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Short Communication

Synthesis of Single-Crystalline Iron Oxide Magnetic Nanorings as Electrochemical Biosensor for Dopamine Detection

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In this paper, uniform iron oxide magnetic nanorings (Fe_3O_4 NRs) were successfully synthesized through hydrothermal method. The electrochemical performance of Fe_3O_4 NRs/glassy carbon electrode (GCE) based biosensor for dopamine (DA) detection has been investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). These results implied the Fe_3O_4 NRs/GCE biosensor exhibited superior electrocatalytic activity and significant electron transfer kinetics for the electrooxidation of DA with a quick response time of 4 s and a low detection limit of 10 nM. These excellent electrochemical results indicate the Fe_3O_4 NRs could be utilized as an extremely promising material for the detection of DA related diseases in biomedical analysis.

Keywords: Fe_3O_4 nanorings, dopamine, electrooxidation, cyclic voltammetry

1. INTRODUCTION

Recently, the application of nanomaterials modified electrodes in electrochemical biosensor has received much attention [1-3]. In these electrodes, magnetic nanomaterials based electrochemical biosensors exhibits excellent properties, because of their high sensitivity, fast response speed, good selectivity, high specific surface area and good electrical conductivity [4-7].

The magnetic nanomaterials modified electrode or incorporated into the electrode can significantly increases the surface area, and accelerates electrons transfer. It is possible to improve the electrode stability, accelerate the response speed, and enhance the selectivity of detection [8].

Dopamine (DA) is considered as one of the most momentous and representative of catecholamine neurotransmitter, which is one of the most important transmission media of mammalian and human important central nervous system [9]. The restricting of DA transmission is likely to cause neurological disorders, such as schizophrenia, Alzheimer's and Parkinson's diseases. Therefore, detection the changes of DA concentrations can prevent a variety of diseases, so fast, highly sensitive and accurate measurement of dopamine is very important. At present, there are many methods to detect DA concentration, such as fluorescence, liquid chromatography and chemiluminescence methods. Because the dopamine is prone to electrochemical oxidation, the electrochemical sensor of DA a detection has many advantages, such as higher accuracy, faster response and lower cost [10].

Wang *et al.*[11] prepared magnetic Fe_3O_4 hybrid nanocomposites then modified them on the glassy carbon electrode (GCE) to generate electrochemical sensor in phosphate buffer solution (PBS) for dopamine detection. And the detection limit is 6.67×10^{-10} M. Peik-See *et al.*[12] described an Fe_3O_4/graphene modified GCE electrode as electrochemical biosensor, where the limits of detection were 0.42 and 0.12 μM for ascorbic acid and dopamine, respectively. Zhang *et al.*[13]prepared nafion covered core–shell structured Fe_3O_4@graphene nanospheres modified GCE, with the detection limit of 0.007 mM.

In the present study, we fabricated high-quality single-crystal Fe_3O_4 nanorings (NRs), and coated them on the surface of GCE for the simultaneous electrochemical determination of DA. The Fe_3O_4 NRs biosensor shows a high sensitivity and selectivity with a wide linear range between 0.01 and 1 mM, and a lower detection limit of 10 nM.

2. EXPERIMENTAL

2.1. Preparation of electrode materials

The uniform Fe_3O_4 NRs were prepared by a hydrothermal method according to Jia *et al* [14]. In a typical procedure, $FeCl_3$, NaH_2PO_4, and Na_2SO_4 aqueous solutions were mixed in 80 mL distilled water and their concentration were controlled as 0.02, 1.8×10^{-4}, and 5.5×10^{-4} mol L^{-1}, respectively. After that, the mixture was reacted at 220 ^oC for 48 h. After cooling to room temperature, the Fe_3O_4 NRs precipitates were separated and washed with distilled water and absolute ethanol at list 3 times. Finally, the precipitates were dried under vacuum at 80 ^oC for 24 h.

