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Original scientific paper

Electrochemical sensing of caffeic acid antioxidant in wine samples using carbon paste electrode amplified with CdO/SWCNTs

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Abstract
An electrochemical sensor was introduced as an analytical tool for monitoring caffeic acid in food samples. This analytical tool was amplified by cadmium oxide decorated on single wall carbon nanotubes as a new catalyst and showed a powerful ability to sensing of caffeic acid in food products. The presence of cadmium oxide decorated on single wall carbon nanotubes catalyst improved the oxidation signal of caffeic acid about 2.4 times at optimum conditions. The pH investigation confirmed that the redox reaction of caffeic acid was pH dependent and showed maximum sensitivity at pH 7.0. The paste electrode amplified with cadmium oxide decorated on single wall carbon nanotubes successfully monitored caffeic acid in the concentration range 0.02–200 μM with a detection limit of 9.0 nM, respectively. The standard addition strategy showed a recovery range of 97.96 to 102.59 % to the measurement of caffeic acid in fruit juice, white and red wine that was acceptable for the fabrication of a new analytical tool in food monitoring.

Keywords
Food sensor, nanocomposite, electroanalysis, modified electrodes, real sample analysis

Introduction

Antioxidants, as one of the most famous substances used in food, prevent the adverse effects of free radicals [1,2]. Antioxidants can be found as natural or artificial and are important in food safety [3,4]. Although the body directly confronts some free radicals, the wide range of radicals makes it important to get antioxidants through food [5]. Caffeic acid is one of the famous natural antioxidants found in various beverages and wine samples [6,7]. Caffeic acid can cause mild effects on insomnia and excessive consumption is not recommended [8]. Therefore, monitoring of caffeic acid in food products was investigated by some analytical methods such as HPLC [9], LC-MS/MS [6], TLC-densitometry [10] and electrochemical sensors.

Electrochemical sensors are a useful and powerful strategy for sensing food products and especially food antioxidants [11-14]. Easy modification to create highly selective and sensitive tools in food products analysis is the main advantage of electrochemical methods compared to other analytical strategies in sensing electrochemically active materials [15-20]. Different modifiers were suggested for the amplification of electrochemical sensors, such as 2D nanomaterials, nanocomposites [21], ionic liquids, composites, conductive polymers, biological compounds, *etc.* [22-24]. Between them, nanomaterials showed more advantages due to easy diversity and high electrical conductivity [25,26]. Many research efforts focused on the modification of electrochemical sensors to trace-level analysis in complex matrixes [27-30].

Nanotechnology changed the approach to pure science and creating unique properties in new materials [31-37]. Nanomaterials showed unbelievable properties and a wide range of applications in different branches of science [38-42]. The application of nanomaterials in the fabrication of modified sensors is increasing significantly [43]. This issue relates to high electrical conductivity and easy modification of nanomaterials with different functionalized groups.

In this study, a nanostructure-based sensor (cadmium oxide decorated on single wall carbon nanotubes (CdO/SWCNTs) modified paste electrode (PE) (CdO/SWCNTs/PE in this case) was suggested as a simple and economical type of sensor for easy monitoring of caffeic acid in food products and results showed the high ability of this sensor.

Experimental

Materials

Cadmium acetate, SWCNTs-COOH, and sodium hydroxide were purchased from Sigma-Aldrich Company and used to synthesize CdO/SWCNTs nanocomposite with the recommended procedure by Cheraghi and Taher [44]. Graphite powder (99.99 %) and paraffin oil were purchased from Merck Company and used to fabricate paste electrodes. Phosphoric acid, sodium dihydrogen phosphate, disodium hydrogen phosphate anhydrous, and trisodium phosphate were purchased from Across company and used to prepare phosphate buffer solution (PBS).

Instruments

All electrochemical signals were recorded by an Ivium-Vertex machine connected to Ag/Ag/KCl$_{sat}$, Pt wire, and CdO/SWCNTs/PE as reference, counter, and working electrodes, respectively. A pH meter model 780 pH Meter, Metrohm was used to prepare PBS solution.

