RESEARCH ARTICLE

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The morphology modulation of graphene to produce wrinkles and folds for effective electrochemical determination of Hg(II)

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Abstract

A highly efficient electrode material, three-dimensional reduced graphene oxide with varying wrinkles and folds (WRGO), applicable for electrochemical determination of Hg(II) was obtained by treating graphene oxide (GO) with KOH aqueous solution. After alkaline etching, the relatively flat graphene was altered and its self-aggregation was significantly alleviated, producing more wrinkles and folds, which provided more active adsorption sites for heavy metal ions. WRGO-5 modified electrode system herein offers a highest sensitivity of (31.83 μ A μ M⁻¹) and a lowest LOD of (16.28 nM). Moreover, the electrode sensor possesses good stability and reproducibility.

K E Y W O R D S

alkaline etching, electrochemical determination, graphene, Hg(II)

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1 | INTRODUCTION

Inorganic mercury (Hg(II)) is considered to be a toxic heavy metal ions (HMI) in nature due to its bio-accumulative property and carcinogenicity on human health [1]. Exposure to mercury which mainly comes from chemicals, batteries, fossil fuel, and the metallurgical industry can bring about severe damage to human brains, kidneys, lungs, and other organs [2]. In addition, Hg(II) in the environment is easier to transform organic mercury (methylmercury, alkylmercury, etc.) with higher toxicity [3]. If the concentration of Hg(II) in drinking water exceeds 30.0 nM, it will not be allowed by the World Health Organization (WHO). Hence, the rapid and effective detection of Hg(II) in the environment is extremely urgent. Nowadays electrochemical analysis method has shown its unique advantages in the field of HMI detection with high sensitivity, stability and low-cost [4]. In this direction, a great deal of effort have been dedicated towards the development of materials from noble metal nanoparticles [5] to transition metal oxides [6] and carbon materials [7] and the like.

Graphene, a two-dimensional and sp²-hybridized honeycomb structure exhibiting excellent chemical and physical properties has been widely used in the field of energy storage materials [8], supercapacitors [9], new energy batteries [10] and sensors [11], etc. In recent years, graphene-based nanomaterials have been widely studied and applied in electrochemical determination [12], such as noble metal particles (Au [13], Pt [14]), metal oxide [15], ILs [16] and DNA [17]), etc. However, the complex synthesis procedure and relatively high cost for the synthesis of nanocomposites restrict their applicability for electrochemical analysis to some degree in natural water resources.

Instead, the intrinsic modification of graphene itself seems to be an effective way of changing the properties of graphene. To the best of our knowledge, three-dimensional (3D) graphene materials have higher surface activity and mass transfer rates than two-dimensional (2D) graphene nanosheets, which may increase their potential for applications in various fields [18]. In particular, the three-dimensional wrinkling produced by chemically synthesized graphene to overcome the thermodynamic instability of a perfect two-dimensional crystal can reduce the surface free energy and stabilize it. Meanwhile, this wrinkling behavior has an effect on the electrical and catalytic properties of graphene. The generated wrinkles make the specific surface area of graphene increases, providing more fully exposed active sites for the target pollutant molecules [19]. From the other side, the three-dimensional crumpling of graphene generates a

large number of pore structures, which are beneficial to accelerate the mass transfer rate of the reaction system [20]. Lin et al. [21] achieved the manipulation of the electron transport properties of graphene-based nanocomposites by adjusting the wrinkles on the three-dimensional graphene architecture. Wang et al. [22] investigated the relationship between surface morphology and adsorption performance using graphene nanosheets with different fold degrees as adsorbents. It was further determined that the adsorption process is controlled by the pore filling mechanism. In recent years, a large amount of research work has been devoted to 3D network graphene materials in the field of adsorption and energy storage, and little has been reported about their application in the electrochemical determination analysis of HMI.

Therefore, the graphene with different degree of wrinkles were synthesized by one-step solvothermal method in the experiment for exploring the electrochemical behavior of Hg(II). Herein, hydrazine hydrate is used as a reducing agent, and KOH is used as an "etching source", which tunes the surface morphology of graphene. Then, these nanostructured materials were used as modifiers to construct electrochemical sensing interfaces for electrochemical analysis of Hg(II). The relevant parameters of the electrochemical experiments were optimized and the electrochemical behavior of Hg-(II) on graphene-modified electrodes with different fold degrees was investigated. In addition, the effect of common heavy metal cations in the aqueous environment on the electrochemical signal of inorganic mercury was examined. Finally, the stability of the constructed sensors was evaluated and their reliability in real water environment was explored.

