

Electrochemical determination of tryptophan at room-temperature ionic liquid-titanium carbide nanoparticle gel modified electrode

Fei Li · Qing Zhang · Dawei Pan · Mingyue Lin · Qi Kang

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Abstract The novel gel composite, based on the ground of ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate, BMIMPF₆) and titanium carbide (TiC) nanoparticles, was used to modify glassy carbon electrode and applied to the electrochemical determination of tryptophan (trp). The physical and electrochemical characterizations of the BMIMPF₆-TiC gel modified electrode were studied in detail by scanning electron microscopy, energy dispersive X-ray spectroscopy, cyclic voltammetry, and differential pulse voltammetry methods. Due to the large specific surface area and strong adsorption property of TiC nanoparticles, as well as the good ionic conductivity and strong electrocatalytic property of BMIMPF₆, the oxidation peak current of trp at BMIMPF₆-TiC gel modified electrode showed good linear relation with its concentrations ranging from 0.50 to 30 μmol/L and 30 to 500 μmol/L, respectively. The detection limit was 0.053 μmol/L. More importantly, the BMIMPF₆-TiC gel modified electrode had good anti-interference ability and can be successfully applied in the electrochemical determination of trp in real food samples.

Keywords TiC nanoparticles · Ionic liquid · Tryptophan · Electrochemical characterizations · Electrode · Ionic conductivity

Introduction

In the past years, electrochemical analysis based on the selective sensors has been improved promptly [1–22] with the use of the novel materials. Room-temperature ionic liquids (RTILs) as a new material have been attracted by scientists in decade years. RTILs are ionic media resulting from the combination of organic cations and various anions; they are liquids at room-temperature and represent a new class of non-aqueous but polar solvents, which are able to dissolve many compounds [23]. They are good solvents for a wide range of inorganic and organic materials, have no appreciable vapor pressure at room-temperature, and have moderate viscosity [24]. These advantages make the ionic liquids more and more popular and widely used in electrochemical analysis [25–29].

Nanomaterials show higher electrocatalytic activity, small size, and large specific surface area, with unique physical properties as a kind of special sensing material of chemically modified electrodes [30–36]. In the past, the voltammetric sensor was developed based on nanomaterials in the presence of RTILs for drug and other important biological compound analysis [37–47]. TiC is representative transition metal carbide. It has high melting point, high thermal and electrical conductivity, high chemical stability, and catalysis activity. TiC nanoparticles not only owe the excellent characteristics of TiC block, but also have the characteristics of nanomaterials. Due to large specific surface area, good biocompatibility, good conductivity, and adsorption performance, TiC nanoparticles have been widely used in the chemical field. Zheng [48] successfully prepared a novel PANI–TiC nanocomposite through the in situ chemical oxidative

F. Li · Q. Zhang · Q. Kang (✉)
The Key Lab in Molecular and Nano-materials Probes of the Ministry of Education of China, College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan, Shandong 250014, People's Republic of China
e-mail: qikang@sdu.edu.cn

D. Pan (✉) · M. Lin
Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research(YIC), Chinese Academy of Sciences(CAS), Shandong Provincial Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai, Shandong 264003, People's Republic of China
e-mail: dwpan@yic.ac.cn

polymerization method, in which PANI and TiC showed an excellent synergic effect. Furthermore, the PANI–TiC exhibited good electrocatalytic activity toward AA. However, the TiC nanoparticles are solid and hard to be modified electrode alone.

