Talanta 88 (2012) 696–700

Contents lists available at SciVerse ScienceDirect

Talanta

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Sensitive electrochemical detection of nitrobenzene based on macro-/meso-porous carbon materials modified glassy carbon electrode

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ARTICLE INFO

Article history:
Received 8 August 2011
Received in revised form
19 November 2011
Accepted 22 November 2011
Available online 28 November 2011

Keywords:
Macro-/meso-porous carbon materials
Electrochemical sensor
Nitrobenzene
Linear sweep voltammetry

ABSTRACT

A sensitive electrochemical sensor for nitrobenzene (NB) detection has been developed based on macro-/meso-porous carbon materials (MMPCMs). MMPCMs were prepared by pyrolysis of the ionic-liquid ([AEIm]BF_4) polymer (PIL) pre-wrapped onto SiO_2 microspheres and then removal of the silica core. The morphology and structure of MMPCMs were characterized by scanning electron microscopy (SEM) and nitrogen adsorption/desorption measurements. Owing to the macro-/meso-porous structure, large specific surface area and accumulation effect of MMPCMs, the MMPCMs modified glassy carbon (MMPCMs/GC) electrode has high catalytic activity towards the reduction of NB. At the optimal pH value and accumulation time, the resulted electrochemical sensor shows satisfactory analytical performance for NB detection. The linear response range is from 0.2 μM to 40 μM and the detection limit is 8 nM based on the signal-to-noise ratio of 3. Moreover, the MMPCMs/GC electrode exhibits good stability and reproducibility, and acceptable selectivity.

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1. Introduction

Nitrobenzene (NB), a compound widely used as munitions, insecticides, herbicides, and industrial feed stock chemicals, etc. [1,2], has been attracted more attention for its suspected carcinogenicity, mutagenicity, teratogenicity or high acute toxicity [3]. The detrimental effects of NB on the environmental human health even in very low concentration inspire scientists to exploit methods for the sensitive detection of NB.

Up to now, various techniques for the quantitative determination of NB in environmental samples, such as ultraviolet spectrophotometry (UV) [4], fluorescence quenching [5–7], high-performance liquid chromatography (HPLC) [8,9] and gas chromatography (GC) [10–12], have been proposed. As compared with the methods above, which usually need time-consuming and complex sample pre-treatment involving separation, extraction and adsorption, electrochemical methods have been recognized as more powerful techniques for inorganic and organic compound determination due to their advantages such as easy operation, low cost, high sensitivity, simple instrument and suitability for portable devices [13,14]. Especially, remarkable accumulation effect and/or electrocatalytic effect of the electrodes used in electrochemical measurements, which results from the chemical modification of the electrode surface with designable molecules or various nanometer-scale or porous materials, can endow the electrode with high sensitivity, special selectivity and good stability [15]. For these reasons, electrochemical techniques based on different modified electrodes, such as carbon nanotubes modified glassy carbon (GC) electrode [16], bismuth-film modified carbon paste electrode [17], ordered mesoporous carbon/didodecyldimethylammonium bromide composite modified GC electrode [18], hanging mercury electrode [19] and C_{60} modified carbon paste electrode [20], have been applied in the detection of NB. These researches have promoted the development of the electrochemical sensor for detecting NB. However, efforts to develop new functional materials for more sensitive detection of NB remain very important due to more and more attention in environmental protection and public security.

On the other hand, macro-/meso-porous materials currently inspire great interest in diverse potential applications such as catalysis, adsorption, sensors, and biotechnologies due to the combined remarkable features of mesoporous and macroporous structure including open pore structure, high specific surface area and efficient mass transportation [21,22]. However, to our best knowledge, there are no works focused on the application of macro-/meso-porous materials in NB determination.

