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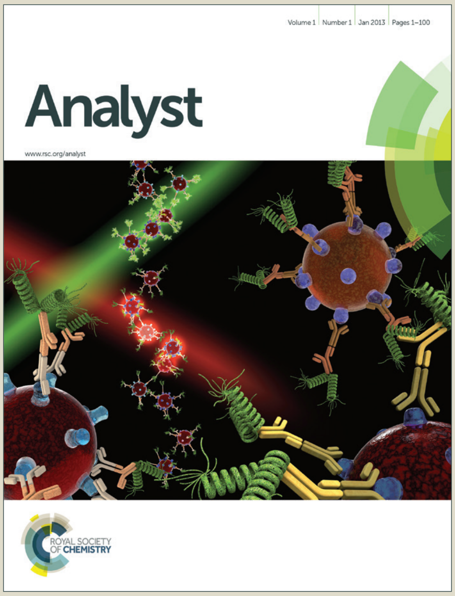

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ARTICLE TYPE

Amperometric sensor for detection of tryptophan based on pristine multi-walled carbon nanotubes/graphene oxide hybrid

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We report the fabrication of a novel amperometric sensor for tryptophan (Trp) based on the pristine multi-walled carbon nanotubes/graphene oxide (pMWCNTs/GO) hybrid obtained through the sonication of pMWCNTs in an aqueous solution of GO. The results of transmission electron microscope and electrochemical impedance spectroscopy demonstrate the successful formation and the excellent charge transfer ability of the resultant hybrid. Compared with the commonly used acid-treated MWCNTs and GO, the resultant hybrid exhibits better electrocatalytic activity towards the oxidation of Trp, which is attributed to the synergistic effect of MWCNTs and GO. The current-time curve reveals that the catalytic oxidation current is linearly dependent on Trp concentration in the range of 50 nM to 4.25 μM with a detection limit of 8 nM (S/N = 3). In addition, the proposed senor is successfully employed to detect Trp in the real samples with satisfactory results.

Introduction

As one of the essential amino acids for the human body, Tryptophan (Trp) plays an important role in biological metabolism and has been commonly used in large scale for the prevention and treatment of schizophrenia, malignant tumour and phenylketonuria, etc[1-3]. Thus, the establishment of a simple and rapid method for the determination of Trp with high selectivity and sensitivity is of great significance to people's health. Electrochemical methods have received considerable interest for the determination of Trp owing to their high sensitivity, simplicity and low cost[4, 5]. However, the direct oxidation of Trp at bare electrodes is not satisfactory due to sluggish electron transfer processes and high overpotential[6, 7]. To overcome these defects, great efforts have been made to design new materials in constructing high-performance electrochemical sensor for Trp analysis. Typical examples include multi-walled carbon nanotubes[8], poly(p-aminobenzene sulfonic acid) film[9], gold nanoparticles[10], butyrylcholine[11], multi-walled carbon nanotubes bridged mesocellulargraphene foam[12], silver nanoparticles-decorated reduced graphene oxide[13], etc. In view of the fact that the modifier materials of the electrode play a key role in the enhancement of electrocatalytic activity, seeking new materials to construct high-performance Trp sensor is still a challenging topic.

Graphene oxide, an oxidative derivative of graphene, has a large abundant of edges that can catalyze the electrochemical reaction of biomolecules[14-17], however, its application in electrochemical sensors has been seriously hindered by the low conductivity due to the defects at the basal plain[18, 19]. Recent advances reveal the interestingly amphiphilic nature of graphene oxide (GO), which allows GO easily forming hybrid with the highly conductive pristine multi-walled carbon nanotubes (pMWCNTs). Because pMWCNTs are ready to behave as electronic bridge to facilitate the electron transfer between GO and electrodes effectively[20, 21], the resultant pMWCNTs/GO hybrid should of course be recognized as one of the state-of-the-art electrode materials in biosensors and can improve the sensing performances dramatically. Recently, Nie and her co-authors reported the application of pMWCNTs/GO hybrid in sensing Azithromycin with satisfactory results[22]. However, till now, the use and the validity of pMWCNTs/GO hybrid in biosensors has not yet been widely described and demonstrated.

