Talanta 115 (2013) 457–461

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of m-dinitrobenzene based on novel type of sensor using thiol-porphyrin mixed monolayer-tethered polyaniline with intercalating fullerenols

Xiaoquan Lu*, Duoliang Shan[1], Jianmin Yang[1], Baomei Huang, Xibin Zhou

Key Laboratory of Bioelectrochemistry and Environmental Analysis of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

ARTICLE INFO

Article history:
Received 17 March 2013
Received in revised form
30 May 2013
Accepted 2 June 2013
Available online 10 June 2013

Keywords:
Porphyrin
Fullerenols
M-dinitrobenzene
Polyaniline

ABSTRACT

A novel sensor based on thiol-porphyrin mixed monolayer-tethered polyaniline (PANI) with intercalating fullerenols was applied to sensitively detect m-dinitrobenzene (m-DNB) by differential pulse voltammetry (DPV). The thiolated polyaniline was examined by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The electrode modification of thiol-porphyrin mixed monolayer-tethered polyaniline with intercalating fullerenols exhibited a higher analytical sensitivity versus that of thiol-porphyrin mixed monolayer-tethered polyaniline, because the fullerenols in mixed monolayer could improve the preconcentration efficiencies of m-DNB. Under optimum conditions, the linear calibration curves ranged from 0.029 to 10,000 nmol L^{-1} for m-DNB, with a limit of detection ($S/N=3$) of 9.72 pmol L^{-1}.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Nitroaromatics are hazardous electrophilic species harmful to human health and environment. Some dinitroaromatics, especially m-dinitrobenzene (m-DNB) finds applications in industry as an intermediate in the chemical synthesis of some rubber chemicals, pesticides, dyes, and explosives [1], and they have been detected also in ground-water near industrial waste disposal sites [2]. Compared with other nitroaromatic compounds, m-DNB could cause methemoglobinemia in animals and in humans [3–5]. It could also produce testicular toxicity [6–8], and brainstem damage [9,10]. Numerous papers have been published on the determination of m-DNB. Among them, spectrophotometry [11,12] and ion-chromatography [13,14] are mainly used. Electrochemical methods offer useful alternatives since they allow faster, cheaper and safer analysis.

The thiols and thiolated chemicals are extensively studied in surface chemistry and synthetic chemistry [15–17]. In addition, the thiol–ene chemistry of some systems is emerging as a new “click chemistry” protocol, for the preparation of functional materials [18]. The thiol–ene chemistry refers to the addition of a S–H bond across a double bond by either free radical or ionic mechanism. Interestingly, polypyrrole (PPy), polyaniline (PANI), and polythiophene (PTH) which are typical conducting polymers (CPs) of high conductivity, as well as good electrochromic property, redox reversibility and stability in aqueous solutions [19–21], could be conveniently thiolated through nucleophilic substitution reactions of thiols with the CPs at their oxidized states [22–27]. The interactions of thiols with conducting polymers in their oxidized states could be conceptually reconsidered as a researching branch of the emerging thiol–ene chemistry, which are thus of high current interest and worthy of more intensive studies.

Polyhydroxylated C_{60}, also known as fullerenols $C_{60}(OH)_x$, one class of the most attractive fullerenic derivative, has drawn extensive attention [28–30]. Because of the strong electrophilic property of the fullerene cage, fullerenols easily release protons and thus provide a new family of proton conductors. Furthermore, fullerenols are excellent free radical scavengers [31–33], making them efficient antioxidants that decrease oxidative stress. In addition, it was reported that attempts have been made in search of superior π-electron donors to interact with nitroaromatic compounds by strong π–π interactions [34]. Because of their structures with highly delocalized π-bonds and unique properties, fullerenols have the ability to participate in hydrogen bonds with the anion to form the hydrogen bond donor–acceptor complexes.

Herein, we report on the thiol–ene chemistry guided preparation of a novel thiolated polymeric nanocomposite involving polyaniline, a functionalized thiol, e.g., thiol-porphyrin (SH-TPP), alkyl thiol ($C_{10}H_{21}SH$) and $C_{60}(OH)_x$ for sensitive differential pulse voltammetry (DPV) determination of m-DNB on a glassy carbon electrode (GCE).

---

* Corresponding author. Tel.: +86 931 7971276; fax: +86 931 7971323.
E-mail address: luxq@nwnu.edu.cn (X. Lu).

[1] These two authors contributed equally to this work.

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.06.002

This biosensor showed promising application in the monitoring of m-DNB with low cost, convenient operation, high sensitivity, and a wide concentration range. In addition, it provided a convenient way to construct a novel biosensing platform, and extended the application of porphyrin and fullerenols in bioanalysis.

