Nitrogen-doped Graphene Modified Glassy Carbon Electrode for Anodic Stripping Voltammetric Detection of Lead Ion

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Nitrogen-doped (NG) graphene modified glassy carbon electrode was prepared for sensitive electrochemical investigation on lead ion (Pb^{2+}) with differential pulse anodic stripping voltammetry. Due to the large surface area, excellent conductivity and good adsorption ability of NG nanosheet, Pb^{2+} can be accumulated and detected with enhanced voltammetric response in the concentration range from 9.0×10^{-9} mol/L to 9.0×10^{-5} mol/L. The detection limit was calculated as 1.91×10^{-9} mol/L and the proposed method was applied to fish powder sample determination.

1. INTRODUCTION

Graphene (GR) is composed of single layer sp^2 hybridized carbon atoms, which is packed into a dense honeycomb crystal structure as nanosheet. Due to the unique properties including large surface area, high conductivity and mechanical strength [1], GR and its related composites have wide applications in different fields such as electrochemistry and electrochemical sensors [2]. GR modified electrodes exhibit electrocatalytic activity to the redox reaction of electroactive substances and further accelerate the electron transfer rate. In recent years doping carbon materials have been reported and investigated. Chemical doping can tailor the property of carbon nanomaterials, and modulate the electronic behaviors and the surface chemistry [3]. Nitrogen atom has similar of atomic size with five valence electron structures, which is often used to dope into the carbon structure with the formation of

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C-N bonds [4]. For example N-doped carbon nanotube (CNT) can fasten direct electron transfer of redox enzymes and the oxygen reduction reaction [5]. Recently N-doped GR (NG) has also been synthesized by different methods such as CVD approach, post-synthesis treatment and solvethermal methods [6]. Nitrogen atom can bond with GR in pyridinic N, pyrrolic N and graphitic C with different ratio. The presence of N in GR can affect the spin density and charge distribution of carbon atoms, which further induces some activation region on the nanosheet with catalytic activity [7].Therefore NG has also been used in the field of fuel cell, biosensor and electrode modification [8,9].

Lead ion (Pb^{2+}) is one of the most serious environmental pollutants that can be accumulated in plant, animal and humans. Because Pb^{2+} cannot be degraded, the low concentrations of Pb^{2+} have great influence on the functions of biological system and organs of both humans and animals [10]. So it is important to establish sensitive and reliable analytical methods for Pb^{2+}. Different methods including atomic spectrophotometry, colorimetry, fluorescence and electrochemistry have been developed for the Pb^{2+} detection [11-13]. However some of them require sophisticated equipment or complex sample treatment procedure. Electrochemical methods, which exhibit high sensitivity and good selectivity with cheaper instruments, have been explored for the detection of Pb^{2+} [14].

In this paper we fabricated a NG modified glassy carbon electrode (GCE), which was used for the sensitive detection of Pb^{2+} with anodic stripping voltammetry (ASV). Pb^{2+} exhibited sensitive ASV response on NG/GCE, which was further used as a sensing platform for Pb^{2+} detection.

2. EXPERIMENTAL

2.1 Reagents and Apparatus

Differential pulse anodic stripping voltammetric (DPASV) measurements were performed on a CHI 1210B electrochemical workstation (Shanghai CH Instrument, China) with conventional three-electrode system. NG/GCE was working electrode with platinum wire as auxiliary electrode and saturated calomel electrode (SCE) as reference electrode. NG was prepared by solvothermal synthesis that reported previously [15]. 0.1 mol/L HOAc-NaOAc buffer solutions were acted as the supporting electrolyte. All the other chemicals were of analytical reagent grade and doubly distilled water was used thoughout.

2.2 Analytical procedure

NG/GCE was fabricated by putting 5.0 μL 1.0 mg/mL NG solution on the GCE surface. After the modified electrode was dried at room temperature, DPASV measurements were performed in 0.10 mol/L pH 4.0 HOAc-NaOAc buffer with pre-concentration at -1.0 V and stirring for 300 s. After a 10 s quiet period, DPASV measurement was performed. The instrumental conditions were selected as: potential range from -0.9 to -0.3V, potential amplitude 50 mV, step potential 8 mV with deposition time 5 min.

