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Short Communication

Electrochemical Sensor Based on Single-Walled Carbon Nanotube-TiN Nannocomposites for Detecting Amaranth

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Currently, as food additives, synthetic colourants have been drawn much attention. This paper studied the electrocatalytic oxidation of amaranth (AM), with a novel electrochemical sensor based on single-walled carbon nanotube-Titanium nitride (SWCNT-TiN) nanocomposites modified glassy carbon electrode. Owing to the high accumulation effect and great catalytic capability of SWCNT-TiN nanocomposites, the developed sensor exhibited well-defined voltammetric peaks for AM. The peak currents of AM increased linearly with its concentration in the ranges of 0.1-100 μM. The detection limit is 40 nM. The developed sensor was successfully applied in the determination of AM in beverage samples. Results indicated that the developed sensor was fast, sensitive and reliable.

Keywords: Single-walled carbon nanotube; Titanium nitride; Electrochemical sensor; Amaranth; Determination

1. INTRODUCTION

Recently, synthetic colorants especially azo dyes have been widely used to enhance the appearance and color of food products in food industry owing to its fascinating color uniformity, good water solubility, inexpensive production cost, low microbiological contamination and high stability to light, oxygen and pH. However, it is reported that many synthetic colorants are pathogenic, especially when they are consumed too much [1]. Amaranth (AM), namely (trisodium (4E)-3-oxo-4-[(4-sulfonato-1-naphthyl) hydrazono] naphthalene-2,7-disulfonate) (Fig. 1), is a typical synthetic azo colorant. It has been applied broadly to give attractive red color and make food more appealing [1]. Unfortunately, studies have demonstrated that AM can cause many adverse health effects such as high genotoxicity, cytostaticity and cytotoxicity [2]. In order to maintain human health and food safety, the content of AM in foods must be accurately controlled. Hence, simple, fast, sensitive determination of AM is very important. Up to now, studies of AM in food products have mainly been carried out using high-performance liquid chromatography (HPLC) [3,4], liquid chromatography-mass spectrometry [5], spectrophotometry [6], capillary electrophoresis [7] et al. Although these methods are well-proven and widely accepted, they require relatively expensive equipment, advanced technical expertise, and are costly and time-consuming [8]. Recently, owing to high sensitivity, short analysis time, good handling convenience and low analytical cost [9], electrochemical techniques have been developed to detect AM.

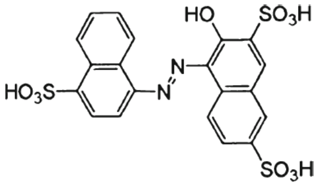

Figure 1. The structure of AM.

Carbon nanotube (CNT) [10], especially single-walled carbon nanotubes (SWCNT), have generated a great deal of interest as novel platforms for sensing because their electrocatalytic properties, chemical functionalities, large specific surface area and high electrical conductivities [11]. In order to further improving its performance, much effort has gone into hybridizing the CNT with other materials [12,13]. Among many candidates, Titanium nitride (TiN) is a promising material due to its desirable physical properties, such as superior conductivity, high chemical stability, excellent biocompatibility and simple synthesis conditions [14-16]. These attractive properties facilitate its applications in many fields.

In this work, to develop a simple, fast and sensitive electrochemical determination method for AM, one electrochemical sensor based on single-walled carbon nanotube-Titanium nitride (SWCNT-TiN) nanocomposites modified glassy carbon electrode has been fabricated. This novel sensor owns wider linear range and lower detection limit compared with the reported literatures. Moreover, to evaluate the proposed sensor, the determination of AM in the real samples was performed and the obtained results were satisfying.

2. EXPERIMENTAL

2.1. Reagents and apparatus

SWCNT (>95% purity) were purchased from Chengdu Organic Chemicals Co. Ltd. Before use, it was purified by refluxing in concentrated nitric acid for 7 h. Tetrabutyl titanate was purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). All chemicals were of analytical grade and without further purification. AM (Sigma) was dissolved into ultrapure water to prepare 0.01 M standard solution, and stored at 4 °C. The acetate buffer solution was prepared by mixing the stock solution of NaAc and HAc.

