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# Sensitive Detection of Hydroxylamine on Poly(3,4-ethylenedioxythiophene)/graphene Oxide Nanocomposite Electrode

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A stable and sensitive hydroxylamine (HA) sensor was developed through a simple one-step electropolymerization of a thin poly(3,4-ethylenedioxythiophene)/graphene oxide (PEDOT/GO) film onto a glassy carbon electrode (GCE) surface (PEDOT/GO/GCE). The sensors were characterized by SEM, FT-IR and UV-vis spectra. The electrochemical performance of the PEDOT/GO/GCE for detection of HA was investigated by cyclic voltammetry and chronamperometry. The PEDOT/GO electrode displayed a synergistic effect of conducting PEDOT and high surface area of GO towards the oxidation of HA, showed higher oxidation current compared with GO/GCE, PEDOT/GCE and bare electrodes. The oxidation of HA on the PEDOT/GO films depended strongly on the solution pH, and the maximum catalytic current was observed at a pH of 8.0. The amperometric response at PEDOT/GO electrode increased linearly to HA concentrations in the range of 0.1 μM to 6 mM, and the detection limit was 0.04 μM. Furthermore, the modified electrode was successfully used for determination of spiked hydroxylamine in water sample. Finally, the modified electrode exhibited good reproducibility and long-term stability, as well as high selectivity.

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**Keywords:** hydroxylamine, poly(3,4-ethylenedioxythiophene), graphene oxide, electropolymerization, sensor

## 1. INTRODUCTION

Hydroxylamine, $NH_2OH$ (abbreviated as HA), is a derivative of ammonium, which is extensively used as intermediate in biological nitrification [1] and reducing agents in synthesis of pharmaceutical intermediates and final drug substances [2]. However, hydroxylamine is a well-known mutagen, moderately toxic and harmful drug to microorganisms that could interfere with biological sewage plant performance [3,4]. Therefore, developing of a rapid, environmental and sensitive analytical method for the determination of HA is much significant. Numerous methods have been used for the determination of HA, including spectrophotometry [5], high performance liquid chromatography [6], polarography [7], gas chromatography [8], and potentiometry [9]. However, the processes involved in many of these methods are extremely complex, and the linear ranges are relatively narrow with low precision. Compared with traditional analytical methods, electrochemical methods present a plenty of advantages such as portable, inexpensive, rapid, and selective detection with low detection limits. Fortunately, HA shows a good electrochemical activity [10], which provides the possibility to detect HA by electrochemical sensor.

Recently, various chemically modified electrodes have been prepared and applied in the determination of HA [11-13], which can significantly lower the overpotentials and increase the oxidation current response. For conductive polymers, Poly(3,4-ethylenedioxythiophene) (PEDOT) is considered as a most potential electrode material because it combines a low oxidation potential and moderate bandgap with good stability in the oxidized state, high conductivity and highly transparent in thin oxidized films, and unusual doping/dedoping character [14]. In particular, advancements in doping technology yielding a suitable dopant and nanostructured forms of PEDOT or its composites [15-20] would accelerate progress in this field. Graphene oxide (GO) sheets are two-dimensional carbon materials that have attracted great interest due to their high surface area, extraordinary electrochemical and mechanical properties. Moreover, owing to the abundance of carboxyl groups that are negatively charged in aqueous solution, GO can act as an excellent dopant for the chemical and electrochemical polymerization of conducting polymers [21,22]. These advantages have led to various applications of PEDOT/GO composites. These composites show enhanced electrochemical properties in the sensing applications, e.g., detection of chemical and biomolecules such as hydroquinone, catechol and nitrite [23]. However, until now, to the best of our knowledge, there has been no report about the electrochemical behaviors and determination of HA at the PEDOT/GO modified electrode.

In this paper, composites of PEDOT and GO are synthesized by in-situ polymerization of EDOT monomer in the presence of GO suspension. PEDOT/GO/GCE exhibited good electrochemical performance and good electrocatalytic activity toward the oxidation of HA. Thus, the prepared PEDOT/GO/GCE was used for the determination of HA as an electrochemical sensor. The proposed method possesses several advantages such as wide linear range, excellent repeatability and long-term stability, low cost, environmentally friendliness and simplicity.

## 2. EXPERIMENTAL DETAILS

### *2.1. Apparatus and chemicals*

Hydroxylamine was purchased from Sinopharm chemical reagent Co. Ltd. Graphene oxide was obtained from Nanjing XFNANO Materials Tech Co., 3,4-ethylenedioxythiophene was obtained from Sigma-Aldrich (USA), lithium perchlorate trihydrate ($LiClO_4$), sodium sulfate ($Na_2SO_4$), disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4$), sodium dihydrogen phosphate dehydrate ($NaH_2PO_4$), potassium ferricyanide ($K_4[Fe(CN)_6]$) and Potassium hexacyanoferrate $K_3[Fe(CN)_6]$ were obtained from Sinopharm chemical reagent Co. Ltd. Phosphate buffer solutions (PBS, 0.1 M) were prepared by varying the ratio of $NaH_2PO_4$, $Na_2HPO_4$ and than adding 0.1 M KCl. All the aqueous solutions were of analytical grade without further purification and doubly distilled water was used throughout the experiments. All electrochemical experiments were carried out at room temperature.