Trp is essential amino acid for humans and a precursor for serotonin (a neurotransmitter), melatonin (a neurohormone), and niacin. The molecular structure of trp is shown in Scheme 1. It has been implicated as a possible cause of schizophrenia in people who cannot metabolize it properly. So, many technologies have been applied to the detection of trp, such as high-performance liquid chromatography [49–52], capillary electrophoresis [53–57], fluorometric methods [58], chemiluminescence [59–63], and ultraviolet detection [64]. Although these methods have the benefits of sensitivity and accuracy, their high cost, time-consuming, and complicated operations limit their extensive application for routine trp analysis. However, electrochemical method for monitoring trp has shown promise compared to the methods above. It is well known that the electrochemical detection of trp at the unmodified electrode is not optimal owing to sluggish electron transfer processes and high over-potential [65]; so, lots of efforts have been contributed to seek the new material for electrode modification in order to promote the electron transfer and reduce the over-potential [66–78].

In this study, ground RTIL BMIMPF₆ and TiC nanoparticles to make the gel compound, which was used to modify glassy carbon electrode and applied to the electrochemical determination of trp. Due to the fact that BMIMPF₆-TiC gel has large specific surface area and adsorption performance and has good electric conductivity and electric catalytic performance, the modified electrode has wide linear range, high sensitivity, low detection limit, excellent reproducibility, and good anti-interfering capability. Under the optimized conditions, the oxidation current of trp with its concentration has a good linear relationship; the detection limit of trp was 0.053 μmol/L. This novel BMIMPF₆-TiC gel modified electrode was applied for the determination of trp in real samples.

Experimental

Reagents

Trp was obtained from Shanghai SSS Reagent Co. Ltd. BMIMPF₆ was supplied by Shanghai Cheng Jie Chemical Co. Ltd. TiC nanoparticles were obtained from Nanjing Emperor Nano Material Co. Ltd. All other chemicals were of analytical reagents and used without further purification. All experiments were conducted at room-temperature, and the solutions were used in the process without nitrogen atmosphere. Deionized water (18.2 MΩ·cm specific resistance)

obtained with a Pall Cascada laboratory water system was used throughout.

A 0.05 mol/L trp solution was prepared daily by dissolving 1.02 g trp in a NaOH solution (0.02 mol/L) in a 100-mL volumetric flask with ultrasonication for several minutes. More diluted solutions were prepared by serial dilutions with water.

Real sample preparation

The milk was bought from supermarket, and the urine was gained from hospital. Before usage, the milk was filtered through a 15~20 μm normal filter paper. The urine and the milk were diluted five times with 0.1 M PBS (pH 5.5) without subjecting it to any further pretreatment.

Apparatus

The morphology and elemental composition of the modified electrodes were characterized by using scanning electron microscopy (SEM Hitachi S-4800 microscope, Japan) and energy dispersive X-ray spectroscopy (EDX HORIBA EX-350), respectively. All the electrochemical experiments were performed in a conventional three-electrode cell controlled by LK2005A Electrochemical Work Station (LANLIKE Instruments, Inc.). A modified glassy carbon (GC) disk (3 mm in diameter) and a platinum foil were used as the working and counter electrodes, respectively. Hg/HgCl₂ reference electrode was adopted in saturated KCl aqueous solution.

