



Cite this: RSC Adv., 2017, 7, 1847

## Electrochemical detection of serotonin based on a poly(bromocresol green) film and $\text{Fe}_3\text{O}_4$ nanoparticles in a chitosan matrix†

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A composite film containing poly(bromocresol green), magnetic nanoparticles and multiwalled carbon nanotubes was fabricated for the sensitive determination of serotonin. The poly(bromocresol green) was prepared by electropolymerization on a glassy carbon electrode surface, then the multiwalled carbon nanotubes and magnetic nanoparticles in a chitosan matrix were dropped onto the surface of the poly(bromocresol green) film. The modified electrode displayed an enhanced differential pulse voltammetric response to serotonin in the presence of dopamine. Its peak current (at an oxidation voltage of 0.36 V vs. Ag/AgCl) increased linearly in the serotonin concentration range 0.5–100  $\mu\text{M}$  with a detection limit of 80 nM (at an S/N of 3). The sensor was highly sensitive and stable. It was applied to the direct determination of serotonin spiked into human serum samples. These results show that the nanocomposite films are good modifying materials for use in the fabrication of electrochemical sensors.

Received 21st October 2016  
 Accepted 29th November 2016

DOI: 10.1039/c6ra25639b  
[www.rsc.org/advances](http://www.rsc.org/advances)

### 1. Introduction

Thin films of conducting polymers have attracted much attention as electrode materials. Conjugated polymers can be used in thin film transistors and biosensors<sup>1–3</sup> as a result of their electronic and electrochemical properties. Conducting polymers can enhance the electrochemical signals produced by the redox reactions of target compounds. Bromocresol green (BCG) has been used as an electrode material in electrochemical sensors;<sup>4,5</sup> its high-electron-density hydroxyl groups and good conductivity give poly(BCG) films a negative charge and they exhibit electrocatalytic activity towards many substances. Iron oxide ( $\text{Fe}_3\text{O}_4$ ) forms magnetic nanoparticles (NPs), which have excellent chemical stability, good biocompatibility and a high electron efficiency<sup>6</sup> and have therefore been widely applied in electrochemistry.<sup>7–10</sup> Multiwalled carbon nanotubes (MWCNTs) have a porous nanostructure and have a high electrical conductivity, large surface area and good chemical stability.<sup>11,12</sup> When used as modifying materials in electrochemical devices, they can promote electron transfer reactions.<sup>13,14</sup> Chitosan (CS) has a good permeability, good adhesion and excellent film-forming abilities. These make CS a good matrix for immobilizing molecules.<sup>15–18</sup>

Serotonin (5-hydroxytryptamine; 5-HT) is an important neurotransmitter and plays a variety of parts in many basic

biological processes, including sensory perception and behavior.<sup>19,20</sup> This has encouraged researchers to look for faster and more sensitive methods to determine 5-HT, including detection using various modified electrodes.<sup>21–27</sup> Sensitivity is a key factor in the detection of serotonin. We describe here nanocomposites films based on magnetic  $\text{Fe}_3\text{O}_4$  NPs, MWCNTs and poly(BCG), which have been used to study the electrochemical behaviour of 5-HT.  $\text{Fe}_3\text{O}_4$  and MWCNTs are ideal modifying materials due to their high conductivity and good absorbability. The poly(BCG) film modified electrode had a large surface area and good conductivity, which led to conjugation between the target analytes and the electrode interface. We describe the preparation and application of the serotonin sensor. The  $\text{Fe}_3\text{O}_4$ –MWCNT–poly(BCG) composite films exhibited strong electrocatalytic ability and enhanced the sensitivity towards 5-HT. Compared with a bare glassy carbon electrode (GCE), the peak currents of 5-HT increased significantly at the electrode coated with a  $\text{Fe}_3\text{O}_4$ –MWCNT–poly(BCG) film. The oxidation peak of 5-HT was not affected by high concentrations of dopamine. 5-HT was detected by the poly(BCG) and nanoparticle films using an electrochemical method. The modified electrode had obvious advantages, such as a wide linear concentration range, low detection limit, good selectivity and reproducibility. The nanocomposite films are thus good materials for the fabrication of electrochemical sensors.