2 | EXPERIMENTAL

2.1 | Chemicals

Graphite powders, ethanol, potassium hydroxide (KOH), hydrazine hydrate (H₄N₂), mercury nitrate (Hg(NO₃)₂), cadmium chloride (CdCl₂), lead nitrate (Pb(NO₃)₂), copper sulfate (CuSO₄), sodium acetate anhydrous (NaC₂H₃O₂), acetic acid (C₂H₄O₂), disodium hydrogen phosphate dodecahydrate (Na₂HPO₄), sodium dihydrogen phosphate dehydrate (NaH₂PO₄), trisodium citrate dihydrate (Na₃C₆H₅O₇), citric acid monohydrate (C₆H₈O₇) were purchased form Sinopharm Chemical Reagent Co. Ltd. To protect researchers, protective suits, activated carbon masks and rubber gloves were worn during the experiment.

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2.2 | Synthesis of WRGO-x

GO was obtained from flake graphite powders by the advanced Hummers' method [23]. The synthesis of WRGOx nanomaterial was carried out by the hydrothermal method. First of all, 50 mg of as-prepared GO powder was added to 80 mL ethanol solution and ultrasonicated for 30 min. In order to prepare reduced graphene oxide varying wrinkles and folds, different masses of KOH (0, 50, 250 or 500 mg) were added to the above suspensions and 4 mL of H_4N_2 was added after complete dissolution. After sufficient stirring, it was transferred to an autoclave containing Teflon lined and kept in an oven at 180°C for 18 h. Then, the reaction products were collected and washed three times successively with ethanol and deionized water. Finally, the ultimate modifier was obtained after drying at 60°C for 24 h and named as WRGO-x (x represents the mass ratio of KOH to GO, x = 0, 1, 5, 10). Among them, WRGO-0 was prepared without the addition of KOH in the subsequent experiments as a control group.

2.3 | Structural characterization of WRGO-x

The morphology of WRGO were collected on the field emission scanning electron microscopy (FESEM, Quanta 200 FEG, FEI Company, USA) at 10 kV. Transmission electron microscopy (TEM) was carried out in a JEM-2100F at 200 kV accelerating voltage. The surface roughness of graphene was examined by Atomic force microscopy (AFM) (Dimension Icon, Bruker). Raman spectra was done on a LabRam HR Evolution (Horiba Jobin Yvon) at a wavelength 532 nm. The X-ray photoelectron spectroscopy (XPS) were recorded on ESCALAB250Xi (USA) in binding energy range of 100 eV~1200 eV. Fourier transform infrared spectroscopy (FTIR) were performed in Nicolet IS50 iN10 (USA). The pore size and specific surface area of the prepared materials were obtained by the Brunauer-Emmett-Teller (BET) method using Autosorb-IQ3 (Quantachrome, USA) at 77K. The ζ potential of the materials was characterized by Zetasizer Nano ZS90 (Britain) and using ultrapure water as solvent.

2.4 | Assessment and preparation of the modified electrode

In the work, electrochemical workstation (CHI760E) was used for all electrochemical measurements. The electrochemical sensor was constructed using a conventional three-electrode system (working electrode: modified glassy carbon electrode; counter electrode: Pt wire; reference electrode: Ag/AgCl). The bare GCE was continuously polished with alumina powder slurries with different particle sizes to a mirror shiny surface before modification. Then ultrasonicated in dilute nitric acid solution, ethanol solution and deionized water for 2 min, respectively, getting rid of any adsorbed impurity on the electrode surface. The well-dispersed WRGO-x suspension was modified on the GCE surface by drop coating and dried at room temperature.

3 | RESULTS AND DISCUSSION

3.1 | Morphologic and structural characterization of WRGO-x

From the Figure 1, TEM images show the microstructures of the as-prepared samples. It can be found that the WRGO-0 (without KOH treatment) revealed the relatively flat surface (Figure 1a). Figure 1b-d shows the respective typical TEM images of WRGO-x with tuning KOH. In contrast, more wrinkles and porous structures were observed in the morphology of WRGO with the increase of KOH, indicating that the KOH dosage has an important role in adjusting the morphology of WRGO. The more KOH, the more serious the wrinkled graphene nanosheet. It was due to the fierce etching of KOH during the whole reaction process [24]. The surface roughness of the prepared material was recorded using AFM and its wrinkling degree was evaluated based on root mean square (RMS) analysis [25]. Figure S1a-d represents the two-dimensional image of WRGO-x. The RMS roughness of the WRGO-0 was approximately 1.45 ± 0.25 nm, lower than



FIGURE 1 TEM images of the synthesized WRGO-0 (a), WRGO-1 (b), WRGO-5 (c) and WRGO-10 (d) samples.

WRGO-1 (2.44 \pm 0.23 nm), WRGO-5 (3.86 \pm 0.18 nm) and WRGO-10 (5.31 \pm 0.32 nm), which shows the same characteristics as the TEM results.