Electrochemical measurements were carried out on a CHI 660D electrochemical workstation (Chenhua Instrument, Shanghai, China) with a conventional three-electrode system. The working electrode is a bare or the SWCNT-TiN nanocomposites modified glassy carbon electrode (GCE, 3 mm in diameter), the reference electrode is an Ag/AgCl electrode, and the counter electrode is a platinum wire. The morphology and microstructure of the samples were analyzed by means of transmission electron microscopy (TEM, JEM-2100F) with a 200 kV accelerating voltage.

2.2. Preparation of SWCNT-TiN nanocomposites

For the preparation of SWCNT-TiN nanocomposites, TiN nanoparticles were firstly synthesized. The TiN nanoparticles were prepared by simply treating TiO_2 nanoparticles with NH_3 gas flow according to the previously reported procedure [17]. Then, the equal amount of SWCNT (5 mg) and TiN nanoparticles (5 mg) was dissolved in water and mixed completely by ultrasonication..

2.3. Fabrication of the sensors

The GCE was carefully polished by 0.3 and 0.05 μm alumina and sonicated successively in distilled water and ethanol for 5 min respectively until a mirror like surface was obtained. Then, 5 μL of as-prepared SWCNT-TiN dispersion was pippetted onto the pretreated GCE surface and dried at room temperature to obtain the SWCNT-TiN/GCE.

2.4. Electrochemical measurement

For the determination of AM, the bare or modified electrode was immersed in 0.1 M acetate buffer solution containing different concentration of AM. The differential pulse voltammogram (DPV) was recorded from 0.4 to 1.0 V. The DPV parameters are as follows: increment potential, 0.004 V; pulse amplitude, 0.05 V; pulse width, 0.05 s; sample width, 0.0167 s; pulse period, 0.2 s; quiet time, 2 s.

3. RESULTS AND DISCUSSION

3.1. Characterization

TEM image was applied to investigate the structural details of SWCNT-TiN nanocomposites. Typical TEM micrographs of SWCNT, TiN and SWCNT-TiN nanocomposites were shown in Fig. 2. The morphology of SWCNT displayed a highly bundled and entangled structure (Fig.2A), which was agreement with the reported literatures [18,19]. As shown in Fig.2B, TiN nanoparticles showed a cuboid shape with a size of approximately 50 nm. From Fig. 2C, it can be seen that TiN nanoparticles were distributed densely on the sidewall of SWCNT, demonstrating the conformation of SWCNT-TiN nanocomposites. Herein, the introduction of TiN nanoparticles to the SWCNT overcame the van der Waals interaction between the SWCNT and thus prevented SWCNT from agglomeration, resulting in the formation of a high dispersed solution.

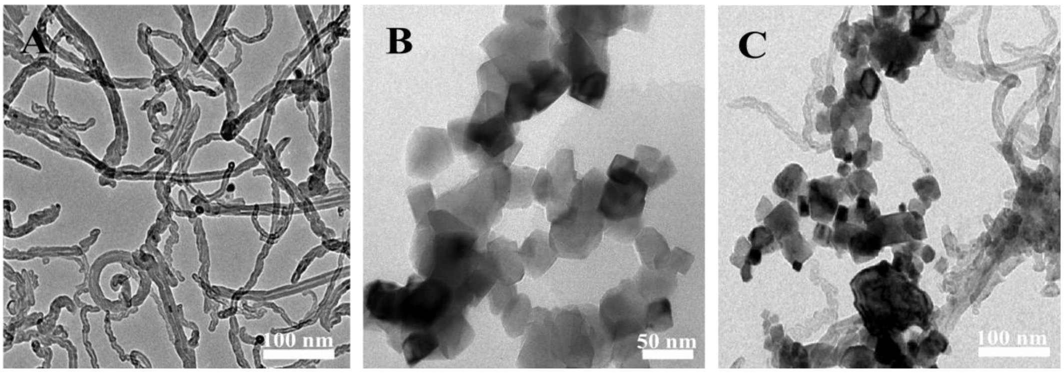

Figure 2. TEM images of SWCNT, TiN and SWCNT-TiN nanocomposites.