Scanning electron microscopy (SEM) analysis was performed using a Hitachi S-3000 N scanning electron microscope. The FTIR spectra were recorded on a Nexus 670 FTIR spectrophotometer (Nicolet Instruments) using a KBr disk at a resolution of 4 $cm^{-1}$. The UV-vis spectra were obtained with an Agilent 8453 UV-vis spectrophotometer. All electrochemical measurements were performed with a CHI660D electrochemical system (Shanghai, China). A three-electrode cell (10 mL) was used with the modified glassy carbon electrode (GCE) and indium tin oxid (ITO) glass substrate as the working electrode, a saturated calomel electrode (SCE) as a reference electrod and a platinum wire electrode as a counter electrode. Inert atmosphere was maintained by passing $N_2$ over the solution during the experiments.

### *2.2. Fabrication of the PEDOT/GO modified GCE*

GO (0.5 mg $ml^{-1}$), EDOT (0.01 M) and $LiClO_4$ (20 mM) solution were dispersed in 5 ml water and ultrasonicated for 40 minute in room temperature. Prior to the modification, the GCE was highly polished to a mirror-like surface with alumina slurry on the polishing cloth, rinsed with water and sequentially ultrasonicated in water, ethanol, and water for 5 min, respectively. The electrochemical in-situ polymerization of EDOT in presence of GO was performed by 25 cycles of potential sweep between -0.2 and 1.1 V at 50 mV $s^{-1}$, under the condition of $N_2$ bubbling.

The electrochemical reduction of the PEDOT/GO (PEDOT/rGO) nanocomposite was carried out in 0.1 M $Na_2SO_4$ by 25 cycles of potential sweep between -0.2 and 0.6 V at 50 mV $s^{-1}$. The electrochemical polymerization of pure EDOT modified GCE was performed by 25 cycles of potential sweep between -0.2 and 1.1 V at 50 mV $s^{-1}$. Inert atmosphere was maintained by passing $N_2$ over the solution during the experiments. GO/GCE was obtained by dropping the GO solution on GCE and dried in a vacuum oven. The preparation of reduced GO/GCE (rGO/GCE) was in consistent with the process of reduction of the PEDOT/GO/GCE modified electrode.

## 3. RESULTS AND DISCUSSION

### *3.1. Characterization of PEDOT/GO film*

SEM was employed to study the nature of the PEDOT/GO composite film (as shown in Fig. 1). From Fig. 1A, it can be clearly seen that the PEDOT film grows compactly and presents twisty reticulate structure. While, the PEDOT/GO composite film shows a high roughness and loose wrinkled paper-like sheets structure (Fig. 1B). During the process of electropolymerization of PEDOT nanocomposite, GO bearing a negative charge acted as the counter ion and were incorporated into the polymer to balance the positive charge on the polymer backbone. Moreover, the π-π interactions and hydrogen bonding between the GO and aromatic PEDOT rings also play a significantly role in the formation of PEDOT/GO nanocomposites [24,25]. The corresponding high magnification image further indicates that the PEDOT/GO shows a lot of nanoflakes. There is no doubt that such open structure of the composite films can promote the adsorption of the ions or target analytes from the electrolyte to the electrode surface. Furthermore, it can be then concluded that the conducting PEDOT/GO film would provide highly accessible surface area for the designing of sensitive electrochemical sensor. The good combination between the GO and PEDOT may be favorable for the charge transfer in the composite.