The experimental conditions for the voltammetric detection of Pb^{2+} were optimized by changing the varieties such as the types of electrolytes, different accumulation potential and
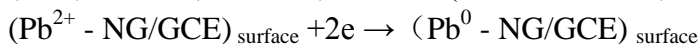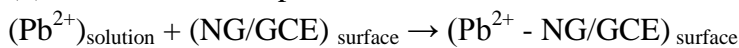
accumulation time. Then the voltammetric responses were recorded at the same instrumental parameters and the data were compared.

3. RESULT AND DISCUSSION

3.1 Voltammetric behavior of Pb^{2+}

The DPASV results of 1.5×10^{-5} mol/L Pb^{2+} on GCE (curve a) and NG/GCE (curve b) were recorded and shown in Figure 1A. After accumulation at the potential of -1.0 V for 300 s, a stripping peak could be observed on GCE at -0.548 V and the reduction peak current was 18.2 μA (curve a), which indicated that Pb^{2+} could be deposited on the GCE surface. Meanwhile, a more obvious stripping peak appeared on NG/GCE and the peak current was 35.8 μA at the same conditions (curve b). Therefore the presence of NG on the electrode can provide more effective active site for the nucleation of lead and more lead could be deposited on the electrode with the response increased greatly. NG has been reported with the characteristics including high conductivity, big surface area and certain catalytic activity. The electrochemical procedure could be shown as the following equations:

(1) Accumulation step
$(Pb^{2+})_{solution} + (NG/GCE)_{surface} \rightarrow (Pb^{2+} - NG/GCE)_{surface}$
$(Pb^{2+} - NG/GCE)_{surface} + 2e \rightarrow (Pb^0 - NG/GCE)_{surface}$

(2) Stripping step
$(Pb^0 - NG/GCE)_{surface} \rightarrow (Pb^{2+})_{solution} + (NG/GCE)_{surface} + 2e$
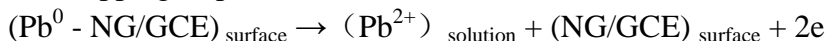
Figure 1B showed the simultaneous DPASV detection of 0.15 μmol/L Pb^{2+} and Cd^{2+} on NG/GCE at the selected conditions. The anodic stripping peak of Cd^{2+} was located at -0.80 V and that of Pb^{2+} was at -0.548 V. Therefore the peak-to-peak (ΔEp) separation was 0.252 V. The large separation of peak potential could be used for the simultaneous determination of Pb^{2+} and Cd^{2+} in the mixture solution.
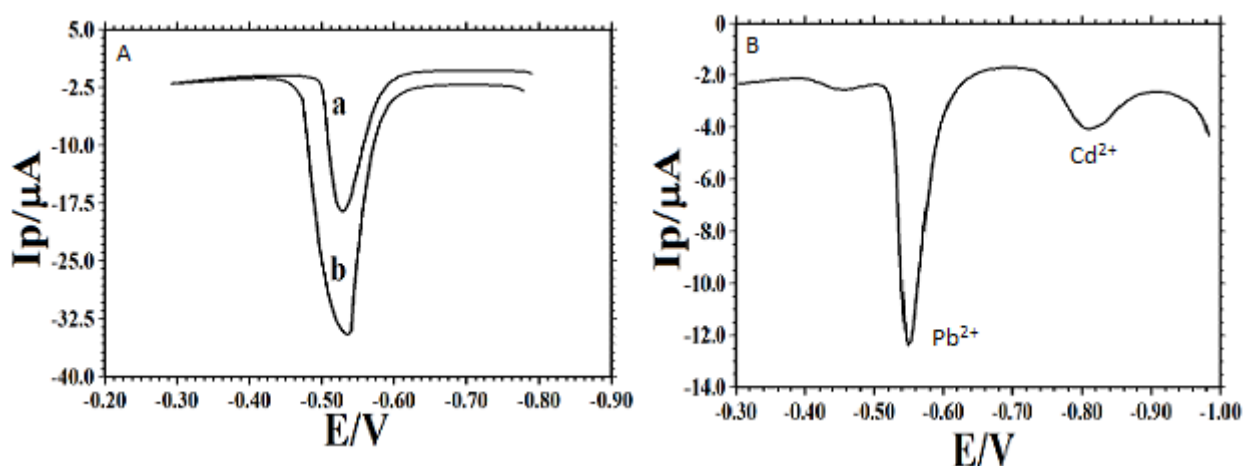

Figure 1. (A) DPASV of 1.5×10^{-5} mol/L Pb^{2+} on (a) GCE and (b) NG/GCE in pH 4.0 HOAc-NaOAc buffer; (B) DPASV of the mixture of 1.5×10^{-7} mol/L Pb^{2+} and 1.5×10^{-7} mol/L Cd^{2+} on NG/GCE in pH 4.0 HOAc-NaOAc buffer. Instrumental conditions: accumulation potential -1.0 V, accumulation time 300 s, pulse amplitude 50 mV, pulse width 50 ms.