1 mg of Fe_3O_4 NRs was dispersed in 5 mL of dimethyl formamide (DMF), and then the suspension was prepared by ultrasonic dispersion for 30 min. After that, the bare GCE was polished to a mirror-like surface with α-Al_2O_3. Subsequently, the bare GCE was rinsed ultrasonic with ethanol for surface cleaning. Then, 5 μL of Fe_3O_4 NRs were coated on GCE surface by evaporation. Finally, the Fe_3O_4 NRs modified GCE electrode was obtained after dried under vacuum at 40 ^oC for 120 min.

2.2. Materials characterization

The morphology and microstructure of the products were characterized by field emission scanning electron microscopy (FSEM, Ultra 55) and transmission electron microscopy (TEM, 200FE Libra). The crystal structure was determined by X-ray diffraction (X'Pert, PRO XRD). The hysteresis loop of the Fe_3O_4 NRs was characterized on a PPMS-9T instrument at 300K.

2.3. Electrochemical characterizations

The electrochemical measurements of the Fe_3O_4 NRs/GCE electrodes were carried out with cyclic scan in the potential range from -1.0 to 0.8 V in 0.1 M PBS (pH 5.0) The electrochemical sensing test of the Fe_3O_4 NRs/GCE electrode was performed with a electrochemistry workstation (IM6, Germany) by a conventional three-electrode system, and then differential-pulse voltammetry (DPV) and cyclic voltammetry (CV) results were recorded.

3. RESULTS AND DISCUSSION

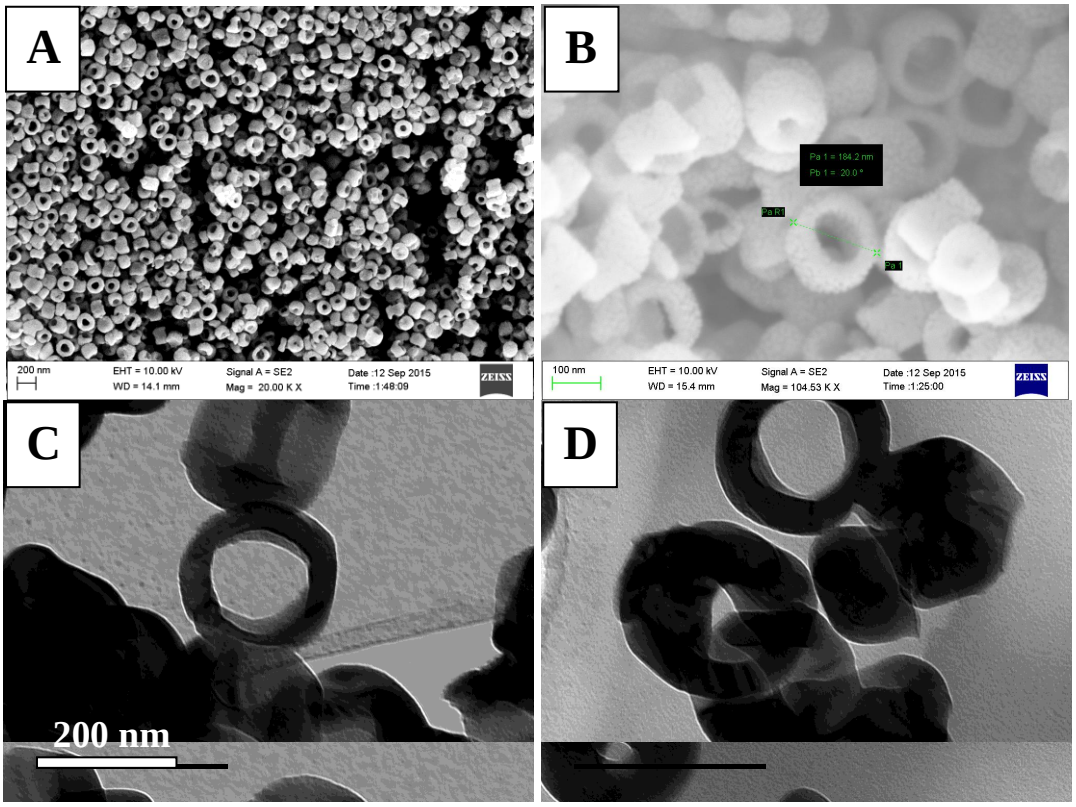

Figure 1. SEM (A, B) and TEM (C, D) images of Fe_3O_4 NRs.