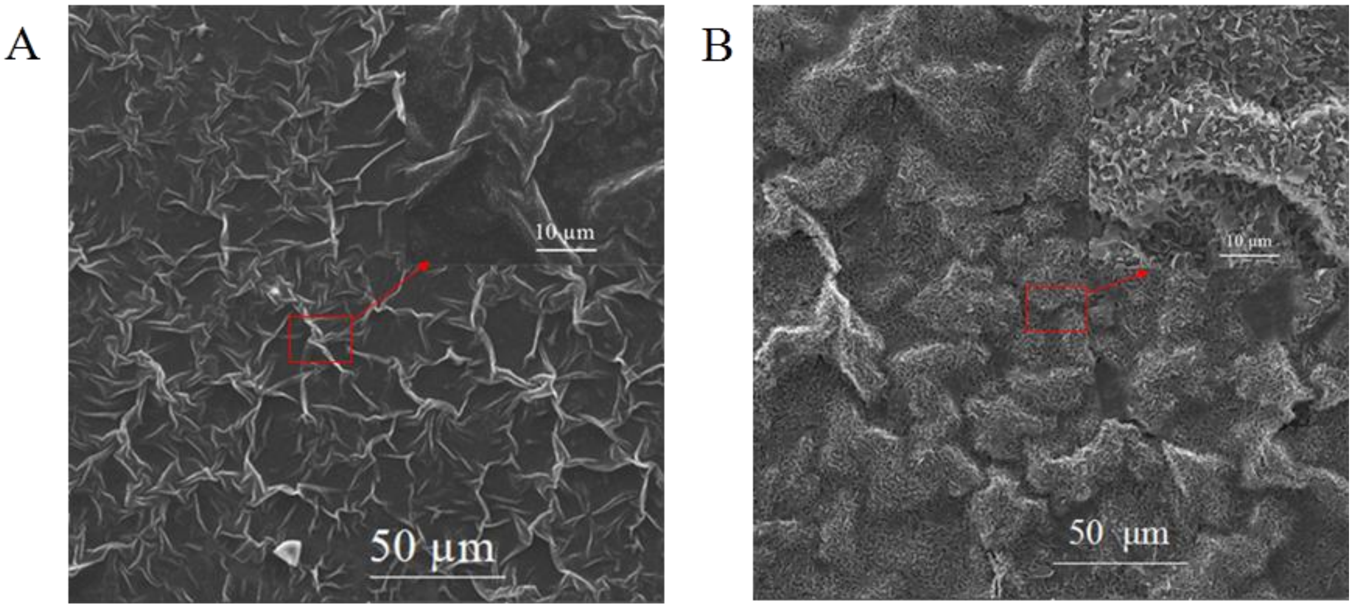

**Figure 1.** SEM image of PEDOT (A), PEDOT/GO (B)

The FT-IR spectra of PEDOT/GO, PEDOT and GO are shown in Fig. 2. For PEDOT (Fig. 2b), the band at 1333 cm$^{-1}$ is assigned to C-C and C=C stretching of quinoidal structure from the thiophene ring. The broad absorption band at 1626 cm$^{-1}$ is assigned to C=C bond, whose position depends on the doping level of the polymer [26]. GO (Fig. 2c) presents a narrow band at 1735 cm$^{-1}$, which originats from the stretching vibrations of carbonyl [27]. The peak of PEDOT/GO at 1333 cm$^{-1}$ shifts to 1343 cm$^{-1}$, which is related to the interaction between PEDOT and GO. And peak at 1626 cm$^{-1}$ shifts to 1642 cm$^{-1}$. It implies that GO acts as a dopant for the conducting PEDOT in the polymer chains [28]. Such an observation provides another piece of evidence to support the formation of PEDOT/GO nanocomposites.

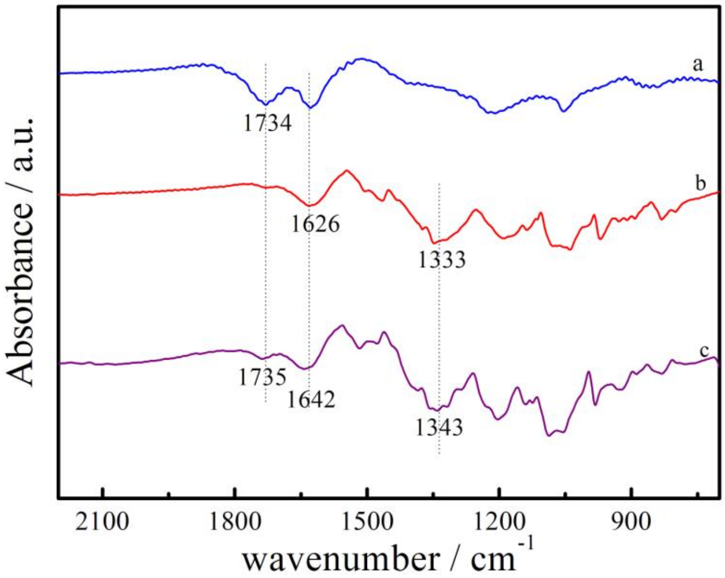

**Figure 2.** FT-IR spectrum of GO (a), PEDOT (b), PEDOT/GO (c)

The structural characterization of GO (a), PEDOT (b), PEDOT/GO (c) were further detected by UV-vis spectrum. It could be observed in Fig. 3 that PEDOT (b), PEDOT/GO (c) present absorption peaks near 370 nm, which may be attributed to π-π* transitions in the bezenoid units of the polymer chain [29]. The appearance of UV-vis absorption at 360 nm which distinguishes from the absorption of PEDOT at 378 nm and that of GO at 229 nm (inset plot, a), indicating the interaction of PEDOT chain and GO sheets.