3.2 Optimization of experimental conditions

The supporting electrolyte has influence on the electrochemical response of Pb^{2+}. Therefore different electrolytes including HCl, KCl, HNO_3, Na_2HPO_4-NaH_2PO_4 and HOAc-NaOAc were investigated. A well-defined anodic stripping voltammetric response of Pb^{2+} could be observed in 0.1 mol/L HOAc-NaOAc solution, which was used in the following experiments. The optimal buffer pH for the determination of Pb^{2+} was checked in the pH range from 3.0 to 5.5. As shown in Figure 2A, the biggest peak current was got at pH 4.0, which was selected for the stripping analysis.

The effect of accumulation potential on the stripping peak currents was studied in 0.10 mol/L pH 4.0 HOAc-NaOAc buffer solution with the results shown in Figure 2B. When the accumulation potential was changed from -0.8 to -1.0 V, the reduction peak current of Pb^{2+} increased gradually. When the accumulation potential was negative than -1.0 V, the peak current did not change significantly. Therefore the accumulation potential of -1.0 V was selected for deposition Pb^{2+}.

The effect of accumulation time on the stripping peak currents was investigated with the results shown in Figure 2C. The stripping peak currents increased gradually with the accumulation time from 100 to 300 s, indicating that more Pb^{2+} was deposited on NG/GCE surface. When the accumulation time was longer than 300 s, the stripping peak currents remained unchanged, which was attributed to the saturation loading of lead on the electrode interface. So 300 s was selected as the optimal accumulation time for the determination of Pb^{2+}.
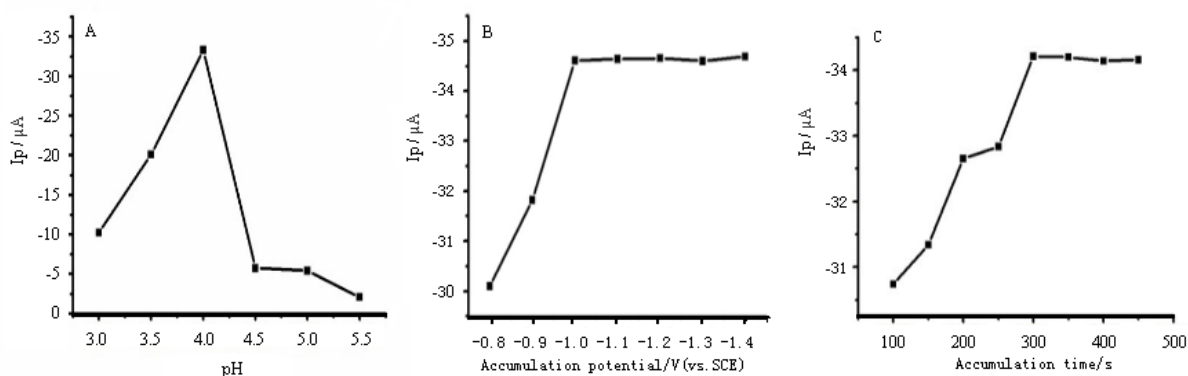

Figure 2. (A) Relationship of pH and Ip value for 1.5×10^{-5} mol/L Pb^{2+} in different pH HOAc-NaOAc buffer; (B) Effect of accumulation potential and (C) Effect of accumulation time on the stripping peak currents of 1.5×10^{-5} mol/L Pb^{2+} in pH 4.0 HOAc-NaOAc buffer. Other conditions are the same as in Figure 1.