Herein, using an ionic liquid polymer as carbon source, macro-/meso-porous carbon materials (MMPCMs) were successfully fabricated by pyrolysis of the ionic-liquid (1-allyl-3-ethylimidazolium tetrafluoroborate, [AEIm]BF_4) polymer (PIL) pre-wrapped onto SiO_2 microspheres and then removal of the silica core. Based on

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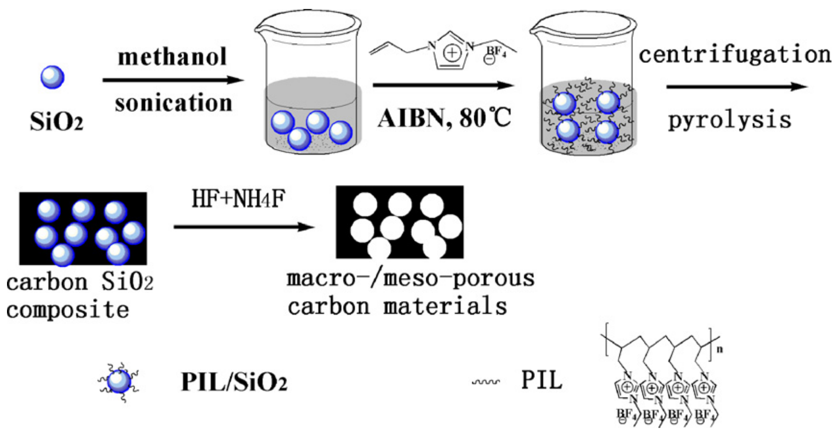
doi:10.1016/j.talanta.2011.11.067



Scheme 1. Schematic diagram for the preparation of MMPCMs.

the MMPCMs, a new electrochemical sensor for NB detection was constructed for the first time. It was found that the MMPCMs modified GC electrode showed a much higher electrocatalytic activity for NB reduction than the bare GC electrode due to the macro-/meso-porous structure, good electrochemical properties and large specific surface area of MMPCMs. Also, the MMPCMs modified GC electrode exhibited attractive analytical features including high sensitivity, excellent stability and reproducibility, and acceptable selectivity for NB determination.

2. Experimental

2.1. Chemicals

NB, purchased from Aladdin, was dissolved in DMF to prepare 1.0 mM stock solution, and stored in a brow volumetric flask at 4 °C. SiO_2 particles (diameter, ~310 nm) were obtained from Alfa Aesar (USA). $[AEIm]BF_4$ (purity > 98%) was purchased from Lanzhou Greenchem ILS, LICP. CAS. China. All the chemicals were of analytical grade unless otherwise stated and used directly without further purification. Doubly distilled water was used throughout.

2.2. Apparatus

The morphology and structure of MMPCMs were characterized by scanning electron microscopy (SEM, JSM 6700F, Japan) and transmission electron microscopy (TEM, JEM 3010, Japan). Nitrogen sorption isotherm and Brunauer–Emmett–Teller (BET) surface area of the sample were determined by an ASAP 2010 Micrometrics sorptometer (USA).

All electrochemical measurements were carried out on a CHI 660A electrochemical workstation (Chenhua Instrument Company of Shanghai, China) at room temperature (25 ± 2 °C). A conventional three-electrode cell was employed with a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. A glassy carbon (GC) electrode (3 mm in diameter) or MMPCMs modified GC electrode was used as the working electrode. All the potentials in this paper were referred to SCE.

2.3. Preparation of MMPCMs

The procedure for the preparation of MMPCMs is illustrated in Scheme 1. In brief, 400 mg silica particles were dispersed into 50 mL methanol with ultrasonic treatment for 30 min to get a homogeneous SiO_2 suspension. Then, 2.15 g $[AEIm]BF_4$ and 75.5 mg 2,2′-azobisisobutyronitrile (AIBN) were added into the above suspension, followed by ultrasonication for 10 min. After that, the obtained mixture was refluxed for 12 h at 80 °C under vigorous stirring and N_2 protection and then aged for another 10 h in N_2 atmosphere. Then, the mixture was centrifuged (12,000 rpm, 2 min) and washed with methanol for three times to remove the physically absorbed polymer and unreacted $[AEIm]BF_4$ monomer from the surface of the SiO_2 particles, followed by drying in vacuum at 50 °C overnight. The resulting yellow powder, labeled as PIL/SiO_2, was then carbonized in a nitrogen atmosphere at 900 °C for 1 h. Finally, MMPCMs were obtained via removal of the silica core in 2 M HF + 8 M NH_4F solution at room temperature for 3 h, followed by successive centrifugation and washing with doubly distilled water for several times, and drying in vacuum at 50 °C.