Generally, the defects of carbon materials are characterized by Raman spectroscopy. Among them, typical graphene Raman peaks include the D-band arising from defects and the G-band caused by in-plane stretching vibrations of sp² carbon atoms. The defect density of graphene is proportional to the intensity ratio of the D peak to the G peak (I_D/I_G) . From Figure 2a, the peaks located at 1350 cm⁻¹ and 1593 cm⁻¹ in WRGO-x were assigned to D peak and G peak, respectively. The I_D/I_G values of the WRGO-0, WRGO-1, WRGO-5, and WRGO-10 were 1.22, 1.15, 1.11 and 1.07, respectively. Obviously, the I_D/I_G value decreases with the increase of the wrinkle degree of graphene [26]. It is found that the reduced graphene oxide varying wrinkles and folds has a smaller size and lower lattice defects compared with ideal graphene. The near-surface functional groups of WRGOx were characterized by FTIR spectroscopy. It can be found that there is no significant difference in the surface chemical states of graphene samples with the change of wrinking and



FIGURE 2 Raman (a) and FTIR (b) spectra of WRGO-0, WRGO-1, WRGO-5, and WRGO-10 samples.

folding degree (Figure 2b). The broadband at 3410 cm^{-1} was attribute to the stretching vibration of O–H. The peak at 1560 cm⁻¹ was related to the C=C skeleton vibrations, and the peaks at 1180 and 1389 cm⁻¹ were bound up with the stretching vibration of C–O, and O–C=O [27].

The surface functional groups of WRGO-x were investigated by XPS analysis. As shown in the Figure S2, the peaks of C1s, N1s, and O1s were observed in XPS spectra, and all samples have a similar distribution of surface functional groups, which agree well with FTIR analysis. Deconvolution of the C1s peak of WRGO-x resolves to the main peak at 284.80 eV, which corresponds to the presence of C=C/C-C. The peaks at 285.83 eV, 286.78 eV and 288.03 eV correlated to C-N, C=O/C-O, and O–C=O, respectively [27-28]. Here, the C–N groups were originated from hydrazine hydrate in the synthesis of modified graphene. In addition, the content of C=C/ C-C was much higher than C-N, C=O/C-O, and O-C=O, demonstrating that most functional groups have been removed under the chemical reaction process (Figure S3).

The pore properties of the prepared graphene materials were described by N2 adsorption-desorption experiments. The specific surface areas of WRGO-0, WRGO-1, WRGO-5 and WRGO-10 were 60.56 m²g⁻¹, 59.06 m²g⁻¹, 40.70 m^2g^{-1} and 31.49 m^2g^{-1} , respectively. This indicated that the addition of KOH did not destroy the large specific surface area of GO nanosheets, and the slight decrease of the specific surface area might be due to the transfer of large and mesopores to small wrinkles or micropores. This conclusion was verified by the four kinds of etched graphene micropore size distribution. As can be seen in the Figure 3a, a sharp peak appears at 3.8 nm, while a new main peak appears at 1.5 nm after KOH treatment. The strength of the original mesopore peak is reduced, indicating that mesopore formed by large ripples on the graphene is transferred to small wrinkles or micropores.

The ζ -potential of the material is influenced by the surface charge, and can be used to predict the adsorption properties of the composite material to ions in solution. Zeta potential analyzer was used to measure the ζ potential of the material at different pH values (Figure 3b). Obviously, the surface charge of WRGO material has different positive and negative properties at different pH values. In the range of pH 4~8, the surface charge of graphene composite material changes from a positive value to negative value with the increase of pH value, which has an advantage in cation adsorption. Under the same weak acidic conditions, WRGO-5 had the smallest ζ potential and showed the strongest adsorption capacity to cations.



FIGURE 3 Pore size distribution (a) and pH-Zeta potential curve (b) of WRGO-0, WRGO-1, WRGO-5, and WRGO-10 samples.

3.2 | Electrochemical behavior of WRGO-x modified electrode

The surface electron transfer capability of the WRGO-x GCE was evaluated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in 0.1 M KCl containing 5 mM $Fe(CN_6)^{3^{-/4^{-}}}$. From the CV diagram (Figure S4a), it can be found that the anode and cathode peak currents of bare GCE and its symmetry were greater than WRGO-x modified GCE, which is due to the thick film deposited on the electrode surface that prevents electron transfer. Specifically, increasing the amount of KOH is beneficial to increase the redox peak current. Note that when the addition amount of KOH reached 250 mg, the fabricated WRGO-5 present the maximum peak current. However, the redox peaks became worse accordingly as KOH amount was further added. Meanwhile, EIS was used to analyze the electrochemical reaction kinetic parameters on the electrode surface by interfacial impedance. As in figure S4b, the impedance curve of the high frequency band has a semicircle shape with a radius equal to half of the electron transfer resistance. And the straight line in the low frequency demonstrates the diffusion control process. The

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data show that the bare GCE has the smallest electron transfer resistance (the R_{et} was about 90 Ω). And the R_{et} of WRGO-x modified GCE were increased, which indicates that the modified material has been successfully attached to the electrode surface. The R_{et} of WRGO-0, WRGO-1, WRGO-5, and WRGO-10 were approximately 600, 500, 200 and 300 Ω , respectively. Compared to other modified electrodes, WRGO-5 GCE shows the lowest Ret, which is due to the pore channels generated by suitable folds that facilitate the electron transfer rate and mass transfer process. This result is consistent with CV.