Figure 1 shows the prepared Fe_3O_4 NRs by hydrothermal method. As can be seen in Figure 1, the Fe_3O_4 NRs exhibit uniform size and morphology with outer diameters of 160-180 nm, inner diameters of 80-110 nm, and heights of 70-110 nm, indicating the Fe_3O_4 NRs have been successfully prepared.

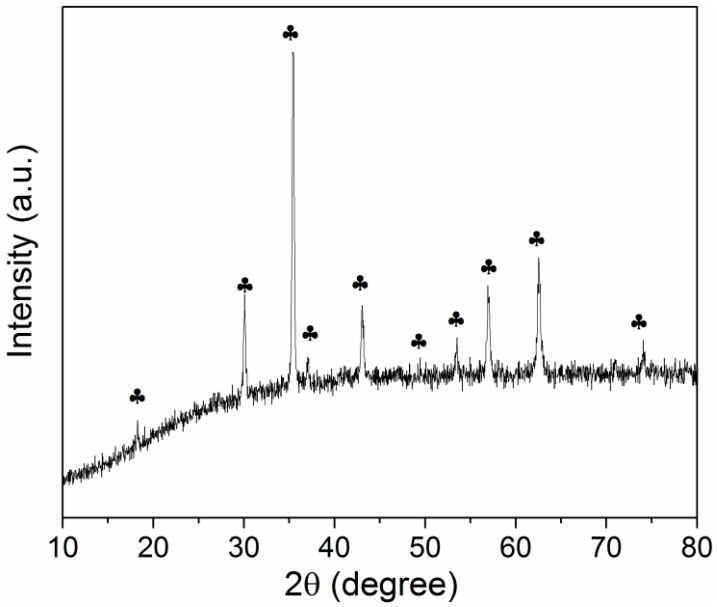

Figure 2. XRD patterns of Fe_3O_4 NRs.

Figure 2 displays the XRD patterns of as-prepared Fe_3O_4 NRs. The diffraction peaks at 18.3°, 30.1°, 35.4°, 37.1°, 43.1°, 47.1°, 53.4°, 56.9° and 62.5° can be assigned to the (111), (220), (311), (222), (400)，(331), (442), (511) and (440) crystal planes of Fe_3O_4, respectively (JCPDS Card No. 87-2334).
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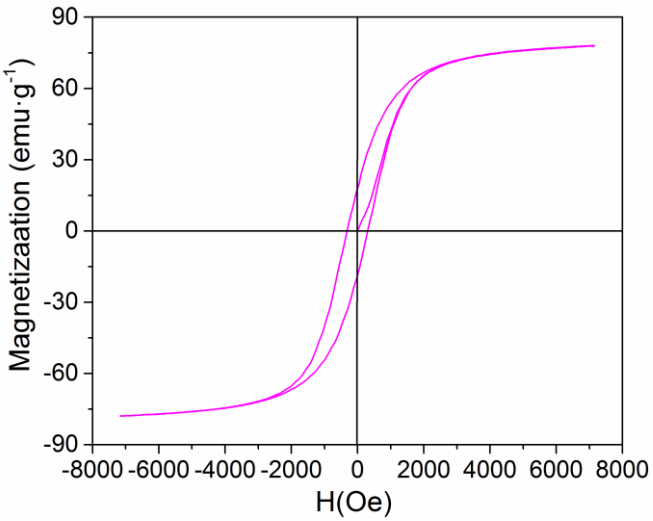

Figure 3. Hysteresis loop of Fe_3O_4 NRs measured at 300 K.

