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Facile Synthesis of Poly(3,4-ethylenedioxythiophene)/Graphene Nanocomposite and its Application for Determination of Nitrite

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Herein, we proposed a facile electrodeposition method to prepare well-defined poly(3,4-ethylenedioxythiophene)/graphene (PEDOT/GR) composite on the glassy carbon electrode (GCE) for the determination of nitrite as an electrochemical sensor. Scanning electron microscopy (SEM), UV-vis spectroscopy (UV-vis) and electrochemical techniques were used for the characterization of the composite. It was found that PEDOT/GR composite was uniform, and formed a kind of encapsulated structures. Electrochemical experiments showed that this proposed PEDOT/GR composite-modified electrode exhibited excellent electrocatalytic properties for nitrite. Under the optimum conditions, the proposed sensor can be applied to the quantification of nitrite with a wide linear range covering from 0.3 to 600 μM and a low detection limit of 0.1 μM. Furthermore, the proposed sensor had good storage stability, reproducibility and anti-interference ability. To further validate its possible application, the method was successfully applied to the determination of nitrite in water samples.

Keywords: Poly(3,4-ethylenedioxythiophene), Graphene, Sensor, Nitrite, Electrocatalytic oxidation

1. INTRODUCTION

Nitrite has been extensively used in food preservation and fertilizing agents, while its excess level in blood leads to the irreversible oxidation of hemoglobin to methemoglobin [1]. Moreover, it can react with amines to form carcinogenic N-nitrosamine [2]. Because of the potential toxicity of nitrite, its quantitative analysis becomes more and more important in environmental protection and public health. There are several analytical techniques used for quantitative determination of nitrite including the spectrophotometry [3], chemiluminescence [4], chromatography [5], capillary electrophoresis [6] and electrochemical method [7,8]. Among these methods, electrochemical method has been proved to be an inexpensive and effective way for quantitative determination because of its intrinsic sensitivity, fast analysis, high selectivity and simplicity. Recently, different kinds of nitrite sensors have been fabricated based on the chemical modification of electrodes [9,10], but there is still an expanding demand for the development of more reliable and efficient sensors for sensitive analysis of nitrite.

As a“rising star”material, graphene (GR), a novel carbon nanomaterial with single layer of carbon atoms arranged in a two dimensional honeycomb lattice, has attracted considerable interests in both the experimental and theoretical communities in recent years [11]. Due to its unique properties, such as high surface area, high electrical conductivity, and strong mechanical strength, GR has been widely applied in synthesizing nanocomposites [12], constructing energy storage devices, such as fuel cells, [13] and ultracapacitors [14], fabricating chemical sensors and biosensors [15,16]. Some works have demonstrated that GR possesses excellent electrochemical catalytic activity, and should be a novel electrode modified material with excellent performance [17]. However, many of the interesting and unique properties of GR can only be realized after it is integrated into more complex assemblies [18,19]. Up to now, various substances have been incorporated with GR layers, including carbon nanotubes [20], metal nanoparticles [21], ionic liquid [22], and so on to fabricate electrochemical sensors.

Conducting polymers are emerging as intelligent materials and they have a wide range of applications in the field of optical, electronic, electro-chromic devices, and sensors etc [23]. Recently, the combination of conducting polymers with GR-based nanomaterials for the development of novel biomaterials and devices has attracted great attention in the field of electrochemical sensors. For example, Xu et al. established an electrochemical method for the dopamine detection based on polypyrrole and GR modified electrode [24]. Fan et al. fabricated polyaniline/GR composite film modified electrode for voltammetric determination of 4-aminophenol [25]. Wang et al. constructed a novel amperometric sensor for the determination of uric acid using poly (acridine orange)/GR modified electrode [26]. In recent years, PEDOT, a comparatively new conducting polymer, has been attracting growing interest due to its high compatibility, very good film forming properties, high stability, high charge mobility, low band gap, and high degree of doping [27]. Owing to these properties, PEDOT has received particular attention for the electroanalytical application, e.g., detection of chemical [28] and biomolecules such as ascorbic acid [29], cysteine [30], etc. However, the combination of GR with PEDOT for electrochemical detection of nitrite has been few reported.

To utilize the advantages of GR and PEDOT, in this paper, we demonstrate a facile electrodeposition method to prepare well-defined PEDOT/GR composite on the GCE for the determination of nitrite as an electrochemical sensor. The novel PEDOT/GR composite modified GCE exhibited good electrochemical performance and good electrocatalytic activity to the oxidation of nitrite, and the sensor based on PEDOT/GR composite showed good stability and acceptable sensitivity. Moreover, the proposed method was also used to determine nitrite in real samples and obtained satisfied results.