The effect of scan rate on the WRGO-x modified GCE were also studied in 5 mM $Fe(CN_6)^{3-/4-}$ redox probe (Figure S5a-d). These data show that the peak currents of the redox reaction indeed rise with scan rate. In the relationship between peak current and scan rate (Figure S6a-d), the anodic peak current (I_{na}) and cathodic peak current (I_{pc}) are linearly related to the square root of scan rate. The linear regression equations of the WRGO-5 modified GCE was I_{pa} (μA) = 7.06 $v^{1/2}$ $(mVs^{-1})^{1/2}$ +4.40 (R²=0.999) and I_{va} (μA) = -7.06v^{1/2} $(mVs^{-1})^{1/2}$ -4.40 (R²=0.999), respectively. The curve between the scan rate and the peak current indicates that the redox process on the WRGO-x modified GCE surface is a diffusion-controlled electrode process. Also of note is that the slope of linear regression equations changes with the folding degree of graphene, WRGO-5 reaches the maximum value. The results were consistent with the CV and EIS data.

3.3 | Electrochemical responses of different electrodes to Hg(II)

To investigate the efficacy of different electrodes, the bare GCE and WRGO-x/GCE was selected to detect known spiked Hg(II) solutions. The Figure 4a shows electrochemical response current of different electrodes towards 1.0 µM Hg(II). The stripping current of WRGOx/GCE is dramatically greater than that of bare GCE, which implies that WRGO-x was beneficial to promote the adsorption for Hg(II) in the accumulation step. This can be attributed to the superiority of the material, intrinsic modification of graphene. In addition, the peak current gradually increased, then decreased with the increase of the mass ratio of KOH and graphene. Among all WRGO-x/GCE, WRGO-5/GCE showed the highest response current (Figure 4b). It can be concluded that the increase of KOH greatly changed the intrinsic properties of graphene, making graphene a more wrinkled, larger specific surface area, which can be further explained by SEM, TEM and AFM analysis. In the study, we used WRGO-5 for all subsequent studies.



FIGURE 4 SWASV responses (a) and comparison of peak currents (b) for 1.0 μ M Hg(II) on the bare GCE and graphene samples (WRGO-0, WRGO-1, WRGO-5, and WRGO-10) modified GCE in NaAc-HAc (pH = 5.0).

3.4 | Optimization of experimental conditions

The experimental parameters such as supporting electrolyte, pH, deposition potential and deposition time were optimized, where the Hg(II) addition concentration was always 1.0 µM. The optimization experiment follows the principle of the single variable. The Figure S7a displays the electrochemical behavior of Hg(II) at pH = 5.0 in acetate buffer solution (0.1 M HAc-NaAc), phosphate buffer saline (0.1 M), and citrate buffer solution (0.1 M), respectively. The deposition potential and time were set at -1.0 V and 150 s. It is obvious that the highest stripping peak of Hg(II) was shown in the HAc-NaAc buffer. Therefore, 0.1 M HAc-NaAc was employed in the next experiments. The effect of pH $(3.0 \sim 7.0)$ on the Hg(II) detection signal was investigated. From the Figure S7 (b), when pH is less than 5.0, the response current of Hg(II) increases with increasing pH. It started to decrease after reaching a maximum value at pH = 5.0. Too low or high pH value will affect the electrochemical reaction process on the electrode surface. At lower pH