Fabrication of CdO/SWCNTs/PE

The working electrode (CdO/SWCNTs/PE in this case) was fabricated after optimization of CdO/SWCNTs compared to graphite powder in the presence of caffeic acid in pH 7.0 as the optimum condition. The maximum sensitivity was obtained in the presence of 9.0 wt.% CdO/SWCNTs nanocomposite at the surface of the paste electrode (Figure 1). Therefore, 910 mg + 90 mg CdO/SWCNTs were mixed in mortar and pestle and converted to paste using paraffin oil and hand mixing for 30 min.

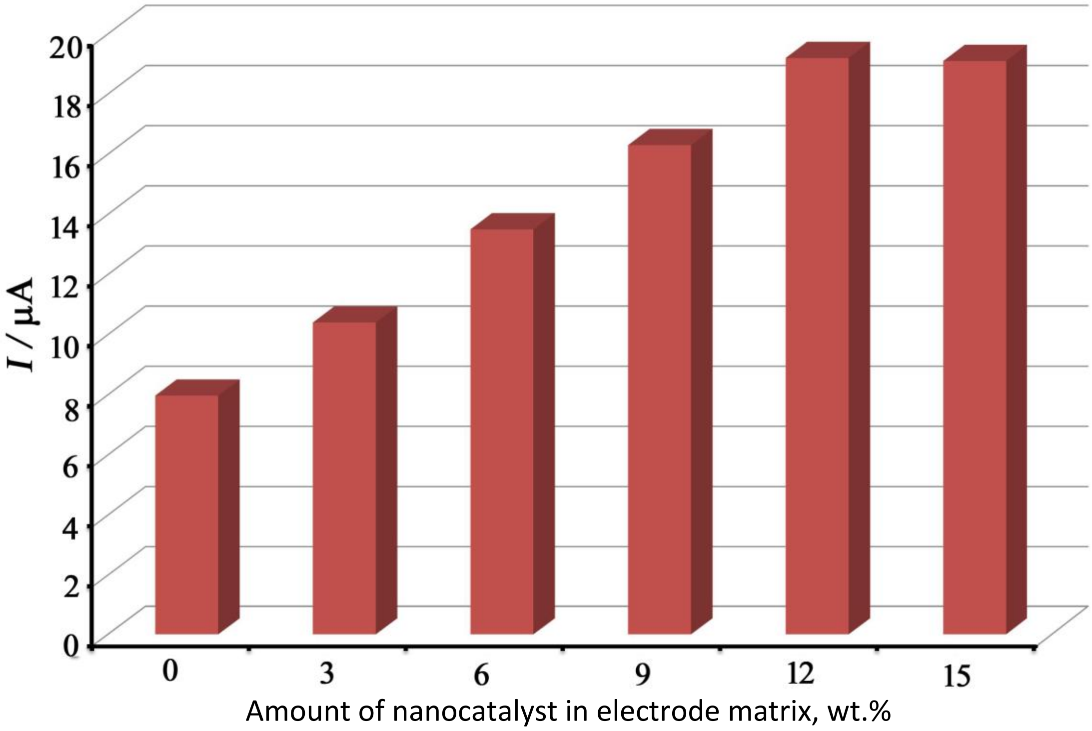


Figure 1. *The oxidation peak current of caffeic acid at surface of paste electrode modified with different amounts of CdO/SWCNTs in carbon paste matrix*

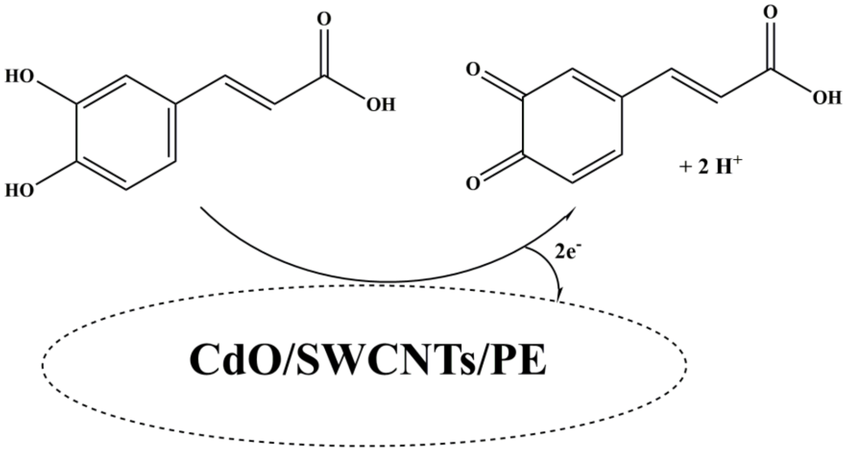
Real sample preparation

10 mL of white, fruit juice and red wines were selected and centrifuged at 4000 rpm for 15 min and, after filtration, diluted into 10 mL PBS (pH 7.0) and transferred to an electrochemical cell for the analysis of caffeic acid using the standard addition method.