2. MATERIALS AND METHODS

2.1. Reagents and chemicals

3, 4-ethylenedioxythiophene (EDOT) was purchased from Sigma-Aldrich (USA). $NaNO_2$, graphite powder and lithium perchlorate trihydrate ($LiClO_4$) were obtained from Sinopharm chemical reagent Co., Ltd. Phosphate buffer solutions (PBS) were prepared from stock solution of 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4. All the used reagents were analytical grade, and used as received without further purification. All solutions were prepared using deionized distilled water as the solvents in experiment.

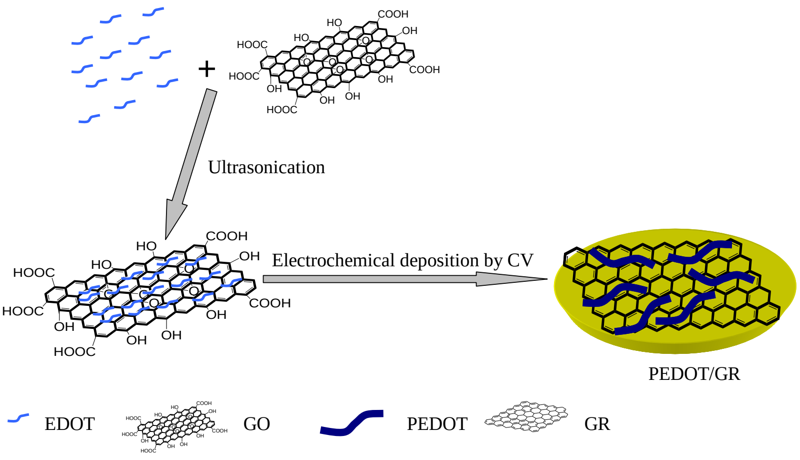
2.2. Apparatus

Scanning electron microscopy (SEM) analysis was performed using a JSM-5600LV microscope (JEOL Ltd., Japan). The UV/vis spectra were obtained using a Perkin-Elmer Lambda 900 ultraviolet-visible-near-infrared spectrophotometer (Germany). The cyclic voltammetric and amperometric measurements were carried out on a CHI 760B electrochemical workstation (Shanghai, China). A three-electrode cell (10 mL) was used with the modified glassy carbon electrode (GCE) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum foil electrode as the counter electrode. All potentials were measured and reported versus the SCE. All experiments were carried out at room temperature and performed in 0.1 M PBS under nitrogen atmosphere.

2.3. Preparation of PEDOT/GR nanocomposite modified GCE

Graphene oxide (GO) was prepared from graphite powder according to the method of Hummers and Offeman [31]. Then EDOT solution was mixed with GO solution and ultrasonicated for 30 min to get a EDOT functionalized GO dispersion solution.

PEDOT/GR nanocomposite film was electrochemically deposited on the GCE by cyclic voltammetry with potential scanning between -1.5 and 1.1 V with a sweep rate of 100 mV s^{-1} at room temperature for 10 cycle in a fresh solution containing 1.0 mg mL^{-1} GO, 0.01 M EDOT monomer and 0.01 M $LiClO_4$ [32]. After deposition, the working electrode was washed with distilled water (shown in Scheme 1).



Scheme 1. Schematic illustration for the synthesis of PEDOT/GR/GCE via a one-step electrochemical approach.

As a comparison, the PEDOT film was prepared by scanning the same potential range and using bare GCE as working electrode in a fresh solution containing 0.01 M EDOT and 0.01 M $LiClO_4$. The pure GR film was synthesized by the same method used to PEDOT/GR except that the suspension was prepared by using pure GO.

3. RESULTS AND DISCUSSION

3.1. Structural and morphological characterizations of PEDOT/GR nanocomposite

UV-Vis spectrophotometry was used to confirm the interaction of PEDOT with GR. Fig. 1 shows the UV-vis spectra of GR (a), PEDOT (b), and PEDOT/GR nanocomposite film (c). All of the above samples were prepared on the indium tin oxide (ITO) coated glass substrate through electrochemical method with similar conditions. There was no obvious absorption of GR because the oxygen functionalities had been removed by electrochemical reduction [33]. As a comparison, PEDOT is a highly conjugated compound, and presents a strong absorption peak at 350 nm and a weak should peak at about 750 nm (curve b), which are attributed to PEDOT oligomers [34] and PEDOT in its oxidized state [35], respectively. The spectrum of PEDOT/GR nanocomposite film was similar to that of PEDOT, except that the absorbance intensity was lower than that of PEDOT, which was indicative of strong π-π stacking interaction between PEDOT and GR.