2.4. Preparation of MMPCMs modified GC electrode

Prior to modification, GC electrode was successively polished with 0.3 and 0.05 μm alumina slurry to a mirror surface, followed by rinsing thoroughly with doubly distilled water. For preparing the MMPCMs modified GC (MMPCMs/GC) electrode, 2.0 mg MMPCMs were dispersed into 2.0 mL doubly distilled water under ultrasonic stirring. Then, the MMPCMs/GC electrode was obtained by casting 4.0 μL MMPCMs suspension on the surface of the pre-treated GC electrode and dried at room temperature.

2.5. Analytical procedure

Unless otherwise stated, all the electrochemical measurements were carried out in the supporting electrolyte solution of 0.1 M phosphate buffer solution (PBS, pH 6.0), which was prepared with Na_2HPO_4, KH_2PO_4 and 0.1 M KCl. The required volume of the NB stock solution was added in the supporting electrolyte to obtain NB solution.

Linear sweep voltammetry (LSV) was used to detect NB in 0.1 M PBS (pH 6.0) with the reduction peak current as the analytical signal. To enhance the detection sensitivity, accumulation by soaking the electrode in the testing solution for proper time prior to the electrochemical measurement was needed.

For real sample analysis, tap water was directly collected from our laboratory without any treatment, while lake water was collected from the local artificial lake named Taozi Lake that lies in Yuelu District of Changsha City (Hunan, China) and filtered through a 0.45-μm filter before measurement. Both tap water and lake water samples were diluted with 0.1 M PBS (pH = 6.0) at a ratio of 1:5 and determined by the same process described above.

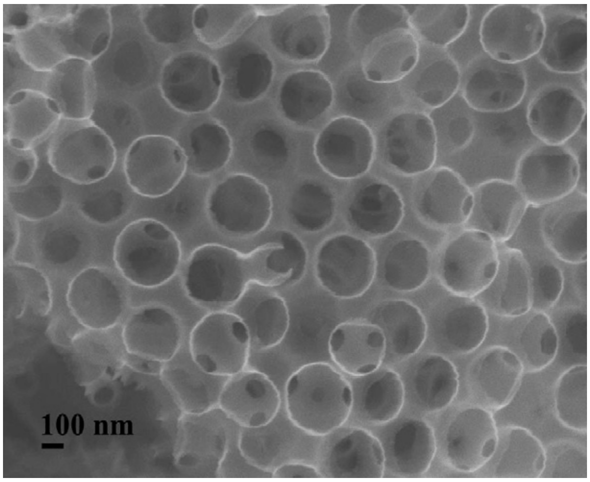


Fig. 1. SEM image of MMPCMs.

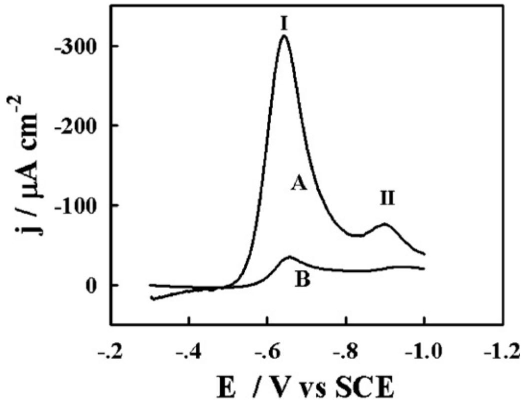


Fig. 2. LSV curves of 6 μM NB at the MMPCMs/GC (curve A) and bare GC (curve B) electrodes in 0.1 M PBS (pH = 6.0) at scan rate of 100 mV s^{-1}. Accumulation time: 60 s.

3. Results and discussion

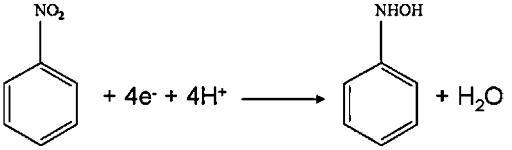
3.1. Characterization of MMPCMs

The morphology of MMPCMs was characterized by SEM and the corresponding result is shown in Fig. 1. It is noted that the macro-porous feature of MMPCMs with honeycomb-like morphology and lots of macro-pores with the diameter of ~330 nm can be clearly observed, which provides effective transport channels for the organic reactants and products moving into or out of the textural materials, and makes the catalytic reactions and sensor analysis achieve good performance [23,24].