In this work, pMWCNTs/GO hybrid, obtained by sonication and centrifugation, is demonstrated to have the better electrocatalytic activity than commonly used acid-treated MWCNTs (AMWCNTs) and even AMWCNTs/GO hybrid towards Trp oxidation, which should be attributed to the combined properties of pMWCNTs and GO. Then, the resultant pMWCNTs/GO hybrid is used as an enhanced electrochemical material for Trp determination, showing a wide linear range between 50 nM to 4.25 μM, a low detection limit of 8 nM (S/N=3)

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and good selectivity. Moreover, the electrochemical sensor can successfully be used for Trp detection in commercial amino acid injection and serum samples with satisfactory results, further confirming the promise of the hybrid as electrode materials in biosensors.

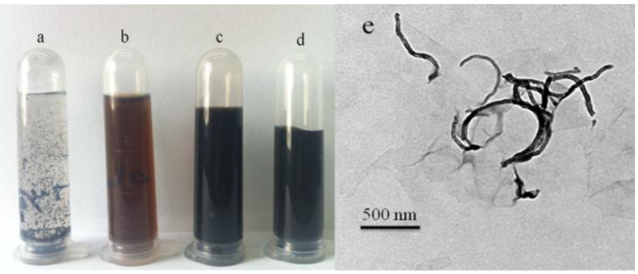

Fig. 1 Photographs of pMWCNTs (a), GO (b), pMWCNTs/GO (c), and the same pMWCNTs/GO dispersion after settling for 3 weeks (d). TEM image of pMWCNTs/GO (e).

Experimental Details

Reagents and instruments

pMWCNTs (Shenzhen Nanotech Port Co.,Ltd.) and graphite powder (Alfa Aesar) were used without further purification. L-tryptophan (Shanghai CapitalBio Corporation) and other chemicals were of analytical grade and used as received. The water used throughout all experiments was purified with the Millipore system. 0.1M phosphate buffersolutions (PBS) were prepared from NaH_2PO_4 and Na_2HPO_4, and pH was adjusted using H_3PO_4 or NaOH.

Transmission electron microscope (TEM) measurements were carried out on a JEM-2010 (Japan) microscope operated at 200 kV. Electrochemical impedance spectroscopy (EIS) studies were performed using a ZAHNER ZENNIUM electrochemical workstation (Kronach, Germany) by applying an AC voltage of 5 mV amplitude in the frequency range of 0.1–100 kHz. Electrochemical measurements were performed using CHI 832C electrochemical workstation (CH Instruments Inc., China). A conventional three-electrode system was used, which consisted of a Ag/AgCl (saturated KCl) electrode as the reference electrode, a platinum wire as the counter electrode, and the pMWCNTs/GO modified glassy carbon electrode (GCE) as working electrode.

Preparation of the pMWCNTs/GO hybrid

GO was synthesized from graphite powder based on a modified Hummers method[23]. Exfoliation of graphite oxide to GO was achieved by ultrasonication for 40 min (1000 W, 20% amplitude). Then, a homogeneous yellow-brown GO aqueous dispersion was obtained and used for further preparation of the pMWCNTs/GO hybrid. pMWCNTs were dispersed in 30% HNO_3 and then refluxed for 24 h at 140 ℃ to acquire acid-treated MWCNTs (AMWCNTs).

The pMWCNTs/GO hybrid was prepared according to the reported method with a slight modification[20, 22]. In brief, 10 mg of pMWCNTs was firstly added into 20 mL of 1 mg mL^{-1} GO suspension, and then the mixture was subjected to sonication for 2h at room temperature. After sonication, the dispersion was centrifugated at 3000 rpm for 20 min to remove the undispersed pMWCNTs. Finally, the obtained supernatant was recentrifugated at 12000 rpm for 30 min and further washed with deionized water to remove the excess GO. The as-prepared pMWCNTs/GO hybrid could be easy dispersed in water and used for further experiments. The preparation of AMWCNTs/GO was similar to that of the pMWCNTs/GO.