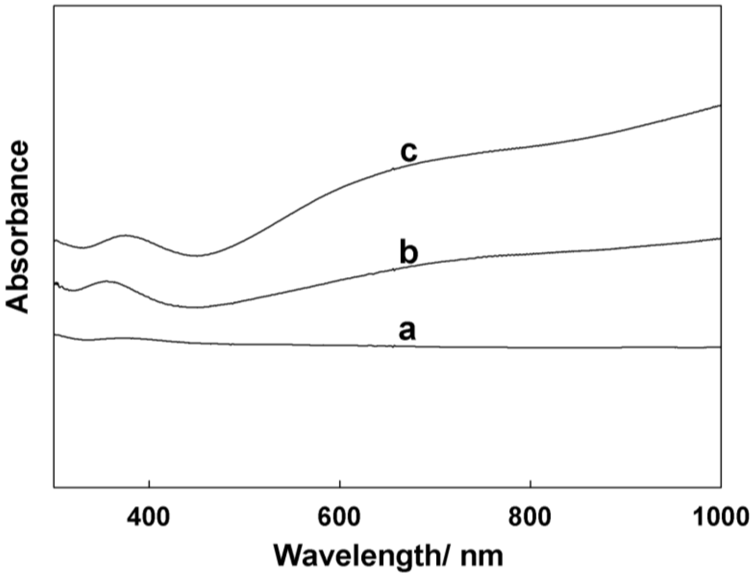


Figure 1 . UV-vis spectra of a) GR, b) PEDOT, and c) PEDOT/GR composite film.

Fig. 2 shows the SEM images of GR and PEDOT/GR composite. The surface of GR thin film (Fig. 2(A)) exhibits well exfoliated, typical wrinkled surface morphology. The in situ electrochemically deposited PEDOT/GR composite film (Fig. 2(B)) manifests the mixed morphology of the layered GR covered by PEDOT molecules obtained by the polymerization of EDOT monomer. It can be seen that during the polymerization of EDOT in electrochemical process, PEDOT molecules have uniformly covered the GR sheets. The GR layer may establish electric conduction pathways throughout the whole system, which is responsible for the electric conductivity and electrochemical sensing.

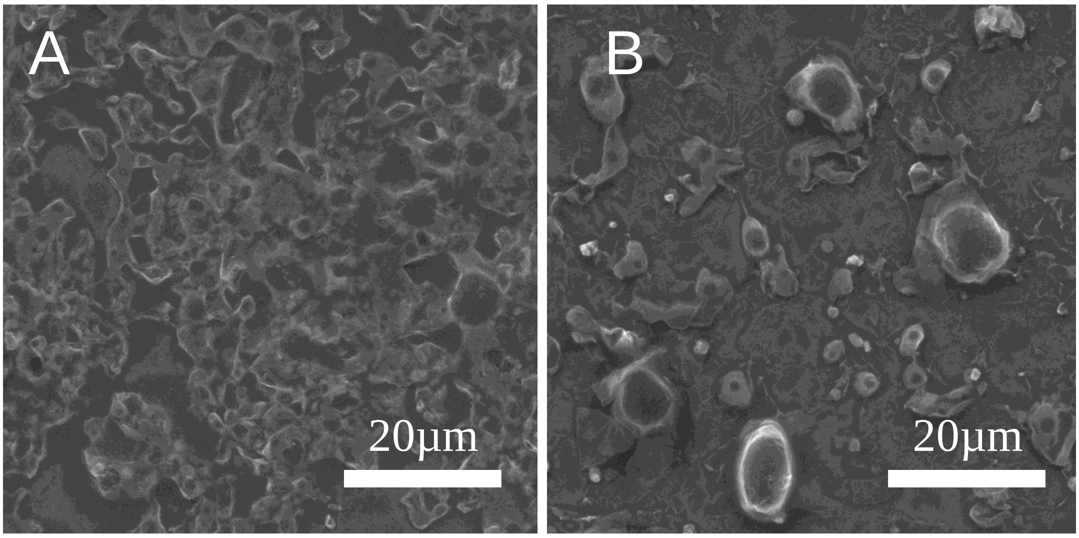


Figure 2. SEM images of (a) GR film and (b) PEDOT/GR composite.