2. Experimental

2.1. Materials and reagents

Stock solutions of m-DNB (1000 mg/L; purchased from Beijing Chemical Co. Ltd.) were dissolved by acetonitrile (ACN). Analyte solutions were prepared by diluting the stock solutions using phosphate buffered saline (PBS) that contained 0.1 M NaCl and protected from light. Aniline was purchased from Shantou Xilong Chemical Engineering Factory (Guangdong, China), which was purified by distillation and stored in a refrigerator prior to use. SH-TPP was synthesized with some modifications according to this literature [35]. $C_{10}H_{21}SH$ was purchased from Alfa Aesar. C_{60} was purchased from Aldrich (USA). Fullerenols ($C_{60}(OH)_x$, $x\sim18$–22) were synthesized according to this literature [36]. All other chemicals were of analytical grade, and Milli-Q ultrapure water (≥18 MΩ cm) was used throughout the experiments.

2.2. Apparatus

The modified films were identified by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS; Princeton Applied Researcher, USA). A conventional three-electrode system consisting of bare and modified glassy carbon electrode as working electrodes (3 mm diameter), a KCl-saturated calomel electrode (SCE) as the reference electrode and a platinum wire electrode as a counter electrode was used. All potentials here were referenced to SCE. EIS was examined in a mixed solution of 1.0 mmol/L $K_3Fe(CN)_6$ containing 0.1 mol/L KCl. The frequency range was from 100 mHz to 10 kHz using an ac voltage of 5 mV amplitude and potential of 0.225 V. The obtained data were analyzed using the fitting program in ZSimpWin software. A PHS-3B pH meter (Leici, Shanghai, China) was used for pH measurements. All measurements were carried out at ambient temperature (18 ± 2 °C).

2.3. Procedure

The preparation of the fullerenols/PANI-mixed-thiol film is depicted in Scheme 1. The GCE was polished with 1.0 and 0.05 μm alumina slurry sequentially and washed ultrasonically in water and ethanol for 15 min. Then, the bare GCE was subjected to potential cycling (−0.2 to 1.0 V, 10 mV s^{-1}) in 0.20 mol L^{-1} aqueous $HClO_4$ until reproducible cyclic voltammogram was obtained. Fullerenols/PANI-mixed-thiol/GCE was prepared as follows. The bare GCE was immersed into 0.1 mol L^{-1} aqueous H_2SO_4 containing 10 mmol L^{-1} aniline, and a PANI film was electrodeposited by CV from −0.2 to 0.85 V for 20 cycles at 50 mV s^{-1}(optimized in Fig. 1) [37]. Afterwards, the PANI/GCE was subjected to potential cycling between −0.1 and 0.8 V at 30 mV s^{-1} for 10 cycles in 0.1 mol/L H_2SO_4 containing SH-TPP and $C_{10}H_{21}SH$ (optimized for the ratio of SH-TPP to $C_{10}H_{21}SH$ is 1:1(c/c)) to form PANI-mixed-thiol/GCE. Finally, the PANI-mixed-thiol/GCE was stirred in fullerenols (1.5 mg/ml) at room temperature for 3 h to sandwich fullerenols.

3. Results and discussion

3.1. Principle of PANI-mixed-thiol film

The thiol–ene chemistry guided preparation of a novel thiolated polymeric nanocomposite is described. As shown in Fig. 2, there are three redox peaks: Pa_1/Pc_1 displayed leucoemeraldine to emeraldine (anion doping), Pa_2/Pc_2 was emeraldine to pernigraniline (partial release of doped anions to the solution from the film), and Pa_3/Pc_3 resulted from the nonideal structures of PANI [38]. All the redox peaks (Pa_1/Pc_1, Pa_2/Pc_2 and Pa_3/Pc_3) decreased cycle by cycle [22].