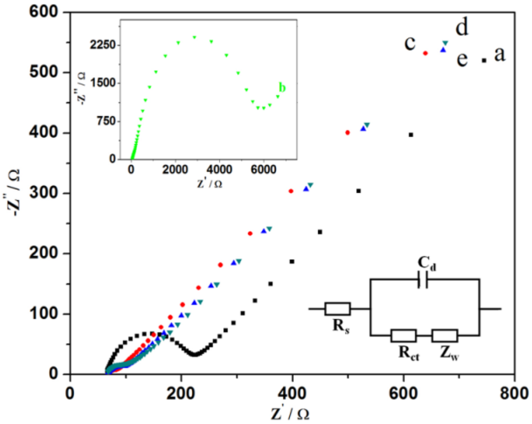

Fig. 2 Nyquist plots for bare GCE (a), GO/GCE (inset, b), AMWCNTs/GCE (c), AMWCNTs/GO/GCE (d) and pMWCNTs/GO/GCE (e) in 5 mM $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1M KCl. Inset (bottom) is the equivalent circuit.

Preparation of the pMWCNTs/GO/GCE

Prior to modification, the GCE was polished successively with 1.0, 0.3 and 0.05 alumina slurry and rinsed with deionized water, followed by sonication in 1:1 nitric acid, acetone and deionized water, respectively. Then, the electrode was allowed to dry with blowing nitrogen. 10 μL of the pMWCNTs/GO or AMWCNTs/GO aqueous solution was cast on the surface of GCE and dried at infrared lamp (noted as pMWCNTs/GO/GCE or AMWCNTs/GO/GCE). For comparison, the GO/GCE was prepared with similar process, and the acid-treated MWCNTs modified electrode was prepared with common way reported elsewhere (noted as AMWCNTs/GCE)[8].

Results

Characterization of the pMWCNTs/GO hybrid

Fig. 1 shows the photographs of pMWCNTs, GO, pMWCNTs/GO and the same pMWCNTs/GO dispersion after settling for 3 weeks, respectively. As shown, due to their hydrophobic outer surface and the strong inter-nanotube van der Waals interactions, pMWCNTs cannot be well dispersed in aqueous solution even after a long time sonication (Fig. 1a). However, GO exhibits great water solubility because of the presence of hydrophilic groups such as hydroxyl, epoxy, and carboxyl groups (Fig. 1b). It can be seen from Fig. 1c that GO can effectively disperse pMWCNTs in water forming a homogeneous black suspension and the pMWCNTs/GO suspension is very stable without any precipitation even for three weeks' storage (Fig. 1d). The structure and morphology of the resultant hybrid was further characterized by TEM. The TEM image (Fig. 1e) reveals that almost all the pMWCNTs are completely disentangled and adhered to the surface of the GO, ascribed to the strong π-π stacking interaction between the surface of pMWCNTs and π-conjugated multiple aromatic domains of GO[20].

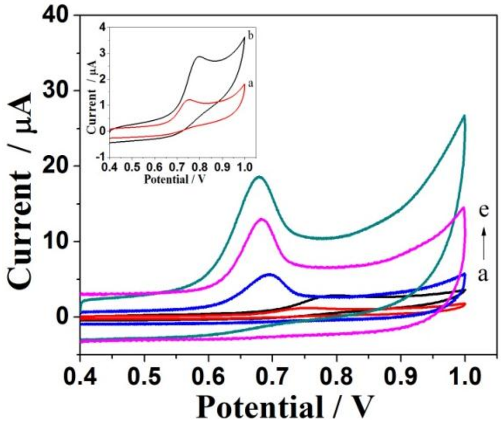

Fig. 3 CVs of GO/GCE (a), bare GCE (b), AMWCNTs/GCE (c), AMWCNTs/GO/GCE (d) and pMWCNTs/GO/GCE (e) in 0.1 M PBS (pH7.4) containing 50 μM Trp.

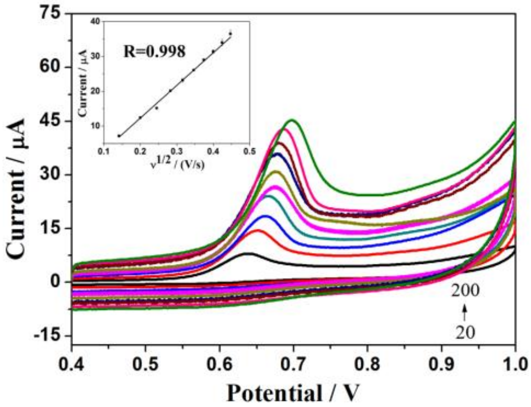

Fig. 4 CVs of 50 μM Trp in 0.1 M PBS (pH 7.4) at the pMWCNTs/GO/GCE with different scan rates: 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14, 0.16, 0.18 and 0.20 V/s. Inset: the plot of the oxidation peak current of Trp versus the square root of the scan rate.