### 2. Experimental

#### 2.1. Reagents and apparatus

CS, BCG and 5-HT were obtained from Sigma. Dopamine (DA), ascorbic acid (AA), uric acid (UA), adrenaline (AD), tryptophan

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† Electronic supplementary information (ESI) available. See DOI: [10.1039/c6ra25639b](https://doi.org/10.1039/c6ra25639b)



(Trp), L-cysteine (L-Cys) and glucose (GLU) were obtained from Alfa Aesar. The MWCNTs were obtained from Nanjing XFNANO Materials Tech. Sulfuric acid, nitric acid, acetic acid, sodium phosphate dibasic and sodium phosphate monobasic were obtained from Sichuan Xilong Chemical. All reagents were of analytical-reagent grade. All solutions used were made with ultrapure water. Phosphate buffers with different pH values were prepared using 0.1 M  $\text{NaH}_2\text{PO}_4$  and 0.1 M  $\text{Na}_2\text{HPO}_4$ . The serum samples were obtained from the hospital of Chongqing Three Gorges University.

A CHI 660D electrochemical workstation (Shanghai CHI Instruments) was used to collect the electrochemical data. The three-electrode system consisted of a modified working electrode, a platinum electrode as the counter electrode and an Ag/AgCl reference electrode. UV absorption spectra were measured on a Cary-300 spectrophotometer (Varian). An EL20K pH meter (Mettler) was used to measure the pH. The morphologies and microstructures of the samples were characterized by an S-4800 scanning electron microscope and H-7500 transmission electron microscope (Hitachi).

## 2.2. Preparation of poly(BCG)/GCE

The GCE was polished successively with 0.3 and 0.05  $\mu\text{m}$  alumina powders, rinsing thoroughly with ultrapure water between each polishing step. The electrode was washed in 1 : 1 nitric acid, then ultrasonicated in ultrapure water before drying in high-purity nitrogen. The GCE was placed in a beaker containing pH 7.4 phosphate buffer and 0.5 mM BCG solution and was cyclically swept for 25 cycles between  $-0.4$  and  $1.8$  V vs. Ag/AgCl at  $100\text{ mV s}^{-1}$  to form the poly(BCG)/GCE (Fig. S1 and S2, ESI†). The anodic peak currents increased with the number of scan cycles, indicating the deposition of BCG on the surface of the GCE by electropolymerization (Fig. 1). The impurities on the electrode surface were removed by ultrapure water. The poly(BCG)/GCE was then stored at room temperature.

## 2.3. Preparation of GCE with composite $\text{Fe}_3\text{O}_4$ -MWCNTs-poly(BCG)

The MWCNTs were sonicated with a strong oxidizing agent consisting of a mixture of concentrated sulfuric and nitric acids

(3 : 1 v/v) for 10 h and then washed with ultrapure water, filtered and centrifuged. A 1.0 mg mass of MWCNTs and 1.0 mL of 0.5 wt% CS were ultrasonicated to obtain a suspension. Magnetic  $\text{Fe}_3\text{O}_4$  NPs were prepared by Batalha's method.<sup>28</sup>  $\text{Fe}_3\text{O}_4$  (1.0 mg) was dispersed in the suspension to obtain an  $\text{Fe}_3\text{O}_4$ -MWCNT solution. The modified electrode was prepared by dropping 5.0  $\mu\text{L}$  of the modified solution onto the surface of the poly(BCG)/GCE. The modified solution was then dried at room temperature.

## 3. Results and discussion

### 3.1. Characterization of $\text{Fe}_3\text{O}_4$ -MWCNT composite films

The TEM image of the  $\text{Fe}_3\text{O}_4$  NPs in Fig. 2a shows that the  $\text{Fe}_3\text{O}_4$  NPs were rounded NPs with a uniform distribution. The SEM images of the MWCNTs and the  $\text{Fe}_3\text{O}_4$ -MWCNT nanocomposite film are shown in Fig. 2b and c. It can be clearly seen that the  $\text{Fe}_3\text{O}_4$  NPs were attached to the MWCNTs. These spherical particles were confirmed to be agglomerations of  $\text{Fe}_3\text{O}_4$  NPs.

To further investigate the  $\text{Fe}_3\text{O}_4$ -MWCNT solution, the modified solution was characterized by its UV absorption spectrum. The UV absorption spectra of different samples in phosphate buffer are shown in Fig. 3. An obvious absorption peak appeared at about 220 nm, originating from the structure of the MWCNTs.<sup>29</sup> The absorption peak of the  $\text{Fe}_3\text{O}_4$ -MWCNTs was influenced by the absorption of the  $\text{Fe}_3\text{O}_4$  NPs, which showed a red shift relative to the pristine MWCNTs. Therefore the  $\text{Fe}_3\text{O}_4$  NPs were attached to the MWCNTs.