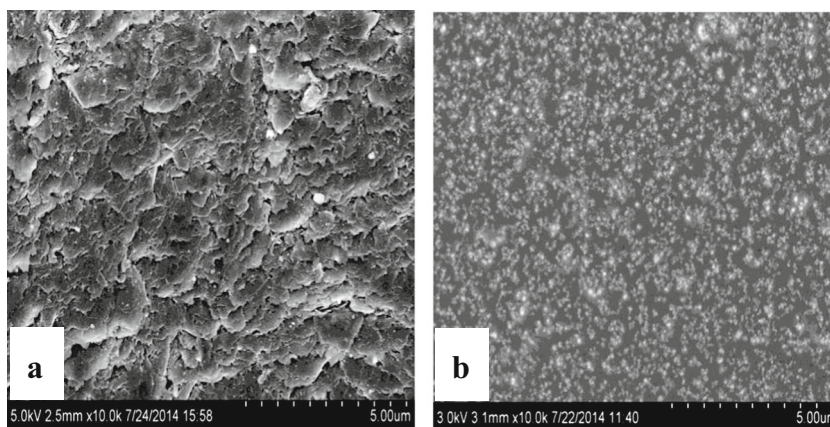
Preparation of the modified electrode

Prior to use, GCE was polished to a mirror finish using a microcloth with 0.05 μm alumina slurry, then rinsed, and ultrasonicated with deionized water. Twenty-five milligram TiC nanoparticles and 20 μL BMIMPF₆ were mixed in an agate mortar grinding at least 20 min [79] until perfect homogeneous BMIMPF₆-TiC gel was obtained. The friction between GCE and smooth slide coated with BMIMPF₆-TiC gel composite will last at least 15 min and resulting in a layer of gel film on GCE surface.

Electrochemical analysis procedure

Unless otherwise stated, 0.1 M phosphate buffer solution (PBS, pH 5.5) was used as the supporting electrolyte for trp determination. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods were adopted. CV was performed under the following parameters: initial potential of -0.2 V, final potential of 0.6 V, scan rate of 0.05 V/s. DPV was performed under the following parameters: initial potential of 0.5 V, final potential of 0.9 V, amplitude of 0.05 V, potential

Fig. 1 SEM micrograph of the bare GCE (a) and BMIMPF₆-TiC/GCE (b)



incremental of 0.01 V, pulse width of 0.2 s, pulse period of 0.45 s, quiet time of 2 s.

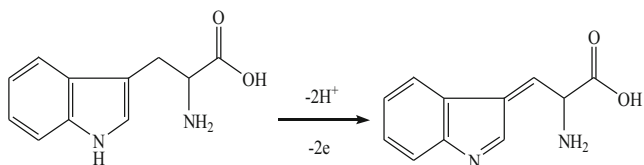
Results and discussion

Characterization of the BMIMPF₆-TiC gel modified electrode

Figure 1 shows the surface morphologies of bare GCE (Fig. 1a) and BMIMPF₆-TiC/GCE (Fig. 1b). As shown in Fig. 1a, the bare GCE was rough and nonuniform. Compared with Fig. 1a, Fig. 2b shows plenty of TiC that appeared in the BMIMPF₆ film. The SEM photograph illustrated that the BMIMPF₆-TiC gel was successfully modified on the surface of the GCE and has a well-defined morphology with almost uniform size and shape. In order to further prove that the BMIMPF₆-TiC gel was successfully modified on the surface of the GCE, BMIMPF₆-TiC/GCE was characterized by EDX (Fig. 2). The EDX result showed that strong Ti, C, F, and P signals were detected. Thus, Ti signal must be contributed by TiC. The source of F and P may be from the BMIMPF₆. The SEM and EDX results indicated that BMIMPF₆-TiC gel was successfully modified on the surface of the GCE.

The active surface areas of the modified electrodes were estimated according to the slope of the *I_p* versus *v*^{1/2} plot for a known concentration of K₃Fe(CN)₆, based on the Randles–Sevcik equation:

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} C_0 \tag{1}$$



Scheme 1 Electrochemical oxidation mechanism of trp on the electrode

I_p refers to the anodic peak current. *n* is the electron transfer number. *A* is the surface area of the electrode. *D* is the diffusion coefficient. *C*₀ is the concentration of K₃Fe(CN)₆, and *v* is the scan rate. For 1.0 mmol/L K₃Fe(CN)₆ in 0.10 mol/L KCl electrolyte, *n* equals 1, and *D* is 7.6 × 10⁻⁶ cm/s. From the slope of the *I_p*-*v*^{1/2} relation, the microscopic areas were calculated. They were 0.076 and 0.066 cm² for BMIMPF₆-TiC/GCE and GCE, respectively. The results show that presence of BMIMPF₆-TiC gel causes the increase of the active surface of the electrode but not very much. The improvement of the sensitivity is due to a fast electron transfer process that can occur at BMIMPF₆-TiC/GCE.