The EIS is an efficient technique to probe the interfacial properties of modified electrodes. Fig. 2 exhibits the Nyquist plots of bare (a), GO (b), AMWCNTs (c), AMWCNTs/GO (d) and pMWCNTs/GO (e) modified GCEs in a 5mM$[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl. The Randles circuit (inset (bottom) of Fig. 2) is chosen to fit the impedance data obtained, where the element R_s is the electrolyte resistance, the resistance to charge transfer (R_{ct}) and the diffusion impedance (Z_w) are both in parallel with the interfacial capacitance (C_d). It can be seen from Fig.2 that the Nyquist plots include a semicircular portion at high frequency and a linear portion at low frequency. The electron transfer resistance at the electrode surface is equal to the semicircle diameter of the Nyquist plot and reveals the interface features of electrodes[24]. Although GO has a lot of edges where heterogeneous electron transfer is fast[15], the R_{ct} of the GO/GCE is estimated to be 5900 Ω in fact, much larger than that of the bare electrode (ca. 120 Ω). The large R_{ct} should be attributed to the well-known poor conductivity of GO. The R_{ct} of pMWCNTs/GO/GCE is 27 Ω, which is about one-twentieth of that of GO/GCE, demonstrating the successful dispersion of pMWCNTs with GO[22]. The R_{ct} of AMWCNTs/GO/GCE is 30 Ω, which is larger than that of AMWCNTs/GCE (18 Ω), reflecting the poor conductivity of GO. Besides, the R_{ct} of pMWCNTs/GO/GCE is similar with that of AMWCNTs/GO/GCE, suggesting that they have almost the same charge transfer ability.

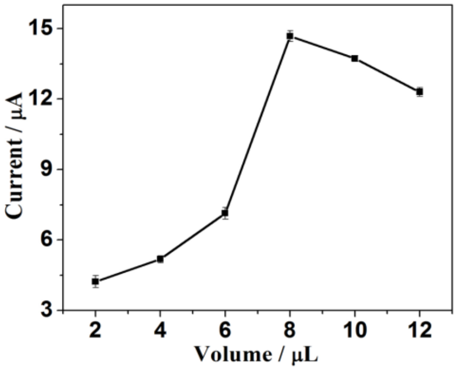

Fig. 5 The relationship between the amount of pMWCNTs/GO hybrid and the peak current of 50 μM Trp in PBS (pH 7.4).

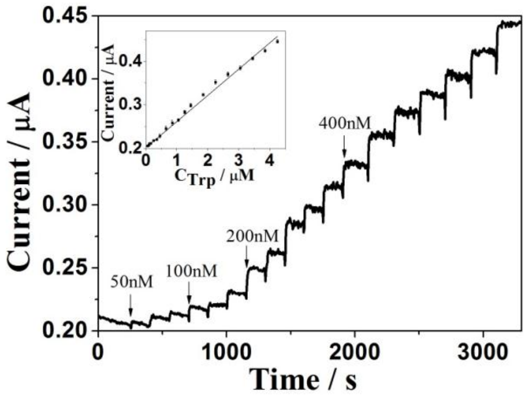

Fig. 6 The amperometric current response at the pMWCNTs/GO/GCE upon successive injection of various concentrations of Trp into PBS (pH 7.4). Inset: calibration plot of the current of Trp versus its concentration. Applied potential: 0.68 V.

Electrochemical behavior of Trp at the pMWCNTs/GO/GCE

Cyclic voltammetry was used to investigate the electrochemical behavior of Trp at the modified electrodes, and Fig. 3 depicts the cyclic voltammograms (CVs) at different electrodes in 0.1 M PBS containing 50 μM Trp. Only one oxidation peak can be observed in the test potential range, indicating the irreversible electrochemical process of Trp at the electrodes. The oxidation peaks appear at 0.80, 0.76, 0.70, 0.68 and 0.68V at the bare GCE, GO/GCE, AMWCNTs/GCE, AMWCNTs/GO/GCE and pMWCNTs/GO/GCE, respectively, and the pMWCNTs/GO/GCE gives the most pronounced peak current. The results mentioned above indicate the pMWCNTs/GO/GCE have the best apparent catalytic activity towards Trp oxidation among the five electrodes used, which can be partially contributed to the high charge transfer capacity due to the combined properties of pMWCNTs and GO (Fig. 2). Since the apparent catalytic activity of modified electrode are related with many factors, for example, adsorption[25, 26], film thickness[27], heterogeneous charge transfer capacity[28], and so on, the exact reason for the high catalytic activity of pMWCNTs/GO/GCE has not yet been understood completely till now.

