# An electrochemical sensor based on rGO/GaN nanowires for Pb(II) determination

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**Abstract.** In this work, rGO/GaN nanowires electrochemical sensors were fabricated on sapphire substrates by metal organic chemical vapor deposition (MOCVD) and electrodeposition method, and it was used for the detection of $Pb^{2+}$ in water. Reduced graphene oxide (rGO) increases the specific surface area and active sites of gallium nitride nanowires (GaN NW), and GaN NW improves the stability of the rGO, thus a highly sensitive electrochemical sensor was established. Square wave anodic stripping voltammetry (SWASV) was used to detect $Pb^{2+}$. Effects of experimental conditions such as rGO modification amount, pH, $Pb^{2+}$ deposition potential/time on the detection performance were investigated. With optimized detection conditions, the rGO/GaN NW sensor features high sensitivity (0.7362 μA $\mu g^{-1}$ L) in the linear range of 2.5-200 μg $L^{-1}$, and the detection limit was 2.5 μg $L^{-1}$. Furthermore, the rGO/GaN NW sensor exhibited a good stability and repeatability.

**Keywords:** GaN nanowires; rGO; Lead ion; Electrochemical sensor.

## 1. Introduction

Heavy metal pollution is becoming more and more serious due to human industrial activities. Heavy metal ions in the environment will enter the human body through the food chain, enriched in the human body, non-degradable serious harm to human health. Lead is one of the most toxic heavy metal ions. Lead can lead to decreased IQ, behavioral problems, cardiac dysfunction, senile dementia and so on. So it is particularly important to develop rapid and sensitive tools to detect lead ions [1, 2].

The commonly used analytical methods include X-ray fluorescence spectrometry (XFS) (which has been used to detect trace heavy metals), inductively coupled plasma mass spectrometry (ICP-MS), etc. [3, 4]. However, the operation of these traditional laboratory analysis methods is complex, the instruments are expensive, and the practical application is limited. In contrast, electrochemical method is widely used in the detection of heavy metal ions because of its simple operation, low cost and easy miniaturization. Square wave anodic stripping voltammetry (SWASV) shows high sensitivity in the detection of heavy metal ions, so it has attracted much attention. The design and modification of working electrode materials are the key to detect heavy metal ions by SWASV. At present, many materials have been used in the detection of heavy metal ions, such as precious metals [5], metal oxides [6], etc.

The third generation wide band gap direct band gap nitride semiconductor GaN material has good electrical conductivity and excellent chemical stability (there is no suitable wet etching agent at present), so it is considered to be an ideal material for electrochemical sensors [7]. In terms of sensors, GaN has shown some excellent performance [7]. Reduced graphene oxide (rGO) material is widely used in the detection of heavy metals because of its high specific surface area and excellent electron transfer velocity [5]. But graphene is easy to agglomerate and its stability is poor.

In this work, GaN nanowire arrays (GaN NW) were prepared by metal organic chemical vapor deposition (MOCVD). GaN NW have high electrical conductivity and large specific surface area. rGO was modified on GaN NW by cyclic voltammetry (CV). rGO increased specific surface area of GaN NW and GaN NW improved the stability of the rGO. The rGO/GaN NW sensor is used to detect $Pb^{2+}$ in water with a detection limit of 2.5 μg $L^{-1}$ and a high sensitivity of 0.7362 μA $μg^{-1}$ L. It has a good practical application prospect in the detection of heavy metal ions in electrochemical sensor applications.

## 2. Experimental

### 2.1 Preparation of rGO/GaN NW

GaN NW was grown by MOCVD at 625 ℃. GaN NW was grown on sapphire substrates coated with 5 nm Ni and 5 nm Au film by self-made MOCVD system. In the process of MOCVD growth of GaN NW, the flow rates of TMGa carrier gas and $NH_3$ are 4 and 100sccm respectively, and the growth time is 3000 s.

