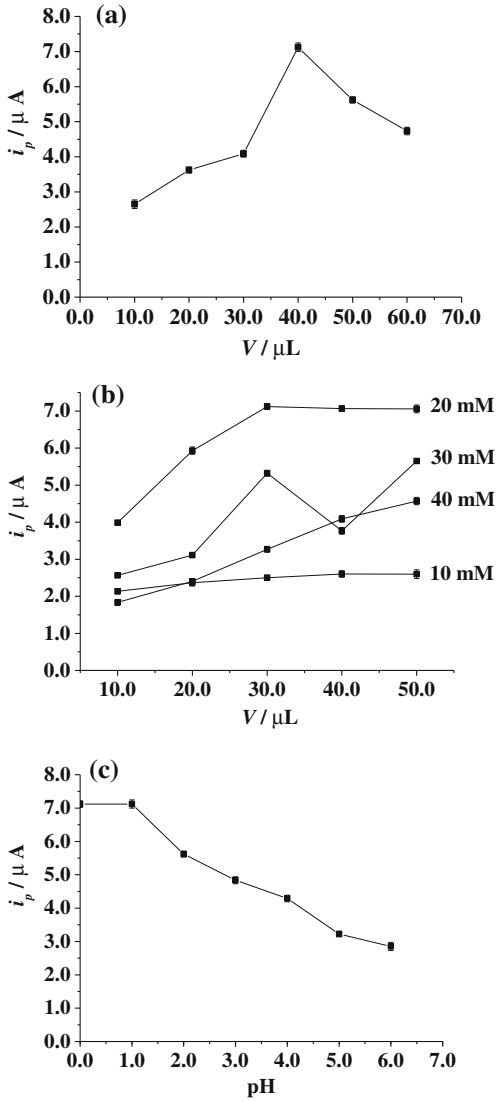


Fig. 3 Effect of (**a**) the volume of GO-AuNPs nanocomposites, **b** the concentration and the volume of MTU and (**c**) the pH of the detection solution on the DPV current for Hg(II)

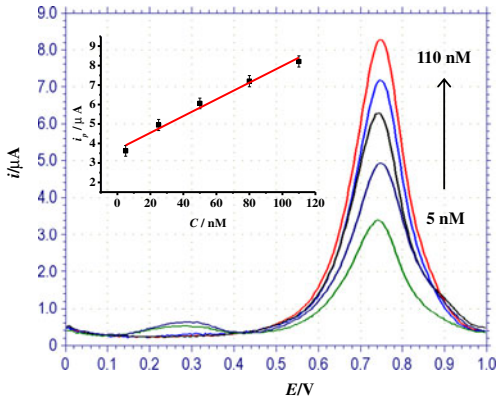


Fig. 4 DPV responses of the GO-AuNPs/MTU modified ITO electrodes to the addition of various concentrations of Hg(II) (5.0, 25.0, 50.0, 80.0 and 110.0 nM) in 0.2 M PBS solutions

advantages, such as high electical conductivity[36, 37], good chemical stability, easy modification and low cost. Compared with glassy carbon electrode, the ITO electrode generally has much larger active area [38]. Moreover, the oxhydryl group of the ITO surface could interact with GO. Therefore, a potentially promissing GO-AuNPs/MTU modified ITO electrochemical sensor was fabricated.

As is well confirmed that T offers a coordination site (N3) to bind with Hg(II) with strong affinity and leads to the T–Hg(II)–T linkage [30]. Herein, the MTU we used can also offer the coordination site (N3) to recognize Hg(II) with strong affinity. Additionally, the small molecule should be coordinated with Hg(II) more easily with weaker space resistance compared with the T chained in the DNA strand [31]. Therefore, Hg(II) ions were attached to the electrode surface via the similar interaction to "T–Hg(II)–T" linkage. The Hg(II) moieties are easily positioned in close proximity to the underlying electrode, allowing facile electron transfer to occur. A large number of Hg(II) in the solutions can be brought to the electrode surface and reduced, which will result in enhanced voltammetric responses based on the synergistic and amplifying effects of GO-AuNPs nanocomposites and the specific binding of MTU and Hg(II).

TEM characterization

Figure 1 shows the typical TEM images of GO and AuNPs. It was clear that the AuNPs were in size with an average of about 10 nm (Fig. 1a), and the typical folds were quite obvious on the edge of the GO material (Fig. 1b). As shown in Fig. 1c, the GO-AuNPs nanocomposites were uniformly dispersed in chitosan film.