To understand the reaction mechanism, the influence of scan rate on peak current and peak potential of Trp at the pMWCNTs/GO/GCE was explored. From Fig. 4, it is obviously that the oxidation peak current of Trp increases linearly with the square root of the scan rate in the range of 0.02–0.2V/s, indicating that the oxidation of Trp at pMWCNTs/GO/GCE is a typical diffusion-controlled process. On the other hand, the peak potential (E_{pa}) shifts positively with increasing scan rate for the oxidation of Trp and the resultant regression equation can be expressed as $E_{pa} = 0.0224\ln v + 0.5703$ (R=0.9957). According to the Laviron's theory[29], the electron transfer number of Trp oxidation is calculated to be 2. The result indicates that two electrons are involved in the electrochemical oxidation of Trp at the pMWCNTs/GO/GCE.

Determination of Trp with the pMWCNTs/GO/GCE

The relationship between the oxidation peak current of Trp and the amount of pMWCNTs/GO hybrid was investigated and the results are shown in Fig. 5. The oxidation peak current of Trp increases continuously with the increasing amount of the hybrid from 2 to 8 μL, while the amount more than 8 μL, the oxidation peak current of Trp decreases gradually. The reason might be that the thicker film at GCE surface makes the interfacial charge transfer difficult. Therefore, an amount of 8 μL is selected for the subsequent analytical experiments.

Fig. 6 shows the amperometric response of the pMWCNTs/GO/GCE upon the successive injection of various concentrations of Trp into PBS at an applied potential of 0.68 V. The total testing volume of PBS is 3 mL and the injection volume of the Trp solution is 3 μL each time. The response of the modified electrode to Trp reaches its 95% steady-state current within about 5 s, validating a free diffusion of Trp onto the surface of modified electrode. Furthermore, there is a good linear relationship (Fig.6 inset) between the catalytic current and the concentration of Trp in the range of 50 nM to 4.25 μM, with a detection limit of 8 nM based on S/N=3.

Table 1 Comparison of the performance at various electrodes for the determination of Trp

Electrode	Linear range (μM)	Detection limit (μM)	References
MCPE/MWCNTs	0.6 to 9	0.033	5
AuNP-CNT/GCE	0.03 to 2.5	0.01	30
4-ABA/GCE	1 to 100	0.2	31
MWNT-Cosal/CPE	0.5 to 50	0.1	32
pMWCNTs/GO/GCE	0.05 to 4.25	0.008	Present work

Table 2 Determination of Trp in amino acid injection samples

Samples	Determined (mg/mL)	Labeled (mg/mL)	RSD (n=3,%)	Recovery (%)
1	2.07	2.00	4.2	103.5
2	1.92	2.00	3.5	96.0
3	1.95	2.00	2.8	97.5

Table 3 Determination of Trp in fetal calf serum samples

Samples	Trp added (μM)	Trp found (μM)	RSD (n=3, %)	Recovery (%)
1	0.5	0.47	1.1	94.0
2	1.0	1.00	0.08	100.0
3	2.0	2.06	2.2	103.0
4	3.0	3.01	0.4	100.3
5	4.0	3.93	1.2	98.5