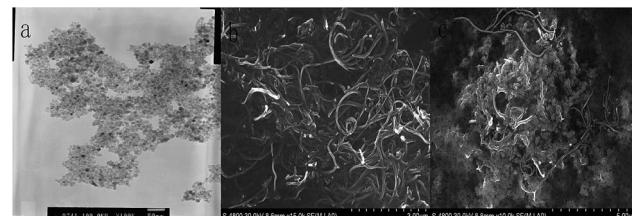


Fig. 2 (a) TEM image of  $\text{Fe}_3\text{O}_4$  NPs and SEM images of (b) MWCNTs and (c)  $\text{Fe}_3\text{O}_4$ -MWCNTs.

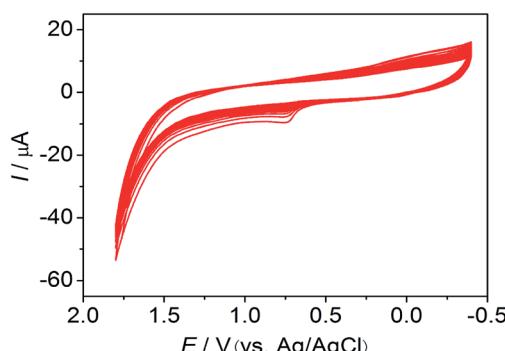


Fig. 1 Repeated cyclic voltammograms in phosphate buffer (pH 7.4) and  $5 \times 10^{-4}$  M BCG. Scan rate:  $100\text{ mV s}^{-1}$ ; no. of sweep circles, 25.

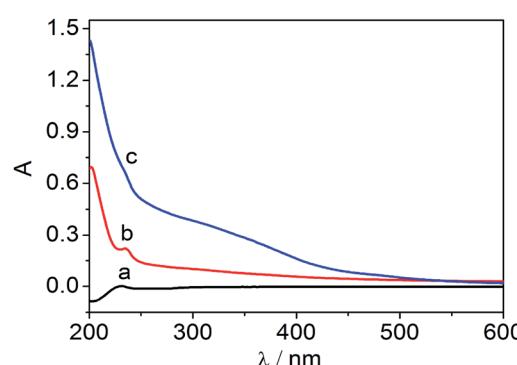


Fig. 3 UV-vis absorption spectra of (a) MWCNTs, (b)  $\text{Fe}_3\text{O}_4$ -MWCNTs and (c)  $\text{Fe}_3\text{O}_4$  in 0.1 M phosphate buffer (pH 7.0).



### 3.2. Electrochemical behaviour of 5-HT at the $\text{Fe}_3\text{O}_4$ –MWCNT–poly(BCG) films

Fig. 4 shows the cyclic voltammograms of different modified electrodes in pH 7.0 phosphate buffer and  $2.0 \times 10^{-5}$  M 5-HT solution. No peak was observed at the bare GCE, (curve a), but an oxidation peak was observed for the poly(BCG)/GCE (curve b). The oxidation peak potentials occurred at 0.400 V vs. Ag/AgCl. An oxidation peak was also observed for the MWCNT–poly(BCG)/GCE (curve c) and  $\text{Fe}_3\text{O}_4$ –MWCNT/GCE (curve d). Under identical conditions, when the bare GCE was modified with the  $\text{Fe}_3\text{O}_4$ –MWCNT–poly(BCG) film, the oxidation peak observed at the  $\text{Fe}_3\text{O}_4$ –MWCNT–poly(BCG)/GCE (curve e) was much larger than for the other modified electrodes and the oxidation peak potential shifted to 0.360 V vs. Ag/AgCl. It was therefore concluded that the  $\text{Fe}_3\text{O}_4$ –MWCNT–poly(BCG) composite enhanced the electron transfer and peak currents of 5-HT. The sensitivity of 5-HT was improved by this electrocatalytic behaviour.