Steady-state CV measurements were performed to characterize the different modified electrodes, as displayed in Fig. 2. A couple of well-defined redox peaks could be observed at the bare ITO electrode (curve a). Peak currents at the AuNPs modified ITO (curve b) increased. The reason was that AuNPs had large specific surface areas which facilitated the electrons transfer. A couple of well-defined redox peaks with the greatest peak currents were exhibited, for the AuNPs-GO modified ITO (curve c). This was very likely because that the synergy of GO and AuNPs in the modified film greatly enhanced the peak currents, and the amplification effect of the nanocomposites to peak currents was remarkable.

Conditions optimization

Since GO-AuNPs nanocomposites, MTU and detection solution acidity play important roles in the performance of the sensor, the influence of solution pH, the amounts of nanocomposites and MTU added to the electrode were investigated.

The amount of GO-AuNPs nanocomposites had a pronounced effect on the performance of the modified electrode. The drop volumes of 10, 20, 30, 40, 50 and 60 μL were experimented. Figure 3a shows the test results. When the drop volume of GO-AuNPs nanocomposites was too low, the DPV response for Hg(II) was limited; when the drop volume was too large, the conductivity of the nanocomposites film modified electrode decreased obviously. Therefore, the optimal amount of 40 μL was chosen in the following experiments.

The concentration and amount of MTU employed in the experiments directly affected the DPV current for Hg(II).

Table 1 Figures of merits of voltammetric methods for determination of mercury(II)

Detection method	Technique in detail	Linear range (nM)	Detection limit (nM)	Ref.
Differential pulse voltammograms	GO-chitosan-AuNPs/MTU modified ITO	5.0–110.0	0.78	This work
Cyclic voltammograms	CuO nanoshuttles/poly(thionine) modified glassy carbon electrode	40–5000	8.5	[7]
Anodic stripping voltammetry	AuNPs-chi-graphene modified GCE	0.008–0.5 ppb	6 ppt (0.03 nM)	[35]
Cyclic voltammograms	Hg^{2+}-induced DNA hybridization	1–10000	0.6	[15]
Anodic stripping voltammetry	Gold films modified screen-printed electrodes and metal ion preconcentration with thiol-modified magnetic particles	2–16 $\mu g L^{-1}$	1.5 $\mu g L^{-1}$ (7.5 nM)	[12]

The signals of Hg(II) with different concentration under different volumes were shown in Fig. 3b. A signal plateau appeared at 20 mM or above under volume of 30 μL. Therefore, 30 μL of 20 mM MTU was selected.

The acidity of the detection solution usually has a large effect on the stripping voltammetry behavior of Hg(II). As seen in Fig. 3c, in the range of pH 1.0–6.0, the DPV current decreased gradually, while in pH 0–1.0, a terrace was reached with the highest current values. Considering real operation, so the detection solution of pH 1.0 was chosen for the subsequent work.

Method linearity and detection limit

The DPV responses of the nanocomposites combined MTU modified electrode, i.e. GO-chitosan-AuNPs/MTU modified ITO electrode, were recorded with various concentrations of Hg(II) in the range from 5.0 nM to 110.0 nM, as shown in Fig. 4. The peak current rose with increasing concentration of Hg(II), with a good linear correlation (R=0.9920). The limit of detection (LOD) was estimated to be 0.78 nM based on a signal-to-noise ratio of 3 (S/N=3), which is much lower than the maximum level of Hg(II) at 5 nM permitted by the WHO. Comparisons with other voltammetric methods [7, 12, 15, 35] are shown in Table 1 for the determination of Hg(II). As can be seen from the table, as a new sensing strategy, the single voltammetry based on specific binding of MTU and Hg(II) but without electro-deposition process is an ideal candidate for sensitive and rapid detection of Hg(II).

Interference study

The selectivity for the Hg(II) sensor is a challenging task. In our work, the potentially interfering ions such as K^+, Na^+, Ca^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Ag^+ and Pt^{4+} were studied to evaluate the selectivity of the GO-AuNPs/MTU modified ITO electrodes. As shown in Fig. 5, it was found that the DPV signals of 100 nM Hg(II) in the presence of 50-fold each element in the solution were changed slightly compared to that in the absence, indicating that these metal ions had no interference with the detection of Hg(II). Evidently, this sensor was very selective for Hg(II) detection over other metal ions.