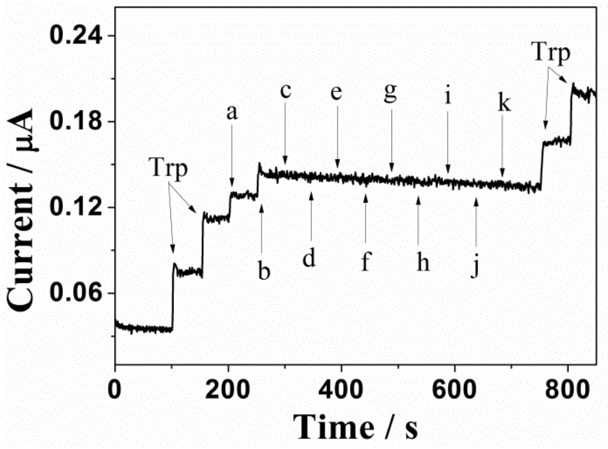

Fig. 7 The amperometric response at the pMWCNTs/GO/GCE upon successive injection of Trp and possible interferents into PBS (pH 7.4). The injection sequence: 1 mM Trp, 1 mM Trp, 1 mM Tyrosine (a), 1 mM ascorbic acid (b), 10 mM histidine (c), 10 mM lysine(d), 10 mM arginineI, 10 mM methionine (f), 10 mM isoleucine (g), 10 mM threonine (h), 10 mM leucine (i), 10 mM valine (j), 10 mM phenylalanine (k), 1 mM Trp , 1 mM Trp. Applied potential: 0.68 V.

Table 1 shows a comparison of pMWCNTs/GO/GCE with other electrodes for the Trp determination. It is evident that the proposed sensor in this work exhibits a wider linear range and lower detection limit compared with some sensors reported previously[5, 30-32], illustrating that the pMWCNTs/GO hybrid possesses unique electrocatalytic performances for the fabrication of electrochemical sensor for Trp.

Moreover, in order to evaluate the anti-interference ability of the pMWCNTs/GO/GCE towards the detection of Trp, several essential amino acids and biomolecules were examined. Fig. 7 shows the amperometric response of Trp and various interferents including tyrosine, ascorbic acid histidine, lysine, arginine, methionine, isoleucine, threonine, leucine, valine and phenylalanine in PBS. As shown, a stepwise growth of amperometric current responses observed with the addition of 1 mM Trp, and the response current is almost unaffected by the addition of various interferents except tyrosine and ascorbic acid. Therefore, the proposed pMWCNTs/GO/GCE can be used to determine Trp in the presence of most of the common interferents and even the low concentrated tyrosine and ascorbic acid.

The reproducibility of the pMWCNTs/GO/GCE was investigated precisely. Six independent measurements of 50 nM Trp using the same modified electrode show a relative standard deviation (RSD) of 4.8%, revealing an acceptable reproducibility. Furthermore, the long-term stability of the modified electrode was also studied by being stored in dry conditions at room temperature. The response current for 50 nM Trp retained 90% of its initial value after two weeks, confirming that the pMWCNTs/GO/GCE has suitable stability for the determination of Trp.

The pMWCNTs/GO/GCE was used to determine Trp concentration in commercial amino acid injection (9AA) (Yichang Sanxia Pharmaceutical Co., Ltd., China) by using the standard addition method. In brief, 10 μL of the diluted (10 times) amino acid injection was injected into 10 mL of the PBS, the results determined by the pMWCNTs/GO/GCE are listed in table 2. As shown, the results of the determination are in satisfactory agreement with the label on the bottle and the recoveries are between 96.0% and 103.5%. Furthermore, fetal calf serum samples were selected to evaluate the applicability of the proposed system. Fetal calf serum samples were diluted 50-fold with 0.1 M PBS without any other treatment. By using the standard addition method, the recoveries of Trp fall in 94.0–103.0%, indicating that the proposed electrochemical sensor can be used for the routine analysis of Trp concentration in real samples.

Conclusions

In summary, the pMWCNTs/GO hybrid has been successfully prepared by utilizing a facile sonication method and used as ideal electrode material for sensitive amperometric determination of Trp because of the combined unique properties of GO and pMWCNTs. The obtained pMWCNTs/GO/GCE exhibited high electrocatalytic activity towards Trp oxidation with a wide linear range of 50nM to 4.25μM and low detection limit of 8nM based on S/N=3. Besides, the proposed amperometric sensor shows good selectivity, reproducibility, stability and has successfully been applied to detect Trp in real samples with satisfactory results. These results indicate that the modified electrode could find its extensive application for the sensitive detection of Trp in practical samples.