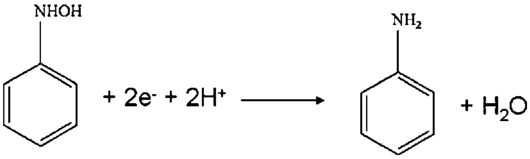
For further understanding the porous texture, N_2 adsorption–desorption isotherm of MMPCMs was measured. The results show that the average pore size of MMPCMs is 2.88 nm, verifying the existence of mesopores in MMPCMs, which may serve to the adsorption of organic molecules onto MMPCMs [25] and bring about accumulation of the organic compounds on the electrode surface during electrochemical analysis. On the other hand, the BET surface area of MMPCMs calculated from the result of nitrogen adsorption/desorption isotherm is 477.1 m^2 g^{-1}, which is much higher than that of graphite powder (38 m^2 g^{-1}) and CNTs (<200 m^2 g^{-1}) [26,27]. Based on the macro-/meso-porous structure and high specific surface area, MMPCMs can be expected to have excellent electrochemical properties and be available to fabricate a sensitive electrochemical sensor for NB.

3.2. Electrochemical reduction of NB at the MMPCMs modified GC electrode

Fig. 2 displays the LSV curves (after background subtraction) at the MMPCMs/GC (curve A) and bare GC (curve B) electrodes in 0.1 M PBS (pH 6.0) containing 6 μM NB at a scan rate of 100 mV s^{-1}. From Fig. 2, one small catholic peak at −0.66 V can be observed at the bare GC electrode, however, two well-defined cathodic peaks at −0.64 V (peak I) and −0.90 V (peak II), respectively, are obtained at the MMPCMs/GC electrode, which may correlate with the electrochemical reduction of NB to phenylhydroxylamine (PHA) and aniline (AN) in the weak acid solution, as demonstrated in Eqs.(1) and (2) [16,25,28]. In particular, it is noted that the reduction current of peak I at the MMPCMs/GC electrode is 22.11 μA, almost 9 times as high as that at the bare GC electrode (2.46 μA). These imply that the MMPCMs/GC electrode has excellent electrocatalytic activity towards the reduction of NB, which results from the good catalytic and accumulation effect of MMPCMs. Because the reduction peak current at peak I (−0.64 V) is much higher than that at peak II (−0.90 V), the reduction peak current at peak I (−0.64 V) is selected as the analytical signal for NB electrochemical detection in this work.



(1)



(2)

3.3. Effects of pH value and accumulation time

The effects of pH on the peak current and peak potential of peak I of NB reduction at the MMPCMs/GC electrode were investigated by LSV, and the corresponding results are shown in Fig. 3. As shown in Fig. 3, with the increase of pH value, the reduction peak current of NB at peak I gradually increases and the related peak potential becomes more and more negative. This implies that the concentration of hydrogen ion affects the rate of the reduction reaction. It is well known that very negative or positive potential is not beneficial to the selective detection of organic compounds. On the other hand, the nature water is usually neuter. Thus, pH 6.0 is selected as the optimum pH value for further studies.

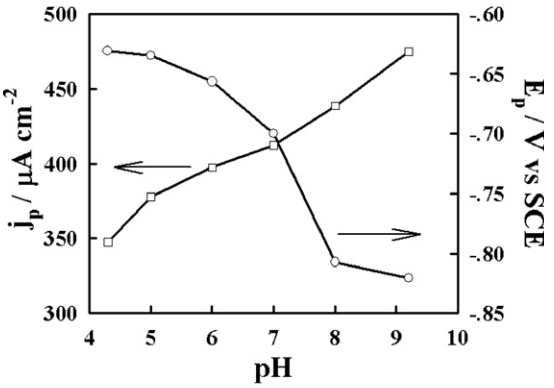


Fig. 3. Effect of pH value on the peak current (□) and peak potential (○) of peak I of 10 μM NB at the MMPCMs/GC electrode. Accumulation time: 60 s, scan rate: 100 mV s^{-1}.