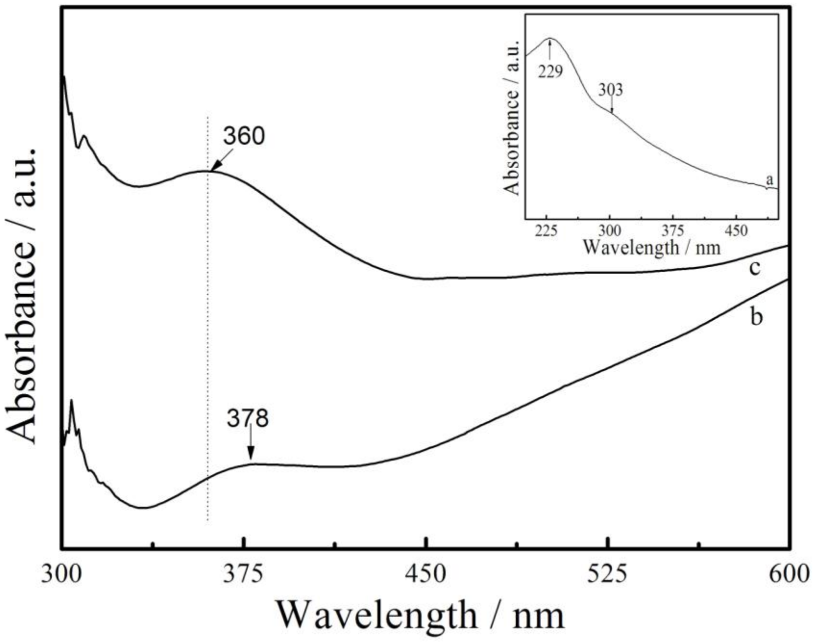

**Figure 3.** UV-vis spectrum of GO (a), PEDOT (b), PEDOT/GO (c)

### *3.2. Electrochemical characterization of the modified electrodes*

$[Fe(CN)_6]^{3-/4-}$, as an electrochemical probe, is usually used to evaluate the electrochemical properties of the electrode. Fig. 4 shows the cyclic voltammograms (CVs) of bare GCE (a), GO/GCE (b), rGO/GCE (c), PEDOT/GCE (d), PEDOT/rGO/GCE (e) and PEDOT/GO/GCE (f) in 5.0 mM $[Fe(CN)_6]^{3-/4-}$ (1:1) containing 0.1 M KCl at a scan rate of 50 mV $s^{-1}$. The bare GCE (a) showed a pair of quasi-reversible peaks. A pair of redox peaks current decreased obviously after the GO deposition onto the bare GCE surface (curve b), which can be attributed to the poor electrical conductivity of GO. An increase peak current was observed when GO was reduced to rGO (curve c), which can be ascribed to the favourable electrical conductivity of graphene. Compared with these electrode materials, PEDOT showed a better pair of quasi-reversible peaks (curve d), which indicated that the conducting polymer film could accelerate the electron transfer between the electrochemical probe $[Fe(CN)_6]^{3-/4-}$ and the GCE. The peak current further increased again (curve e), when GO incorporated with PEDOT, showing that GO accelerated electron transfer to some extent. As for PEDOT/rGO (curve e), the peak current increased slightly. This result may be attributed to the fact that GO in the nanocomposite is reduced to the more conductive rGO [30].

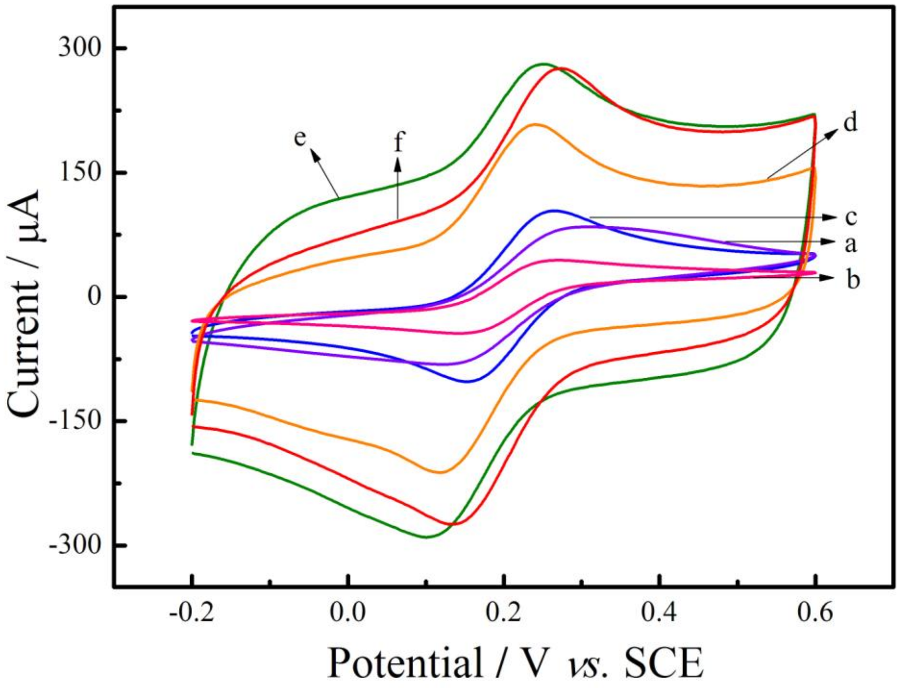

**Figure 4.** CVs of bare GCE (a), GO/GCE (b), rGO/GCE (c), PEDOT/GCE (d), PEDOT/rGO/GCE (e) and PEDOT/GO/GCE (f) in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.1 M KCl at a scan rate of 50 mV $s^{-1}$.

Fig. 5 shows the CVs of the PEDOT/GO electrode recorded in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.1 M KCl at different scan rates. It was found that both the anodic and cathodic peak current clearly increased with increasing potential scan rate, which implied the electrode reactions of

HA were adsorption-controlled processes, according to the following equations: Ipa (μA) = 81.48 + 1.918 v (mV $s^{-1}$) ($R^2$ =0.991), Ipc (μA) = -80.22 - 1.809 v (mV $s^{-1}$) ($R^2$ =0.990).