Graphene oxide of 20 mg was dispersed in 0.1M phosphate buffer solution (PBS), PBS pH is 7. After ultrasonic for 1 hour, the suspension was uniform and stable. Then drop the above suspension of 5 μL on GaN NW and dry naturally. Finally, graphene oxide was reduced by cyclic voltammetry with a scanning rate of 50 mV/s, a potential range of -1.5 V and a scanning cycle of 20 times. The preparation of rGO/GaN NW was completed. rGO/GaN NW is electrically connected to copper wire with silver epoxy resin. In order to avoid contact with the electrolyte, the connecting area of the wire is sealed with neoprene. The exposed area of the working electrode is 0.6 × 0.7$cm^2$.

### 2.2 Material Characterizations

The morphology of rGO/GaN NW was characterized by ultra-high resolution field emission scanning electron microscopy (SEM, JEM7900F, JEOL, Japan) with energy dispersion spectra. Electrochemical experiments were carried out on CHI630E electrochemical workstation (China Chenghua instrument).

### 2.3 Determination method of $Pb^{2+}$

The electrochemical detection of $Pb^{2+}$ was carried out on CHI630E electrochemical workstation (China Chenghua instrument), and SWASV was used. RGO/GaN NW, Ag/AgCl and Pt foils are used as working electrodes, reference electrodes and opposites, respectively. The electrolyte used for the detection was 0.1M HAc-NaAc buffer solution (pH 5.5) containing 300 μg $L^{-1}$ bismuth ion as supporting electrolyte. The experimental process is as follows: (1) firstly, $Pb^{2+}$ was agglomerated on the surface of rGO/GaN NW electrode by stirring for 300 s at -1 V constant potential. (2) then dissolve $Pb^{2+}$ by SWASV. (3) finally, clean the electrode with 0.4 V potential for the next detection.

## 3. Results and discussion

### 3.1 Characterization of rGO/GaN NW

The surface morphologies of GaN NW and rGO/GaN NW were characterized by SEM. Figure 1a shows the SEM image of GaN NW, which shows that the surface of nanowires is smooth and grows perpendicular to the substrate, forming nanowire arrays. Figure 1b shows the SEM image of rGO/GaN NW. In the figure, the rGO is uniformly attached to the nanowires, and the array structure of the nanowires makes the rGO more stable. The rGO does not completely cover the nanowires, which verifies that the performance of rGO/GaN electrochemical sensor for detecting $Pb^{2+}$ is due to the joint action of rGO and GaN NW. Figure 1c, d are the EDS analysis of GaN NW and rGO/GaN NW, respectively. It can be seen that the nanowires contain two elements of Ga, N, and the

rGO/GaN NW sensor contains four elements of Ga, N, C and O, which proves that rGO/GaN NW has been successfully prepared.

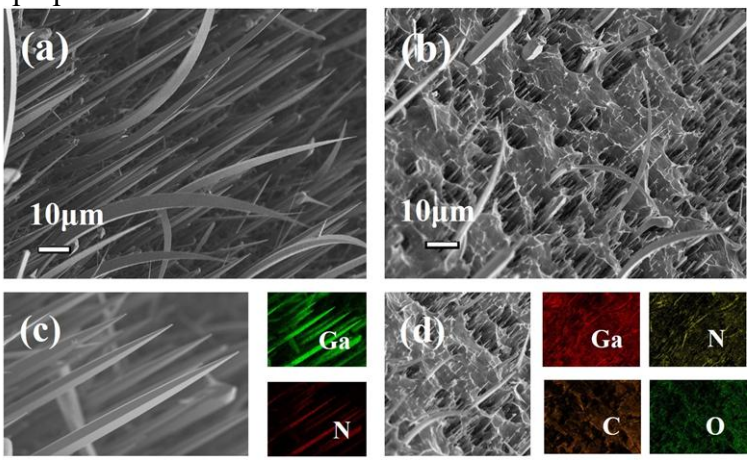


Fig. 1 SEM image of GaN NW (a) SEM image of rGO/GaN NW (b) EDS analysis of GaN NW (c) EDS analysis of rGO/GaN NW (d)