3.2. Electrochemical behavior of the modified electrode

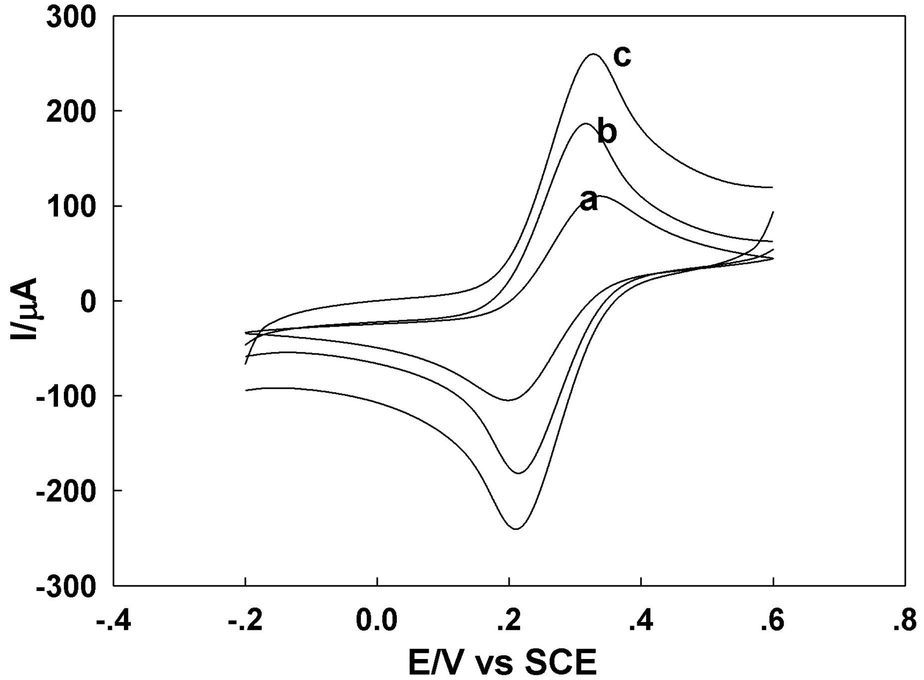


Figure 3. The cyclic voltammograms of bare GCE (a), GR/GCE (b) and PEDOT/GR/GCE (c) in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.1 M KCl at 100 mV s^{-1}.

As a traditional electrochemical technique, cyclic voltammogram (CV) of ferricyanide is a valuable tool to monitor the barrier of the modified electrode, and to investigate the changes to the electrode behavior after each assembly. Fig. 3 represents the CVs of bare GCE (a), PEDOT/GCE (b) and PEDOT/GR/GCE (c) in 5.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.1 M KCl with a scan rate of 100 mV s^{-1}. As shown in Fig. 3, an increase in peak current was observed when PEDOT (curve b) was modified onto the GC electrode (curve a), indicating that PEDOT could accelerate the electron transfer between the electrochemical probe $[Fe(CN)_6]^{3-/4-}$ and the GC electrode. The GR assembled on the PEDOT modified electrode (curve c) made the peak current further increased again, which is attributed to the significantly improved electrical conductivity of PEDOT/GR film.

3.3. Electrocatalytic oxidation of nitrite

Fig. 4 shows CVs responses at bare GCE, PEDOT/GCE, GR/GCE and PEDOT/GR/GCE in the presence of 1 mM nitrite in pH 6.0 PBS. As can be seen, there is a small and broad oxidation peak at about 0.97 V at the bare GCE (Fig. 4, curve a), which was corresponding to the conversion of NO_2^- to NO_3^- through a two-electron oxidation process [36]. The rather broad peak might be due to the slow electron transfer kinetics of nitrite oxidation process. However, in comparison with that at the bare GCE, a remarkable increase in oxidation current and negative shift of peak potential can be observed at the PEDOT/GR/GCE (Fig. 4, curve d). The 1.75-fold enhancement of peak current and the 190 mV reduction of overpotential indicated an efficiently catalytic capability of the PEDOT/GR/GCE towards the oxidation of nitrite. Although similar electrocatalytic response to nitrite can also be observed at PEDOT/GCE and GR/GCE (Fig. 4, curves b and c), the best electrocatalytic activity with the lowest overpotential occurred at the PEDOT/GR/GCE. The extraordinarily electrocatalytic activity could be attributed to the synergistic reaction of PEDOT and GR.