3.3 Interferences

At the optimal conditions, we investigated the influence of commonly coexisting inorganic ions on the stripping response of 1.0 μmol/L Pb^{2+} and the results were summarized in table 1. It can be seen that same concentrations of Mn^{2+}, Mg^{2+}, Na^+, Al^{3+}, K^+, Cl^-, SO_4^{2-} etc. had no significant influences to the peak current of Pb^{2+} with the deviation less than ±5%. While Hg^{2+} in the solution resulted in the increase of peak response, which could be ascribed to the reduction of Hg^{2+} on the electrode. Then a mercury film was formed on the surface with more Pb deposited to the formation of amalgam.

Table 1. Influence of ions on the determination of 1.0 μmol/L Pb^{2+}

Interference	Concentration (μmol/L)	Ralative error (%)	Interference	Concentration (μmol/L)	Ralative error (%)
Mn^{2+}	1.0	+0.75	K^+	1.0	+1.21
Mg^{2+}	1.0	+3.24	Cl^-	1.0	+0.32
Na^+	1.0	+1.14	SO_4^{2-}	1.0	-1.05
Al^{3+}	1.0	+2.17	Hg^{2+}	1.0	+16.8

3.4 Calibration curve

At the selected conditions Pb^{2+} solution was measured by DPASV. As expected the increase of Pb^{2+} concentration in the solution resulted in the enhancement of the stripping response gradually. As shown in Figure 3, the stripping peak current exhibited good linear ranges with Pb^{2+} concentration from 9.0×10^{-9} mol/L to 9.0×10^{-5} mol/L and the detection limit was 1.91×10^{-9} mol/L (3σ). The linear regression equation was got as Ip(μA)= - 0.456C (μmol/L) - 7.175(γ=0.998), which could be used for sample detection.
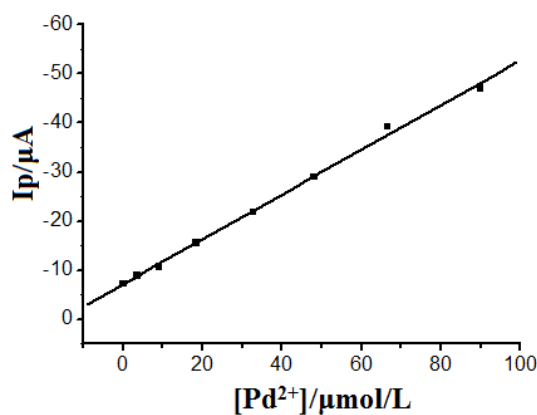
Figure 3. Calibration curve for Pb^{2+} detection with NG/GCE in pH 4.0 HOAC-NaOAC solution

Table 2. Comparison of analytical parameters for Pb^{2+} detection by modified electrodes

Electrodes	Linear range (μmol/L)	Deterction limit (μmol/L)	Reference
BTPSBA/CPE	0.3-7.0	0.04	16
L-cys-rGO/GCE	0.4-1.2	0.02	17
$Mo_6S_{9-x}I_xNWs$/GCE	0.007-2.2	0.002	18
Bi/Sb-Sn/SPE	0.024-0.22	0.004	19
NA-SbFE(pyrogallol red)	0.004-0.58	0.004	20
RGO/Bi/CPE	0.097-0.58	0.0027	21
NG/GCE	0.009-90.0	0.0019	This work

A comparison of this method with other modified electrodes for Pb^{2+} detection was summarized in table 2. It can be seen that NG/GCE had a wider linear range for the Pb^{2+} detection with lower detection. Also the fabrication procedure was easy with the casting of NG directly on the electrode surface.

3.5 Stability and reproducibility

A same NG/GCE was used to eight parallel detections of 1.5×10^{-7} mol/L Pb^{2+} with the relative standard deviations (RSD) as 4.5%. After 4 weeks storage, the modified electrode remained 96.7% of its initial response, and after one month the stripping peak current still retained for 90%. The results indicated that NG/GCE had good reproducibility and long-time stability.

3.6 Sample detection

In order to illustrate its application, NG/GCE was employed to detect Pb^{2+} in fishmeal samples, which was processed with the following digestion procedure [22]. 0.5 g fishmeal samples were mixed with a little deionized water, 8 mL nitrate and 2 mL hydrogen peroxide in the clean digestion tank for a period of time. Until the digestion tank cooling the digestion solution was put into microwave digestion system and set digestion process. Lastly the digestion solution was shifted into beaker on a hot plate to catch the acid to about 0.5 mL, and then transferred to 10 mL colorimetric tube to get the sample solution. The pretreated real fishmeal samples solution were diluted with 0.1 mol/L HOAC-NaOAC buffer solution (pH 4.0) and detected by the proposed procedure with the results listed in table 3. It can be seen that the results of electrochemical detection were in good agreement with those obtained by AAS, which confirmed the accuracy and reliability of this method.