Results and discussion

pH optimization

Caffeic acid is a phenolic antioxidant and according to reported papers and Scheme 1 [45], its oxidation in signal changes with the changes in the pH of the solution, and optimization of this factor is so important in the first step.



Scheme 1. *Redox reaction of caffeic acid*

Therefore, linear sweep voltammograms of caffeic acid were recorded in the pH range of 5.0 – 9.0 and the results are shown in Figure 2 inset. Results showed that maximum oxidation current to caffeic acid was observed at pH = 7.0 (Figure 2), and this condition was selected as the optimal condition for monitoring caffeic acid in food samples.

Catalytic activity of senor

The oxidation signal of 500 µM caffeic acid at the surface of PE (Figure 3, curve a) and CdO/SWCNTs/PE (Figure 3, curve b) was recorded and results showed oxidation currents of 7.97 and 19.2 µA at oxidation potentials of 563 and 460 mV, respectively.

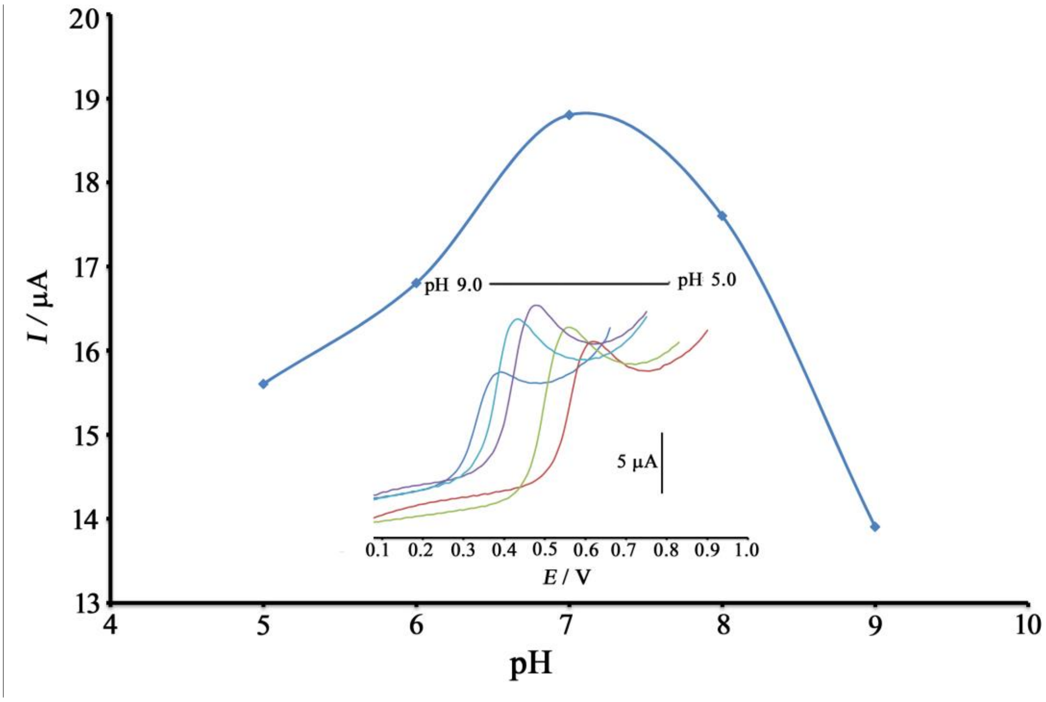


Figure 2. *Current-pH curve to electrooxidation of 500 µM caffeic acid. Inset: linear sweep voltammograms of 500 µM caffeic acid in the pH range 5.0 to 9.0*

