An electrochemically reduced graphene oxide chemiresistive sensor for sensitive detection of Hg²⁺ ion in water samples

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Abstract: Divalent mercuric (Hg^{2+}) ion is one of the most prevalent forms of mercury species in waters with high toxicity and bioaccumulation in the human body, for which sensitive and selective detection methods are highly necessary to carry out its recognition and quantification. Here an electrochemically reduced graphene oxide (RGO) based chemiresistive sensor was constructed and used for the detection of Hg^{2+} ion in various water samples. Monolayer GO sheets were assembled onto interdigitated electrodes, followed by reduction through linear sweep voltammetry and then modification with a single-stranded DNA aptamer. The electrochemically derived RGO based sensor showed selective response to as low as 0.5 nM Hg^{2+} ion in presence of other metal ions and matrices. A comparison between chemiresistive sensors prepared with electrochemically and chemically derived RGO showed that the former had better response performance for sensing Hg^{2+} ion. The proposed method provides a simple tool for rapid, selective and sensitive monitoring of Hg^{2+} ion in environmental samples.

Keywords: Reduced graphene oxide; Electrochemical; Mercury(II) ion; Environment monitoring; Aptamer

1. Introduction

Mercury is a widespread pollutant, which exists as metallic, inorganic and organic species in environments. Divalent mercuric (Hg^{2+}) ion is one of the most prevalent forms of mercury species in environmental waters, which can further transform into the more poisonous methylmercury by microbial methylation [1, 2]. Hg^{2+} ion can accumulate in animal and human bodies through the food cycle, with a high enrichment factor (10^6) [3], and then affect the nervous, immune, and digestive systems and cause serious damage of kidney, liver, and brain [4, 5]. Hence, there is a great need to develop reliable analytical methods for sensitive detection of trace Hg^{2+} ion in the fields of environmental monitoring, food safety and toxicity assessment.

The traditional techniques for Hg^{2+} ion detection include cold vapor atomic absorption spectrometry (CVAAS) [6], inductively coupled plasma atomic emission spectrometry (ICPAES) [7], atomic fluorescence spectrometry (AFS) [8], liquid chromatography inductively coupled plasma mass spectrometry (LCICPMS) [9], and anodic stripping voltammetry (SV) [10, 11]. Although these methods are reliable and sufficiently sensitive for routine analysis, there are several shortcomings, such as the need for expensive equipment, well-trained operators and complicated sample preparation, and not being competent for on-site detection in emergent pollution events. Alternatively, several sensors have been developed for the detection of Hg^{2+} ion, such as colorimetric [12, 13], fluorescent [14, 15], electrochemical [16, 17], and surface-enhanced Raman scattering, [18], where metal nanoparticles or carbon nanotubes were typically used as the signal transducer and enhancement factor to improve the response speed and sensitivity due to their large surface area and excellent structural, electronic and optical characteristics. Despite these advancements, novel sensors with simple operation, low cost, fast response, and reliability results are still

needed.

In recent years, field-effect transistor (FET) or chemiresistor based on one-dimensional and two-dimensional nanomaterials, such as carbon nanotube, silicon nanowire, and graphene, has attracted increasing attention as a transducer combined with biological sensing element for highly selective and sensitive, real-time response, and label-free detection capabilities [19-21]. Graphene not only has excellent electron mobility, thermal conductivity, mechanical strength, and large surface-to-volume ratio, but also shows unique tunable ambipolar characteristics and extremely low thermal and electrical noise due to high conductivity and few surface defects. Additionally, graphene overcomes the limitation of almost inevitable metallic impurities present in carbon nanotubes, which compromises the nanotubes' performance in FET [22]. These merits have made graphene as an attractive channel material of FET/chemiresistor transducer and also as sensing element for the detection of various analytes [23-25].