Table 3. Determination of Pb^{2+} concentration in fishmeal samples (n=3)

Samples	Detected	Added (10^{-8} mol/L)	Found (10^{-8} mol/L)	Recovery (%)	AAS (10^{-8} mol/L)
1	0	8.00	7.75	96.88	7.01
2	0	8.00	7.82	97.75	7.23
3	0	8.00	7.88	98.50	7.18

4. CONCLUSION

NG was modified on the surface of GCE and anodic stripping analysis of Pb^{2+} was realized on NG/GCE. At the optimal conditions, the anodic stripping peak current had good linear relationship with Pb^{2+} concentration from 9.0×10^{-9} to 9.0×10^{-5} mol/L with the detection limit as 1.91×10^{-9} mol/L

(3σ). The proposed method has a simpler fabrication procedure and high sensitivity for Pb^{2+} detection due to the modification of NG on the working electrode, which extended the application of NG in the field of electroanalysis.

References

1. A. K. Geim and K. S. Novoselov, *Nat. Mater.,* 6 (2007) 183.
2. M. Pumera, *Chem. Soc. Rev.,* 39 (2010) 4146.
3. Y. C. Ma, A. S. Foster and A. V. Krasheninnikov, *Phys. Rev. B,* 72 (2005) 205416.
4. K. P. Gong, F. Du and Z. H. Xia, *Science,* 323 (2009) 760.
5. N. Q. Jia, L. Liu and Q. Zhou, *Electrochim. Acta,* 51 (2005) 611.
6. H. B. Wang, T. Maiyalagan and X. Wang, *ACS Catal*., 2 (2012) 781.
7. Y. Y. Shao, S. Zhang and M. H. Engelhard, *J. Mater. Chem.,* 20 (2010) 7491.
8. W. Sun, L. F. Dong, Y. Deng, J. H. Yu and W. C. Wang, *Mat. Sci. Eng. C-Mater.,* 39 (2014) 86.
9. W. Sun, L. F. Dong, Y. X. Lu, Y. Deng and J. H. Yu, *Sensor. Actuat. B-Chem.,* 199 (2014) 36.
10. J. Du, C. Cao and L. Jiang, *Gene,* 563 (2015) 155.
11. Q. Song, M. G. Li and L. Huang, *Anal. Chim. Acta,* 787 (2013) 64.
12. D. P. Zhang, L. Yin and Z. H. Meng, *Anal. Chim. Acta,* 812 (2014) 161.
13. X. Y. Zhang, R. X. Hu and N. Shao, *Talanta,* 107 (2013) 140.
14. S. R. Tang, W. Lu and F. Gu, *Electrochim. Acta,* 134 (2014) 1.
15. Q. Q. Zhu, J. H. Yu, W. S. Zhang, H. Z. Dong and L. F. Dong, *J. Renew Sustain Ener.*, 5 (2013) 021408.
16. I. Cesarino, G. Marino, J. R. Matos, E. T. G. Cavalheiro, I. Cesarinoetal, *Talanta,* 75 (2008)15.
17. S. Muralikrishna, K. Sureshkumar, T. S. Varley, D. H. Nagaraju, T. Ramakrishnappa, *Anal. Methods,* 6 (2014) 8698.
18. H. Lin, M. X. Li, D. Mihailovič, *Electrochim. Acta,* 154 (2015) 184.
19. M. Maczuga, A. Economou, A. Bobrowski, *Electrochim. Acta,* 114 (2013) 758.
20. V. Arancibia, E. Nagles, C. Rojas, M. Gomez, *Sensor. Actuat. B,* 182 (2013) 368.
21. P. K. Sahoo, B. Panigrahy, S. Sahoo, A. K. Satpati, D. Li, D. Bahadu, *Biosen. Bioelectron.,* 43 (2013) 293.
22. R. J. Zhao, *Journal of Qingdao Agricultural University (Natural Science),* 31 (2014) 50.