The typical CVs for BMIMPF₆-TiC/GCE and bare GCE were recorded between -0.2 and 0.6 V in 1 mmol/L Fe(CN)₆^{3-/4-} and 0.1 M KNO₃ solution (Fig. 3). The CVs of the bare GCE (Fig. 3a) and BMIMPF₆-TiC/GCE (Fig. 3b) showed a well-shaped reduction–oxidation (redox) peak. However, the peak-to-peak potential of Fe(CN)₆^{3-/4-} at BMIMPF₆-TiC/GCE is slightly wider than that at bare GCE. This may be due to the electrostatic repulsion force between the negatively charged Fe(CN)₆^{3-/4-} and BMIMPF₆-TiC gel. However, the peak currents of Fe(CN)₆^{3-/4-} at BMIMPF₆-TiC/GCE are higher than those at bare GCE, which indicated that a fast electron transfer process can occur at BMIMPF₆-TiC/GCE.

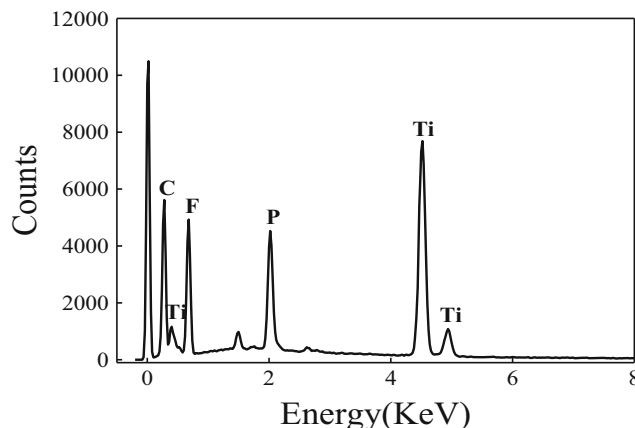


Fig. 2 EDX spectrum of BMIMPF₆-TiC/GCE

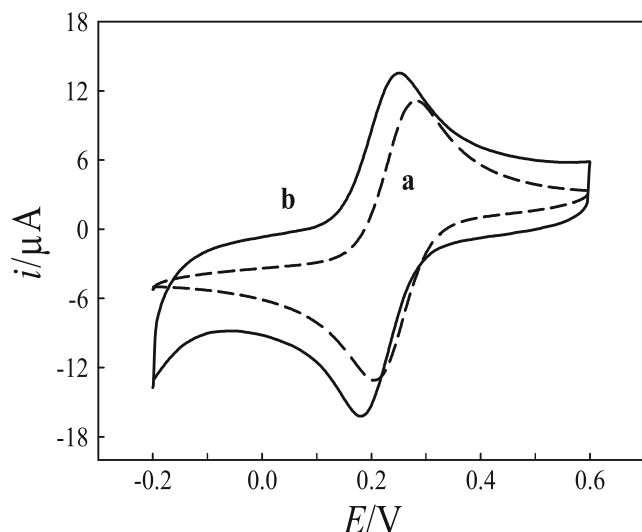


Fig. 3 CVs of **a** bare GCE and **b** BMIMPF₆-TiC/GCE in 1 mmol/L [Fe(CN)₆]^{3-/4-} and 0.1 M KCl solution in the potential range of -0.2 to 0.6 V. Scan rate 50 mV/s

Electrochemical behavior of trp on the BMIMPF₆-TiC modified GCE

Figure 4 shows the DPVs of bare GCE (Fig. 4a) and BMIMPF₆-TiC/GCE (Fig. 4b) in 0.1-mol/L PBS solution (pH 5.5) containing 10 μmol/L trp. The small oxidation peak of trp was obtained at bare GCE. The peak potential of trp is 0.72 V, and the peak current is 0.62 μA (Fig. 4a), while the peak potential of trp at BMIMPF₆-TiC/GCE is 0.68 V and the peak current is 3.68 μA (Fig. 4b). The peak current of trp at the BMIMPF₆-TiC/GCE showed up to the fivefold improvement than that at bare GCE. As a result of the catalysis of BMIMPF₆, the oxidation peak potential of trp shifted negatively. These results suggested that the BMIMPF₆-TiC gel not only possess strong electrocatalytic activity toward the redox