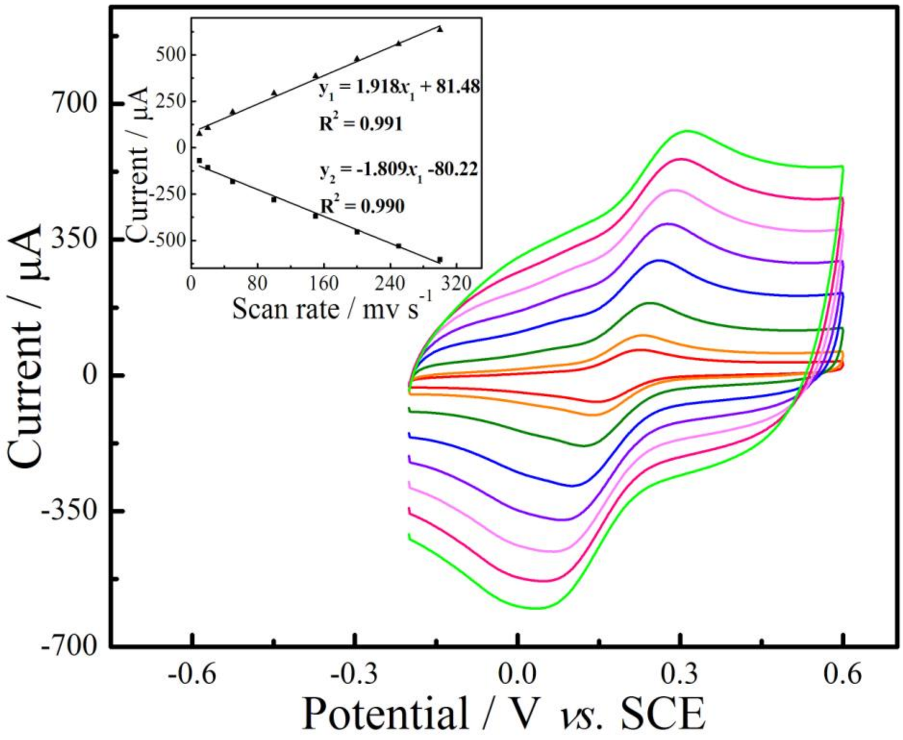

**Figure 5.** CVs of PEDOT/GO/GCE in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.1 M KCl at different scan rate from: 10, 20, 50, 100, 150, 200, 250, 300 mV $s^{-1}$.

### *3.3. Electrocatalysis of HA at the PEDOT/GO/GCE*

The electrocatalytic activity of different modified electrodes toward HA were investigated by CVs. Fig. 6A shows the results of 2.0 × $10^{-4}$ M HA in 0.1 M PBS (pH = 8.0) at the different electrodes. The order of the oxidation peak currents of HA on these electrodes are as follows: PEDOT/GO/GCE > PEDOT/rGO/GCE > PEDOT > rGO/GCE > GO/GCE > bare GCE, which implies that the electrochemical oxidation behavior of HA on the bare GCE was improved significantly by PEDOT and GO. As shown in Fig. 6B, at an applied potentials 0.5 V, the amperometric responses for 1.0 × $10^{-4}$ M HA are similar to the current responses of CVs. The enhancement effect may be due to the large surface area and high adsorption capability of GO, and good electrochemical properties, good electrocatalytic properties of PEDOT. This result further confirms that the PEDOT/GO/GCE has excellent electrocatalytic properties for the oxidation and sensitive detection of HA.

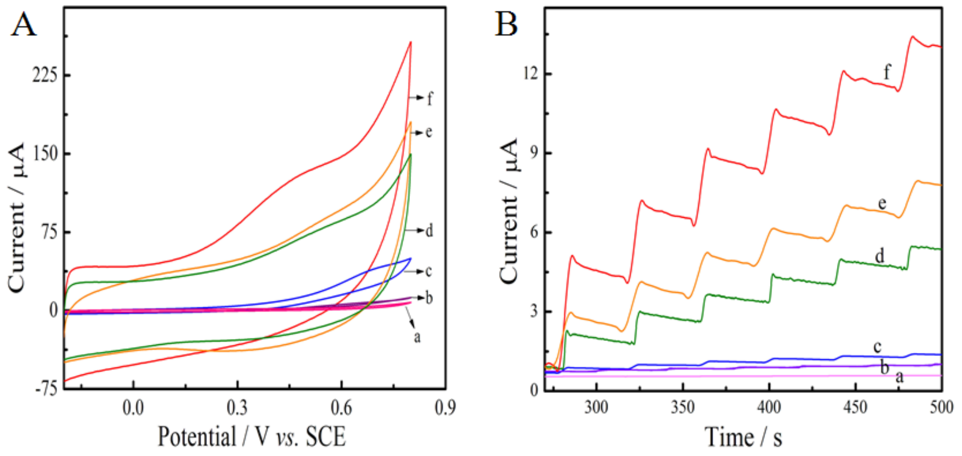

**Figure 6.** (A) CVs of 2.0 × $10^{-4}$ M hydroxylamine at bare (a), GO (b), rGO (c), PEDOT (d), PEDOT/rGO (e) and PEDOT/GO (f) modified GCEs in 0.1 M PBS (pH 8.0). (B) Amperometric responses of 1.0 × $10^{-4}$ M hydroxylamine at bare (a), GO (b), rGO (c), PEDOT (d), PEDOT/rGO (e) and PEDOT/GO (f) modified GCEs at 0.5 V in 0.1 M PBS (pH 8.0).