**3.2.1. Optimum amounts of  $\text{Fe}_3\text{O}_4$  and MWCNTs.** The optimum amounts of  $\text{Fe}_3\text{O}_4$  and MWCNTs were investigated. The total concentration of  $\text{Fe}_3\text{O}_4$  and MWCNTs was fixed at  $6.0 \text{ mg mL}^{-1}$ , but we changed the concentration of  $\text{Fe}_3\text{O}_4$  from 0 to  $6.0 \text{ mg mL}^{-1}$ .<sup>30</sup> Fig. 5 shows that the peak currents gradually increased with an increase in the concentration of  $\text{Fe}_3\text{O}_4$  from 0 to  $3.0 \text{ mg mL}^{-1}$ . When the concentration of  $\text{Fe}_3\text{O}_4$  reached  $3.0 \text{ mg mL}^{-1}$ , the peak currents reached the highest value. However, the peak currents gradually decreased with an increase in the concentration of  $\text{Fe}_3\text{O}_4$  from  $3.0$  to  $6.0 \text{ mg mL}^{-1}$ . Therefore the optimum proportion of  $\text{Fe}_3\text{O}_4$  to MWCNTs was 1 : 1.

**3.2.2. Effects of scan rate and solution pH.** The scan rate influenced the electrode reaction of the peak potential ( $E_{\text{pa}}$ ) and the peak current ( $I_{\text{p}}$ ) (Fig. 6a). In the range  $40– $180 \text{ mV s}^{-1}$ ,  $I_{\text{p}}$  was linearly related to the square root of the scan rate. The linear regression equation was  $I_{\text{p}} (\mu\text{A}) = 0.081 + 0.699 \text{ V mV}^{-1} \text{ s}^{-1}$  ( $R^2 = 0.997$ ), meaning that the oxidation process was diffusion controlled. As the scan rate increased,  $E_{\text{pa}}$  shifted to a more positive potential, indicating that the electron transfer process$

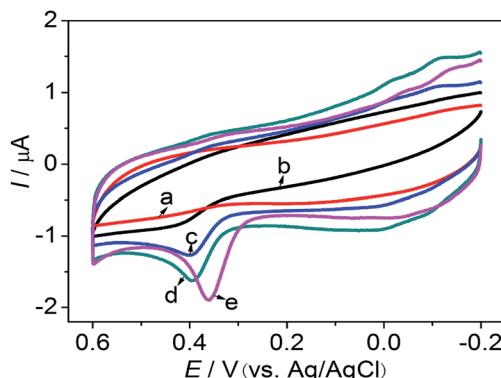


Fig. 4 Cyclic voltammograms obtained with (a) a bare GCE, (b) the poly(BCG)/GCE, (c) the MWCNT/GCE, (d) the  $\text{Fe}_3\text{O}_4$ –MWCNT/GCE and (e) the  $\text{Fe}_3\text{O}_4$ –MWCNT–poly(BCG)/GCE in 0.1 M phosphate buffer (pH 7.0) and  $2.0 \times 10^{-5}$  M 5-HT.

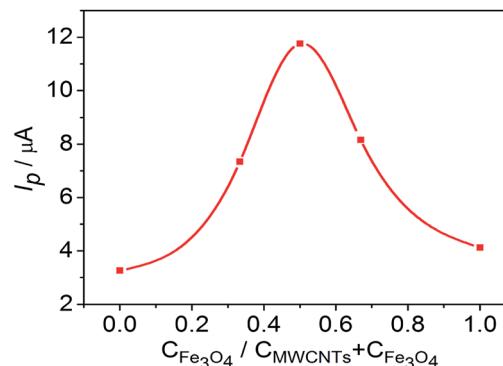


Fig. 5 Peak currents of different proportions of  $\text{Fe}_3\text{O}_4$  and MWCNTs in 0.1 M phosphate buffer (pH 7.0) and  $1.0 \times 10^{-4}$  M 5-HT.

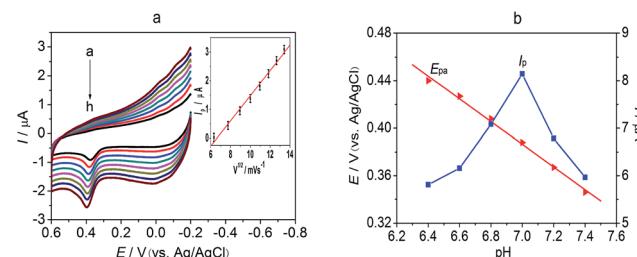


Fig. 6 (a) Cyclic voltammograms of the  $\text{Fe}_3\text{O}_4$ –MWCNT–poly(BCG)/GCE at different scan rates from 40 to  $180 \text{ mV s}^{-1}$ . The inset shows the relationship between  $I_{\text{p}}$  and the square root of the scan rate. (b) Effect of pH on the peak current ( $I_{\text{p}}$ ) and peak potential ( $E_{\text{pa}}$ ) at the  $\text{Fe}_3\text{O}_4$ –MWCNTs–poly(BCG)/GCE in phosphate buffer (pH 7.0) and  $1.0 \times 10^{-4}$  M 5-HT.