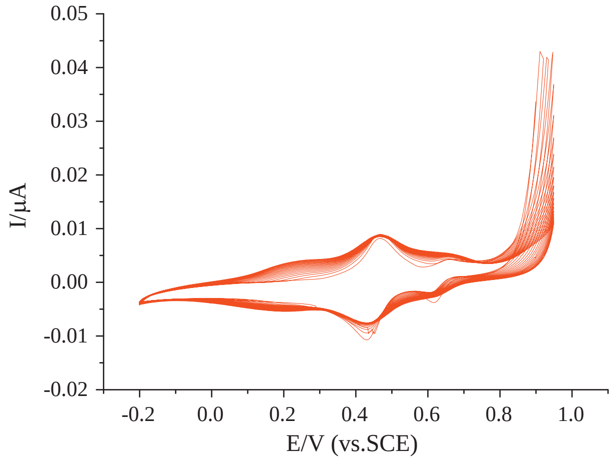
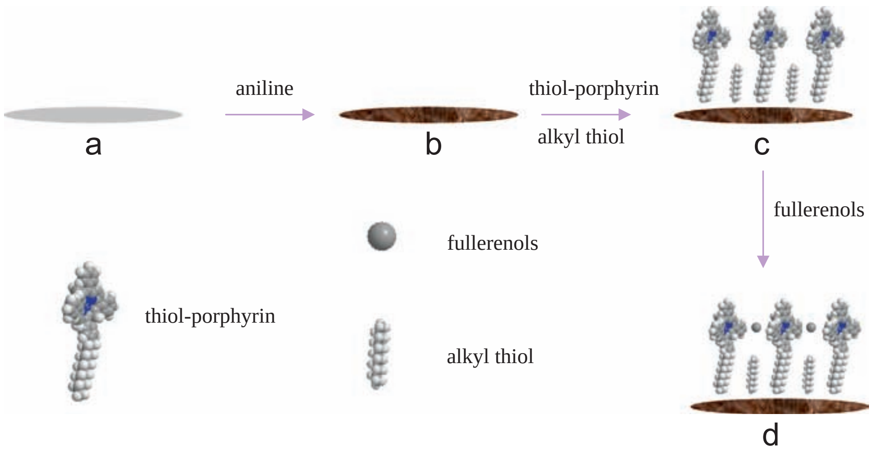


Fig. 1. CVs of bare GCE during potential cycling between −0.2 and 0.85 V for 20 cycles at 50 mV s^{-1} in 10 mmol/L aniline containing 0.1 mol L^{-1} H_2SO_4.



Scheme 1. The preparation of the fullerenols/PANI-mixed-thiol film: (a) bare GCE, (b) PANI/GCE, (c) PANI-mixed-thiol/GCE and (d) fullerenols/PANI-mixed-thiol/GCE.

Structural details of fullerenols/PANI-mixed-thiol/GCE are described in Scheme 2, which show the feasibility of intercalating $C_{60}(OH)_x$ between porphyrin molecules on PANI-mixed-thiol-film but not on PANI-thiol-porphyrin film. The average distance between two porphyrin molecules on PANI surface was about 5 Å (Scheme 2a) [39] which was insufficient to provide such a void space for intercalating $C_{60}(OH)_x$ molecule (the diameter of a $C_{60}(OH)_x$ molecule was about 9.9 Å; Scheme 2b). With one $C_{10}H_{21}SH$ molecule standing in the middle of two porphyrin molecules, which not only filled up the potential space on PANI surface between bulky porphyrin molecules but also provided space for further insertion of $C_{60}(OH)_x$ molecules, the distance was about 10 Å (Scheme 2c). It was about 26 Å (Scheme 2d) from the center of porphyrin to the surface of PANI, and the longest chain length of $C_{10}H_{21}SH$ was 13.4 Å (Scheme 2e). It can be calculated as 12.6 Å from the center of porphyrin ring to $C_{10}H_{21}SH$ chain, which is much larger than the diameter of a $C_{60}(OH)_x$ molecule [40,41]. The closest distance between $C_{60}(OH)_x$ and the center of the porphyrin ring has been reported as 2.856 Å [40]. Thus, the smallest center-to-center distance of two porphyrin rings which could sandwich a $C_{60}(OH)_x$ molecule was about 15.6 Å (Scheme 2f); it was also larger than the diameter of a $C_{60}(OH)_x$ molecule. The above mentioned data about porphyrin and $C_{10}H_{21}SH$ were calculated in Chem3D of ChemOffice.