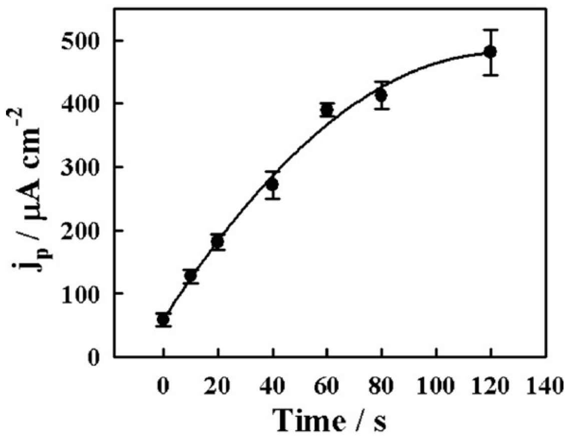


Fig. 4. Influence of the accumulation time on the reduction peak current (peak I) of 10 μM NB in 0.1 M PBS (pH = 6.0) at MMPCMs/GC electrode. Scan rate: 100 mV s^{-1}.

Since it could affect the adsorption degree of NB on MMPCMs, accumulation time may be another important factor that affects the analytical performance of the MMPCMs modified GC electrode. Therefore, the effect of accumulation time on the reduction of NB was also examined by LSV, and the dependence of the catholic peak current (peak I) of 10 μM NB in 0.1 M PBS (pH = 6.0) on the accumulation time is shown in Fig. 4. It is noted that the peak current increases rapidly with the increase of the accumulation time in the range of 0–60 s, while further increase of the accumulation time (60–120 s) generates relatively slow increase of the peak current owing to progressive saturation of NB on the MMPCMs/GC electrode. Considering the sensitivity and time saving, 60 s is employed as the appropriate accumulation time for NB detection.

3.4. Electrochemical detection of NB

The LSVs at the MMPCMs/GC electrode in 0.1 M PBS (pH = 6.0) containing different concentration of NB were investigated under the optimized experimental condition, and the corresponding results are shown in Fig. 5. From Fig. 5B, the peak current (peak I) of NB increases linearly with the increase of the NB concentration from 0.2 to 40 μM with a correlation coefficient of 0.9967. The sensitivity is 2.36 μA μM^{-1} and the detection limit is 8 nM on the basis of the signal-to-noise ratio of 3 (S/N = 3). Comparing with the results reported in the previous literatures (Table 1), the MMPCMs/GC electrode shows the improved performance, especially in detection limit and sensitivity, due to the unique macro-/meso-porous structure, high specific surface area, and the catalytic and accumulation effect of MMPCMs. This implies that the MMPCMs/GC electrode has potential application in the sensitive detection of NB.

3.5. Stability, reproducibility and anti-interferent ability of the MMPCMs/GC electrode

In order to investigate the stability of the MMPCMs/GC electrode, the reduction peak current (peak I) to 1.0 μM NB after its store in the atmosphere was measured. The results show that the current response has no lost after storage for 3 days, and only 1.5% decrease after a week of storage, which reveals good storage stability of the proposed electrode. The reproducibility of the MMPCMs/GC electrode was also estimated by recording the responses for four parallel measurements with different electrodes. The relative standard deviation (R.S.D.) is 4.87%, thus indicating good reproducibility of the MMPCMs/GC electrode.

Possible interferences for the detection of NB at the MMPCMs/GC electrode were also investigated by addition of various ions and organic pollutants to 0.1 M PBS (pH = 6.0) in the presence of 10.0 μM NB. The results suggested that NO_3^-, Mn^{2+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, CH_3COO^- and Mg^{2+} with their concentrations of 100-fold higher than that of NB had no significant interference with the detection of NB. It was also found that 10-fold Zn^{2+}, Co^{2+} and 5-fold Pb^{2+} produced negligible contributions to the signal of NB. As to organic pollutants, no interference for the detection of NB was observed when the concentration ratio of pollutants-to-NB is 100:1 for toluene, and 5:1 for 4-chlorobiphenyl. These imply that the MMPCMs/GC electrode has excellent anti-interference ability and may have promising application in NB assay in real water samples.