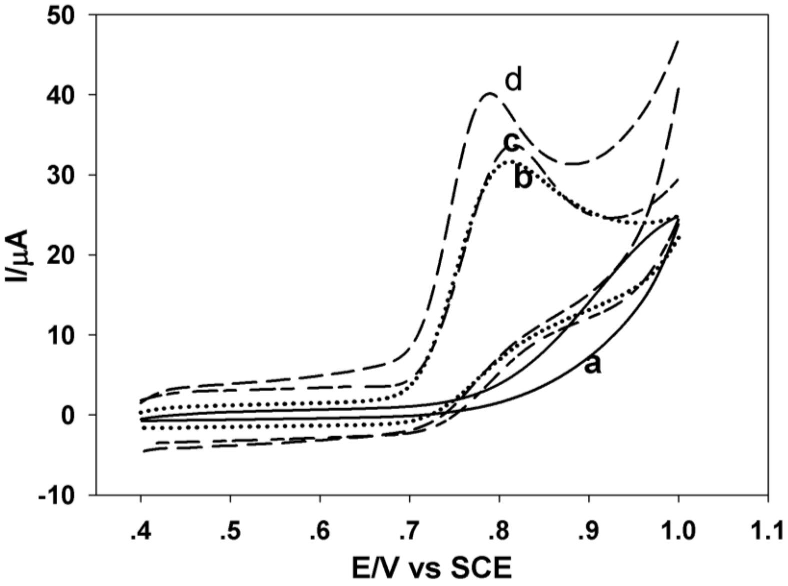


Figure 4. Cyclic voltammograms of 1 mM nitrite at: (a) bare GCE, (b) PEDOT/GCE, (c) GR/GCE and (d) PEDOT/GR/GCE in pH 6.0 PBS. Scan rate: 50 mV s^{-1}.

For investigation of reaction mechanism, the CVs of PEDOT/GR/GCE recorded in 0.1 M PBS (pH 6.0) contain 0.5 mM nitrite at various scan rates were also investigated. As shown in Fig. 5, it can be seen that the anodic peak current clearly increases with increasing potential scan rate. Besides this, the anodic peak currents are proportional to the scan rate, v (inset of Fig. 5). The linear relationship between the peak current and scan rate can be expressed by the linear regression equation as: I_{pa} (μA) = 0.163 v (mV s^{-1}) + 5.950 (R^2 = 0.995). This result indicates that the electrochemical reaction of nitrite on the PEDOT/GR is a surface-controlled process.

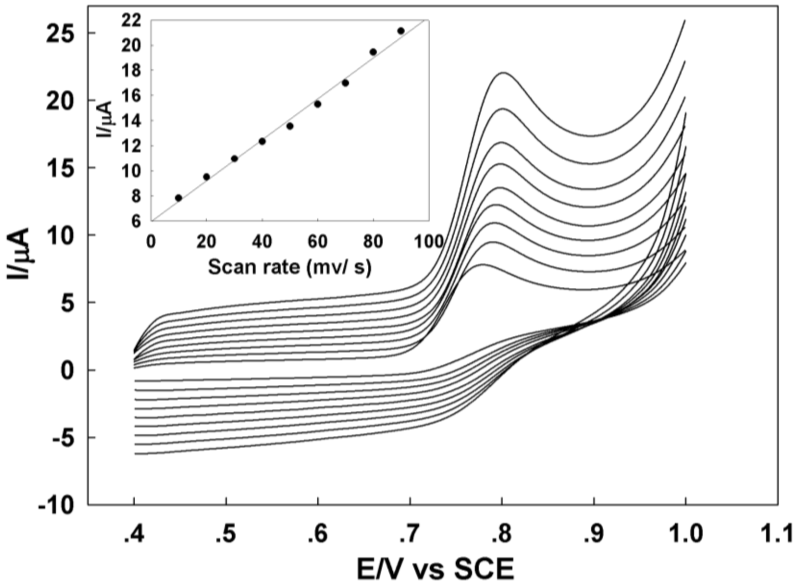


Figure 5. The cyclic voltammograms of the PEDOT/GR/GCE recorded in pH 6.0 PBS containing 0.5 mM nitrite at different scan rates (inner to outer: 10, 20, 30, 40, 50, 60, 70, 80 and 90 mV s^{-1}). Inset: plots of peak current vs. the scan rate (v).

3.4. Effect of pH value

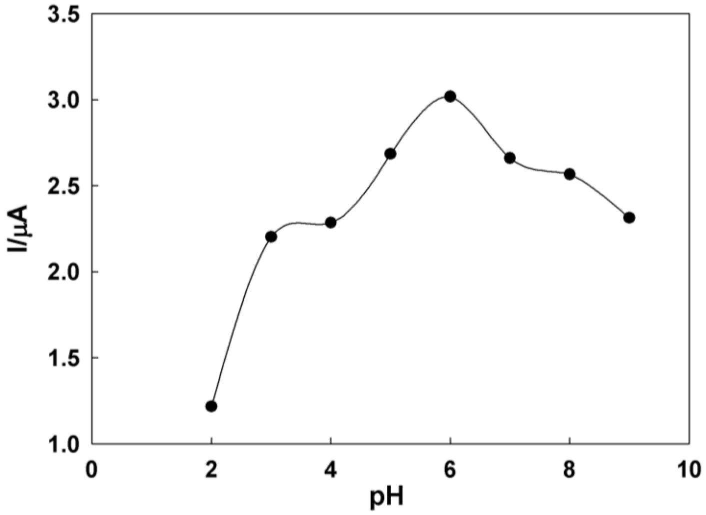


Figure 6. Effects of pH on amperometric response of the PEDOT/GR/GCE to 100 μM nitrite in the pH range 2.0-9.0.