Notes and references

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1. Y. Fan, J.-H. Liu, H.-T. Lu and Q. Zhang, *Microchimica Acta*, 2011, **173**, 241-247.
2. M. H. Fernstrom and J. D. Fernstrom, *Life Sci.*, 1995, **57**, PL97-PL102.
3. W. K. H. Steinhart;, *L-Tryptophan—Current Prospects in Medicine and Drug Safety*, Walter de Gruyter.
4. S. Boonchiangma, S. Srijaranai, T. Tuntulani and W. Ngeontae, *J. Appl. Polym. Sci.*, 2014, **131**, 40356.
5. T. Thomas, R. J. Mascarenhas, O. J. D'Souza, P. Martis, J. Dalhalle and B. E. K. Swamy, *J. Colloid Interface Sci.*, 2013, **402**, 223-229.
6. A. Babaei, M. Zendehdel, B. Khalilzadeh and A. Taheri, *Colloids Surf., B*, 2008, **66**, 226-232.
7. S. M. MacDonald and S. G. Roscoe, *Electrochim. Acta*, 1997, **42**, 1189-1200.
8. F.-H. Wu, G.-C. Zhao, X.-W. Wei and Z.-S. Yang, *Microchimica Acta*, 2004, **144**, 243-247.
9. Y. Ya, D. Luo, G. Zhan and C. Li, *Bull. Korean Chem. Soc.*, 2008, **29**, 928-932.
10. C. Li, Y. Ya and G. Zhan, *Colloids Surf., B*, 2010, **76**, 340-345.
11. G.-P. Jin and X.-Q. Lin, *Electrochem. Commun.*, 2004, **6**, 454-460.
12. H. Li, Y. Wang, D. Ye, J. Luo, B. Su, S. Zhang and J. Kong, *Talanta*, 2014, **127**, 255-261.
13. B. Kaur, T. Pandiyan, B. Satpati and R. Srivastava, *Colloids Surf., B*, 2013, **111**, 97-106.
14. A. Ambrosi and M. Pumera, *Phys. Chem. Chem. Phys,*, 2010, **12**, 8943-8947.
15. M. Pumera, A. Ambrosi, A. Bonanni, E. L. K. Chng and H. L. Poh, *TrAC, Trends Anal. Chem.*, 2010, **29**, 954-965.

16. M. Zhou, Y. Zhai and S. Dong, *Anal. Chem.*, 2009, **81**, 5603-5613.
17. F. Zhao, F. Wang, W. Zhao, J. Zhou, Y. Liu, L. Zou and B. Ye, *Microchimica Acta*, 2011, **174**, 383-390.
18. I. Jung, D. A. Dikin, R. D. Piner and R. S. Ruoff, *Nano Lett.*, 2008, **8**, 4283-4287.
19. S. Pei, J. Zhao, J. Du, W. Ren and H.-M. Cheng, *Carbon*, 2010, **48**, 4466-4474.
20. J. Kim, L. J. Cote, F. Kim, W. Yuan, K. R. Shull and J. Huang, *J. Am. Chem. Soc.*, 2010, **132**, 8180-8186.
21. C. Zhang, L. Ren, X. Wang and T. Liu, *J. Phys. Chem. C*, 2010, **114**, 11435-11440.
22. K. Zhang, L. Lu, Y. Wen, J. Xu, X. Duan, L. Zhang, D. Hu and T. Nie, *Anal. Chim. Acta*, 2013, **787**, 50-56.
23. Y. Li and Y. Wu, *J. Am. Chem. Soc.*, 2009, **131**, 5851-5857.
24. D. Wen, S. Guo, S. Dong and E. Wang, *Biosens. Bioelectron.*, 2010, **26**, 1056-1061.
25. J. Li, D. Kuang, Y. Feng, F. Zhang, Z. Xu, M. Liu and D. Wang, *Microchimica Acta*, 2013, **180**, 49-58.
26. J. Li, D. Kuang, Y. Feng, F. Zhang, Z. Xu and M. Liu, *J. Hazard. Mater.*, 2012, **201–202**, 250-259.
27. M. Gholamian, J. Sundaram and A. Q. Contractor, *Langmuir*, 1987, **3**, 741-744.
28. A. S. Adekunle, B. O. Agboola, J. Pillay and K. I. Ozoemena, *Sens. Actuators B*, 2010, **148**, 93-102.
29. E. Laviron, *J. Electroanal. Chem. Interfac*, 1974, **52**, 355-393.
30. Y. Guo, S. Guo, Y. Fang and S. Dong, *Electrochim. Acta*, 2010, **55**, 3927-3931.
31. K.-J. Huang, C.-X. Xu, W.-Z. Xie and W. Wang, *Colloids Surf., B*, 2009, **74**, 167-171.
32. S. Shahrokhian and L. Fotouhi, *Sens. Actuators B*, 2007, **123**, 942-949.