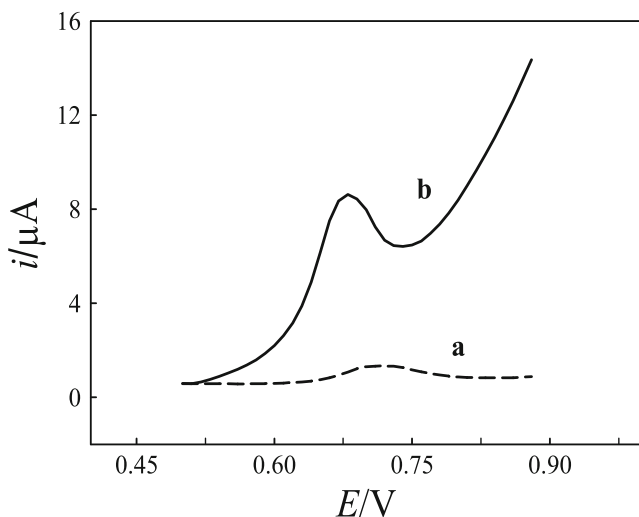


Fig. 4 DPVs of **a** bare GCE and **b** BMIMPF₆-TiC/GCE in 0.1 M PBS (pH 5.5) containing 10 μmol/L trp. Scan rate 50 mV/s

reaction but also promoted the electron transfer rate on the surface of the electrode. The relationship between scan rate and the peak current of trp was also investigated. The anodic peak currents of trp were proportional to the square root of the scan rate from 5 to 100 mV s⁻¹ (Fig. 5). This result indicated that the electro-oxidation reaction of trp at BMIMPF₆-TiC/GCE was a typical diffusion-controlled process.

Optimization for trp measurement on BMIMPF₆-TiC/GCE

Effect of the ratio of TiC nanoparticles in BMIMPF₆

To optimize the electrocatalytic response of the BMIMPF₆-TiC/GCE for trp oxidation, the ratio of TiC nanoparticles (mg) in BMIMPF₆ (μL) was studied between 0.6 and 2 with 10 μmol/L trp in 0.1 mol/L PBS (pH 5.5). The largest oxidation peak current of trp is obtained at the BMIMPF₆-TiC/GCE incorporating TiC nanoparticles (*m/v* 1.25) in BMIMPF₆ from Fig. 6. Thus, the BMIMPF₆ incorporating TiC (*m/v* 1.25) nanoparticles is selected for trp detection.

Effect of pH values

The pH value of the supporting electrolyte is an important factor that affects the voltammetric response of trp. The existing form of trp in the solution is highly affected by the pH values. There is a pair of unpaired electron on the nitrogen atoms in the amino group. In strong acid solution, it will combine with H⁺ and is not conducive to the formation of free radicals of nitrogen; thus, the oxidation reaction is more difficult. When in strong alkaline solution, the OH⁻ in aqueous solution will produce oxygen evolution reaction easily on electrode and will affect the stability of system. So, too low or too high pH values are not conducive to the determination of