Figure 3 shows of the magnetization of as-prepared Fe_3O_4 NRs. The coercivity of these Fe_3O_4 NRs are 120 Oe. The saturation magnetization (M_s) of the Fe_3O_4 NRs is about 86.2 emu/g, which is smaller than the bulk Fe_3O_4 (92 emu/g) [15], because of the decreasing of the particle size. Two kinks near zero magnetization appeared in the *M-H* loop, indicating the possibility of an opposite direction of the two vortex states [14].

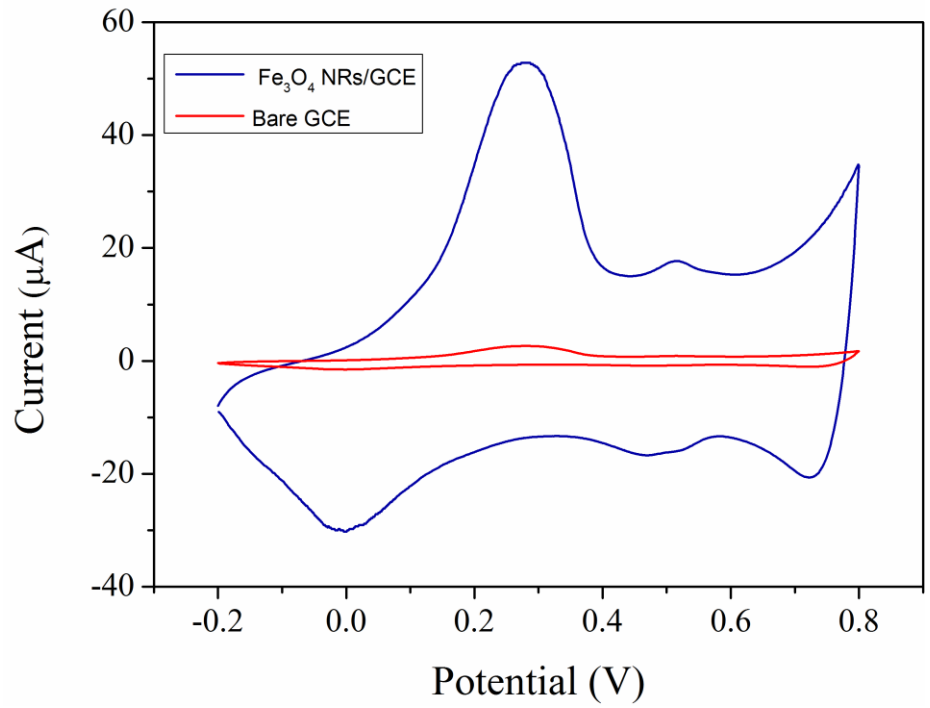

Figure 4. CV results of bare GCE and Fe_3O_4 NRs/GCE with 1 mM DA in PBS (0.1M, pH 5.0) at scan rate of 20 mV s^{-1}.