3.2. Electrochemical behaviours of AM at GCE and SWCNT-TiN/GCE

DPV was an electrochemical method with a high sensitivity and a low detection limit and was employed to characterize the prepared sensor [20]. Fig. 3 shows the DPVs of AM at a bare GCE (curve a) and SWCNT-TiN/GCE (curve b), respectively. As can be seen, at bare GCE, AM produced a small oxidation peak at 0.85 V. After GCE modified with SWCNT-TiN nanocomposites, besides the oxidation peak current of AM enhanced significantly, the oxidation peak potential shifted to 0.78 V, suggesting a pronounced electrocatalytic activity of this nanocomposites for the AM oxidation reaction. The enhancement was ascribed to a synergistic effect between SWCNT and TiN in the nanocomposites. Accordingly, such SWCNT-TiN nanocomposites could provide a useful sensing platform for detection of AM.

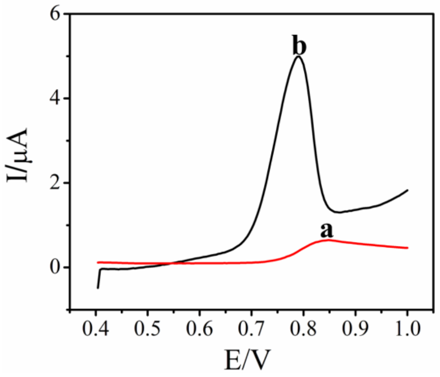

Figure 3. Differential pulse voltammograms of 50 μM AM at bare GCE (a) and SWCNT-TiN/GCE (b) in 0.1 M acetate buffer solution.

3.3. Optimization studies

The effects of several parameters, such as the electrolyte, pH and the amount of SWCNT-TiN dispersion on the voltammetric responses of AM were then investigated.

To obtain suitable supporting electrolyte, the electrochemical behaviors of AM in different solutions were studied using DPVs. The used supporting electrolytes included 0.1 M acetate buffer solution, phosphate buffer solution, citrate buffer solution, H_2SO_4, NaOH, $NaNO_3$, $HClO_4$, HCl and Na_2SO_4. It was found that the best voltammogram shape and the highest oxidation peak current can be obtained in acetate buffer solution. So, it was selected as the supporting electrolyte. In 0.1 M acetate buffer solution, we subsequently studied the effect of pH on the oxidation peak currents of AM at the SWCNT-TiN/GCE. As seen in Fig. 4(A and B), the oxidation peak currents of AM gradually enhanced with pH value from 3.0 to 5.0, and then decreased gradually as further increasing pH value to 8.0. To obtain high response signal, pH 5.0 of 0.1 M acetate buffer solution was used for the detection of AM.