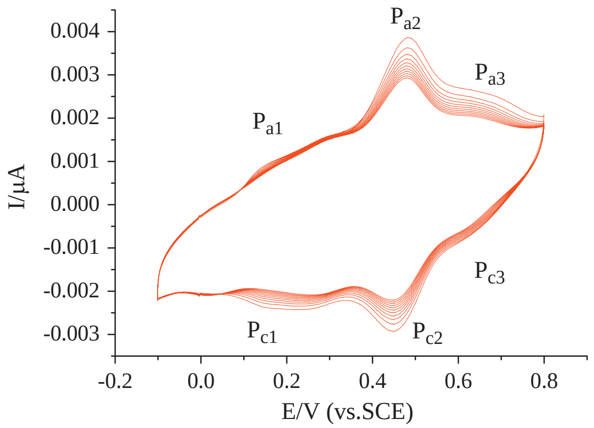
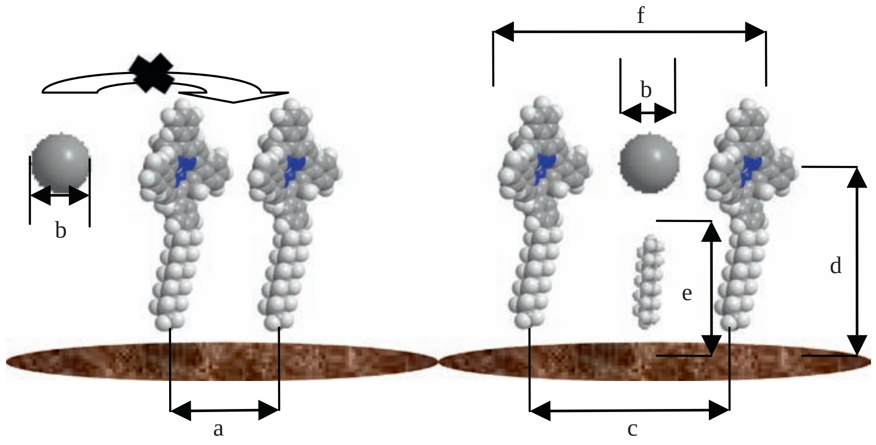


Fig. 2. CVs of the PANI film in SH-TPP and $C_{10}H_{21}SH$(1:1(c/c)) during potential cycling between −0.1 and 0.8 V at 30 mV s^{-1} for 10 cycles in 0.1 mol L^{-1} H_2SO_4.

3.2. Films characterization

Typical CV and Nyquist plots were obtained to study the surface properties of different films using the redox couple $Fe(CN)_6^{3-/4-}$ as redox probe (Fig. 3). For the bare GCE (Fig. 3A-a), there was a reversible electrochemical behavior, which was controlled by diffusion of a $Fe(CN)_6^{3-/4-}$ redox couple. For PANI/GCE (Fig. 3A-b), the peak current increased and the redox reaction became more reversible. The result demonstrated that the PANI conductive film could greatly accelerate the electron transfer to produce a well-defined redox couple of $Fe(CN)_6^{3-/4-}$. For PANI-mixed-thiol/GCE (Fig. 3A-c) and fullerenols/PANI-mixed-thiol/GCE (Fig. 3A-d), the curves became flat, that is, the peak current decreased and the redox reaction



Scheme 2. Structural details of fullerenols/PANI-mixed-thiol/GCE: $a=5$ Å, $b=9.9$ Å, $c=10$ Å, $d=26$Å, $e=13.4$ Å and $f=15.6$ Å.

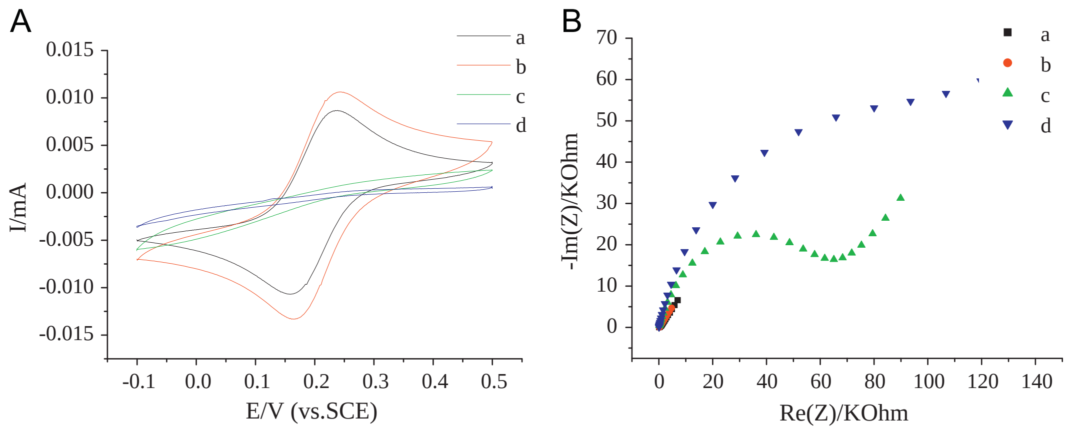


Fig. 3. CVs (A) and EIS (B) in solution of 1.0 mmol/L $K_3Fe(CN)_6$ containing 0.1 mol/L KCl, corresponding to (a) bare GCE, (b) PANI/GCE, (c) PANI-mixed-thiol/GCE and (d) fullerenols/PANI-mixed-thiol/GCE. Scan rate: 50 mV s^{-1}.

became irreversible. This indicated that the electron transport was blocked by mixed-thiol and fullerenols between $Fe(CN)_6^{3-/4-}$ and the GCE.