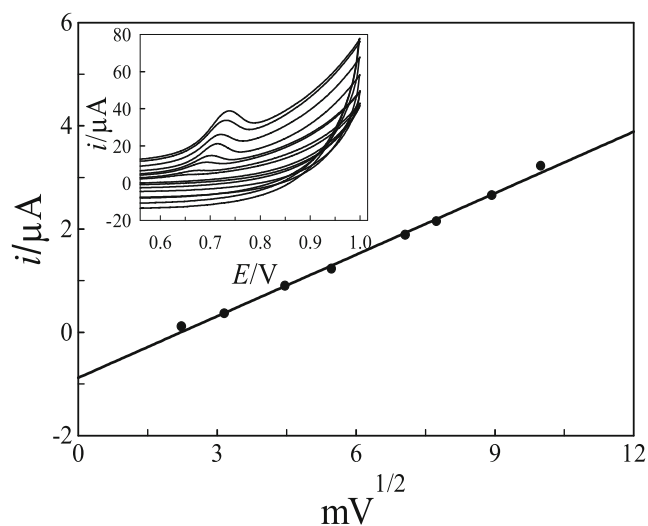


Fig. 5 Linear relationship of square root of scan rate versus oxidation current response of 10 μmol/L trp in 0.1 M PBS (pH 5.5). *Insert* CVs of the BMIMPF₆-TiC/GCE at different scan rates (from 5 to 100 mV/s)

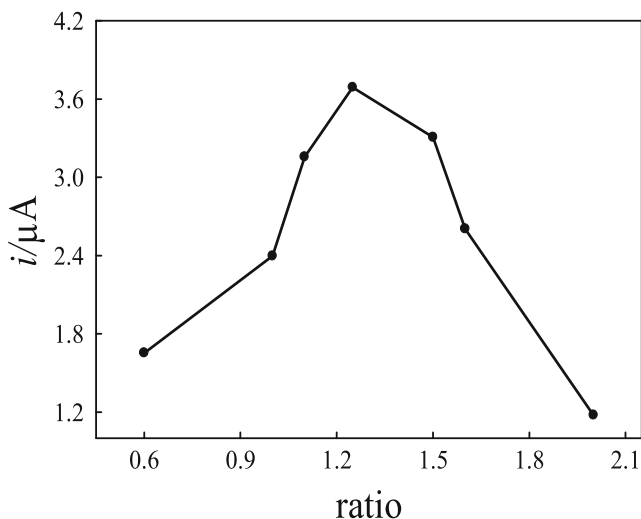


Fig. 6 Effect of the ratio of TiC nanoparticles in BMIMPF₆ on the oxidation current response of 10 μmol/L trp in 0.1 M PBS (pH 5.5) on BMIMPF₆-TiC/GCE

trp. The effect of pH on the peak current of trp was investigated by recording DPV on BMIMPF₆-TiC Gel/GCE of 10 μmol/L trp in 0.1 M PBS of different pH ranging from 4.5 to 7.0, and the results are displayed in Fig. 7a. The anodic peak current gradually increases from pH 4.5 to pH 5.5. The maximum current was observed at pH 5.5. However, the anodic peak current decreased when pH was further increased from pH 5.5 to 7.0. Thus, pH 5.5 was chosen. In addition, the peak potential shifted negatively and linearly as the solution pH increased from pH 4.5 to 7.0 (Fig. 7b). The slope value of the *E_p*/pH plots was −52 mV/pH, which implies that H⁺ transfer was involved in the electrode reaction. In the experiment, the relationship between the oxidation peak potentials and scan rates can be described as following: *E_{pa}* = 0.049log*v* + 0.8, *r* = 0.999. According to Laviron’s theory, the slope was equal to 2.303RT/n(1-α)F. Then, the value of *n* was