was quasi-reversible.<sup>31</sup> When the pH of the phosphate buffer changed, the oxidation  $E_{\text{pa}}$  and the  $I_{\text{p}}$  of 5-HT also changed. When the pH of the phosphate buffer was 7.0, the peak current of 5-HT reached a maximum value at the  $\text{Fe}_3\text{O}_4$ –MWCNT–poly(BCG)/GCE (Fig. 6b) and therefore pH 7.0 was selected as the optimum pH for the determination of 5-HT. By contrast, when the pH increased, the peak potential of 5-HT shifted to a negative potential and  $E_{\text{pa}}$  was linear with pH. The linear regression equation was  $E_{\text{pa}} (\text{mV}) = 654.4 - 38.3 \text{ pH}$  ( $R^2 = 0.990$ ). The slope of  $-38.3 \text{ mV pH}^{-1}$  indicates that only one proton was involved in the two-electron oxidation process.<sup>32</sup>

### 3.3. Electrochemical response of 5-HT in the presence of DA at the modified electrode

Differential pulse voltammetry (DPV) has a much better current sensitivity than cyclic voltammetry, so it was used to determine the concentration of 5-HT in the presence of DA at the  $\text{Fe}_3\text{O}_4$ –MWCNT–poly(BCG)/GCE and to estimate the limit of detection. The anodic peak currents were linearly related to the 5-HT concentration in the range 0.2–100  $\mu\text{M}$  (Fig. 7a). The linear regression equation was:  $I_{\text{p}} (\mu\text{A}) = 0.3088 + 0.5279C (\text{M})$  ( $R^2 = 0.998$ ) and the detection limit was 60 nM ( $S/N = 3$ ). The oxidation peak current was linearly related to the concentration of 5-HT in the range 0.5–100  $\mu\text{M}$  in the presence of 10  $\mu\text{M}$  DA

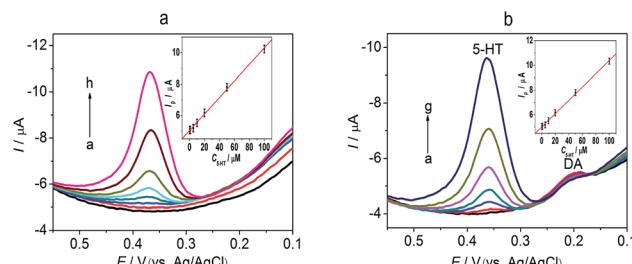


Fig. 7 (a) DPV for 5-HT at the  $\text{Fe}_3\text{O}_4$ -MWCNT-poly(BCG)/GCE in phosphate buffer (pH 7.0). 5-HT concentrations (from a to h): 0, 0.2, 0.5, 1, 5, 10, 50 and 100  $\mu\text{M}$ . (b) DPV of 5-HT at the  $\text{Fe}_3\text{O}_4$ -MWCNTs-poly(BCG)/GCE in phosphate buffer (pH 7.0) and  $1.0 \times 10^{-5}$  M DA. 5-HT concentration (from a to g): 0, 0.5, 1, 5, 10, 50 and 100  $\mu\text{M}$ . The inset shows the relationship between  $I_p$  and different concentrations of 5-HT.

(Fig. 7b). The regression equation was  $I_p (\mu\text{A}) = 0.3183 + 0.5309C (\mu\text{M})$  ( $R^2 = 0.996$ ) and the detection limit was 80 nM ( $S/N = 3$ ). The measured parameters of this electrode are compared with other previously reported modified electrodes in Table 1. Compared with these other modified electrodes, the  $\text{Fe}_3\text{O}_4$ -MWCNT-poly(BCG)/GCE had a low detection limit.