The EIS plots are shown in Fig. 3B. For the bare GCE (Fig. 3B-a), a straight line at low frequency and a small semicircle at high frequency were observed in the Nyquist plot. This demonstrated that the process was essentially diffusion-controlled for the redox couple on the bare GCE, and it is consistent with the result of CV at the bare GCE. When the bare GCE was functionalized with PANI film (Fig. 3B-b), a smaller semicircle appeared at higher frequency, which indicated that the PANI film was immobilized on the electrode surface and increased the electron-transfer efficiency. When the bare GCE was functionalized with PANI-mixed-thiol film (Fig. 3B-c) and fullerenols/PANI-mixed-thiol film (Fig. 3B-d), a larger semicircle appeared, indicating that the GCE was fully coated with nonconductive film, and these were also consistent with the results of CVs.

3.3. *Detection of m-DNB*

The electrochemical response of different modified films to the m-DNB is shown in Fig. 4. It obeyed the order fullerenols/PANI-mixed-thiol/GCE > PANI-mixed-thiol/GCE > GCE and the intercalation of fullerenols gave the greatest signal-increase. The cathodic peaks at −0.598 V, −0.714 V and −0.891 V correspond, respectively, to the consecutive reduction of nitro-groups to nitroso (1), hydroxylamino (2), and amino-derivatives (3), according to the mechanism for the reduction of nitro-groups [42,43].

$$RNO_2+2e^-+H^+ \rightarrow RNO_2H^- \qquad RNO_2H^- - OH^- \rightarrow RNO \tag{1}$$

$$RNO+2e^-+H^+ \rightarrow RNOH^- \qquad RNOH^-+H^+ \rightarrow RNHOH \tag{2}$$

$$RNHOH+2e^-+H^+ \rightarrow RNH_2OH^- \qquad RNH_2OH^- - OH^- \rightarrow RNH_2 \tag{3}$$

The reduction involved “electron–proton transfers”. The proton donor was depleted by neutralization of basic component which was produced by the electrochemical reduction of m-DNB, and this was attributed to an acute change of pH at the surface of the electrode. The proton concentration decreased rapidly at the surface of the electrode, making the remaining electron transfer, that is, reduction of the remaining RNO or RNHOH, more difficult.

For bare GCE (Fig. 4a), the amount of the proton component of the buffer was insufficient to neutralize basic component which was produced by the electrochemical reduction, so only two reduction peaks appeared, corresponding to (1) and (2), and the final product was hydroxylamino derivatives; for PANI-mixed-thiol/GCE (Fig. 4b), the proton was provided from porphyrin, so reduction peak (3) appeared, and the final product was amino-derivatives; for fullerenols/PANI-mixed-thiol/GCE (Fig. 4c), the reduction peak (3) current value became larger, but reduction peaks of corresponding (1) did not appear. These could be attributed to the reason that the fullerenols were found to be a water soluble compound with weak acidity and the charge carrier was a proton which could act as proton donor offering lots of proton [44–47,28]. In addition, the reaction rate constant of (1) is far less than the rate constant of (2) and (3). And the final product was amino-derivatives.

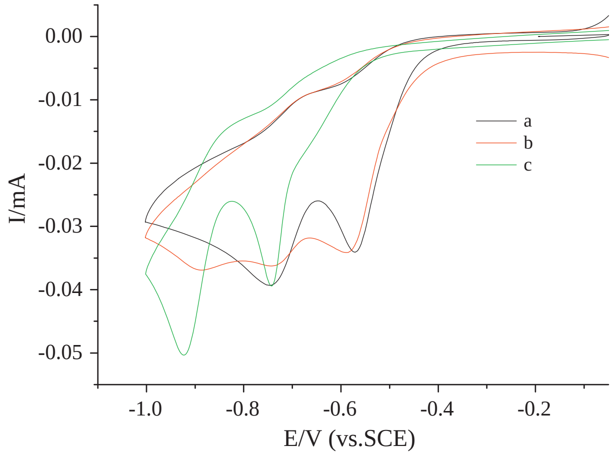


Fig. 4. The electrochemical response of different modified films in PBS (pH=7) that contained 0.5 mol L^{-1} m-DNB at scan rate 50 mV s^{-1}: (a) GCE, (b) PANI-mixed-thiol/GCE and (c) fullerenols/PANI-mixed-thiol/GCE.