values, high concentrations of hydrogen ions compete with Hg(II) on the electrode surface. When pH exceeded 5.0, the formation of hydroxide complexes by hydrolysis of Hg may precipitate on the electrode surface, resulting in lower stripping current [29]. Thus, 0.1 M HAc-NaAc (pH = 5.0) was selected for the work. The optimal deposition potential for the sample modified electrode was examined in 0.1 M HAc-NaAc (pH = 5.0). The deposition potential at the modified electrode was changed between -1.3 and -0.7 V, as shown in the Figure S7c. As the stripping peak current for Hg(II) increased, and reached a maximum at potential -1.0 V. However, when the deposition potential exceeded -1.0, the peak current became unstable and reduced somewhat. As the potential becoming more negative, the hydrogen evolution reaction would have occurred [30] on the surface of WRGO-x modified GCE, which might affect the whole experimental process. Thus, the potential at -1.0 V was chosen. Finally, the deposition time from the 60 s to 240 s was studied in the work (Figure S7d), the peak current of Hg(II) increased with the time-varying 30 to 150 s, and the trend of subsequent growth was slow or even unchanged, which may be due to the surface saturation at high Hg(II) concentration. Therefore, the 150 s were chosen as the optimal deposition time throughout the experiment for considering the efficiency. According to the above discussion, the following optimized experimental conditions were set to 0.1 M NaHc-HAc (pH = 5.0), deposition potential -1.0 V and time 150 s.

3.5 | Electrochemical detection of Hg(II) with WRGO-5 modified GCE

Under the optimum condition, Hg(II) was electrochemically determined by SWASV using WRGO-5 nanomaterials modified GCE at a series of concentrations varying 0.5 to $1.6 \,\mu$ M. Figure 5a showed that the plot of voltammetric stripping peak current vs. Hg-(II) concentration. It can be observed that the current peak appearing at potential of 0.28 V is denoted as Hg-(II), and its intensity increases with increasing Hg(II) concentration. From the Figure 5b, the corresponding linear equation was Y (μ A) = 31.83X (μ M)-16.69, with a high correlation coefficient of 0.998. where X is the concentration of Hg(II) and Y is the current response. The sensitivity of the WRGO-5/GCE was 31.83 µA μM^{-1} , and the calculated limit of detection (LOD) of Hg(II) was 16.28 nM at a signal to noise 3 (3σ method [31]). The Figure S8 displayed the results of the other samples (WRGO-0, WRGO-1, and WRGO-10) for detection of Hg(II). The sensitivities of the WRGO-x GCE followed modified the order: WRGO-0

 $\begin{array}{ll} (18.61 \ \mu A \mu M^{-1}) < WRGO-1 & (25.85 \ \mu A \mu M^{-1}) < WRGO-10 & (28.00 \ \mu A \mu M^{-1}) < WRGO-5(31.83 \ \mu A \mu M^{-1}). & The electrochemical performance of the materials prepared by adding KOH was better than that of the raw$



FIGURE 5 Typical SWASV signals of Hg(II) (a) and the corresponding calibration plot (b) on a WRGO-5 modified GCE under optimized conditions.

graphene material. This is due to the relatively high atomic and electron density at the wrinkles and folds of graphene, which facilitates the enhancement of the preenrichment process of heavy metal ions [32]. When x < 5, the sensitivity of Hg(II) enhanced with the increment of KOH amount, proper KOH made wrinkles and folds during the preparation process to form more active reaction sites. The maximum value is reached at x = 5, which shows a more saturated degree of graphene folding towards Hg(II). When the surface folds and defects of the graphene were further increased, which might be not suitable for Hg(II) determination, accounting for the decrease of the electrochemical in properties of WRGO-10/GCE. The relative results were good agreement with the Figure S6. The detection performance of electrochemical sensors for Hg(II) using other modified materials were summarized in Table 1. As shown in Table S1, a comparative overview of analytical performance data with other methods in the literature. It can be concluded that the graphene with surface wrinkles modified electrode system offers excellent sensitivity and LOD compared to other methods.

3.6 | Interference

The interfering effect of other cations were examined by WRGO-5 modified GCE sensor. Figure 6a–c showed the individual interfering effect towards Hg(II), and the concentration of single additions of foreign metal ions were all fixed at $0.5 \,\mu$ M. Figure 6d showed the simultaneous effect of three interfering ions (Cd(II), Pb(II), and Cu(II) were fixed at $1.0 \,\mu$ M, $1.0 \,\mu$ M and $0.5 \,\mu$ M, respectively. The stripping of Cd(II), Pb(II), and Cu(II) on WRGO-5 electrode appeared at -0.80, -0.60 and $-0.10 \,$ V,

TABLE 1 Comparison of the detection performance of electrochemical sensors for Hg(II) using other modified materials.