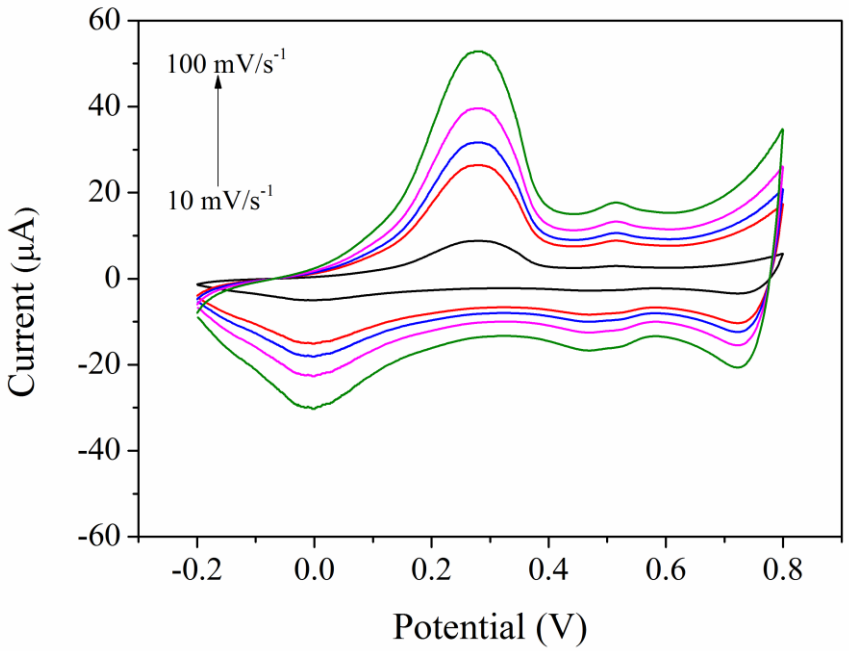

Figure 5. CV results of 0.1 mM DA in 0.1 M PBS at the Fe_3O_4 NRs at scan rate of 10-100 mV s^{-1}.

To investigate the application of Fe_3O_4 NRs, the electrochemical properties in the present of DA were detected on the Fe_3O_4 NRs/GCE. The electrochemical sensing characteristics of bare GCE and Fe_3O_4 NRs/GCE electrode was analyzed in PBS as a redox probe at rate of 20 mV/s.

Figure 4 depicts the typical CV rsponses of 1 mM DA on the bare GCE and the Fe_3O_4 Fe_3O_4

NRs/GCE. At the bare GCE, DA has a reversible electrochemical behavior and minimal small current, indicating that it detects DA inefficiency. After functionalized with Fe_3O_4 NRs, a couple of small redox peaks was observed [16], due to DA is easily oxidized to form dopaminequinone (DAQ) after exchange of 2 electrons and 2 protons [17].

To study the influence of the scan rate on the oxidation current of 0.1 mM DA, the Fe_3O_4 NRs/GCE electrode was applied in 0.1 M PBS (pH 5.5) by varying the scan rates from 10 to 100 mV s^{-1}. As can be seen in Figure 5, with the increasing of the scan rate, the anodic peak currents are rised and moved to more positive positions. In contrast, the cathodic peak currents are slightly moved to more negative positions. These results indicate that the electron transfer rate of Fe_3O_4 NRs/GCE electrode decreased, and the electrochemical performance of DA tended to be less reversible [18].

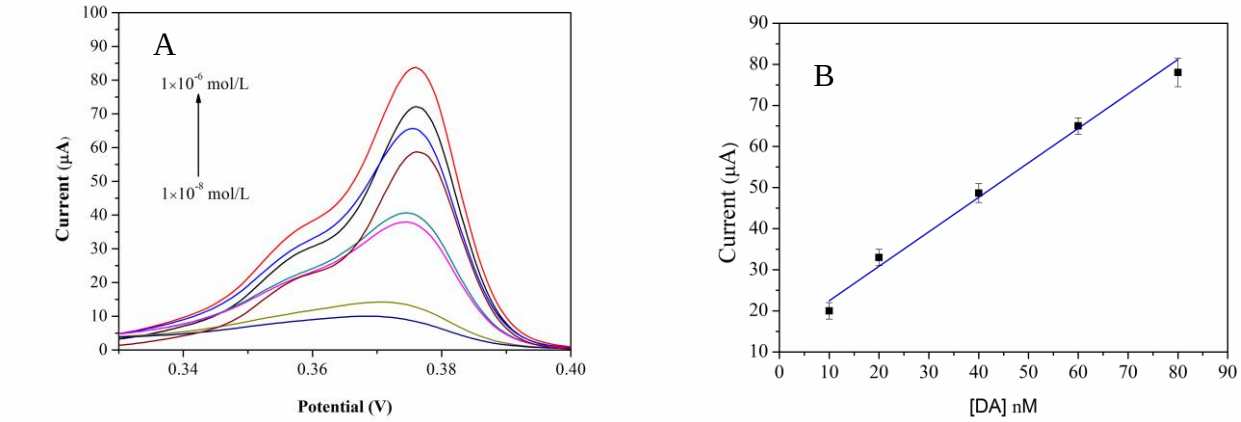

Figure 6. DPV results of different DA concentration for Fe_3O_4 NRs/GCE based biosensor.

