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Ultrasensitive and selective sensing of heavy metal ions with modified graphene[†]

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Swift fabrication of a non-covalently modified reduced graphene oxide electronic sensor has been developed. An unparalleled detection limit is demonstrated for Hg²⁺, down to the picomolar range.

Graphene is a single layer of high crystalline graphite with a two-dimensional hexagonal honeycomb-like structure. Because of its excellent physicochemical and extraordinary electronic properties,¹ this amazing planar sheet of carbon material has been used in many applications, such as transparent electrodes,² electronic devices,³ energy storage⁴ and sensors.⁵ A variety of preparation methods of graphene sheets have been reported including mechanical exfoliation,³ epitaxial growth,⁶ chemical vapor deposition,⁷ and reduction of graphene oxide (RGO).⁵ RGO can be prepared through graphene oxide (GO) by chemical reduction (hydrazine, tetrathiafulvalene and vitamin C),^{5,8} thermal reduction,9 and electrochemical reduction.10 RGO has unique properties such as easy preparation, patterning, miniaturization and facile modification. In addition, it exhibits high sensitive response to certain environments.¹¹ These outstanding advantages have attracted tremendous interest in RGO and made it promising for application in detecting DNA,¹² living cells,¹³ gas molecules,⁵ H₂O₂,¹⁴ or metal ions.¹⁵ With respect to heavy metal ion sensors, mercury-containing species are special pollutants of drinking water because a small amount of these species would cause detrimental effects on the renal, reproductive, cardiovascular, genetic, and immune systems of the human body.¹⁶ Several methods for detecting inorganic mercury (Hg²⁺) ions have been developed including atomic absorption spectrometry,17 fluorescence spectroscopy,18 inductively coupled plasma mass spectrometry,19 and the electrochemical method.20

Recently, electronic sensors based on RGO for detecting Hg^{2+} have attracted increasing attention. In order to enhance sensitivity, an effective strategy is to modify RGO with recognition structures which could selectively bind the analyte. Sudibya *et al.* reported a RGO-based Hg^{2+} sensor with the detection limit (DL) of 1 nM. In their sensor, metallothionein type II had been chosen as an intermediate binder of the analyte.²¹ Chen *et al.* reported another RGO-based field-effect transistor (FET) sensor for detecting Hg^{2+} ions, in which RGO was modified through gold nanoparticles with a 25 nM DL.²² However, these FET detectors for Hg^{2+} still need a relatively complex modification process and a complicated electrochemical workstation. Thus the realization of superior sensing performance for Hg^{2+} with a simple fabrication and detection method would be promising for the development of low-cost detectors.

In this study, we have designed an ultra-sensitive and highly selective Hg^{2+} sensor through non-covalent modification of an electrochemically reduced GO (ERGO)-based diode with *N*-[(1-pyrenyl-sulfonamido)-heptyl]-gluconamide (PG) as the modifier. PG is composed of a glucose residue and a pyrene residue. The glucose residue has imines and hydroxyl functional groups, which can work as multiple-receptor sites for Hg^{2+} in the medium. The large π system in the pyrene can be stably attached on the ERGO surface (see Fig. 1). The DL of this sensor for Hg^{2+} reaches 0.1 nM, which is the best result of electronic sensors and is about 10 times as low as the previously reported results.²¹

The fabrication procedures for the ERGO-based electronic sensor are shown in Scheme S1 (ESI[†]). Two gold (Au) electrodes were deposited on the substrate through a shadow mask. Then an aqueous GO suspension was dropped on the surface of two Au electrodes, and a fixed voltage (0–4 V) was applied. The reduction process was repeated more than 5 times, and then ERGO sheets were deposited between the two electrodes. The transformation of GO to ERGO is represented by the equation $GO + H^+ + e^- \rightarrow RGO + H_2O$. In this equation, protons can be released from the carboxylic acid groups of the GO suspension and electrons are provided by the cathode.¹¹ Raman spectroscopy is employed to characterize the structure changes of GO. The D and G bands at ~1350 cm⁻¹ and ~1590 cm⁻¹

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Fig. 1 A proposed mechanism for an ultra-sensitive and highly selective ${\rm Hg}^{2+}$ sensor based on the modified ERGO.