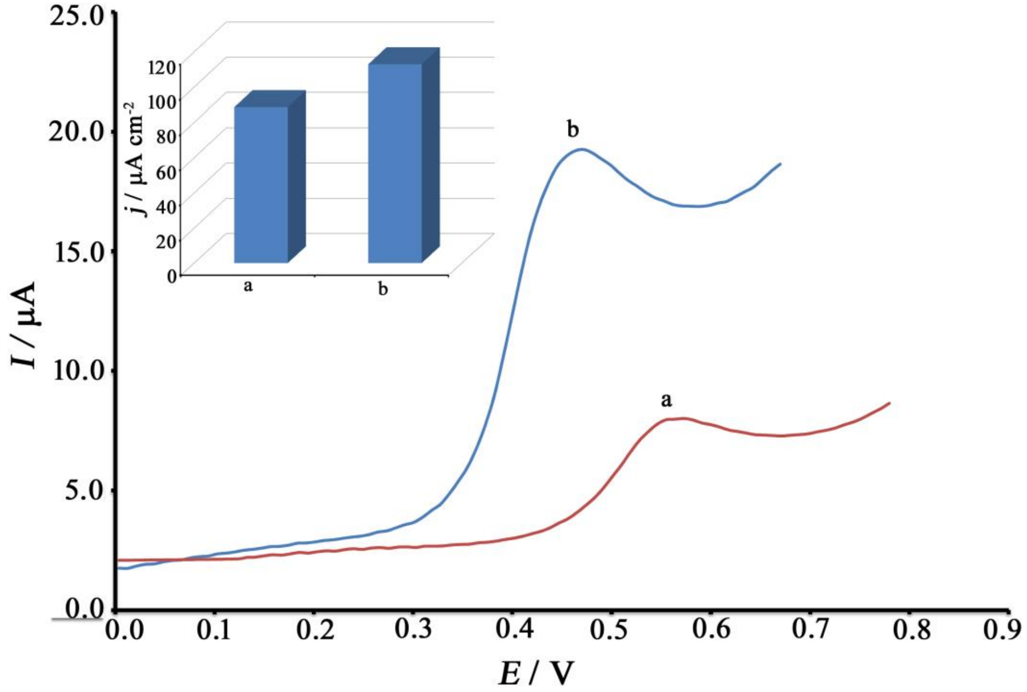


Figure 3. *LS voltammograms 500 µM caffeic acid at surface of a) PE and b) CdO/SWCNTs/PE. Inset: Oxidation peak current density diagram relative to LS voltammogarms*

Comparing of these values clearly showed that the presence of CdO/SWCNTs at the surface of PE plays a catalytic role in the redox behavior of caffeic acid. On the other hand, the active surface area of PE and CdO/SWCNTs/PE were determined to be about 0.09 and 0.17 cm^2, respectively. The active surface was determined by the recording of cyclic voltammograms of $[Fe(CN)6]^{3-/4-}$ in the presence of 0.1 M KCl and Randles–Ševčik equation.. This confirms that CdO/SWCNTs increases the active surface area of the electrode. Oxidation peak current densities relative to two electrodes are shown in Figure 3 inset.

Scan rate investigation

The role of scan rate on the potential and current of caffeic acid signal was investigated and results showed in Figure 4 inset. The results showed a positive shift in the oxidation potential of caffeic acid and also increase in the oxidation current at the surface of CdO/SWCNTs/PE at the scan rate range 5 – 80 mV s^{-1}. The linear relationship between current of caffeic acid and $\nu^{1/2}$ with an equation of $I = 1.6197\nu^{1/2} +4.8775$ (R^2= 0.9944) confirms a diffusion-controlled process. Also, a positive shift in oxidation potential indicates a kinetic limitations of the redox reaction of caffeic acid at the surface of CdO/SWCNTs/PE.

Analytical parameters

The limit of detection and linear dynamic range are two main analytical factors in the design of new types of analytical methods. The linear dynamic range between 0.02 to 200 µM with equation $I = 0.0481C + 0.7410$ ($R^2 = 0.9911$) was determined. A detection limit of 9.0 nM was determined to for this method of caffeic acid at the surface of CdO/SWCNTs/PE at optimum conditions using equation $Y_{\rm LOD} = 3\sigma/m$.