### *3.4 Optimization conditions for the sensor*

#### *3.4.1 Effect of pH Values*

In most case, the solution pH was an important influence factor to the electrochemical reaction. The effect of pH value on the determination of HA in the mixture at PEDOT/GO/GCE was systemically investigated by amperometric responses (shown in Fig. 7). The current of HA increased with an increasing in the solution pH until it reached 8.0 and then increased slightly when the pH exceeded 8.0. These phenomena are attributed to the fact that HA present two forms, the nonprotonated form $NH_2OH$ for pH value higher than 5.9 and protonated form $NH_3$ $OH^+$ at lower pH than 5.9. The protonated form is less active, while the higher pH could promote the anodic oxidation of HA [31]. In order to obtain high sensitivity and selectivity, pH 8.0 was selected as the optimum value in the following measurements.

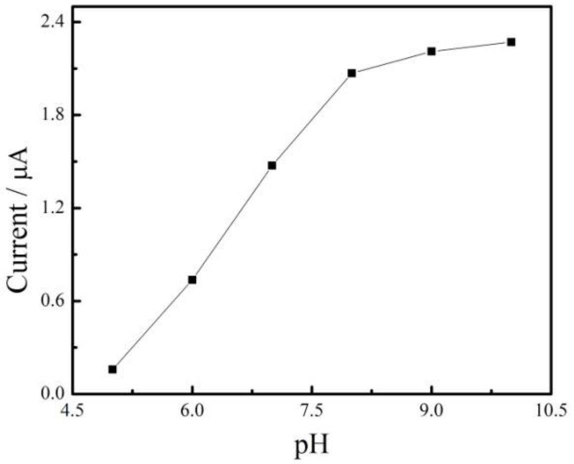

**Figure 7.** Influence of the pH values on the electrochemical response of 1.0 × $10^{-4}$ M hydroxylamine.

### *3.4.2. Effect of the concentration of GO*

In order to achieve high sensitivity, the concentration of GO suspension was explored. Fig. 8 showed the changes of the amperometric current with different concentrations of GO, while the concentration of EDOT was fixed to 0.01 M. As can be seen from Fig. 8, the amperometric current of 1.0 × $10^{-4}$ M HA increased remarkably with the concentration of GO suspension from 0 to 0.5 mg $mL^{-1}$. The reason might be that GO contains large number of oxygen-containing functional groups, and the incorporation of GO into PEDOT matrix can enhance the adsorptive capability for HA. In this case, the oxygen groups on the surface of GO can form hydrogen bonds with HA and enhance the electrostatic interaction between the modified electrode and HA [32]. Then a small concentration of GO could notably enhance the current response. However, when the concentration of GO further improved, the amperometric current of HA gradually decreased, which might be that amount of GO sheet lead to strong π-π accumulation, at a higher coincentration GO sheets restacked and aggregated and the efficient surface area of the composites was reduced [33]. Moreover, more GO sheets incorporating into PEDOT matrix will decreased the electric conductivity of PEDOT.

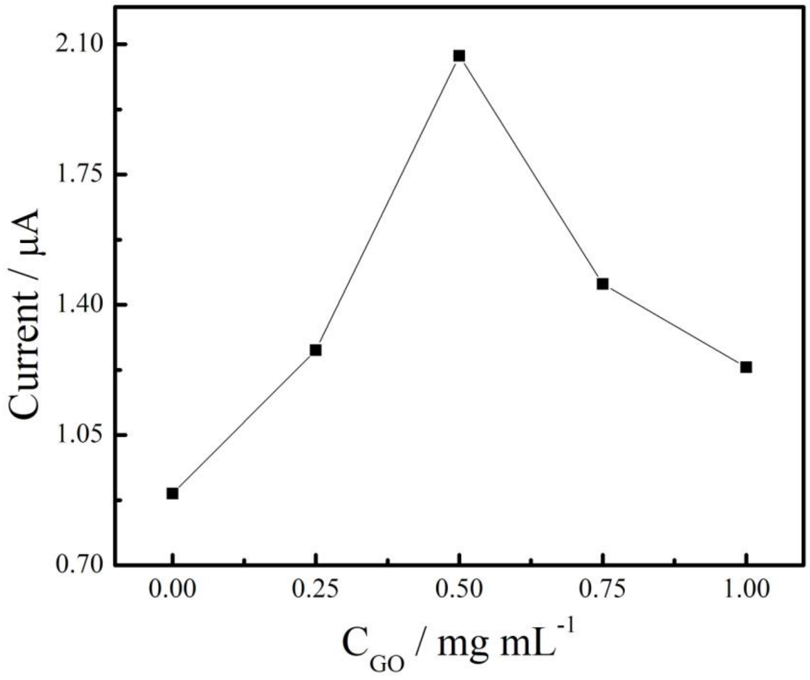

**Figure 8.** Influence of the concentration of GO on the electrochemical response of 1.0 × $10^{-4}$ M hydroxylamine.

### *3.4.3. Effect of the scan number in the electrodeposition process*

The effect of the scan number in the electrodeposition process was also evaluated by amperometric responses; the tendency was shown in Fig. 9. Amperometric response was performed by varying the scan number of the PEDOT/GO at applied potential 0.5 V for successively adding 1.0 × $10^{-4}$ M HA. It can be easily seen that current response increased remarkably when the scan number increased. And the response reached a maximum when the scanning number was 25. Further increasing the scanning number only resulted in a decrease of electrochemical response. This was probably because too thin a film possessed few catalytically active sites, while too thick a film would block the electron transfer and sites for electrochemical reactions on the surfaces of the electrodes [34,35], both cases might result in the small current response. Thus 25 cycles were selected as the optimal cycle value of electrodepositing.