There were weak electrochemical responses for bare GCE and PANI-mixed-thiol/GCE, while, fullerenols/PANI-mixed-thiol/GCE showed strong electrochemical response, associating it with endemic preconcentration capability of fullerenols to concentrate hydrophobic organic compounds at the surface of fullerenols [48]. At fullerenols/PANI-mixed-thiol/GCE, the attachment of fullerenols based on PANI-mixed-thiol matrix provided more receptor sites to m-DNB compound. The electron-rich hydroxyl group of fullerenols could interact with the electron-deficient nitro-group of m-DNB to form acid–base pairing firstly. And the interaction between the π-macrocycle of fullerenols and the benzene ring was a parallel-planar one to form strong electron donor–acceptor (EDA) complexes, which resulted in the improvement of response and sensitivity. These results indicated that fullerenols were a crucial element to the hybrid film and the introduction of PANI improved electrochemical response of m-DNB. We anticipated that the additional hydroxyl group could provide more opportunities to form hydrogen bond with nitro-group of m-DNB and the π-donor–acceptor interaction between fullerenols and m-DNB should be enhanced by the additional hydroxyl group. This information also provided a platform for a practical strategy for rational design of the sensor of explosives.

3.4. *Differential pulse voltammetry at the fullerenols/PANI-mixed-thiol/GCE*

As shown in Fig. 5, when the concentration was low, step (1) corresponding to $RNO_2 \rightarrow RNO$ was dominant; this could be attributed to the fact that proton in the solution formed electrostatic interaction with the hydroxyl group of fullerenols which did not form acid–base pairing with the electron-deficient nitro-group of m-DNB, and the result was not enough protons for the reaction. While the reduction peak current value of step (1) decreased with the increase

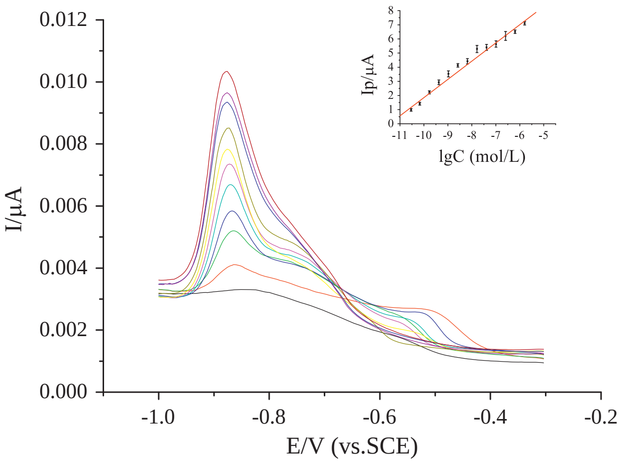


Fig. 5. DPV of m-DNB at fullerenols/PANI-mixed-thiol/GCE for peak at 0.891 V in PBS (pH=7). From bottom to top concentration: 0, 1×10^{-5}, 4×10^{-6}, 1.6×10^{-6}, 6.4×10^{-7}, 2.56×10^{-7}, 1.0×10^{-7}, 4.1×10^{-8}, 1.6×10^{-8}, 6.6×10^{-9}, 2.6×10^{-9}, 1.0×10^{-9}, 4.1×10^{-10}, 1.7×10^{-10}, 6.7×10^{-11}, 2.9×10^{-11} mol L^{-1} and the inset shows standard curve of the relation between the peak current value at 0.891 V and concentration of m-DNB.

Table 1
Line range and detection limit for different m-DNB sensors.

Modified electrode	Linear range	Detection limit	Reference
Mesoporous carbon	5.0×10^{-8}–2.1×10^{-5}	2.5×10^{-8}	[50]
IL–GNs	3.0×10^{-8}–1.5×10^{-6}	4.0×10^{-9}	[51]
MIP/MWCNT	4.5×10^{-8}–8.5×10^{-6}	2.5×10^{-8}	[52]
MIMs–AuNPs–GCE	4.0×10^{-8}–3.2×10^{-6}	1.3×10^{-8}	[53]
Porphyrin/CNTs film	8.0×10^{-9}–5.0×10^{-7}	2.0×10^{-9}	[54]
Fullerenols/PANI-mixed-thiol film	2.9×10^{-11}–1.0×10^{-5}	9.7×10^{-12}	This paper

of concentration, those of steps (2) and (3) increased. This could be attributed to the fact that proton in the solution which formed electrostatic interaction with the hydroxyl group of fullerenols was released, and there were enough protons for the reaction.

DPV was exploited to investigate the response of m-DNB due to its potential-controlled preconcentration at the surface of functionalized film [49]. Calibration curves are presented in the inset of Fig. 5, in which the proposed sensor exhibited good linear response ranging from 0.029 to 10,000 nmol L^{-1} for m-DNB and correlation coefficient of 0.99352 for peak −0.891 V with a detection limit of 9.72 pmol mol L^{-1} (signal to noise ratio of 3). The result based on this sensor was compared with those from the other methods that reported about m-DNB detection in solution [50–54] (Table 1). It was noted that this method with a simple preparation provided a better linear range and detection limit.