### 3.2 Electrochemical behavior of modified electrode

CV is an effective method to study the surface and electrochemical activity of modified electrodes [8]. Figure 2a shows the electrochemical characteristics of GaN NW and rGO/GaN NW electrodes at 5 mM $[Fe(CN)_6]^{3-/4-}$and 0.1 M KCl, with a scanning rate of 0.05 V/s. It can be seen from the figure that both CV curves show symmetrical redox peaks, indicating that both GaN nanowires and rGO/GaN NW electrodes have good reversibility in the redox process. Compared with GaN NW, rGO/GaN NW has a larger redox peak current, indicating that the addition of rGO promotes the electron transfer of GaN NW and improves the specific surface area and electrochemical activity of the electrode.

In order to evaluate the response of modified electrodes to $Pb^{2+}$, two electrodes were tested by SWASV method. The electrolyte used in the experiment is 0.1M HAc-NaAc buffer solution of pH=5, the potential range is from -0.85 v to 0.35 v, the deposition potential is -1 V, the deposition time is 300 s, the concentration of bismuth ion is 300 μg $L^{-1}$, the concentration of lead ion is 200 μg $L^{-1}$. The results are shown in figure 2b. The response current of the GaN NW sensor to $Pb^{2+}$ is 6.891 μA, the response current of rGO/GaN NW sensor to $Pb^{2+}$ is 54.7 μA, and the response is 100.5 μA after adding $Bi^{3+}$. The response of the modified electrode rGO/GaN NW sensor is increased by more than 6.9 times, while the response current of the rGO/GaN NW sensor is nearly doubled after the addition of $Bi^{3+}$, indicating that $Bi^{3+}$ can also increase the response current. The results show that rGO/GaN NW nanocomposites have good electrochemical properties.

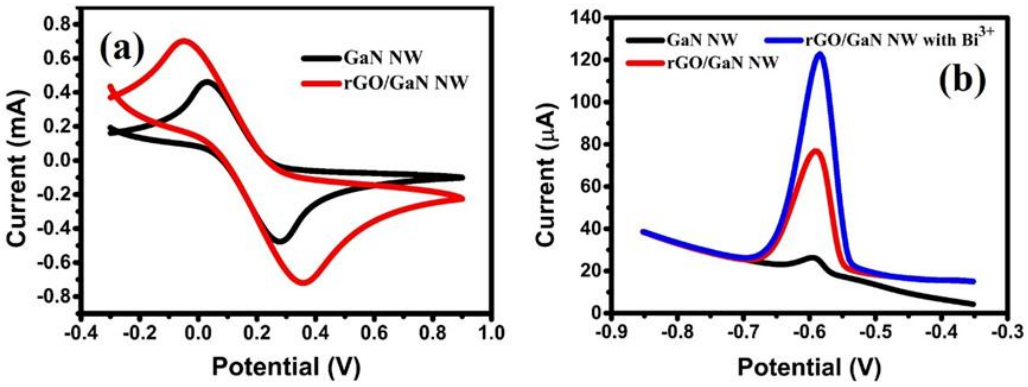


Fig. 2 The CV curves of GaN NW and rGO/GaN NW in 55 mM $[Fe(CN)_6]^{3-/4-}$and 0.1 M KCl (a) SWASV responses for GaN NW, rGO/GaN NW without $Bi^{3+}$ and rGO/GaN NW with $Bi^{3+}$ SWASV responses in 0.1M HAc-NaAc (pH=5) buffer solution containing 200μg $L^{-1}$ $Pb^{2+}$

### 3.3 Optimization of experimental conditions

3.3.1 Optimization of electrode operating conditions

The concentration of $Bi^{3+}$ has a great influence on the response current, so it is necessary to determine the best concentration of $Bi^{3+}$. The experimental results are shown in figure 3a, the concentration of $Bi^{3+}$ is from 100 to 500 μg $L^{-1}$. When the concentration of $Bi^{3+}$ increased from 100 to 300 μg $L^{-1}$, the response current increases, which may be due to the formation of alloy between $Bi^{3+}$ and $Pb^{2+}$. When the concentration of $Bi^{3+}$ exceeds 300 μg $L^{-1}$, the response current decreases because the thickness of bismuth film may hinder the electron transfer in the process of $Pb^{2+}$ dissolution. To sum up, the concentration of $Bi^{3+}$ is 300 μg $L^{-1}$.