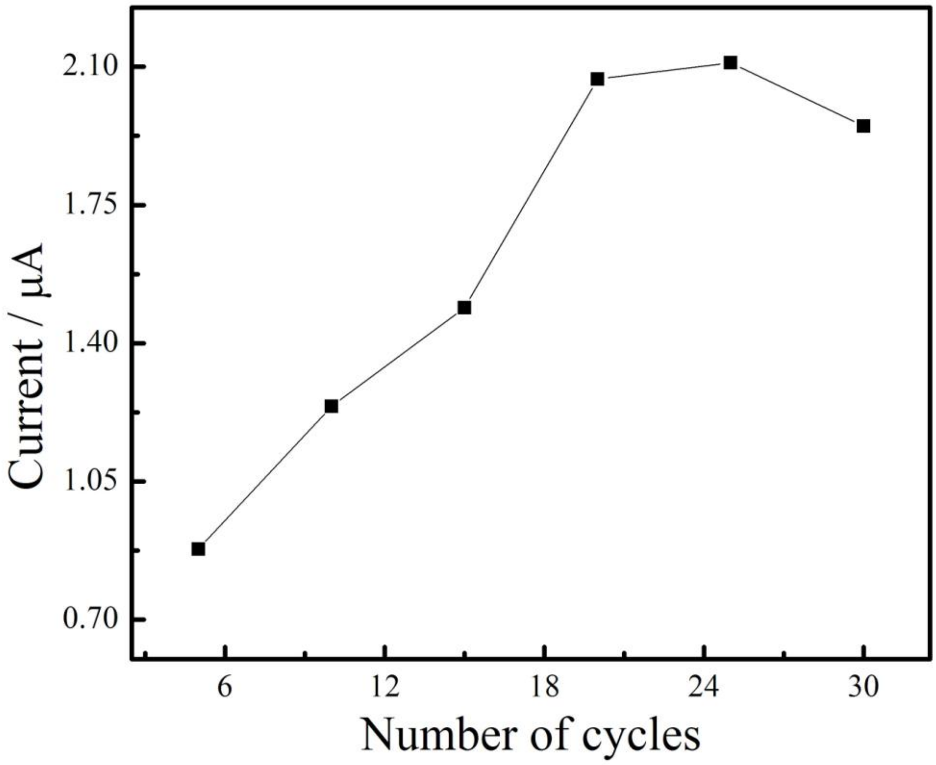

**Figure 9.** Influence of the scan number in the electrodeposition process on the electrochemical response of 1.0 × $10^{-4}$ M hydroxylamine.

### 3.5. *Amperometric detection of HA*

The amperometric response of HA at PEDOT/GO/GCE was further evaluated under the optimized experimental conditions. Fig. 10 shows the typical current-time dynamic response for the different amount of HA at 0.50 V in stirred PBS (pH = 8.0). The electrochemical response of HA increases linearly with the increase of HA concentration. The linear relationship existed between the amperometric current and the concentrations of HA in the range from 1.0 × $10^{-7}$ M to 6.0 × $10^{-3}$ M with limit of detection of 4.0 × $10^{-8}$ M. Table 1 gives the comparison of some of the analytical parameters obtained for HA in this study with other previous literatures. It can be observed that the proposed electrode displays good superiority in terms of linear ranges and limit of detection.

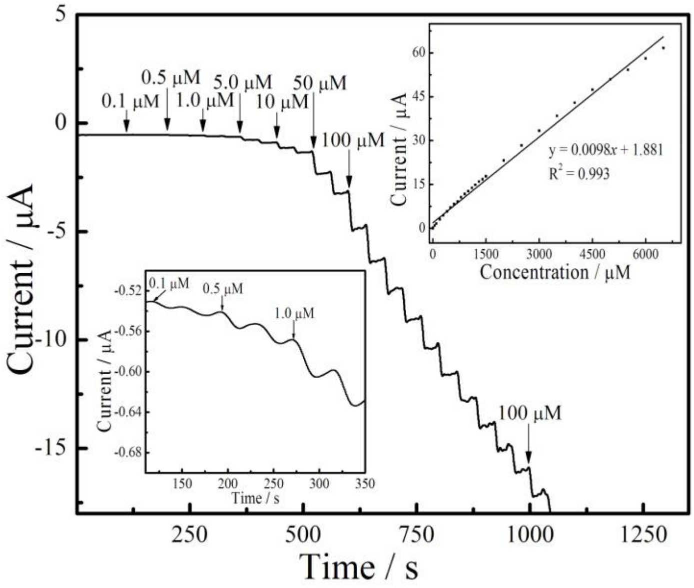

**Figure 10.** Amperometric responses of PEDOT/GO/GCE to successive additions of $1.0 \times 10^{-7}$ M – $1.0 \times 10^{-4}$ M hydroxylamine in 0.1 M PBS (pH = 8.0) at applied potential 0.5 V.