Electrodes	Linear range (µM)	Sensitivity (μΑμΜ ⁻¹)	LOD (nM)	Correlation coefficient	Ref.
rGO-Fe ₃ O ₄ /GCE	0.4~1.8	24.19	4	0.997	[15a]
MoS ₂ /rGO/GCE	0.4~2.0	9.76	90	0.998	[33]
MnFe ₂ O ₄ /GCE	1.0~3.0	3.70	-	0.991	[34]
Chitosan-CPE	1.0~38.5	1.27	628	0.999	[35]
MnFe ₂ O ₄ @Cys/GCE	1.4~3.0	11.7	208	0.996	[36]
[Ru(bpy) ₃] ²⁺ /GO/Au	0.1~1.2	3.71	350.2	0.950	[37]
Nanoplate-stacked Fe ₃ O ₄ / GCE	1.0~8.0	5.48	521	0.990	[38]
NH ₂ -CMS/GCE	1.0~1.9	29.08	370	0.943	[39]
WRGO-5/GCE	0.5~1.6	31.83	16.28	0.998	Present work

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respectively. The relative sensitivity of the WRGO-5 electrode sensor decreased to some degree under individual and simultaneous interfering effect comparing to the result without interference. The reduced sensitivity of WRGO-5 GCE towards Hg(II) may be attributed to the formation of amalgam on the electrode surface or to the competition between interfering metal ions for active sites during the enrichment of HMI. In addition, the response signal of the interfering cation gradually increased with the adding concentration of Hg(II), which attributed to the generation of the thin Hg film on the electrode surface. In the past any Hg film or Hg-electrodes were used widely broadly in the field of electrochemical detection to enhance the capability of detecting heavy metal ions. However, these electrodes are harmful to the environment and should be banned [40]. It is noteworthy that the peak shape and correlation coefficient of Hg(II) still remain excellent under single interference and simultaneous interference (The relative fitting data were shown in Figure S9). Furthermore, the interference test of the proposed electrode toward Hg(II) with other coexisting ions, such as As(III), Bi(III),

Fe(III), Fe(II), Mn(II), Ni(II), Zn(II) was investigated (Figure S10). The results show that most of these metal ions do not interfere with the detection of mercury, and the interference rate is less than 10%.

3.7 | Stability of the WRGO-5 modified GCE

The stability of WRGO-5 modified electrode for the detection of Hg(II) was examined. Here, electrochemical detection of 1.0 μ M spiked Hg(II) was carried out in the fifteenth cycles using the same WRGO-5 modified electrode. Multiple measurement data show no significant difference in response current, and the relative standard deviation (RSD) was 1.28% (Figure S11a). On the other side, the reproducibility measurements were implemented for the same Hg(II) concentration (1.0 μ M) using six different WRGO-5 modified electrodes (No. E1-E6). A comparison of the electrochemical signal intensity of Hg(II) on the six modified electrodes is shown in Figure S11b, and the RSD was calculated as 3.31%.



FIGURE 6 SWASV responses of the WRGO-5/GCE towards Hg(II) with the interfering ions (a) 0.5 μM Cd(II), (b) 0.5 μM Pb(II), (c) 0.5 μM Cu(II) and (d) 1.0 μM Cd(II), 1.0 μM Pb(II) and 0.5 μM Cu(II) simultaneously.

The RSD of stability and reproducibility measurement were less than 5.00%, which was allowed. Therefore, the WRGO-5 modified electrode possesses excellent stability and reproducibility, which provide useful support for the helpful electrochemical analysis of Hg(II) in the practical water sample.

3.8 | Spiked water analysis

To determine the potential applications of the newly developed sensor, its reliability was evaluated by detection of mercury concentrations in real water samples. Water samples were collected from Hubing pond water (HeFei University of technology, China). The samples were filtered and acidified to pH = 5.0 using NaAc-HAc buffer. There was no electrochemical signal obtained for Hg(II) in water sample. Hence, The recoveries of Hg(II) in lake water samples were determined by the standard addition method (Figure S12). In the concentration range of 0.5–1.0 μ M, the recoveries of the spiked water sample was in the range of 96.3 to 106.4%, and the RSD was between 1.59 and 3.58% (Table S2). Therefore, WRGO-5 modified electrode can be effectively employed in inorganic mercury monitoring of environmental samples.

4 | CONCLUSION

Here, graphene varying wrinkles were prepared by onestep facile thermally treated with KOH, which was used to modify the glass carbon electrode (GCE) for electrochemical detection of inorganic mercury ion (Hg(II)). Graphene morphology alternation creates more wrinkles and folds with a large surface area and more adsorption for Hg(II). The effects of KOH amount on the morphology and electrocatalytic properties of reduced graphene oxide were investigated. The different experimental parameters such as supporting electrolyte, pH, deposition potential and deposition time that exert an effect on the signal response at the sensing interface were optimized. With the participation of tuning concentration of KOH (the quality ratio of GO and KOH is 1:5), the obtained WRGO-5 was endowed with the highest response of Hg-(II) with 31.83 $\mu A\mu M^{-1}$ sensitivity and 16.28 nM detection limit. This improvement was attributed to the structural defects produced by KOH etching, which increases the active sites of graphene and accompanied enlarged specific surface area of the resultant nanostructure material. Simultaneously, the WRGO-5/GCE was demonstrates high stability and reproducibility for the electrochemical detection of Hg(II). The surface morphology modulation of graphene might be an effective way to enrich its

properties and provide a promising prospect for the design of new sensor materials in the application field of electrochemical Hg(II) detection.