observed in the Raman spectrum of GO or ERGO, respectively (see Fig. S1, ESI[†]). As shown in Fig. S1 (ESI[†]), the two bands for GO appear at 1328 cm⁻¹ and 1596 cm⁻¹, respectively. After electrochemical reduction, the bands shift to 1324 cm⁻¹ and 1594 cm⁻¹, respectively. Furthermore, the intensity ratios of the two bands (D/G), representing defects of the carbon material in structure, are found to be 1.18 for GO and 1.31 for ERGO, respectively. It is indicated that new small-sized graphitic domains are formed after electrochemical reduction, which is consistent with the reported result.¹¹

The synthesis routes to PG are shown in Scheme S2 (ESI[†]). The compound with a glucose residue and a pyrene residue has unique properties: (1) one-step functionalization for ERGO sheets; (2) organic compounds containing rich hydroxyl groups show great affinity to Hg^{2+} in aqueous phase;²³ (3) the π structure in the pyrene unit of the compound guarantees its adsorption on the ERGO sheets *via* a strong π - π interaction.²⁴ The other side of the compound, the glucose residue, is hydrophilic and tends to stretch in aqueous medium to bind Hg^{2+} .

In the experiment, ERGO sheets were modified through dipping in 1 mM PG solution and rinsed off with deionized (DI) water to remove extra PG molecules. The micro-morphologies of the ERGO and the modified ERGO surface were studied using SEM and the results are shown in Fig. S2 (ESI[†]). The Raman spectra of ERGO, PG and ERGO decorated with the PG surface are illustrated in Fig. 2a, respectively. It has been confirmed that regardless of several rinsing and drying cycles, PG molecules are firmly attached on ERGO surfaces due to the π system between pyrene units of PG and ERGO. Fig. 2b shows the current *versus* voltage plots for the unmodified and modified ERGO device, respectively. Clearly, the device strictly follows



Fig. 2 (a) The Raman spectra of PG, ERGO + PG and ERGO surface; (b) current *versus* voltage plots of the ERGO and the modified ERGO sensor.



Fig. 3 (a) The real-time current recording of the modified ERGO sensor upon addition of Hg²⁺ solutions of different concentrations; (b) conductivity changes of the modified ERGO sensor with Hg²⁺ solutions of different concentrations. Inset: plot of the conductivity changes against the concentrations of the ion in aqueous phase ($R^2 = 0.972$); (c) the conductivity changes of the devices in the presence of different metal ions, of which blue shows the results obtained for the modified device.

Ohm's law no matter whether it is modified or not. It can be observed in the figure that the resistance of a modified device increases only slightly when compared with the resistance of an unmodified device.

To show the efficacy of our modified ERGO sensor, its sensing performances for Hg2+ have been explored. 35 µL of Hg²⁺ solution with specific concentrations was added to a PDMS cell of the sensor and then the responsive current was continually monitored at a constant voltage of 1 V. The results are shown in Fig. 3a. It is seen that a concentration of 0.1 nM of Hg²⁺ solution could result in a conductivity change ($\Delta G/G$) of -11.3%which was calculated using the equation $(\varepsilon G_{\text{ion}} - \varepsilon G_{\text{DI}})/\varepsilon G_{\text{DI}}$, in which $\varepsilon G_{\text{ion}}$ and $\varepsilon G_{\text{DI}}$ are conductivities recorded in the presence of mercury ions and DI water after background correction, respectively. There is no doubt that the DL obtained using our method for the determination of Hg²⁺ is significantly lower than the value of 0.1 nM, which is, to the best of our knowledge, the lowest concentration to be directly detected by a mercury electronic sensor.^{21,22} The fact that the maximum concentrations of Hg²⁺ allowed in drinking water are 30 nM and 10 nM, respectively, according to the requirements of the World Health Organization (WHO) and that of the United States Environmental Protection Agency (USEPA) is considered. Combining the results described above, it may be concluded that the sensor device developed has the potential to be developed into a micro-sized mercury detection device. Furthermore, the response of the sensor to the analyte is almost instantaneous even though nearly 10 min is needed to reach equilibrium. To be clear, the dynamic responses of our sensor device to some Hg²⁺ solutions of different concentrations are shown in Fig. S3 (ESI⁺). The greater conductivity phenomenon after addition of DI water observed in the present study may be understood by considering that water may function as an acceptor of ERGO, which makes the charge carriers of ERGO more mobile.³ As for the decrease in the conductivity resulting

from the appearance of Hg^{2+} , it can be attributed to the complex formation between the ions and the PG molecules adsorbed on the ERGO surface, which may inhibit the electron transmission on the modified ERGO surface, implying decreased conductivity.