In the earlier reports of graphene-based FET biosensors, pristine graphene was prepared by the micromechanical cleavage of graphite. While elegant for demonstration of applications of this material for biosensors, the micromechanical cleavage is time-consuming, inefficient and hard to control. Alternative methods for the preparation of graphene, such as decomposition of silicon carbide (SiC) and chemical vapor deposition (CVD) [26, 27] on Cu or other metallic substrates at a high temperature, have been developed. However, the lack of a reliable and scalable transfer method remains a challenging issue [28]. On the other hand, reduced graphene oxide (RGO) could be prepared by chemical [29], thermal [30, 31], or electrochemical [32] reduction of single or few-layer graphene oxide (GO), which are easily obtained from graphite following the treatment of strong acid. These reduction methods allow for a low-cost and large-scale production of RGO. RGO has shown to possess low

electronic noise and excellent electronic conductivity similar to those of pristine graphene and is becoming an alternative graphene material for developing functional electronic biosensors. For example, RGO (synthesized by chemical or thermal reduction of GO) FETs have been constructed and used for the detection of Hg^{2+} ion [33, 34], Pb^{2+} ion [35], proteins [36], DNA [37, 38], dopamine [39] and NH_3 [40].

Compared with chemical and thermal methods, electrochemical reduction (EC) is a more controlled, safer, simpler, and more economical method for the preparation of RGO since it doesn't use toxic hydrazine or reducing gases such as H_2 or He gas at high temperatures for the reduction. In the present work, an electrochemically derived RGO chemiresistive sensor was prepared and characterized and then used for the detection of Hg^{2+} ion in water samples. Further, a comparison between chemiresistive devices prepared with electrochemically and chemically derived RGO for sensing Hg^{2+} ion was carried out. The proposed strategy provides a useful tool for rapid and sensitive analysis of Hg^{2+} ion in water.

2. Experimental

2.1 Material

1-Pyrenebutanoic acid succinimidyl ester (PASE) and 3-aminopropyltriethoxy silane (APTES) were purchased from Sigma-Aldrich (USA). A single-stranded DNA aptamer with a sequence of 5'-(NH_2)-TTCTTTCTTCCCCTTGTTTGT-3' was synthesized by Takara Biotechnol. Co., Ltd (Dalian, China), which was prepared in 10 mM phosphate buffer (PB, pH 7.4). Hg^{2+} and other metal ion solutions (1 mM) were prepared by adding mercury sulfate or their nitrate or chloride salt (analytical grade) in 100 μL sulfuric acid (98%, analytical grade) and deionized (DI) water, then diluted by 10 mM PB (pH 7.4) to different concentrations. Milli-Q® ultrapure water (18.2 $\text{M}\Omega$)

was used in all experiments.

GO powder was purchased from Nanjing XFNANO Materials Tech. Co. Ltd (Nanjing, China). 0.5 mg/mL of GO aqueous solution was prepared by sonication at 250 W for 2 h. The resulting GO dispersion was centrifuged at 3000 rpm for 2 h by an Anke TGL-16G centrifuge (Shanghai, China). The supernatant of the centrifugation was collected and centrifuged at 8000 rpm for 2 h. The pellet from this centrifugation was collected and redispersed in DI water. The final concentration of the uniform GO solution was measured to be ~50 $\mu\text{g/mL}$ by a colorimetric method referring to a known GO solution.

2.2 Device Fabrication

The sensor fabrication process is schematically shown in Scheme. 1. Sensing device was microfabricated according to our previous report [41]. Each device contained five Au interdigitated electrode units, and each electrode unit consisted of ten pairs of fingers. The interdigitated electrodes were cleaned sequentially with acetone and piranha solution (a mixture of sulfuric acid and 30% hydrogen peroxide (3:1 v/v)) followed by DI water and drying with N_2 after each step, and then incubated with APTES for 30 min after which the electrodes were rapidly washed with plenty of DI water and dried with N_2 . Five μL of the GO solution was dropped onto the interdigitated electrodes for 1 h, which was kept in a high humidity container to prevent drying of the GO solution, followed by washing with DI water. During the process, GO sheets strongly assembled onto the bottom surface of the interdigitated electrodes gap and the electrode surface by the electrostatic interaction between carboxylic groups on the GO surface and amino groups of APTES. Excessive GO was removed by washing with DI water.