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CONFLICT OF INTEREST STATEMENT The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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REFERENCES

- a) D. Obrist, J. L. Kirk, L. Zhang, E. M. Sunderland, M. Jiskra, N. E. Selin, *Ambio* **2018**, *47*, 116–140; b) G. Bjorklund, M. Dadar, J. Mutter, J. Aaseth, *Enviro Res.* **2017**, *159*, 545–554.
- S. S. Ghasemi, M. Hadavifar, B. Maleki, E. Mohammadnia, J Water Process Eng. 2019, 32, 100965.
- a) H. H. Harris, I. J. Pickering, G. N. George, *Sci. J.* 2003, 301, 1203; b) J. Aaseth, B. Hilt, G. Bjørklund, *Enviro Res.* 2018, 164, 65–69; c) T. Syversen, P. Kaur, *J. Trace Elem. Med. Biol.* 2012, 26, 215–226.
- L. Li, Y. Qiu, Y. Feng, Y. Li, K. Wu, L. Zhu, J. Electroanal. Chem. 2020, 865, 114121.
- J. Gong, T. Zhou, D. Song, L. Zhang, X. Hu, Anal. Chem. 2010, 82, 567–573.
- a) M. Fayazi, M. A. Taher, D. Afzali, A. Mostafavi, Sens. Actuators B 2016, 228, 1–9; b) B. Maleki, M. Baghayeri, M. Ghanei-Motlagh, F. Mohammadi Zonoz, A. Amiri, F. Hajizadeh, A. Hosseinifar, E. Esmaeilnezhad, Measurement 2019, 140, 81–88; c) M. Baghayeri, A. Amiri, B. Maleki, Z. Alizadeh, O. Reiser, Sens. Actuators B 2018, 273, 1442–1450.
- 7. A. K. Wanekaya, Analyst 2011, 136, 4383-4391.
- M. Mehrali, S. T. Latibari, M. Mehrali, T. M. Indra Mahlia, H. S. Cornelis Metselaar, *Energy* 2013, *58*, 628–634.
- Y. Wang, Z. Shi, Y. Huang, Y. Ma, C. Wang, M. Chen, Y. Chen, J. Phys. Chem. C 2009, 113, 13103–13107.
- Z. Yin, J. Zhu, Q. He, X. Cao, C. Tan, H. Chen, Q. Yan, H. Zhang, *Adv. Energy Mater.* 2014, *4*, 1300574.
- 11. S. H. Bae, Y. Lee, B. K. Sharma, H. J. Lee, J. H. Kim, J. H. Ahn, *Carbon* **2013**, *51*, 236–242.
- a) K. Chen, G. Lu, J. Chang, S. Mao, K. Yu, S. Cui, J. Chen, Anal. Chem. 2012, 84, 4057–4062; b) J. Gong, T. Zhou, D. Song,

15214109, 0, Downloaded doi/10.1002/elan.202200493 by University Of Nevada Las Vegas Libraries Wiley Online Library on [06/02/2023]. See the Term on Wiley Online Library for QA are gover: ned by the applicable Creative

10 of 10 **FCTROANALYSIS**

L. Zhang, Sens. Actuators B 2010, 150, 491-497; c) M. Baghayeri, H. Alinezhad, M. Fayazi, M. Tarahomi, R. Ghanei-Motlagh, B. Maleki, Electrochim. Acta 2019, 312, 80-88.