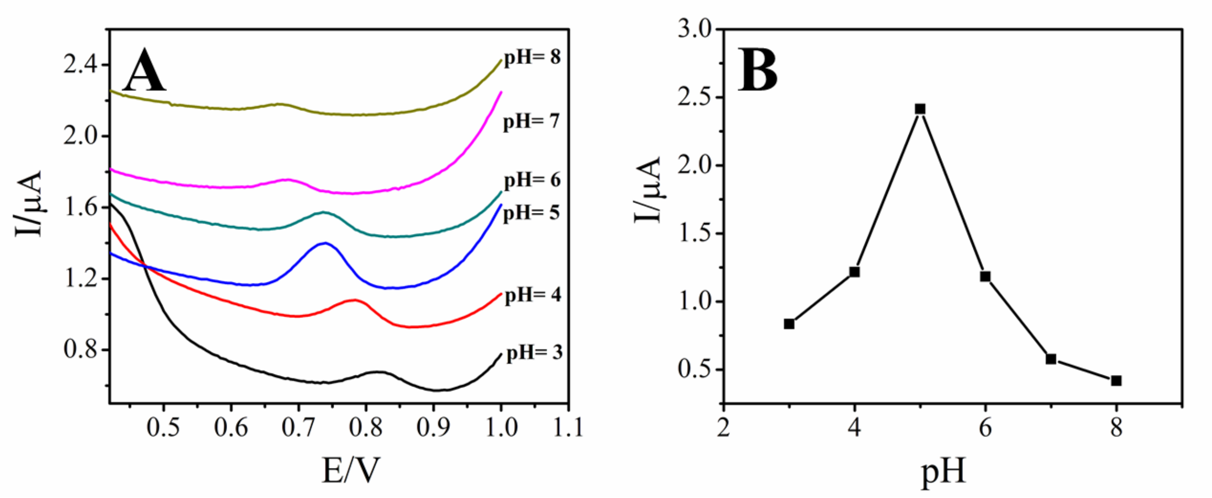

Figure 4. Effect of pH values of 0.1 M acetate buffer solution on the oxidation peak currents of AM.

The amount of SWCNT-TiN dispersion had a significant influence on the voltammetric response of AM. The effect of amount of SWCNT-TiN dispersion was studied by dropping different volumes dispersion onto the GCE surface (Fig. 5). It was found that 4 μL of SWCNT-TiN dispersion gave the highest peak current towards oxidation of AM. An increase in the oxidation peak current from 1-4 μL is due to the increase in conductivity with the amount of SWCNT. Further increasing the volume of SWCNT-TiN dispersion, the peak current decreased, probably due to the decrease of the conductivity of thicker layer of SWCNT-TiN dispersion [21]. Hence 4 μL of SWCNT-TiN dispersion was found to be ideal for the determination of AM.

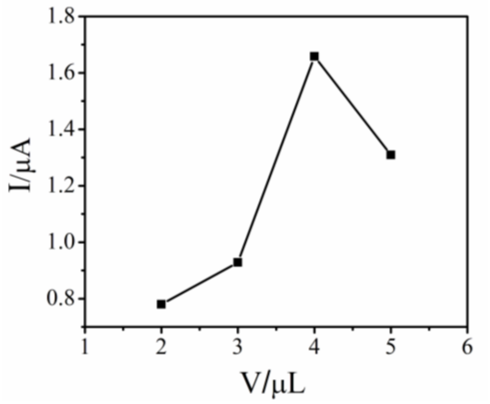

Figure 5. Effect of the amount of SWCNT-TiN dispersion on the oxidation peak currents of AM.

3.4. Determination of AM

Under the optimal conditions, a calibration curve of AM was obtained at SWCNT-TiN/GCE with different concentrations of AM. As shown in Fig. 6A, with the concentration increasing, the peak current of AM increased accordingly. The calibration plot for AM was illustrated in Fig. 6B. A linear relationship between the peak current and AM concentration was obtained from 0.1-100 µM. The detection limit was 40 nM (S/N = 3). The detection limit was lower than or closed to that at multiwalled carbon nanotube modified gold electrode (68 nM) [22] and expanded graphite paste electrode (36 nM) [23]. The lower detection limit and wider linear range were due to the excellent electrocatalytic activity of SWCNT-TiN nanocomposites.