In order to investigate the influence of pH value on the response current of $Pb^{2+}$, we investigated the response current of $Pb^{2+}$ (100 μg $L^{-1}$) when the pH value is from 3 to 7. As shown in figure 4b, the deposition potential is 1 V and the deposition time is 300 s. When the pH of the buffer solution is from 3 to 5.5, the response current of $Pb^{2+}$ increases. In the overly acidic environment, too many protons in the solution are not conducive to the adsorption of heavy metal ions on the electrode surface. The response current of $Pb^{2+}$ decreases with the increase of pH from 5.5 to 7.0. It is possible that due to the increase of pH value of the buffer solution, some $Pb^{2+}$ are hydrolyzed into $Pb(OH)_2$, $Pb(OH)_3^-$ [9]. Therefore, the HAC-NaAc buffer solution of pH=5.5 is selected as the supporting electrolyte in the follow-up experiment.

Figure 4c shows the effect of different deposition potential on the detection of $Pb^{2+}$. The concentration of $Pb^{2+}$ is 100 μg $L^{-1}$ and the deposition time is 300 s. When the deposition potential ranging from -0.8 to -1 V, the response current of $Pb^{2+}$ increases. The excessive deposition potential will be close to the oxidation potential of $Pb^{2+}$, which is not conducive to its deposition on the electrode surface. The response current of $Pb^{2+}$ decreases when the deposition potential exceed -1 V. This is because too low deposition potential will lead to hydrogen evolution on the electrode surface, and too many hydrogen bubbles reduce the effective area of the electrode and greatly reduce the adhesion of metals on the electrode surface [10]. Therefore, the optimum deposition potential is -1 V.

Deposition time is also an important parameter that affects the electrochemical behavior of $Pb^{2+}$ detected by the sensor. As shown in figure 4d, the concentration of $Pb^{2+}$ is 100 μg $L^{-1}$. When the deposition time increases from 60 s to 300 s, the $Pb^{2+}$ response current increases. It tends to saturated when the deposition time further increases beyond to 300 s. Therefore, considering the work efficiency, 300 s is chosen as the best deposition time.

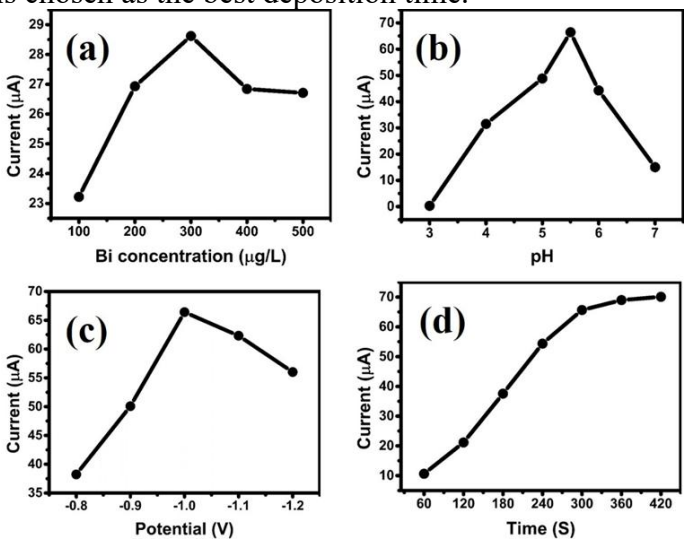


Fig. 3 Effect of $Bi^{3+}$ concentration on $Pb^{2+}$ (50 μg $L^{-1}$) response current in 0.1M HAc-NaAc (pH=5) buffer solution containing 50 μg $L^{-1}$ $Pb^{2+}$ (a) effect of pH in 0.1M HAc-NaAc buffer solution containing 100 μg $L^{-1}$ $Pb^{2+}$ (b) deposition potential (c) deposition time (d)