The assembled GO was reduced by a CHI 660D electrochemical workstation

(Shanghai, China) with a standard three electrodes system, where the interdigitated electrodes with the assembled GO was used as a working electrode (WE), a Pt wire as a counter electrode (CE), and an Ag/AgCl electrode as a reference electrode (RE). The electrochemical reduction was carried out in 100 mM PB (pH 7.4) through a linear sweep voltammetry at a potential ranging from 0 V to -1.5 V for seven cycles, at a scan rate of 100 mV/s. Subsequently, the interdigitated electrodes were annealed at 150 °C for 1 h in ambient air. The electrodes were further incubated with 6 mM PASE in dry dimethylformamide (DMF) for 30 min, washed with DMF and 10 mM PB (pH 7.4), and incubated with 500 nM aptamer solution for 2 h at room temperature. Then the electrodes were incubated with 100 mM ethanolamine (EA) for 1 h to passivate residual ester groups of PASE, and rinsed thoroughly with the PB. The resulting electrodes were maintained in 10 mM PB (pH 7.4) at 4°C. Here each functionalized interdigitated electrode unit was a sensing channel or a chemiresistive sensor.

A chemically derived RGO chemiresistive sensor was prepared using the same procedure as described above except that the assembled GO on the interdigitated electrodes was reduced chemically with hydrazine vapor at 60 °C for 12 h.[33]

2.3 Characterization

Morphological characterization of the interdigitated electrodes with the electrochemically derived RGO was performed with a Nova nanoSEM 450 scanning electron microscope (SEM) of FEI (Eindhoven, The Netherlands). Raman spectra of the GO and electrochemically and chemically derived RGO were obtained by a DXR Raman spectrometer (Thermo Fisher Scientific, USA) with an excitation wavelength of 532 nm. Transmission electron microscope (TEM) and atomic force microscope (AFM) images of the GO were obtained by a FEI Tecnai G2 20 and Molecular Imaging with PicoScan controller, respectively.

2.4 Sensing experiments

A 200 μL volume polydimethylsiloxane (PDMS) chamber, used to contain the measurement electrolyte solution, was attached onto the sensing channels of the device. The sensing channels were first exposed to 100 μL PB (10 mM, pH 7.4) through the chamber until the resistance of all the channels was stable. The drain current (I_{ds}) versus drain voltage (V_{ds}) or I_{ds} versus time (t) at a fixed V_{ds} were recorded in real-time with a CHI 660D electrochemical workstation 149 (Shanghai, China) as different concentrations of Hg^{2+} ion or other metal ions were added into the solution chamber.

2.5 Real samples analysis

Water samples analyzed included tap water from our laboratory and river water from Lingshui River, Dalian, China. Prior to analysis, water samples were filtered with a 0.22 μm membrane to remove large particles and then spiked with Hg^{2+} ion standard solution. Ten μL of spiked samples were added into the PB for measurements. To quantify Hg^{2+} ion concentration in the real samples, first a calibration curve between $(R-R_0)/R_0$ versus Hg^{2+} concentrations was obtained by a device which contained five same sensing channels, where R_0 and R were average resistances of the five channels before and after exposure to Hg^{2+} ion, respectively. Then the samples were analyzed by the device with the same procedure as above.

3. Results and discussion

The prepared GO was characterized by AFM and TEM, as shown in Fig. 1a and 1b. AFM images showed the topographic height of the GO was 1.0~1.2 nm, indicating the GO was monolayer according to the typical thickness of single-layer GO (~1.0 nm) [30]. The size of the GO sheets typically ranged from hundreds of nanometers to several micrometers, according to the scale bars in the AFM and TEM images.