To prove the sensitivity of the Fe_3O_4 NRs/GCE based biosensor, DPV was utilized to show the detection of DA. As can be seen in Figure 6, with the DA concentration increasing, the oxidation peak current (Ipa) rising relatively.

Furthermore, the peak current and DA concentration show linearly proportional in the range from 1.0×10^{-8} to 1.0×10^{-6} M (see Figure 6 (B)). The linear regression equations for DA is I(μA)=14.3+0.839 C (10^{-8} M). The limit for DA detection was conformed to be 8.67×10^{-9} M, which is comparable with other reports [19, 20].

Table 1. Comparison of measurement results of the analytical performance with standard and previous measurement methods.

Modified materials	Linear ranges (M)	Detection limits (M)	reference
GO	1.5×10^{-7} to 1×10^{-6}	0.27×10^{-6}	21
Meso-SiO_2/CPE	4×10^{-6} to 5.2×10^{-5}	1.00×10^{-7}	22
Fe_3O_4/r-GO	4×10^{-7} to 1.6×10^{-4}	8.00×10^{-8}	23
HPLC	2.6×10^{-6} to 2.55×10^{-5}	2.50×10^{-6}	24
Fe_3O_4 NRs/GCE	1.0×10^{-8} to 1.0×10^{-6} M	8.67×10^{-9}	This work

Table 1 shows the comparison of measurement results of the analytical performance Fe_3O_4 NRs/GCE with standard high-performance liquid chromatography (HPLC) method and other dopamine detection methods reported recently. Based on the results, the Fe_3O_4 NRs/GCE biosensor in this work has comparable and even better performance than the standard HPLC method and others, indicating that Fe_3O_4 NRs/GCE electrode based biosensor has extraordinary potential for DA detection.

Table 2. Determination results of DA in real urine samples (n=3).

Detected (μM)	Added (μM)	Found (μM)	RSD (%)	Recovery (%)
0	5.00	5.05±0.12	2.4%	102.4
5.00	10.0	14.92±0.27	1.8%	101.1
10.0	20.0	29.82±0.47	2.2%	101.2

Table 2 summarized the reliability of the Fe_3O_4 NRs/GCE electrode based detection results of the real human urine samples. In the experiment, the human urines were diluted 5 times with 0.10 M PBS (pH 6.0) before characterization. Then different amounts of DA were added into the sample to test recoveries. The recovery of the spiked samples ranged between 101.1% and 102.4%. Hence, the Fe_3O_4 NRs/GCE electrode based detection method can be applied to real biological samples in the determination, and obtain satisfactory results.

4. CONCLUSION

In conclusion, we have successfully prepared Fe_3O_4 NRs *via* a low cost and simple method. The Fe_3O_4 NRs/GCE electrode was applied as electrochemical biosensor for DA detection, showing excellent electrocatalytic activity and electron transfer rate in the oxidation of DA. Furthermore, compared with the similar DA detection biosensor, the Fe_3O_4 NRs/GCE electrode exhibited higher sensitivity, selectivity and lower detection limit. These results reveal that Fe_3O_4 NRs/GCE electrode could be a potential candidate as electrochemical and biological sensors.