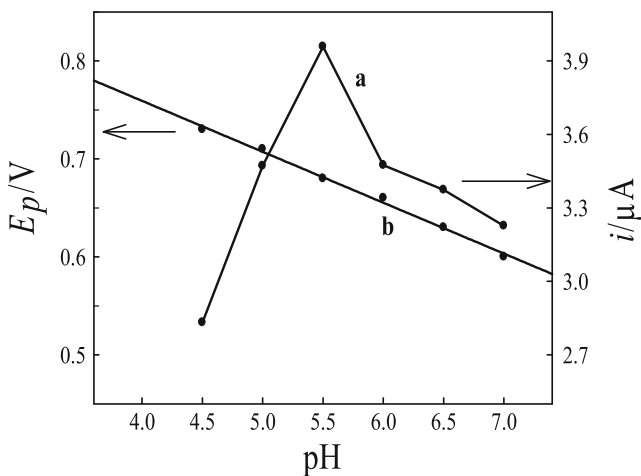


Fig. 7 Effect of pH on **a** the oxidation current response and **b** oxidation peak potential of 10 μmol/L trp in 0.1 M PBS (pH 5.5) on BMIMPF₆-TiC/GCE

calculated as 2.34. As for a totally irreversible electrode reaction process, α was assumed as 0.5, which indicated that two electrons were involved in the oxidation process of trp at the gel modified electrode. Since equal numbers of electron and proton took part in the oxidation of trp, therefore the transfer of two electrons and two protons was involved in the electrode reaction process. The mechanism of the oxidation of trp at the gel modified electrode is shown in Scheme 2, which is in accordance with the report [80].

Calibration curve

The calibration curve of the trp determination was derived from the DPVs obtained on the BMIMPF₆-TiC/GCE in 0.1 M PBS (pH 5.5) under the optimum conditions (Fig. 8). Two linear dynamic ranges as shown in Fig. 8 from 0.5 to 30 μmol/L and 30 to 500 μmol/L and a detection limit of 0.053 μmol/L were obtained. If the concentration of trp is less than the value of 30 μmol/L, trp may be related to the formation of a monolayer on the surface of the modified electrode. However, if the concentration of trp is higher than the value of 30 μmol/L, trp may be related to the formation of a multilayer on the surface of a modified electrode [81]. Meanwhile, the forces of the interaction were changed between trp and gel compound. So, the calibration curve plots of trp were broken at low and high concentrations. Linear regression equations for the two regions are as follows:

$$I_p(\mu A) = 0.57 + 0.236C(\mu mol/L)(0.5-30\mu mol/L, R = 0.9750) \quad (2)$$

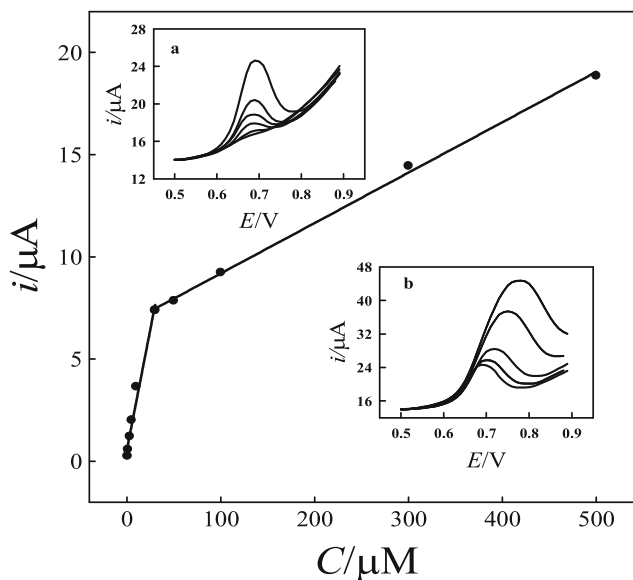


Fig. 8 The calibration curve for trp determination. *Insert* DPVs of the BMIMPF₆-TiC/GCE at different trp concentrations (from **a** 0.5 to 30 μmol/L and **b** 30 to 500 μmol/L) in 0.1 M PBS (pH 5.5). Scan rate 50 mV/s

Table 1 Comparison of response characteristic on different modified electrodes

Electrodes	Linear range (μM)	Detecting limit (μM)	References
BDD ^a	400–3000	0.2	82
GNP ^b -CNT ^c /GCE	0.03–2.5	0.01	69
GNP/CILE ^d	5–900	1.2	83
GCE modified with butyrylcholine	2–60	0.25	66
Iron(III)-doped zeolite modified CPE ^e	0.2–150	0.02	76
BMIMPF ₆ -TiC/GCE	0.5–500	0.053	Present work