Fig. 3b shows the plot of the conductivity changes $(\Delta G/G)$ against the concentrations of Hg²⁺ ions. It is observed in this figure that there are two regions in the plot: the linear region and the saturation region. In the linear region, the conductivity changes linearly increase with increasing Hg²⁺ concentrations from 0.1 nM to 4 nM. As shown in the inset of the figure, the correlation coefficient, R^2 , of the measurements is 0.972. Compared with the linear region, the conductivity changes in the saturation region in which the Hg²⁺ concentration is greater than 4 nM are nearly constant. These two regions may be ascribed to an adsorption accumulation process. In the linear region, the amount of Hg2+ adsorbed on the ERGO surface increases with the increasing analyte concentrations. In the saturation region, increasing the analyte concentrations has little effect on the amount of Hg²⁺ adsorbed on the ERGO sheet due to its exhausted binding sites.

The selectivity of the ERGO modified Hg²⁺ sensor was also evaluated through examining its responses to common interfering ions, such as K⁺, Na⁺, Cu²⁺, Zn²⁺, Fe³⁺ and Cd²⁺. Compared with its response to 10 nM of Hg²⁺, very weak conductivity change was observed for the modified sensor upon addition of any of the interfering metal ions at a concentration of 100 nM, except for Cd²⁺. The results are collectively presented in Fig. 3c (blue). It is clearly seen that the presence of ten times' higher concentration of the interfering ions only results in less than 1/8th response to Hg²⁺. As for Cd²⁺, its interference in the determination of Hg²⁺ is obvious only when its concentration exceeds 2 nM, suggesting that the Hg²⁺ sensor developed in the present study is also selective to Cd2+ provided the measurement is conducted at a concentration lower than 2 nM (see Fig. S4, ESI[†]). The selectivity of our Hg²⁺ sensor device could be attributed to the high binding affinity of PG to Hg^{2+} .

Responses of the sensor developed to the interfering ions with the exception of Cd²⁺ at even higher concentrations were also studied. The results are shown in Fig. S5-S9 (ESI⁺) displayed in the ESI.[†] It is seen that the conductivity changes induced by these ions at these concentrations of the micro-molar level are still very low, actually significantly lower than that induced by Hg²⁺ at the nano-molar level, demonstrating clearly that the PG modified ERGO-based sensor is not only sensitive to the presence of Hg²⁺, but also highly selective to it. Furthermore, a control experiment was also performed to demonstrate the key role of PG. In the control, no PG was used, and the results obtained for this control are shown in Fig. S10 (ESI^{\dagger}). The figure reveals that 4 nM of Hg^{2+} only results in a change of -10.2% in the conductivity of the sensor, which is much lower than that, a change more than 60%, observed using the PG modified device to conduct the same measurement. Additionally, the detection performances of the unmodified ERGO sensor for other ions were also explored. The results are depicted in Fig. 3c (red). Clearly, this sensor is not only insensitive to the presence of Hg²⁺ but also less selective to it, indicating that introduction of PG is crucial to the improvement of the sensing performance of the ERGO based electronic sensor device.

In conclusion, the PG modified ERGO-based electronic sensor device can be used as a highly sensitive and selective sensor for detecting Hg^{2+} in aqueous phase. The DL of the sensor to the analyte is 0.1 nM, which is about 10 times as low as that reported previously. The superior sensor performance is based on the introduction of the PG compound as the modifier. The simple fabrication method and excellent sensor performance suggest that the modified ERGO sensor device has the potential to be developed into an integratable Hg^{2+} practical detector.

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