4. Conclusions

In summary, we reported a novel electrochemical sensor for m-DNB based on mixed-thiol-conducting polymers with intercalating fullerenols film. The study demonstrated that the attachment of fullerenols on hybrid film led to more receptor sites that could detect explosive compounds and the high conductivity effect of conducting polymers enlarged the performance of the sensor for m-DNB. On one hand, fullerenols utilized the endemic preconcentration capability to accumulate m-DNB. On the other hand, π-donor–acceptor complexes formed on fullerenols film. On the basis of this designed strategy, it should be possible to develop a novel class of m-DNB probe based on fullerenols and thiolated conducting polymers.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 20927004, 20965007, 20775060, 20875077, and 21005063) and the Key Laboratory of Polymer Materials of Gansu Province, China.

References

[1] N. Arshad, N.K. Janjua, S. Ahmed, A.Y. Khan, L.H. Skibsted, Electrochim. Acta 54 (2009) 6184–6189.

[2] S.R. Myers, M.T. Pinorini-Godly, P. Godly, T.V. Reddy, F.B. Daniel, G. Reddy, Int. J. Toxicol. 18 (1999) 317–325.

[3] P.A. Cossum, D.E. Rickert, Pharmacologist 27 (1985) 250–255.

[4] M.F. Obasaju, D.F. Katz, M.G. Miller, Fundam. Appl. Toxicol. 16 (1991) 257–266.

[5] T. Beritic, Br. J. Ind. Med. 13 (1956) 114–118.

[6] T.E. Cody, S. Witherup, L. Hastings, K. Stemmer, R.T. Christian, J. Toxicol. Environ. Health. 7 (1981) 829–847.

[7] R.E. Linder, R.A. Hess, L.F. Strader, J. Toxicol. Environ. Health. 19 (1986) 477–489.

[8] P.A. Cossum, D.E. Rickert, P.K. Working, Pharmacologist 28 (1986) 178–182.

[9] M.A. Philbert, C.C. Nolan, J. Cremer, E.D. Tucker, A.W. Brown, Neuropathol. Appl. Neurobiol. 13 (1987) 371–389.

[10] I. Romero, A.W. Brown, J.B. Cavanagh, C.C. Nolan, D.E. Ray, M.P. Seville, Neuropathol. Appl. Neurobiol. 17 (1991) 495–508.

[11] K. Sharma, S.C. Lahiri, Spectrochim. Acta, Part A 79 (2011) 1063–1070.

[12] G. Paraskevas, J. Atta-Politou, M. Koupparis, J. Pharm. Biomed. Anal. 29 (2002) 865–872.

[13] O.S. Bamidele, A.O. Kolawole, J.O. Ajele, Aquat. Toxicol. 112 (2012) 39–45.

[14] S.A. Burns, Y.-J. Hong, A.E. Mitchell, J. Chromatogr. B 809 (2004) 331–337.

[15] A.C. Templeton, M.J. Hostetler, C.T. Kraft, R.W. Murray, J. Am. Chem. Soc. 120 (1998) 1906–1911.

[16] R.P. Carney, G.A. DeVries, C. Dubois, H. Kim, J.Y. Kim, C. Singh, P.K. Ghorai, J.B. Tracy, R.L. Stiles, R.W. Murray, S.C. Glotzer, F. Stellacci, J. Am. Chem. Soc. 130 (2007) 798–799.

[17] O. Uzun, Y. Hu, A. Verma, S. Chen, A. Centrone, F. Stellacci, Chem. Commun. 2 (2008) 196–198.

[18] J.R. Kramer, T.J. Deming, J. Am. Chem. Soc. 134 (2012) 4112–4115.

[19] D.M. DeLongchamp, P.T. Hammond, Chem. Mater. 16 (2004) 4799–4805.

[20] J.M. Sansinena, V. Olazabal, T.F. Otero, C.N.P. daFonseca, M.A. DePaoli, Chem. Commun. 25 (1997) 2217–2218.

[21] W.J.E. Beek, M.M. Wienk, R.A.J. Janssen, Adv. Funct. Mater. 16 (2006) 1112–1116.

[22] L. Chen, Z. Su, X. He, Y. Liu, C. Qin, Y. Zhou, Z. Li, L. Wang, Q. Xie, S.Z. Yao, Electrochem. Commun. 15 (2012) 34–37.

[23] N. Oyama, T. Tatsuma, T. Sato, T. Sotomura, Nature 373 (1995) 598–600.

[24] B. Bergman, T.W. Hanks, Macromolecules 33 (2000) 8035–8042.

[25] Y. Zhou, B. Yu, K. Levon, Synth. Met. 142 (2004) 137–141.