^a Boron-doped diamond electrode

^b Gold nanoparticle

^c Carbon nanotube

^d Carbon ionic liquid electrode

^e Carbon paste electrode

$$I_p(\mu\text{A}) = 6.72 + 0.025C(\mu\text{mol/L})(30\text{--}500\mu\text{mol/L}, R = 0.9983) \quad (3)$$

The response characteristics of the BMIMPF₆-TiC/GCE were compared with those in previously published works. As shown in Table 1, the proposed BMIMPF₆-TiC/GCE had wider linear dynamic range and lower detection limit than most of the materials used in other works for trp determination.

Reproducibility, repeatability, and selectivity

The reproducibility of BMIMPF₆-TiC/GCE was investigated by detecting a certain amount of trp in 0.1 M PBS (pH 5.5) for one electrode in ten measurements. The relative standard deviation (RSD) of the anodic peak current was 2.8 % for trp determination. The repeatability of the developed method was also evaluated by using five different BMIMPF₆-TiC/GCEs, and the obtained RSD was 2.9 %. Therefore, BMIMPF₆-TiC/GCE showed good reproducibility and repeatability.

The selectivity of the BMIMPF₆-TiC/GCE for the trp determination was investigated by adding various foreign species into PBS (pH 5.5) containing 10 $\mu\text{mol/L}$ trp. Moreover, 500-fold Na⁺, K⁺, NO₃⁻, 150-fold lactose, 100-fold urea, sucrose, Mg²⁺, SO₄²⁻, Ca²⁺, 50-fold glucose, fructose, 5-

fold ascorbic acid, histidine, aspartic acid, glycine, serine, 2-fold dopamine, threonine, valine, phenylalanine did not affect the determination of trp (<5 % of response current change). These results indicated good selectivity of the proposed electrode.

Practical application of BMIMPF₆-TiC/GCE

The practical utility of BMIMPF₆-TiC/GCE was evaluated by employing it for the determination of trp in the human urine and cow's milk. The concentration of trp was estimated by standard addition method. The amperometric response of trp was recorded at BMIMPF₆-TiC/GCE, and the results are displayed in Table 2. From the good quantitative recoveries and precision of the results observed, BMIMPF₆-TiC/GCE can be successfully employed for the determination of trp in real samples. The present method is reliable and suitable for the determination of trp in food and biological samples.

Conclusions

In this work, a simple and effective method for the quantification of trp by modifying the GCE with BMIMPF₆-TiC gel was used. SEM and EDX results demonstrated that BMIMPF₆ and TiC nanoparticles were successfully doped into the GCE. Compared with bare GCE, the obtained BMIMPF₆-TiC/GCE exhibited significantly enhanced electrocatalytic performance in trp determination. The detection limit of trp was 0.053 $\mu\text{mol/L}$. In addition, the BMIMPF₆-TiC/GCE showed excellent reproducibility, repeatability, and selectivity and can be applied for determination in real samples. The fabricated electrode may serve as an electrochemical sensor for high sensitive trp determination. This work provides a simple and easy approach to selectively detect trp and had wider linear dynamic range and lower detection limit. It showed good

Table 2 Results of real sample analysis at BMIMPF₆-TiC/GCE

Real samples	Trp added (μM)	Trp found (μM)	Recovery(%)
Milk	5.0	5.16±0.024	103.2
	10.0	10.61±0.042	106.1
	15.0	15.66±0.033	104.4
Urine	5.0	5.28±0.040	105.7
	10.0	10.73±0.047	107.3
	15.0	15.54±0.063	103.6

reproducibility and repeatability and had good anti-interference ability. BMIMPF₆-TiC/GCE can be successfully employed for the determination of trp in real samples.

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