3.3.2 Determination of $Pb^{2+}$ by rGO/GaN NW Sensor

Under the best experimental conditions, different concentrations of $Pb^{2+}$ were added to 0.1M HAc-NaAc buffer solution (pH=5.5) to study the response current of rGO/GaN NW sensor for $Pb^{2+}$ detection. As shown in figure 4a, the response current increases gradually with the increase of $Pb^{2+}$ concentration from 2.5 to 200 μg $L^{-1}$. According to the experimental results, the relationship between response current and $Pb^{2+}$ concentration is shown in figure 4b, and the illustration is a low concentration response curve. The linear regression equation obtained from the calibration curve is I (μA) = -4.348 ± 0.7362C (μg $L^{-1}$), and the correlation coefficient is $R^2$ = 0.996. The sensitivity of the rGO/GaN NW sensor is 0.7362 μA $μg^{-1}$ L, and the linear range is 2.5 ~ 200 μg $L^{-1}$. As shown in the illustration of figure 6a, the detection limit (LOD) of the sensor can be clearly identified, and the LOD is 2.5 μg $L^{-1}$, which is lower than the $Pb^{2+}$ concentration specified by the World Health Organization ($Pb^{2+}$~ 10 μg $L^{-1}$).

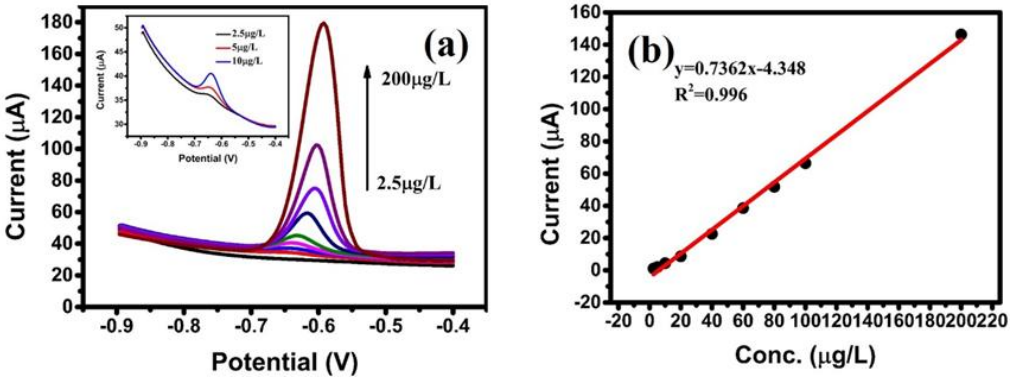


Fig. 4 SWASV responses of rGO/GaN NW electrodes to different concentrations of $Pb^{2+}$ (a), The illustration shows its calibration curve (b)

3.3.3 Repeatability and Stability

In order to verify the repeatability of the rGO/GaN NW sensor, the same modified electrode was repeated for 5 times in 0.1 M HAc-NaAc buffer solution containing 100 μg $L^{-1}$ $Pb^{2+}$. As shown in figure 5a, the response current range of the rGO/GaN NW sensor to $Pb^{2+}$ is from 65.65 μ A to 68.05 μA. The relative standard deviation (RSD) of the response current calculated is 1.38%, indicating that the rGO/GaN NW sensor has good repeatability. The long-term stability of rGO/GaN NW sensor is another important parameter in practical application. We compared the response current changes of 100 μg $L^{-1}$ $Pb^{2+}$ detected by the same electrode on the first day and the 15th day, and the electrode was stored in air. In the figure 5b, the response current can still be maintained at 93.9% on the 15th day, indicating that the sensor has good stability.