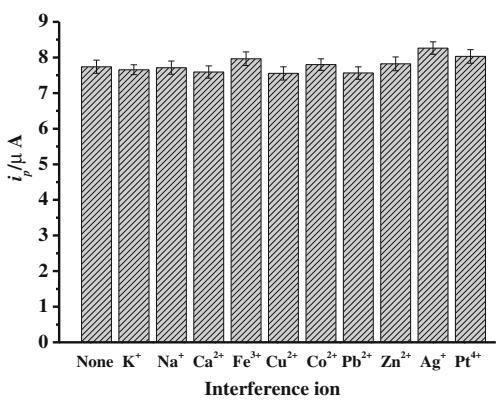


Fig. 5 Effects of various ions on the electrochemical stripping signals of Hg(II) at GO-AuNPs/MTU modified ITO electrodes. 100 nM Hg(II); 100 nM Hg(II) and 5 μM each for K^+, Na^+, Ca^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Ag^+ and Pt^{4+}, respectively

Table 2 Linear correlations and detection limits for Hg(II) determination in water samples (n=5)

Water samples	Linear range (nM)	Slope	Intercept	R	LOD (nM)
Tap water	10.0–60.0	0.046	1.063	0.9921	6.9
Bottled water	3.0–80.0	0.039	0.917	0.9895	1.0
Lake water	6.0–50.0	0.051	1.129	0.9916	1.9

Detection of Hg(II) in real water samples

Quantitation correlations assessed using tap water, bottle water and lake samples water samples spiked at different concentration levels were obtained between peak current height and the corresponding concentrations of Hg(II), listed in Table 2. LODs for Hg(II) in the water samples, calculated as the analyte concentration for which the peak current height was three times the background noise (3S/N), were obtained of 6.9, 1.0 and 1.9 nM, respectively (Table 2). In this work, four LOD values were given, different LOD in different sample solutions. Especially, the LOD in tap water (6.9 nM) is about 9 times of that in standard solution (0.78 nM). It is a general case that lower LODs are obtained in standard solutions than in real samples. This LOD difference is very likely owing to the matrix difference, for example, tap water and standard solution. There are more ions in tap water than in standard solution, so the ionic effects possibly discourage sensitivity and greater LOD is given. On the other hand, the difference in LODs among the

Table 3 Method recoveries for the determination of Hg(II) in spiked water samples (n=5)

Water samples	Spiked (nM)	Recovery (%)	RSD (%)
Tap water	8.0	93.5	3.6
	50.0	90.3	5.2
	100.0	87.9	3.3
Bottled water	8.0	96.8	3.9
	50.0	91.6	4.6
	100.0	83.9	3.8
Lake water	8.0	95.8	4.1
	50.0	89.5	3.6
	100.0	85.7	5.1

three real water samples was not very big, and in a certain sense, it also suggested the developed GO-AuNPs/MTU based DPV determination had wide applicability without significant matrix interferences.

In order to evaluate the method performance in different water samples, the recovery was obtained by spiking the Hg(II) standard at three levels of 8.0, 50.0 and 100.0 nM, respectively. Recoveries were from 83.9 % to 96.8 % with the RSDs of 3.3–5.2 %, shown in Table 3. The results indicated that there were no significant matrix effects on the determination. Therefore, the developed method proved greatly applicable to Hg(II) analysis in environmental and drinking water samples.

Conclusions

In conclusion, a novel electrochemical sensor for trace Hg(II) determination in water samples was successfully developed by the combination of GO-AuNPs nanocomposites and MTU. Taking advantage of amplification effects of nanocomposites and specific interactions of MTU and Hg(II), the sensor was demonstrated highly sensitive and selective towards Hg(II). Besides, this sensing strategy offered other advantages and possible inspirations: (1) The use of a simple and commercially available MTU containing coordination site (N3) as a Hg(II) acceptor avoids any design or molecular modification or optimization of the Hg(II)-binding oligonucleotide. (2) This sensing platform is easily constructed in solution without any other labeling or modification steps. (3) The detection procedure is also rather simple: all it takes is recording the DPV responses after the addition of analyte to the sensing system. This simple, rapid and cost-effective sensing method opens attractive perspectives for Hg(II) determination in real samples.