[26] C. Bieniarz, M. Husain, P.J. Tarcha, Macromolecules 32 (1999) 792–795.

[27] Z. Su, J. Huang, Q. Xie, Z. Fang, C. Zhou, S. Yao, Phys. Chem. Chem. Phys. 11 (2009) 9050–9061.

[28] K. Hinokuma, M. Ata, Chem. Phys. Lett. 341 (2001) 442–446.

[29] M.E. Rincón, H. Hu, J. Campos, J. Ruiz-García, J. Phys. Chem. B 107 (2003) 4111–4117.

[30] T.H. Goswami, B. Nandan, S. Alam, G.N. Mathur, Polymer 44 (2003) 3209–3214.

[31] L.Y. Chiang, F.J. Lu, J.T. Lin, J. Chem. Soc. Chem. Commun. 12 (1994) 1283–1284.

[32] S. Trajmar, I. Kanik, Chem. Phys. Lett. 262 (1996) 241–246.

[33] U.S. Jeng, T.L. Lin, T.S. Chang, H.Y. Lee, C.H. Hsu, Y.W. Hsieh, T. Canteenwala, L.Y. Chiang, Prog. Colloid Polym. Sci. 118 (2001) 232–237.

[34] H.X. Zhang, Q. Chen, R. Wen, J.S. Hu, L.J. Wan, Anal. Chem. 79 (2007) 2179–2183.

[35] F. Zhi, X. Lu, J. Yang, X. Wang, H. Shang, S. Zhang, Z. Xue, J. Phys. Chem. C 113 (2009) 13166–13172.

[36] K. Kokubo, K. Matsubayashi, H. Tategaki, H. Takada, T. Oshima, ACS Nano 2 (2008) 327–333.

[37] Z.M. Wang, H.W. Guo, E. Liu, G.C. Yang, N.W. Khun, Electroanalysis 22 (2009) 209–215.

[38] Q. Xie, Z. Li, C. Deng, M. Liu, Y. Zhang, M. Ma, S. Xia, X. Xiao, D. Yin, S. Yao, J. Chem. Educ. 84 (2007) 681.

[39] G.E. Poirier, Chem. Rev. 97 (1997) 1117–1128.

[40] T. Hasobe, H. Imahori, P.V. Kamat, T.K. Ahn, S.K. Kim, D. Kim, A. Fujimoto, T. Hirakawa, S. Fukuzumi, J. Am. Chem. Soc. 127 (2004) 1216–1228.

[41] Q. Peng, G. Chen, H. Mizuseki, Y. Kawazoe, J. Chem. Phys. 131 (2009) 214–226.

[42] M. Mohammad, M.S. Subhani, W. Begum, Res. Chem. Intermediat. 16 (1991) 29–43.

[43] D.H. Evans, Chem. Rev. 108 (2008) 2113–2144.

[44] L.Y. Chiang, J.W. Swirczewski, C.S. Hsu, S.K. Chowdhury, S. Cameron, K. Creegan, J. Chem. Soc. Chem. Commun. 24 (1992) 1791–1793.

[45] L.Y. Chiang, R.B. Upasani, J.W. Swirczewski, J. Am. Chem. Soc. 114 (1992) 10154–10157.

[46] L.Y. Chiang, R.B. Upasani, J.W. Swirczewski, S. Soled, J. Am. Chem. Soc. 115 (1993) 5453–5457.

[47] L.Y. Chiang, L.Y. Wang, J.W. Swirczewski, S. Soled, S. Cameron, J. Org. Chem. 59 (1994) 3960–3968.

[48] F. Su, C. Lu, S. Hu, Colloids Surf. Physicochem. Eng. Aspects 353 (2010) 83–91.

[49] M.I.D. Scanlon, G.G. Herzog, D.W.M. Arrigan, Anal. Chem. 80 (2008) 5743–5749.

[50] D. Nie, P. Li, D. Zhang, T. Zhou, Y. Liang, G. Shi, Electrophoresis 31 (2010) 2981–2988.

[51] S. Guo, D. Wen, Y. Zhai, S. Dong, E. Wang, Biosens. Bioelectron. 26 (2011) 3475–3481.

[52] Y. Qu, Y. Liu, T. Zhou, G. Shi, L. Jin, Chin. J. Chem. 27 (2009) 2043–2048.

[53] D. Nie, D. Jiang, D. Zhang, Y. Liang, Y. Xue, T. Zhou, L. Jin, G. Shi, Sens. Actuators B 156 (2011) 43–49.

[54] X. Lu, Y. Quan, Z. Xue, B. Wu, H. Qi, D. Liu, Colloids Surf. B Biointerfaces 88 (2011) 396–401.