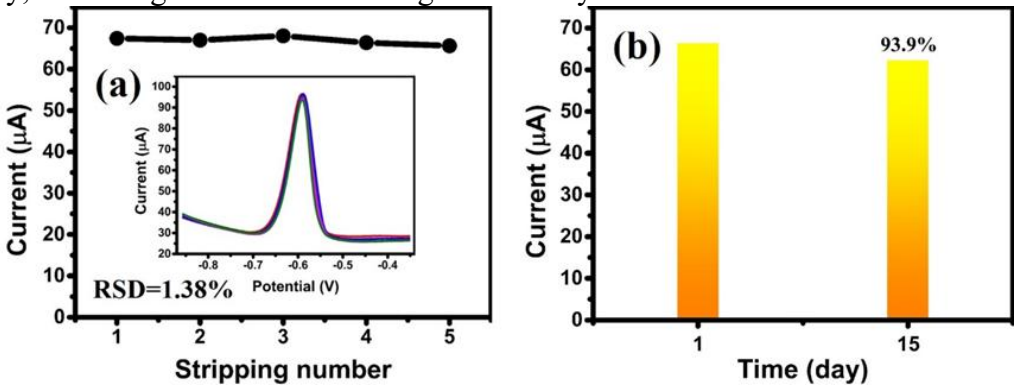


Fig. 5 Reproducibility measurements repeated five times using the rGO/GaN NW (a) the stability of rGO/GaN NW, and the sensor was stored in air for 15 days.

Table 1 shows the comparison of the analytical performance of different electrodes. Compared with other electrodes, the prepared electrodes have high sensitivity and linear range [5,6,11-13]. For conventional nanomaterials, the LOD of $Pb^{2+}$ is generally between 0.129 with 29.21 μg $L^{-1}$, and the

sensitivity of $Pb^{2+}$ is generally between 0.0719 with 0.6523 μA $μg^{-1}$ L. The rGO/GaN NW sensor is used for electrochemical detection of $Pb^{2+}$ with the LOD is 2.5 μg $L^{-1}$ and the sensitivity is 0.7362 μA $μg^{-1}$ L. Compared with traditional nanomaterials, our rGO/GaN NW has high sensitivity. Therefore, rGO/GaN NW has high sensitivity, easy to manufacture and contains no binder.

Table 1 Comparison of $Pb^{2+}$ testing performance between different electrode materials and rGO/GaN NW materials

| Electrodes | Sensitivity ( μ A μ g-1 L) | Linear range ( μ g L-1) | LOD ( μ g L-1) | References |
|---|---|---|---|---|
| Fe3O4 | 0.0719 | 60-260 | 23.8 | [6] |
| Co3O4 | 0.6523 | 1-100 | 0.52 | [11] |
| Fe2O3 – BCN/Nafion/ GCE | 0.537<br>0.212 | 0.5-40<br>40-140 | 0.129 | [12] |
| MnFe2O4/GO/GCE | 0.1636 | 41.44-227.92 | 18.23 | [13] |
| AgNPs/RGO/GCE | 0.2348 | | 29.21 | [5] |
| rGO/GaN NW | 0.7362 | 2.5-200 | 2.5 | This work |

## 4. Summary

In this work, the rGO/GaN NW sensor was prepared by MOCVD and electrodeposition. The rGO/GaN NW sensor was applied to the detection of $Pb^{2+}$ in water. Reduced graphene oxide (rGO) increases the specific surface area and certain active sites of GaN nanowires, which makes the sensor have high sensitivity. GaN NW improves the stability of rGO. Our sensor features good repeatability and stability in $Pb^{2+}$ detection. The electrochemical performance of rGO/GaN NW modified electrode for the detection of SWASV $Pb^{2+}$ ions compared with the nanomaterial modified electrode, our sensor has high sensitivity for the detection of $Pb^{2+}$ (0.7362 μA $μg^{-1}$ L). The linear range of $Pb^{2+}$ detection by rGO/GaN NW sensor is 2.5 ~ 200 μg L-1, and the detection limit is 2.5 μg $L^{-1}$.

## 5. Acknowledgment

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