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References

1. Tchounwou PB, Ayensu WK, Ninashvili N, Sutton D (2003) Environmental exposure to mercury and its toxicopathologic implications for public health. Environ Toxicol 18:149–175
2. Nolan EM, Lippard SJ (2008) Tools and tactics for the optical detection of mercuric ion. Chem Rev 108:3443–3480
3. Clemens S, Monperrus M, Donard OFX, Amouroux D, Guerin T (2012) Mercury speciation in seafood using isotope dilution analysis: a review. Talanta 89:12–20
4. Matusiewicz H, Stanisz E (2012) Evaluation of the catalyzed photo-cold vapour generation for determination of mercury by AAS. J Brazilian Chem Soc 23:247–257
5. Shekhar R (2012) Improvement of sensitivity of electrolyte cathode discharge atomic emission spectrometry (ELCAD-AES) for mercury using acetic acid medium. Talanta 93:32–36
6. Zhao YQ, Zheng JP, Fang L, Lin Q, Wu YN, Xue ZM, Fu FF (2012) Speciation analysis of mercury in natural water and fish samples by using capillary electrophoresis–inductively coupled plasma mass spectrometry. Talanta 89:280–285
7. Yin Z, Wu J, Yang Z (2010) A sensitive mercury (II) sensor based on CuO nanoshuttles/poly(thionine) modified glassy carbon electrode. Microchim Acta 170:307–312
8. Wang GQ, Chen ZP, Wang WH, Yan B, Chen LX (2011) Chemical redox-regulated mesoporous silica-coated gold nanorods for colorimetric probing of Hg^{2+} and S^{2-}. Analyst 136:174–178
9. Wang G, Lim C, Chen L, Chon H, Choo J, Hong J, deMello AJ (2009) Surface-enhanced Raman scattering in Nanoliter droplets: towards high sensitivity detection of mercury (II) ions. Anal Bioanal Chem 394:1827–1832
10. Wang YQ, Yan B, Chen LX (2013) SERS tags: novel optical nanoprobes for bioanalysis. Chem Rev. doi:10.1021/cr300120g
11. Li JH, Lu WH, Ma JP, Chen LX (2011) Determination of mercury(II) in water samples using dispersive liquid-liquid microextraction and back extraction along with capillary zone electrophoresis. Microchim Acta 175:301–308
12. Mandil A, Idrissi L, Amine A (2010) Stripping voltammetric determination of mercury(II) and lead(II) using screen-printed electrodes modified with gold films, and metal ion preconcentration with thiol-modified magnetic particles. Microchim Acta 170:299–305
13. Pan DW, Wang YE, Chen ZP, Lou TT, Qin W (2009) Nanomaterial/ionophore-based electrode for anodic stripping voltammetric determination of lead: an electrochemical sensing platform toward heavy metals. Anal Chem 81:5088–5094
14. Chen LX, Zhou N, Li JH, Chen ZP, Liao CY, Chen JN (2011) Synergy of glutathione, dithiothreitol and N-acetyl-L-cysteine self-assembled monolayers for electrochemical assay: sensitive determination of arsenic (III) in environmental and drinking water. Analyst 136:4526–4532
15. Niu X, Ding Y, Chen C, Zhao H, Lan M (2011) A novel electrochemical biosensor for Hg^{2+} determination based on Hg^{2+}-induced DNA hybridization. Sensor Actuat B-Chem 158:383–387
16. Baca AJ, Zhou FM, Wang J, Hu JB, Li JH, Wang JX, Chikneyan ZS (2004) Attachment of ferrocene-capped gold nanoparticle-streptavidin conjugates onto electrode surfaces covered with biotinylated biomolecules for enhanced voltammetric analysis. Electroanalysis 16:73–80
17. Martín-Yerga D, González-García MB, Costa-García A (2012) Use of nanohybrid materials as electrochemical transducers for mercury sensors. Sensors Actuat B-Chem 165:143–150
18. Zhou N, Li JH, Chen H, Liao CY, Chen LX (2013) A functional graphene oxide-ionic liquid composites–gold nanoparticle sensing platform for ultrasensitive electrochemical detection of Hg^{2+}. Analyst 138:1091–1097
19. Song YH, He ZF, Hou HQ, Wang XL, Wang L (2012) Architecture of Fe_3O_4–graphene oxide nanocomposite and its application as a platform for amino acid biosensing. Electrochim Acta 71:58–65
20. Pérez-López B, Merkoçi A (2012) Carbon nanotubes and graphene in analytical sciences. Microchim Acta 179:1–16
21. Boisselier E, Astruc D (2009) Gold nanoparticles in nanomedicine: preparations, imaging, diagnostics, therapies and toxicity. Chem Soc Rev 38:1759–1782
22. Gan T, Hu S (2011) Electrochemical sensors based on graphene materials. Microchim Acta 175:1–19
23. Fu XL, Chen LX, Li JH, Lin M, You HY, Wang WH (2012) Label-free colorimetric sensor for ultrasensitive detection of heparin