The pH value is one of the parameters that affect the response of the PEDOT/GR/GCE to nitrite. Fig. 6 presents the pH dependence of the amperometric response of 100 μM nitrite in the pH range 2.0-9.0. It can be seen that the current increased as the pH changed from 2.0 to 6.0, following by a largely decrease in the pH range of 6.0-9.0. The small peak current at lower pH (<6.0) may be attributed to the instability of nitrite in strong acidic conditions due to its decomposition reaction of the conversion of nitrite to NO and NO_3^- [37]. While the peak current decreased at higher pH above 6.0, which might be due to a shortage of protons [38]. The maximum response was obtained at pH 6.0, which was adopted as the optimum pH value in our experiments.

3.5. Amperometric detection of nitrite

The amperometric response of the PEDOT/GR/GCE to successive additions of nitrite was further evaluated under the optimized experimental conditions. Fig. 7 shows the typical current-time dynamic response of the PEDOT/GR/GCE towards nitrite. The electrode responded quickly to the change of nitrite concentration and reaches about 95% of the steady-state current within 8 s. The amperometric signal shows linear correlation to nitrite concentration in the range from 0.3 to 600 μM with a correlation coefficient of 0.995, which covers four orders of magnitude of nitrite concentrations. The detection limit was estimated to be 0.1 μM (based on S/N=3) for nitrite. The performances of the fabricated sensor are compared with different nitrite sensors and the results are shown in Table 1. It can be observed that the PEDOT/GR/GCE offers a reasonable linear range for nitrite determination and the detection limit is lower than some previously reported.

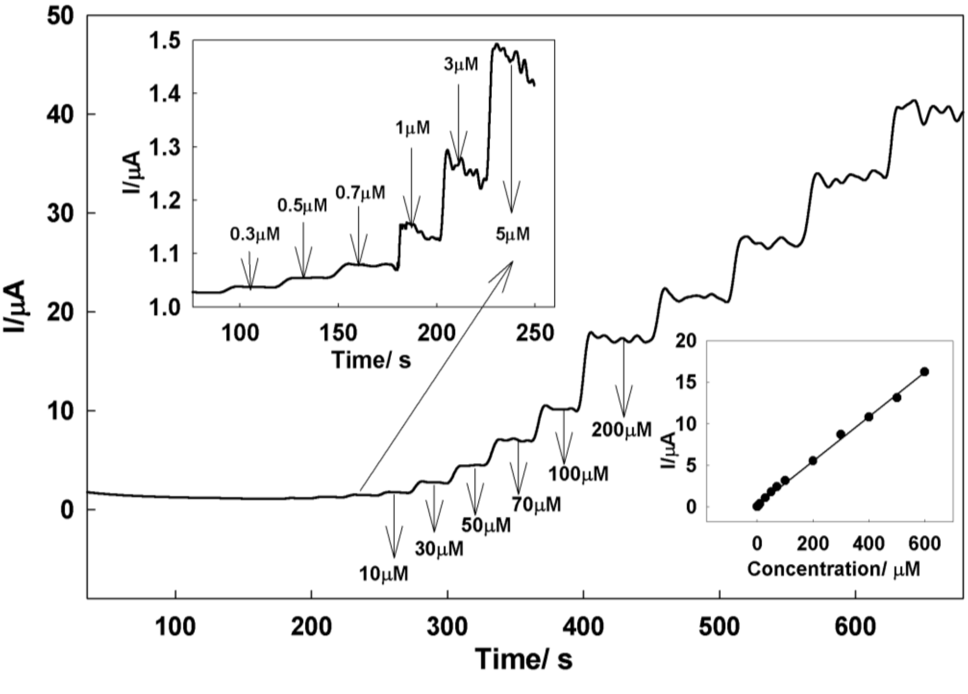


Figure 7. The typical current-time dynamic response of PEDOT/GR/GCE with successive injection of nitrite at an applied potential 0.78 V (Inset: the relationship of catalytic current with the concentration of nitrite).