GO is essentially insulating because of the high number of sp^3 bonds and rich content of carboxylic, hydroxyl and epoxy groups [42]. In this work a linear sweep voltammetry (LSV) method was used for the reduction of the assembled GO on the interdigitated electrodes. The original resistances of the channels between the electrodes that were on the order of tens of $G\Omega$ prior to the LSV reduction reduced to $\sim 120\text{ K}\Omega$ following the reduction. This decrease is attributed to the transformation of the assembled GO into conductive RGO, resulting in a conductive channel between the interdigitated electrodes. Annealing further improved the contact between the RGO and gold electrodes [41], resulting in further decrease in the resistance of the RGO channels. The detailed resistance data are shown in Table S1. Fig. 1C shows SEM of the interdigitated electrodes with the GO following the electrochemical reduction. As shown in the figure, the electrochemically derived RGO was mainly distributed on the bottom of the interdigitated electrodes gap while few large RGO sheets covered the gap and electrodes. The adjacent RGO at the electrodes gap contacted each other to bridge the interdigitated fingers.

The reduction of the assembled GO on the electrodes was also confirmed by Raman analysis. In general, RGO has a higher D/G peak intensity ratio (I_D/I_G) than that of GO [29], thus the I_D/I_G ratio could be used to differentiate GO and RGO and reflects the extent of GO reduction. Fig. 2 shows the Raman spectra of the adsorbed GO before and after the LSV reduction. Two characteristic peaks at 1600 cm^{-1} and 1340 cm^{-1} were observed, which corresponds to D and G bands of GO/RGO, respectively. The I_D/I_G ratio increased from 0.91 to 1.31 following the reduction, indicating a transformation from GO to RGO. Further, the results showed that the I_D/I_G ratio increased with increasing number of LSV cycles (Fig. 2), an indication the assembled GO was gradually changed to RGO, plateauing at seven cycles of LSV.

To compare between the reduction by LSV and the traditional chemical using hydrazine, we used one device prepared in the same batch following the assembly of GO for a chemical reduction. Results showed that the resistances of the chemically reduced GO channels were larger than those by the LSV, as shown in Table S1. Additionally, the RGO prepared by the hydrazine reduction achieved a lower I_D/I_G ratio than that of the RGO by the LSV (Table S1). These facts indicate that the LSV was more effective than the chemical method for the reduction of GO assembled on the interdigitated electrodes.

To perform Hg^{2+} ion sensing, RGO channel was functionalized with single-stranded DNA aptamer (5'-(NH₂)-TTCTTTCTTCCCCTTGTTTGT-3') which specifically capture Hg^{2+} ion by forming a rigid hairpin structure due to the strong coordination of the spatially separated thymine bases for Hg^{2+} ion. The aptamer immobilization on RGO was achieved through a bi-linker PASE that attached onto the RGO channel through π - π interaction between pyrene and RGO and single-stranded DNA aptamer by nucleophilic substitution of the succinimidyl ester group with the amine group of the aptamer [43]. The unreacted succinimidyl ester of PASE attached to RGO was neutralized with EA to prevent any nonspecific adsorption. Fig. 3A shows the curves of the drain current versus drain voltage (I_{ds} - V_{ds}) before and after the immobilization of the aptamer onto the RGO channel. The slope (I_{ds}/V_{ds}) of the plot, corresponding to the conductance of the channel, decreased following the immobilization of aptamer, which can be attributed to the electron transfer from the electron-rich nucleotide bases in the aptamer to the RGO [37]. In the presence of Hg^{2+} ion, there was a great increase in the conductance of the channel (Fig. 3A). This was because the positive charge of Hg^{2+} ion has an electrostatic effect on the RGO/solution interface, which forces the holes away from the RGO/solution interface and into the

p-type RGO channel, leading to an increase in carrier concentration in the channel and subsequently an increase in conductance [44]. Additionally, the aptamer/ Hg^{2+} ion interaction also weakened the electron transfer, contributing to the increase in conductance. Fig. 3B shows relative average resistance change $(R-R_0)/R_0$ of five electrically derived RGO channels in a chip after each modification step and exposure to Hg^{2+} ion. It can be seen that there was a great increase of $(R-R_0)/R_0$ value upon DNA modification and a definite decrease upon exposure to Hg^{2+} ion ($p < 0.05$).