based on color quenching of gold nanorods by graphene oxide. Biosens Bioelectron 34:227–231
24. Fu XL, Chen LX, Li JH (2012) Ultrasensitive colorimetric detection of heparin based on self-assembly of gold nanoparticles on graphene oxide. Analyst 137:3653–3658
25. Ma JC, Zhang WD (2011) Gold nanoparticle-coated multiwall carbon nanotube-modified electrode for electrochemical determination of methyl parathion. Microchim Acta 175:309–314
26. Xi Q, Chen X, Evans DG, Yang WS (2012) Gold nanoparticle-embedded porous graphene thin films fabricated via layer-by-layer self-assembly and subsequent thermal annealing for electrochemical sensing. Langmuir 28:9885–9892
27. Zhu ZQ, Su YY, Li J, Li D, Zhang J, Song SP, Zhao Y, Li GX, Fan CH (2009) Highly sensitive electrochemical sensor for mercury(II) ions by using a mercury-specific oligonucleotide probe and gold nanoparticle-based amplification. Anal Chem 81:7660–7666
28. Bernalte E, Marín Sánchez C, Pinila Gil E (2012) Determination of Mercury in indoor dust samples by ultrasonic probe microextraction and stripping voltammetry on gold nanoparticles-modified screen-printed electrodes. Talanta 97:187–192
29. Sheng Y, Cao XY, Yu M (2012) Electrochemical immunoassay based on gold nanoparticles and reduced graphene oxide functionalized carbon ionic liquid electrode. Microchem J 103:125–130
30. Liu X, Qi C, Bing T, Cheng X, Shangguan D (2009) Highly selective phthalocyanine−thymine conjugate sensor for Hg^{2+} based on target induced aggregation. Anal Chem 81:3699–3704
31. Chen L, Lou TT, Yu CW, Kang Q, Chen LX (2011) N-1-(2-Mercaptoethyl)thymine modification of gold nanoparticles: a highly selective and sensitive colorimetric chemosensor for Hg^{2+}. Analyst 136:4770–4773
32. Li H, Zhai J, Tian J, Luo Y, Sun X (2011) Carbon nanoparticle for highly sensitive and selective fluorescent detection of mercury(II) ion in aqueous solution. Biosens Bioelectron 26:4656–4660
33. Xu SF, Chen LX, Li JH, Guan YF, Lu HZ (2012) Novel Hg^{2+}-imprinted polymers based on thymine–Hg^{2+}–thymine interaction for highly selective preconcentration of Hg^{2+} in water samples. J Hazard Mater 237–238:347–354
34. Tang XM, Liu HX, Zou BH, Tian DB, Huang H (2012) A fishnet electrochemical Hg^{2+} sensing strategy based on gold nanoparticle-bioconjugate and thymine–Hg^{2+}–thymine coordination chemistry. Analyst 137:309–311
35. Gong JM, Zhou T, Song DD, Zhang LZ (2010) Monodispersed Au nanoparticles decorated graphene as an enhanced sensing platform for ultrasensitive stripping voltammetric detection of mercury(II). Sensors Actuat B-Chem 150:491–497
36. Chen YT, Jiang YY, Lin ZY, Sun JJ, Zhang L, Chen G (2009) Fabrication of an electrically heated indium-tin-oxide electrode for electrochemiluminescent detection system. Analyst 134:731–737
37. Oh SY, Yun YJ, Kim DY, Han SH (1999) Formation of a self-assembled monolayer of diaminododecane and a heteropolyacid monolayer on the ITO surface. Langmuir 15:4690–4692
38. Cummins CM, Koivunen ME, Stephanian A, Gee SJ, Hammock BD, Kennedy IM (2006) Application of europium(III) chelate-dyed nanoparticle labels in a competitive atrazine fluoroimmunoassay on an ITO waveguide. Biosens Bioelectron 21:1077–1085