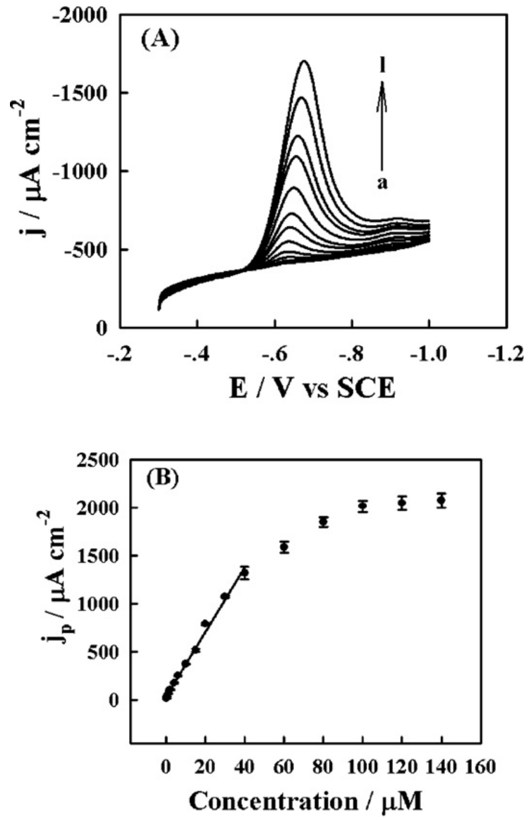


Fig. 5. (A) LSVs at the MMPCMs/GC electrode in 0.1 M PBS (pH = 6.0) containing different concentration of NB. Arrow direction: blank, 0.2, 0.4, 1, 2, 4, 6, 10, 15, 20, 30, 40 μM. (B) Plot of peak current (Peak I) vs. concentration of NB. Accumulation time: 60 s, scan rate: 100 mV s^{-1}.

3.6. NB assay in real water samples

To ascertain its practical application, the MMPCMs/GC electrode was used to analyze NB in tap water and lake water samples. Since no detectable NB was found in original tap water and lake water, certain amounts of NB were spiked in the water samples. After diluted with 0.1 M PBS, the concentration of NB in each sample was determined by the standard addition method and the results are shown in Table 2. From Table 2, the recovery is from 97.7% to 100.5% for tap water samples and from 93.3% to 99.4% for lake water samples, respectively. On the other hand, to testify the accuracy of this method, the NB content of these samples was also analyzed by high-performance liquid chromatography (HPLC) and the results are also listed in Table 2. As can be seen in Table 2, the results obtained by the proposed electrode are in good agreement with those detected by HPLC (perkinElmer series 200). These imply that the proposed electrochemical sensor (the MMPCMs/GC electrode)

Table 1
Comparison of the analytical performance of the different modified electrodes for NB detection.

Modified electrode	Linear response range (μM)	Sensitivity (μA μM^{-1})	Detection limit (μM)	Correlation coefficient	Reference
BiF/CP	1.0–100	0.289	0.83	0.9980	[17]
OMC/DDAB/GC	20–2900	–	10	0.999	[18]
Hanging mercury drop electrode	14.7–1000	–	5	0.9995	[19]
C_{60} modified carbon paste electrode	50–6000	–	30	0.9998	[20]
MMPCMs/GC	0.2–40	2.36	0.008	0.9967	This work

Table 2
NB recovery studies in real water samples ($n = 3$).

Sample	Added (μM)	This method		By HPLC (μM)
		Found (μM)	Recovery (%)	
Tap water 1	4.0	3.91	97.7	3.98
Tap water 2	10.0	10.05	100.5	10.02
Tap water 3	20.0	19.80	99.0	18.74
Lake water 1	4.0	3.73	93.3	3.85
Lake water 2	10.0	9.79	97.9	9.83
Lake water 3	20.0	19.88	99.4	19.27

has great potential application for NB detection in environmental water.

4. Conclusion

Macro-/meso-porous carbon materials were fabricated by pyrolysis of the ionic-liquid (1-allyl-3-ethylimidazolium tetrafluoroborate) polymer wrapped on SiO_2 microspheres and removal of the silica core, and then used to construct an electrochemical sensor for NB detection. Due to the unique macro-/meso-porous structure and high specific surface area of MMPCMs, the MMPCMs modified GC electrode show remarkably improved catalytic activity for NB electrochemical reduction. Compared with those reported in previous literatures, the sensor exhibits improved analytical characteristics: higher sensitivity (2.36 μA μM^{-1}), lower detection limit (8 nM) and excellent stability and reproducibility as well. Additionally, for real water sample analysis, a satisfactory recovery is obtained. These imply that the proposed electrochemical sensor has promising application for NB detection in environmental water.