Table 1. Comparisons of the proposed PEDOT/GR/GCE performance with other nitrite sensors

Type of electrode	Linear range (µM)	Detection limit (µM)	Reference
Chitosan-carboxylated multi-wall carbon nanotube-modified electrode	0.5-100	0.1	[39]
Thionine modified aligned carbon nanotubes modified electrode	3.0-500	1.12	[40]
Carbon nanotubes/poly(Azure A) electrode	3-4500	1	[41]
PdCu alloy nanoclusters modified electrode	1.0-1100	0.3	[42]
Hollow Fe_2O_3 polyhedrons electrode	9-300	2.6	[43]
Graphene-poly(3,4-ethylenedioxythiophene) nanocomposite electrode	0.3-600	0.1	This work

3.6. Selectivity, reproducibility and stability of PEDOT/GR/GCE

Possible interferences for the detection of nitrite at the PEDOT/GR/GCE were investigated by adding various foreign species into a fixed amount of nitrite (0.1 mM). A relative error of 5% was considered tolerable. The results showed that most of the ions, as K^+, Na^+, Ag^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Zn^{2+}, Cl^-, NO_3^- , SO_4^{2-} and PO_4^{3-} in a 200-fold concentration, BrO_3^-, IO_3^-, H_2O_2, glucose, methanol and Uric acid in a 20-fold concentration had no effect on the detection of nitrite.

The reproducibility and repeatability of the developed sensor were determined. In a series of 10 sensors prepared in the same way, a relative standard deviation of 3.9% was obtained toward 0.1 mM nitrite, indicating the reliability of the method. A set of 10 different amperometric measurements for 0.1 mM nitrite with a single sensor yield a R.S.D. of 3.1%. Thus, the proposed method had an excellent reproducibility for nitrite determination.

The stability of the nitrite sensor was explored. The response to 0.1 mM nitrite was tested each week, after 35 days of storage, the response of the sensor only decreased 9% compared to the initial response, which shows long-term stability.

3.7. Real sample analysis

In order to verify the performance and feasibility of the proposed method for analysis of nitrite in environmental samples, the PEDOT/GR/GCE was applied to the determination of nitrite in river water. Recovery studies were carried out on samples by nitrite standards added. An appropriate volume of the sample was placed in an electrochemical cell for the determination of nitrite by amperometric determination. The results are listed in Table 2. It can be seen that this proposed method can be successfully applied for the detection of nitrite in real samples.

Table 2. Determination of nitrite in water samples

Sample	Added (mM)	Found (mM)	Recovery(%)
1	0.09	0.092	102.1
2	0.16	0.17	105.6
3	0.58	0.56	96.7
4	1.20	1.24	103.5
5	5.00	4.90	98.0

[a] R.S.D. (%) calculated from three separate experiments.

4. CONCLUSIONS

In this work, PEDOT/GR nanocomposite was prepared by a simple electrochemical method. It was found that such nanocomposite modified electrode exhibited good catalytic activity toward the oxidation of nitrite. Under the optimized conditions, a sensitive and simple method for the determination of nitrite was established with a wide linear range and low detection limit. Moreover, the proposed method has been successfully applied to the determination of nitrite in real samples and obtained satisfied results. The facile and easy electrochemical approach used for the preparation of PEDOT/GR nanocomposite may open up new horizons in developing of cost effective sensors.

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References

1. R. Yue, Q. Lu, Y. Zhou, *Biosens. Bioelectron*, 26 (2011) 4436
2. Y.G. Huang, J.D. Ji, Q.N. Hou, *Mutation. Res*, 358 (1996) 7
3. M. Bru, M.I. Burguete, F. Galindo, S.V. Luis, M.J. Marin, L. Vigara, *Tetrahedron Lett*, 47 (2006) 1787
4. P. Mikuska, Z. Vecera, *Anal. Chim. Acta*, 495 (2003) 225
5. I.M. Ferreira, S. Silva, *Talanta*, 74 (2008) 1598
6. E. Szoko, T. Tabi, A. Halasz, M. Palfi, K. Magyar, *J. Chromatogr. A*, 1051 (2004) 177
7. A. Lagalante, P. Greenbacker, *Anal. Chim. Acta*, 590 (2007) 151
8. B. Strehlitz, B. Grundig, W. Schumacher, P.M.H. Kroneck, K.D. Vorlop, H. Kotte, *Anal. Chem*, 68 (1996) 807
9. W.J. Santos, A.L. Sousa, R.C. Luz, F.S. Damos, L.T. Kubota, A.A. Tanaka, S.M. Tanaka, *Talanta*,