- 13. a) D. Martín-Yerga, M. B. González-García, A. Costa-García, Sens. Actuators B 2012, 165, 143-150; b) P. K. Sahoo, S. Sahoo, A. K. Satpati, D. Bahadur, Electrochim. Acta 2015, 180, 1023-1032.
- 14. J. M. Pinilla, L. Hernández, A. J. Conesa, Anal. Chim. Acta 1996, 319, 25-30.
- 15. a) S. Xiong, B. Yang, D. Cai, G. Qiu, Z. Wu, Electrochim. Acta 2015, 185, 52-61; b) S. Fang, X. Dong, Y. Zhang, M. Kang, S. Liu, F. Yan, L. He, X. Feng, P. Wang, Z. Zhang, New J. Chem. 2014, 38, 5935-5942.
- 16. A. Shirzadmehr, A. Afkhami, T. Madrakian, J. Mol. Liq. 2015, 204, 227-235.
- 17. a) Y. Zhang, J. Xie, Y. Liu, P. Pang, L. Feng, H. Wang, Z. Wu, W. Yang, Electrochim. Acta 2015, 170, 210-217; b) Z. Zhang, X. Fu, K. Li, R. Liu, D. Peng, L. He, M. Wang, H. Zhang, L. Zhou, Sens. Actuators B 2016, 225, 453-462.
- 18. C. Li, G. Shi, Nanoscale 2012, 4, 5549-5563.
- 19. a) X. Chen, B. Chen, Environ. Sci. Technol. 2015, 49, 6181-6189; b) J. G. Radich, P. V. Kamat, ACS Nano 2013, 7, 5546-5557.
- 20. a) H. Yu, J. Zhu, H. Ren, S. Liu, Int. J. Nanosci. 2019, 18, 1850019; b) W. Li, S. Gao, L. Wu, S. Qiu, Y. Guo, X. Geng, M. Chen, S. Liao, C. Zhu, Y. Gong, M. Long, J. Xu, X. Wei, M. Sun, L. Liu, Sci. Rep. 2013, 3, 2125.
- 21. J. D. Lin, X. B. Yin, H. Pang, L. Zhang, B. Liao, M. L. Xin, Y. Su, Y. Liu, L. Wu, K. L. Jia, B. B. Zhong, Y. L. Mai, Y. Q. Dai, Adv. Mater. Interfaces 2020, 7.
- 22. J. Wang, B. Chen, B. Xing, Environ. Sci. Technol. 2016, 50, 3798-3808.
- 23. W. S. Hummers, R. E. Offeman, J. Am. Chem. Soc. 1958, 80, 1339-1339.
- 24. Y. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach, R. S. Ruoff, Sci. J. 2011, 332, 1537.
- 25. a) L. A. L. Tang, W. C. Lee, H. Shi, E. Y. L. Wong, A. Sadovoy, S. Gorelik, J. Hobley, C. T. Lim, K. P. Loh, Small 2012, 8, 423-431; b) A. Sinitskii, D. V. Kosynkin, A. Dimiev, J. M. Tour, ACS Nano 2010, 4, 3095-3102.
- 26. S. Liu, W. Peng, H. Sun, S. Wang, Nanoscale 2014, 6, 766-771.
- 27. J. Wang, Z. Chen, B. Chen, Environ. Sci. Technol. 2014, 48, 4817-4825.

- 28. Z. Pei, L. Li, L. Sun, S. Zhang, X.-q. Shan, S. Yang, B. Wen, Carbon 2013, 51, 156-163.
- 29. R. X. Xu, X. Y. Yu, C. Gao, Y. J. Jiang, D. D. Han, J. H. Liu, X. J. Huang, Anal. Chim. Acta 2013, 790, 31-38.
- 30. A. Królicka, A. Bobrowski, A. Kowal, Electroanalysis 2006, 18, 1649-1657.
- 31. D. MacDougall, W. B. Crummett, Anal. Chem. 1980, 52, 2242-2249.
- 32. H. Tang, Y. Zhao, S. Shan, X. Yang, D. Liu, F. Cui, B. Xing, Environ. Sci. Technol. 2018, 52, 7689-7697.
- 33. Y. F. Sun, J. H. Sun, J. Wang, Z. X. Pi, L. C. Wang, M. Yang, X. J. Huang, Anal. Chim. Acta 2019, 1063, 64-74.
- 34. X. J. Han, S. F. Zhou, H. L. Fan, Q. X. Zhang, Y. Q. Liu, J. Electroanal. Chem. 2015, 755, 203-209.
- 35. L. H. Marcolino-Junior, B. C. Janegitz, B. C. Lourenção, O. Fatibello-Filho, Anal. Lett. 2007, 40, 3119-3128.
- 36. S. F. Zhou, J. J. Wang, L. Gan, X. J. Han, H. L. Fan, L. Y. Mei, J. Huang, Y. Q. Liu, J. Alloys Compd. 2017, 721, 492-500.
- 37. M. B. Gumpu, M. Veerapandian, U. M. Krishnan, J. B. B. Rayappan, Talanta 2017, 162, 574-582.
- 38. W. J. Li, X. Z. Yao, Z. Guo, J. H. Liu, X. J. Huang, J. Electroanal. Chem. 2015, 749, 75-82.
- 39. Y. F. Sun, L. J. Zhao, T. J. Jiang, S. S. Li, M. Yang, X. J. Huang, J. Electroanal. Chem. 2016, 760, 143-150.
- 40. a) H. P. Wu, Anal. Chem. 1996, 68, 1639-1645; b) C. Agra-Gutiérrez, J. C. Ball, R. G. Compton, J. Phys. Chem. B 1998, 102, 7028-7032; c) T. M. Florence, J. Electroanal. Chem. Interfacial Electrochem. 1970, 27, 273-281; d) R. Ouyang, Z. Zhu, C. E. Tatum, J. Q. Chambers, Z.-L. Xue, J. Electroanal. Chem. 2011, 656, 78-84.

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