**Table 1.** The comparison of PEDOT/GO/GCE with other HA sensors.

| Electrode | Detection limit (μM) | Linear range(μM) | Sensitivity μA $\mu M^{-1}$ | Method | Reference |
|---|---|---|---|---|---|
| PEDOP/MWCNTs[a]-Pd/GCE | 0.2 | 1–5000 | 0.0098 | Amperometry | [36] |
| PEDOT/MWCNTs-Pd/GCE | 0.25 | 1–6000 | 0.027 | Amperometry | |
| Au/PPY[b]/GCE | 0.21 | 1-500 | 0.0639 | DPV | [37] |
| BaMWCNT[c]/GCE | 0.1 | 0.5–400 | 0.0274 | Amperometry | [11] |
| ZnO/MWCNTs/GCE | 0.12 | 0.4–19,000 | 0.0075 | Amperometry | [38] |
| PEDOT/GO | 0.05 | 0.1 - 6500 | 0.0098 | Amperometry | This work |

[a] multi-wall carbon nanotubes

[b] polypyrrole

[c] baicalin multi-wall carbon nanotubes

### *3.6. Reproducibility, stability and selectivity of the PEDOT/GO/GCE*

Stability is another advantage of the PEDOT/GO/GCE, which was tested by measuring the response current decay during repetitive amperometrical detection. Fig. 11 shows repetitive measurements examined in PBS containing $1.0 \times 10^{-4}$ M HA with 30 successive determinations using the same modified electrode. The relative standard deviation (RSD) of the amperometric response was 0.59%, indicating that the modified electrode had good reproducibility. The long-term stability of the sensor was also investigated in the same solution. The current response of the sensor decreased gradually and retained 87% of its original activity after 3 weeks and displayed excellent response to HA. This achievement manifested that PEDOT/GO film had ability to prevent the electrode from fouling by the oxidation product and to be very stable on the electrode surface for a long time.

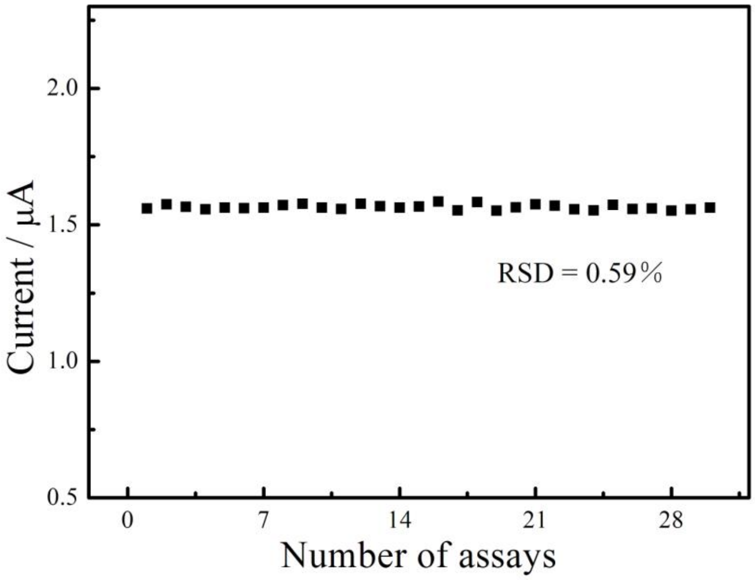

**Figure 11.** The repeatability of the current response of the PEDOT/GO/GCE in 0.1 M PBS (pH 8.0) to successive additions of 0.1 μM hydroxylamine for 30 successive assays.

Possible interferences for the detection of HA at the PEDOT/GO/GCE were investigated by adding various interfering materials into a fixed amount of $1.0\times10^{-4}$ M HA in PBS (pH 8.0). No significant interference was observed from common cations and anions, for 100-fold quantities of $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $Br^-$, $F^-$, $SO_4^{2-}$, $NH_4^+$ and $NO_3^-$ ions, 10-fold quantities of $Pb^{2+}$, $Ba^{2+}$, $Ag^+$, $Cu^{2+}$, $Al^{3+}$, $Pd^{2+}$, and 5-fold quantities $NO_2^-$.

### *3.7 Preliminary application of the PEDOT/GO/GCE*

To illustrate the feasibility of the PEDOT/GO electrode in practical analysis, it was applied to detect HA in tap water by amperometric method. The tap water samples were diluted 500 times with 0.1 M PBS (pH 8.0) before the measurement to fit the calibration curve. HA in tap water was determined by the standard addition method to prevent any matrix influence. The analytical results are presented in table 2. The obtained results showed that the recoveries were satisfactory. Thus, the modified electrode can be successfully applied for the detection of HA in real sample analysis.

**Table 2.** Determination and recovery results of HA in tap water by PEDOT/GO/GCE.

| Sample | Hydroxylamine added (μM) | Hydroxylamine found (μM) | Recovery (%) |
|---|---|---|---|
| 1 | 300 | 301 | 100.3 |
| 2 | 400 | 406 | 101.5 |
| 3 | 500 | 503 | 100.6 |

## 4. CONCLUSIONS

Herein, a biocompatible conducting polymer based nanocomposite was electrochemically synthesized through the electropolymerization of PEDOT in the presence of GO as an anion dopant. It was found that such nanocomposite modified electrode exhibited good catalytic activity toward the oxidation of HA. Under the optimized conditions, a sensitive and simple method for the determination of HA was established with a wide linear range and low detection limit. Moreover, the proposed method has been successfully applied to the determination of HA in real samples. These obtained satisfied results including the simple fabrication procedure, wide linear range, low detection limit, high stability and good reproducibility for repeated determination suggest that this electrode will be a good and attractive candidate for practical applications.

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