Fig. 4A shows the real-time response of the RGO chemiresistor at a fixed drain voltage (V_{ds}) upon exposure to DI water and different concentrations Hg^{2+} ion. There was no change in the drain current (I_{ds}) after the addition of DI water. However, the sensor produced observable responses (ΔI_{ds}) upon exposure to Hg^{2+} ion, implying that the addition of Hg^{2+} ion resulted in increased channel conductance. The response time was ~ 50 s, which is longer compared to previous reports [34, 44]. The longer time was attributed to the use of a large solution chamber (200 μL) for detection, which results in a longer diffusion path from the liquid drop to the sensing channel. From the insert in Fig. 4a, it can be seen that 0.5 nM Hg^{2+} was definitely detected by the sensor (signal-to-noise: ~ 20), which is four-fold lower concentration than the maximum contaminant level (MCL) of 2 ppb enforced by the United States Environmental Protection Agency (EPA) for inorganic mercury in drinking water [45]. A calibration curve was obtained using the response signal (ΔI_{ds}) and Hg^{2+} ion concentrations ranging from 0.5 nM to 990 nM ($y=0.00161x - 0.0044$, $R^2=0.987$, Fig. S1). A control experiment was carried out using the electrochemically reduced GO whose RGO channel was not functionalized with the DNA aptamer. As shown in Fig. S2, there was no obvious response to Hg^{2+} ion concentrations below 5 nM. Higher Hg^{2+} ion concentrations resulted in small responses, but the sensitivity was far lower

than that of the aptamer-functionalized RGO chemiresistor biosensor. The responses may be attributed to the residual carboxylic groups of the RGO, which could bind Hg^{2+} ion, resulting in the increase of the channel conductance. This fact indicates that the response of the present RGO chemiresistor biosensor is mainly attributed to the binding of the immobilized aptamer to Hg^{2+} ion in a hairpin structure.

For a comparison, Fig. 4B shows the real-time response of the chemically reduced GO chemiresistive sensor upon exposure to Hg^{2+} ion. There was a linear relationship between the response and Hg^{2+} ion concentrations ranging from 5 nM to 1020 nM ($y=7.64\times10^{-4}x-0.0016$, $R^2=0.997$, Fig. S1). From the slopes of the two calibration equations, it can be seen that the electrochemically derived RGO chemiresistor biosensor was at least two times more sensitive than made from the chemically derived RGO. Furthermore, the former had a ten-fold lower the lowest concentration detected. The above superior analytical performance characteristics for the electrochemically derived RGO based sensor is attributed to a better reduction of the assembled GO by LSV.

To investigate the present sensor specificity, responses of the sensor to Hg^{2+} and other common metal ions in waters were measured. The drain current (I_{ds}) was monitored when the different metal ions were sequentially added into the solution chamber/reservoir. As shown in Fig. 5, no measurable change in the I_{ds} was observed when the sensor was exposed to 2.9 μM ~ 4.8 μM of Na^+ , K^+ , Li^+ , Cd^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Mg^{2+} , Cu^{2+} , Pb^{2+} , Ag^+ , Ca^{2+} or Fe^{3+} ions, respectively, and a ~0.5% increase in the I_{ds} was produced upon addition of 3.0 μM Mn^{2+} ion. However, when the sensor was further exposed to 100 nM Hg^{2+} ion, a very large increase, ~15.1%, of the I_{ds} was obtained. This response was far larger than that of other metal ions, including Mn^{2+} ion. A more detailed real-time response for the various metal ions tested is given in Fig. S3.

These results indicate that the sensor preferentially detected Hg^{2+} ion even in presence of other metal ions. The high selectivity of the sensor is attributed to the specific binding of the aptamer to Hg^{2+} ion by forming a rigid hairpin structure derived from the strong coordination of the thymine bases for Hg^{2+} ion, as shown in Scheme 1.