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References

1. L. Reverté, B. Prieto-Simón and M. Campàs, *Anal. Chim. Acta.*, 908 (2016) 8-21.
2. J.I. A. Rashid, N.A. Yusof, J.Abdullah, U.Hashim and R.Hajian, *J. Mater. Sci.*, 51 (2016) 1083-1097.
3. Y. Zhou, H. Yin, J. Li, B. Li, X. Li, S. Ai and X. Zhang, *Biosens. Bioelectron.*, 79 (2016) 79-85.

4. W. Wei, P. Ma, D. Hui, H.J. Krause, Z. Yi, D. Willbold, A. Offenhaeusser and Z. Gu, *Biosens. Bioelectron.*, 80 (2016) 661–665.
5. M.E. Cortina, L.J. Melli, M. Roberti, M. Mass, G. Longinotti, S. Tropea, P. Lloret, D.A. Serantes, F. Salomón and M. Lloret, *Biosens. Bioelectron.*, 80 (2016) 24-33.
6. D. Wu, Y. Wang, Y. Zhang, H. Ma, X. Pang, L. Hu, B. Du and Q. Wei, *Biosens. Bioelectron.*, 82 (2016) 9-13.
7. B. Feng and Y.N. Liu, *Int. J. Electrochem. Sci.*, 10 (2015) 4770-4778.
8. O. Galović, M. Samardžić and M. Sak-Bosnar, *Int. J. Electrochem. Sci.*, 10 (2015) 5176-5193.
9. L. Liu, N. Xia, J.J. Meng, B.B. Zhou and S.J. Li, *J. Electroanal. Chem.*, 775 (2016) 58–63.
10. A. Azadbakht, M. Roushani, A. R. Abbasi and Z. Derikvand, *Anal. Biochem.*, 507 (2016) 47–57.
11. Y. Wang, C. Hou, Y. Zhang and M. Liu, *Rsc Adv.*, 5 (2015) 98260-98268.
12. T. Peiksee, A. Pandikumar, H. Nayming, L. Hongngee and Y. Sulaiman, *Sensors*, 14 (2014) 15227-15243.
13. W. Zhang, J. Zheng, J. Shi, Z. Lin, Q. Huang, H. Zhang, C. Wei, J. Chen, S. Hu and A. Hao, *Anal. Chim. Acta*, 853 (2015) 285–290.
14. C.J. Jia, L.D. Sun, F. Luo, X.D. Han, L.J. Heyderman, Z.G. Yan, C.H. Yan, K. Zheng, Z. Zhang and M. Takano, *J. Am. Chem. Soc.*, 130 (2008) 16968-16977.
15. Q.A. Pankhurst, J. Connolly, S.K. Jones and J. Dobson, *J. Phys. D Appl. Phys.*, 36 (2003) R167-R181.
16. Y. Li, Y. Jiang, T. Mo, H. Zhou, Y. Li and S. Li, *J. Electroanal. Chem.*, 767 (2016) 84-90.
17. S. Palanisamy, X. Zhang and T. He, *J. Mater. Chem. B*, 3 (2015) 6019-6025.
18. W. Dan, Y. Li, Z. Yong, P. Wang, W. Qin and B. Du, *Electrochim. Acta*, 116 (2014) 244-249.
19. T. Peiksee, A. Pandikumar, N.M. Huang, L. Hongngee and Y. Sulaiman, *Sensors*, 14 (2014) 15227-15243.
20. Z. Terzopoulou, G. Kyzas and D. Bikiaris, *Materials*, 8 (2015) 652-683.
21. F. Gao, X. Cai, X. Wang, C. Gao, S. Liu, F. Gao and Q. Wang, *Sens. Actuators, B*, 186 (2013) 380-387.
22. D. Sun, X.F. Xie, H.J. Zhang, *Colloids Surf. B*, 75 (2010) 88-92.
23. H. Teymourian, A. Salimi and S. Khezrian, *Biosens. Bioelectron.*, 49 (2013) 1-8.
24. V. Sirisha, C. Sreedhar and T. Sreenivasa Rao, *Open Access Sci. Rep.*, 2 (2013) 1-4.