Acknowledgements

This work was supported by the National Basic Research Program of China (No. 2009CB421601), NSFC (20975033), the Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT), the Project from Hunan Provincial Natural Science Foundation of China (10JJ5055) and the Fundamental Research Funds for the Central Universities (2009).

References

[1] A. Agrawal, P.G. Tratnyek, Environ. Sci. Technol. 30 (1996) 153–160.
[2] Y. Mu, H.Q. Yu, J.C. Zheng, S.J. Zhang, G.P. Sheng, Chemosphere 54 (2004) 789–794.
[3] M. Algarra, B.B. Campos, M.S. Miranda, J.C.G. Esteves da Silva, Talanta 83 (2011) 1335–1340.
[4] S. Cui, X.Y. Liu, Y. Liu, X.D. Shen, B.L. Lin, G.F. Han, Z.W. Wu, Sci. China. Technol. Sci. 53 (2010) 2367–2371.
[5] M.S. Meaney, V.L. McGuffin, Anal. Chim. Acta 610 (2008) 57–67.
[6] H.H. Li, J.P. Kang, L.P. Ding, F.T. Lu, Y. Fang, J. Photochem. Photobiol. A: Chem. 197 (2008) 226–231.
[7] G.H. Shi, Z.B. Shang, Y. Wang, W.J. Jin, T.C. Zhang, Spectrochim. Acta A 70 (2008) 247–252.
[8] K.G. Furton, L.M. Wu, J.R. Almirall, J. Forensic Sci. 45 (2000) 845–852.
[9] S.P. Wang, H.J. Chen, J. Chromatogr. A 979 (2002) 439–446.
[10] Y. Nishikawa, T. Okumura, Anal. Chim. Acta 312 (1995) 45–55.
[11] X. Li, J.M. Chen, L.C. Du, J. Chromatogr. A 1140 (2007) 21–28.
[12] H. Ebrahimzadeh, Y. Yamini, F. Kamarei, Talanta 79 (2009) 1472–1477.
[13] J. Wang, Electroanalysis 19 (2007) 415–423.
[14] C.M.A. Brett, Pure Appl. Chem. 73 (2001) 1969–1977.
[15] H.X. Zhang, A.M. Cao, J.S. Hu, L.J. Wan, S.T. Lee, Anal. Chem. 78 (2006) 1967–1971.
[16] Y.P. Li, H.B. Cao, C.M. Liu, Y. Zhang, J. Hazard. Mater. 148 (2007) 158–163.
[17] L.Q. Luo, X. Wang, Y.P. Ding, Q.X. Li, J.B. Jia, D.M. Deng, Anal. Methods 2 (2010) 1095–1100.
[18] B. Qi, F.Y. Lin, J. Bai, L. Liu, L.P. Guo, Mater. Lett. 62 (2008) 3670–3672.
[19] S.X. Liang, H.K. Zhang, D. Lu, Environ. Monit. Assess. 129 (2007) 331–337.
[20] H. Qian, J. Ye, L. Jin, Anal. Lett. 30 (1997) 367–381.
[21] Z.K. Sun, Y.H. Deng, J. Wei, D. Gu, B. Tu, D.Y. Zhao, Chem. Mater. 23 (2011) 2176–2184.
[22] Y. Zhao, X.T. Zhang, J. Zhai, L. Jiang, Z.Y. Liu, S. Nishimoto, T.Murakami, A. Fujishima, D.B. Zhu, Micropor. Mesopor. Mater. 116 (2008) 710–714.
[23] P.T. Tanev, T.J. Pinnavaia, Science 271 (1996) 1267.
[24] J.J. Pietron, R.M. Stroud, D.R. Rolison, Nano Lett. 2 (2002) 545.
[25] J.F. Zang, C.X. Guo, F.P. Hu, L. Yu, C.M. Li, Anal. Chim. Acta 683 (2011) 187–191.
[26] C.X. Guo, Z.S. Lu, L. Yu, C.M. Li, Electrochem. Commun. 12 (2010) 1237–1240.
[27] F.P. Hu, P.K. Shen, Y.L. Li, J.Y. Liang, J.Wu, Q.L. Bao, C.M. Li, Z.D.Wei, Fuel Cells 8 (2008) 429–435.
[28] E. Laviron, A. Vallata, R. Meunier-Presta, J. Electroanal. Chem. 379 (1994) 427–435.