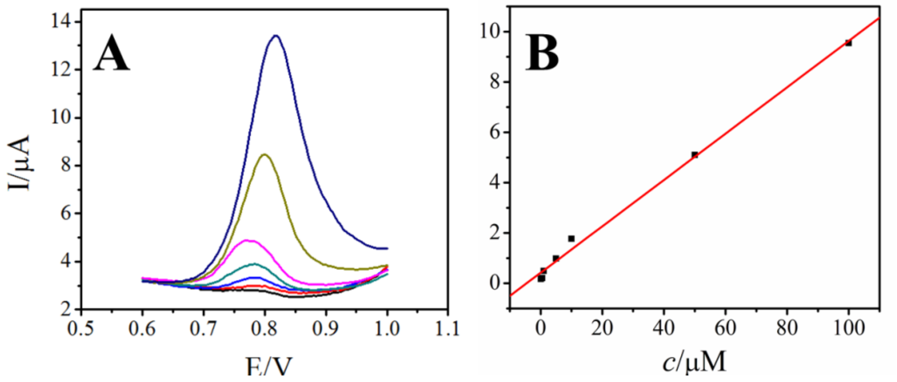

Figure 6. (A) Differential pulse voltammograms for the different concentration of AM in 0.10 M acetate buffer solution (pH 5.0) on the SWCNT-TiN/GCE, (B) Dependence of peak current on the concentration of AM.

3.5. Interference

The potential interferences for the detection of AM were studied. Under the optimal conditions, the oxidation peak currents of AM were individually measured in the presence of different concentrations of interferents and then the peak current change was recorded. The results were shown in Table 1. As observed, no influence on the detection of 50 μM AM was found after the addition of 1000-fold concentrations of glucose, sucrose, citric acid, glycine, nitrite, acetaminophen, cysteine and glutathione; 50-fold concentration of erythrosine, new coccine and allure red.

Table 1. Results for determination of 50 μM AM with some interferences.

Interference	Concentration	Peak current change
No interference	-	0 μA
glucose	50.0 mM	0.125 μA
sucrose	50.0 mM	0.088 μA
citric acid	50.0 mM	0.146 μA
glycine	50.0 mM	0.122 μA
nitrite	50.0 mM	0.186 μA
acetaminophen	50.0 mM	0.212 μA
cysteine	50.0 mM	0.057 μA
glutathione	50.0 mM	0.112 μA
erythrosine	2.50 mM	0.208 μA
new coccine	2.50 mM	0.197 μA
allure red	2.50 mM	0.234 μA

3.6. Reproducibility, stability and reusability

The reproducibility between multiple sensors was investigated by parallel determination of the oxidation peak current of 50 μM AM. The relative standard deviation (RSD) is 3.6% for 10 sensors, demonstrating an excellent fabrication reproducibility and detection precision (Table 2). When the SWCNT-TiN/GCE was not in use, it was stored at 25 °C. 92.8% of the initial response for AM was remained, after three weeks. This result indicated the SWCNT-TiN/GCE had good stability.

Table 2. Results for parallel determination of 50 μM AM with different electrodes prepared under the same conditions (n=10).

number	1	2	3	4	5	6	7	8	9	10
I/μA	4.872	4.908	5.089	5.202	4.966	5.384	5.157	4.758	5.093	5.123
I_n/μA	5.055									
SD	0.1822									
RSD	3.60%									

3.7. Real samples analysis

To verify the practical application of this new developed method, it was used to detect AM in beverage samples. The beverage samples were obtained from local markets. To remove the dissolved gas, the samples were firstly ultrasonicated for 30 min. Then, the samples were diluted with ultrapure water. Each sample was detected by three times, and the RSD was 4.2%, suggesting good precision (Table 3). The content of AM was achieved by the standard addition method, and the value was 33.2 μg/mL. To test the accuracy, the content of AM was also determined by HPLC. The result obtained by HPLC and our method were in good agreement, suggesting that the newly developed method is accurate.

Table 3. Results for determination of three samples (n=3).

Sample	1			2			3		
I/μA	2.427	2.437	2.426	2.683	2.652	2.662	2.511	2.527	2.464
I_n/μA	2.532								
SD	0.1063								
RSD	4.20%								

4. CONCLUSION

In this work, a novel, sensitive and fast electrochemical method based on the SWCNT-TiN nanocomposites was developed for the detection of AM. Due to the excellent electrocatalytic activity of SWCNT-TiN nanocomposites, the proposed method for detection of AM exhibited a wide linear range and a low detection limit. This method may provide a useful platform for the determination of other additives, and could be readily extended toward the on-site monitoring of the hazard components in food.

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