Table 1 compares the analytical performance of the present sensor to other reported FET or chemiresistive biosensors employing carbon nanostructures, i.e. graphene, RGO and single-walled carbon nanotubes (SWCNTs), as channel material for Hg^{2+} ion. The sensitivity of the present biosensor was comparable or better than most of previous reported biosensors, and had sensitivity necessary to detect Hg^{2+} for real-life applications considering the MCL value in drinking water and has high selectivity. Additionally, the EC reduction used in this work does not employ explosive gases such as methane and hydrogen at high temperature and/or low pressure required for growing graphene or reducing GO or toxic hydrazine; can be completed in less than 3 min compared to at least two hours required for growing CVD graphene and SWNTs or thermal and chemical reduction of GO. Further, the ssDNA aptamer biological recognition element is more stable and less oxygen sensitive and selective than metallothionein and thioglycolic acid [33, 42].

The effect of matrices in waters on the response was evaluated with Hg^{2+} ion spiked DI, tap, and river water samples. Fig. 6 shows relative resistance change $(R-R_0)/R_0$ of the sensor after exposure to 50 nM, 300 nM, 600 nM, and 1000 nM Hg^{2+} ion spiked water samples. As evidenced in the figure, the sensor had similar sensitivities for the three water samples with different matrices and good reproducibility (relative standard deviations (RSDs) of 3.8~10.6%). These results imply that the developed sensor is suitable for the detection of Hg^{2+} ion in real water samples.

The intra- and inter-batch reproducibility of the sensor fabrication was evaluated. Three sensing devices were prepared in one batch (each device contained five same sensing channels, i.e. sensors) to detect Hg^{2+} ion at 50 nM, 300 nM, and 1000 nM concentrations in DI water. The largest RSDs of five sensors within one device were 14.9%, 8.0%, and 8.4% for the samples while the RSDs between the devices were 17.1%, 4.2%, and 4.0%. Furthermore, three devices were prepared in different batches and evaluated. The RSDs between the devices were 17.2%, 11.1%, and 13.7% for the samples. Considering the devices were handmade, the data showed that the sensing devices could be fabricated repeatedly by the described protocol.

To evaluate the applicability of the present method for practical applications, the RGO sensor was applied to detect Hg^{2+} ion in tap water and river water. Water samples collected were filtered to remove any large suspended particles before usage. The initial detection showed no presence of Hg^{2+} ion in the samples. In this case, Hg^{2+} standard solution was spiked in the samples with the final concentrations of 50 nM and 600 nM, and then detected by the sensor. The recoveries ranged from 98.6~116.7% and the RSDs ranged from 3.4% to 10.4% (Table 2). This shows the competence of the proposed sensor for the analysis of real samples.

4. Conclusion

In conclusion, we have fabricated an electrochemically reduced GO chemiresistive sensor for sensitive and specific detection of Hg^{2+} ion in water samples. The sensing channel of the sensor consisted of electrochemically reduced GO functionalized with single-stranded DNA aptamer. The sensor showed selective response to Hg^{2+} ion in presence of other metal ions, with the lowest detected concentration being 0.5 nM. There were no obvious differences for the detection of Hg^{2+} ion in presence of

different matrixes (DI, tap, and river waters). The sensor fabrication was facile, safe and had good intra and inter batch reproducibility. Compared with the chemically reduced GO chemiresistor, the present electrochemically reduced GO chemiresistor showed better response performance for sensing Hg^{2+} ion. Overall, the proposed method provides a powerful platform for rapid and sensitive analysis of Hg^{2+} ion in water samples.

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Notes

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Figure captions

Scheme 1 Schematic diagrams of the electrically derived RGO chemiresistive sensor fabrication

Fig. 1 AFM (A) and TEM (B) of the GO sheets and SEM (C) of the interdigitated electrodes with electrically derived RGO

Fig. 2. Raman spectra of the adsorbed GO on the IEs following different LSV scans; a: GO without LSV scan; b: GO with 3 LSV scans; c: GO with 7 LSV scans; d: GO with 10 LSV scans.