#### 3.4. Interference studies

To explore the selectivity of the  $\text{Fe}_3\text{O}_4$ -MWCNT-poly(BCG)/GCE, four small biological molecules (AA, UA, DA and 5-HT) were detected simultaneously. Four oxidation peaks were separated. Interference from AA coexisting in 5-HT at the  $\text{Fe}_3\text{O}_4$ -MWCNT-poly(BCG)/GCE was analysed by DPV with the concentration of AA increasing from 0 to  $4.0 \times 10^{-3}$  M in solution. The results showed that a 400-fold excess AA did not obviously influence the detection of 5-HT (Fig. S3, ESI†). The same experiments were carried out in the presence of DA, UA, AD, Trp, L-Cys and GLU. We found that 20-fold DA, 10-fold UA, 15-fold AD, 200-fold Trp, 150-fold L-Cys and 150-fold GLU did not obviously interfere in the detection of 5-HT. To test the repeatability of the  $\text{Fe}_3\text{O}_4$ -MWCNT-poly(BCG)/GCE, the electrode was stored in

Table 1 Performance of previously reported modified electrodes in the detection of 5-HT<sup>a</sup>

Modified electrode	Linear region ( $\mu\text{M}$ )	Detection limit ( $\mu\text{M}$ )	Ref.
Ru/WGE	0.3–9.0	0.1	23
5-HTP/GCE	5.0–35.0	1.7	25
ACh/GCE	1.0–30.0	0.5	33
Carbon fibre electrode	2.5–10.0	1.0	34
CNT-IL/GCE	5.0–900.0	2.0	35
PM-PG/GCE	1.0–100.0	0.49	36
$\text{Fe}_3\text{O}_4$ -MWCNT-poly(BCG)/GCE	0.5–100.0	0.08	This work

<sup>a</sup> Ru: rutin; WGE: paraffin-impregnated graphite electrode; 5-HTP: 5-hydroxytryptophan; GCE: glassy carbon electrode; ACh: acetylcholine; CNT: carbon nanotube; IL: ionic liquids; PM: polymelamine; PG: pyrolytic graphite.

Table 2 Recovery for the determination of 5-HT in serum samples

Sample	Original ( $\mu\text{M}$ )	Added ( $\mu\text{M}$ )	Found <sup>a</sup> ( $\mu\text{M}$ )	Recovery (%)
1	ND <sup>b</sup>	2.00	1.89	94.50
2	ND <sup>b</sup>	3.00	2.79	93.00
3	ND <sup>b</sup>	4.00	3.75	93.75

<sup>a</sup> Mean of three determinations. <sup>b</sup> Not detected.

a refrigerator at 4 °C after the first measurement. Compared with the initial response, the current response was reduced by about 3.7% 3 days later, by 7.5% 7 days later and by 16.4% after 15 days. Therefore this sensor displays high selectivity and good stability in the detection of 5-HT.

#### 3.5. Determination of 5-HT in human blood serum

The  $\text{Fe}_3\text{O}_4$ -MWCNT-poly(BCG)/GCE was applied to the detection of 5-HT in human blood samples. Serum samples were analysed under the optimum conditions, but 5-HT was not detected. Therefore different concentrations of 5-HT standards were added to the sample matrix to carry out the recovery test. The experimental results are shown in Table 2. The results show that the  $\text{Fe}_3\text{O}_4$ -MWCNT-poly(BCG)/GCE could detect 5-HT in serum samples.

## 4. Conclusions

A serotonin sensor was fabricated using a  $\text{Fe}_3\text{O}_4$ -MWCNT-poly(BCG) nanocomposite film. It was shown that the  $\text{Fe}_3\text{O}_4$ -MWCNT-poly(BCG) nanocomposite film had a strong electrocatalytic effect in the oxidation of 5-HT and enhanced electron transfer between the target analytes and the electrode interface. The MWCNTs provided many active sites and enhanced the sensitivity of the sensor. Compared with previously reported methods, the serotonin sensor exhibited high sensitivity, good selectivity and a low detection limit. The sensor was successfully applied to the determination of 5-HT in blood serum samples.

## Acknowledgements

The authors give heartfelt gratitude for the financial support of this study by the Scientific and Technological Research Program of Chongqing Municipal Education Commission (No. KJ1501026), the research program of Wanzhou District Science Commission (No. 201503051) and the Key Laboratory of Water Environment Evolution and Pollution Control in the Three Gorges Reservoir fund project (No. WEPKL2016LL-01; WEPKL2016LL-06).

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