70 (2006) 588
10. S. Wang, Y. Yin, X. Lin, *Electrochem. Commun*, 6 (2004) 259
11. J.C. Meyer, A.K. Geim, M.I. Katsnelson, *Nature*, 446 (2007) 60
12. J.P. Avinash, L.V. Jemma, B.S. Thomas, M. Stephen, *Adv. Mater*, 21 (2009) 3159
13. J.J. Liang , Y. Huang , L. Zhang , Y. Wang , Y.F. Ma , T.Y. Guo , Y.S. Chen, *Adv. Funct. Mater*, 19 (2009) 2297
14. M. D. Stoller , S. Park , Y. Zhu , J. An , R. S. Ruoff , *Nano Lett*, 8 (2008) 3498
15. Y. Wang , Y.Y. Shao , J.H. Li , Y. H. Lin , *ACS Nano*, 4 (2010) 1790
16. T.T. Baby, S.S. Aravind, T. Arockiadoss, R.B. Rakhi, S. Ramaprabhu, *Sens. Actuators* B, 145 (2010) 71
17. K.J. Huang, D.J. Niu, J.Y. Sun, C.H. Han, Z.W. Wu, Y.L. Li, X.Q. Xiong, *Colloids Surf.*, B, 82 (2011) 543
18. C.L. Fu, W.S. Yang, X. Chen, D.G. Evans, *Electrochem. Commun*, 11 (2009) 997
19. J. Li, S. Guo, Y. Zhai, E. Wang, *Anal. Chim. Acta*, 649 (2009) 196
20. H.S. Yin, Y. Zhou, X. Meng, K. Shang, S.Y. Ai, *Biosens. Bioelectron*, 30 (2011) 112
21. F. Liu, Y.X. Piao, K.S. Choi, T.S. Seo, *Carbon*, 50 (2012) 123
22. J.Y. Sun, K.J. Huang, S. Zhao, Y. Fan, Z.W. Wu, *Bioelectrochemistry*, 82 (2011) 125
23. S. Harish, J. Mathiyarasu , K.L. Phani, V. Yegnaraman, *J. Appl. Electrochem*, 38 (2008) 1583
24. 24. P. Si, H.L. Chen, P. Kannan, D.H. Kim, *Analyst*, 136 (2011) 5134
25. Y. Fan, J.H. Liu, C.P. Yang, M. Yu, P. Liu, *Sens. Actuators* B, 157 (2011) 669
26. Z.h. Wang, J.F. Xia, L.Y. Zhu, Y.Z. Xia, *Sens. Actuators* B, 161 (2012) 131
27. C.Y. Lin, A. Balamurugan, Y.H. Lai, K.C. Ho, *Talanta*, 82 (2010) 1905
28. A. Balamurugan, S.M. Chen, Electroanal, 21 (2009) 1419
29. S.S. Kumar, J. Mathiyarasu, K.L. Phani, Y.K. Jain, V. Yegnaraman, *Electroanal*, 17 (2005) 2281
30. W.Y. Su, S.H. Cheng, *Electrochem. Commun*, 10 (2008) 899
31. W.S. Hummers, R.E. Offeman, *J. Am. Chem. Soc*, 80 (1958) 1339
32. L.M. Lu, O. Zhang, J.K. Xu, Y. Wen, X. Duan, H. Yu, L. Wu, T. Nie, *Sens. Actuators* B, 181 (2013) 567
33. H.J. Ahonen, T. Hellstrom, J. Mattila, J. Kankare, *Synth Met*, 119 (2001) 119
34. M. Turbiez, P. Frere, J.Roncali, *J. Org. Chem*, 68 (2003) 5357
35. H.J. Ahonen, J. Lukkari, J. Mattila, J.Kankare, *Synth. Met*, 119 (2001) 119
36. A.L. Sousa, W.J. Santos, R.C. Luz, F.S. Damos, L.T. Kubota, A.A. Tanaka, S.M. Tanaka, *Talanta*, 75 (2008) 333
37. O. Brylev, M. Sarrazin, L. Roué, D. Bélangér, *Electrochim Acta*, 52 (2007) 6237
38. X. Huang, Y. Li, Y. Chen, L. Wang, *Sens. Actuators B*, 134 (2008) 780
39. L.Y. Jiang, R. Wang, X. Li, L. Jiang, G.H. Lu, *Electrochem. Commun*, 7 (2005) 597
40. K. Zhao, H.Y. Song, S.Q. Zhuang, L.M. Dai, P.G. He, Y.Z. Fang, *Electrochem. Commun*, 9 (2007) 65
41. J.X. Zeng, W.Z. Wei, X. Zhai, P. Yang, J. Yin, L. Wu, X. Liu, K. Liu, S. Gong, *Microchim. Acta*, 155 (2006) 379
42. X.H. Zhu, G.F. Kang, X.Q. Lin, *Microchim. Acta*, 159 (2007) 141
43. X. Cao, Y.J. Xu, N. Wang, *Electrochim. Acta*, 59 (2012) 81