Fig. 3. (A) $I_{ds}-V_{ds}$ characteristics of one electrically derived RGO chemiresistor in 10 mM PB (pH 7.4) (1) electrochemically derived RGO; (2) after PASE modification; (3) after ssDNA aptamer immobilization; (4) after blocking with EA; and (5) after exposure to 450 nM of Hg^{2+} ion. (B) Relative average resistance change $(R-R_0)/R_0$ of five channels in a chip after each modification, where R_0 is the initial resistance of the channels, and R is the resistance of the channels after each modification ($p < 0.05$ at 95% confidence interval).

Fig. 4 Real-time response of the electrically derived RGO chemiresistor (A) and chemically derived RGO chemiresistor (B) biosensors upon exposure to different concentrations Hg^{2+} ion ($V_{ds} = 0.1$ V). The concentrations shown in the figures are the cumulative concentrations after sequential addition of Hg^{2+} ion.

Fig. 5 Responses of the electrically derived RGO chemiresistor ($V_{ds} = 0.1$ V) to Hg^{2+}

ion (100 nM) and other metal ions including Na^+ , K^+ , Li^+ , Cd^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Mg^{2+} , Cu^{2+} , Pb^{2+} , Ag^+ , Ca^{2+} , Mn^{2+} and Fe^{3+} ions (final concentrations: $2.9\text{ }\mu\text{M} \sim 4.8\text{ }\mu\text{M}$).

Fig. 6 Response of the ERGO chemiresistor to Hg^{2+} ion spiked samples. R_0 is the initial resistance of the channels, and R is the resistance of the channels after exposure to the samples, respectively.

Table 1 Analytical performance of carbon nanomaterials based FET or chemiresistive Hg^{2+} ion biosensors

Detection method	Sensing material	Recognition element	Sample	LOD ¹ or LCD ² (nM)	Ref.
chemiresistor	SWCNT	PolyT oligonucleotide	Water	100 ²	[19]
chemiresistor	SWCNT	PolyT oligonucleotide	Saliva	0.5 ²	[46]
FET	Thermally reduced GO	Thioglycolic acid	Water	25 ²	[34]
FET	Graphene prepared by CVD	DNA aptamer	Mussel	0.01 ²	[44]
FET	Chemically reduced GO	Metallothionein	Water	1 ²	[33]
FET	GO	DNA aptamer	Water	25 ¹	[47]
FET	Chemically reduced GO	polyfuran	/	0.01 ¹	[48]
ASV+DPV	GO-IL-Au nanoparticles	/	Water	0.03 ¹	[49]
DPV	ITO/-GO-Au nanoparticles	5-methyl-2-Thiouracil	Water	1 ¹	[50]
CV, SWV	Graphene-Au nanoparticle	ssDNA	Water	0.001 aM ¹	[16]
CV, impedance	GO	ssDNA		1 ¹	[51]
CV	Chemically reduced GO	ssDNA	Water	1 ¹	[52]
chemiresistor	Electrically	DNA aptamer	Water	0.5 ²	This

reduced GO	work
<p>Abbreviations: ASV-anodic stripping voltammetry; DPV-differential pulse voltammetry; IL-ionic liquid; ITO-indium tin oxide; CV-cyclic voltammogram; SWV-square wave voltammogram; ssDNA-single-stranded DNA.</p> <p>LOD¹-detection limit, which is based on a signal-to-noise ratio of 3σ; LCD²-lowest detected concentration, which the concentration which can be definitely detected and quantified by the sensor.</p>	

Table 2 Analytical results of spiked real water samples by the proposed method (n = 4~5). The original concentrations were measured by inductively coupled plasma mass spectrometry (ICPMS)

Samples	Original Conc.	Spiked (nM)	Determined (nM)	Recovery (%)	<i>RSD</i> (%)
Tap water	nd	50	49.3	98.6	3.4
	nd	600	671.3	111.9	10.4
River water	nd	50	45.27	90.5	0.8
	nd	600	700.59	116.7	8.4

nd: not found

Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6