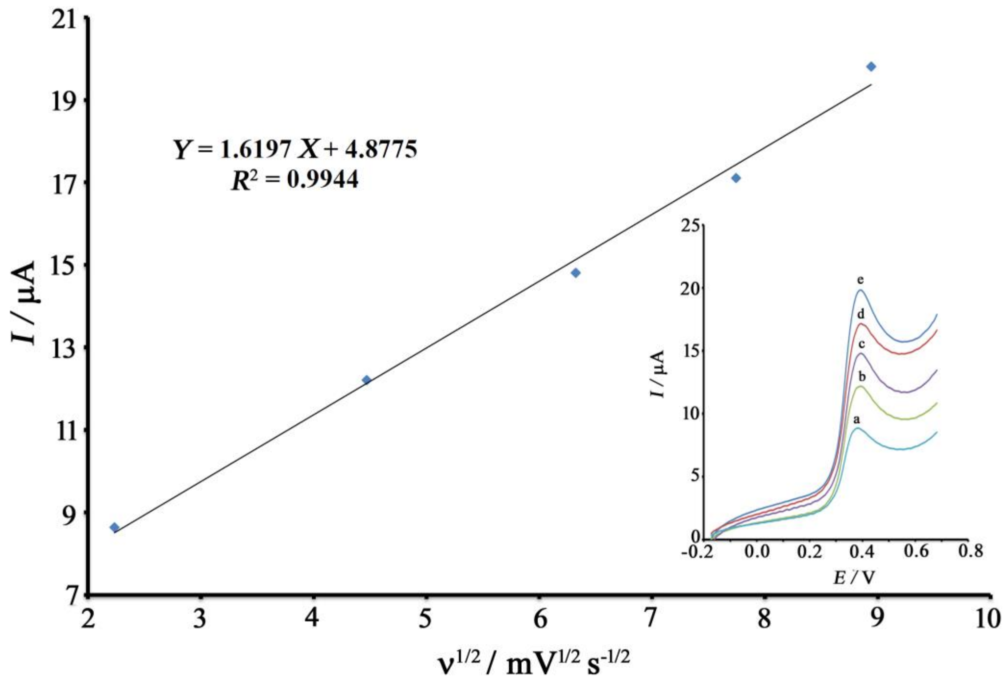


Figure 4. *Oxidation peak current - $\nu^{1/2}$ curve for electro-oxidation of 450 µM caffeic acid at surface of CdO/SWCNTs/PE. Inset: LSVs at scan rates a) 5; b) 20; c) 40; d) 60 and e) 80 mV s^{-1}*

Selectivity of CdO/SWCNTs/PE to sensing of caffeic acid

The selectivity of CdO/SWCNTs/PE as a new catalyst for sensing of 15.0 µM caffeic acid was investigated at pH 7.0 as the optimum condition. The results are reported with an acceptable error of

5 % in Table 1. Data were repeated five times and confirmed the high selectivity of CdO/SWCNTs/PE as a new sensor for sensing caffeic acid in an aqueous solution.

Table 1. *Interference study to sense 15.0 µM caffeic acid using CdO/SWCNTs/PE*

Species	Tolerance limit (Interference mass, g / caffeic acid mass, g)
Li$^+$, K$^+$, Br$^-$ and Na$^+$	1000
Sucrose, glucose, fructose and lactose	600
Vitamin B$_9$ and glycine	400
Starch	Saturated

Determination of caffeic acid in real samples

The fruit juice and wine samples were prepared according to the reported procedure in Experimental section and transferred to an electrochemical cell for electrochemical monitoring by standard addition methods. The results were repeated three times and compared with one published sensor and data shown in Table 2. F-test and t-test were used to investigate accuracy data and results clearly confirmed CdO/SWCNTs/PE's high ability to sense caffeic acid in real samples.

Table 2. *Determination of caffeic acid using CdO/SWCNTs/PE (n=3)*

Sample	Content of caffeic acid, µM			Recovery, %	F_{tab}	F_{exp}	t_{tab}	t_{exp}
	Added	Founded	Founde by HPLC					
White wine	---	3.11±0.13	2.96±0.13	---	---	---	---	---
	10.00	13.45±0.34	13.67±0.55	102.59	19.0	6.7	3.8	1.5
Red wine	---	2.85±0.22	2.94±0.13	---	---	---	---	---
	5.00	7.69±0.45	8.05±0.49	97.96	19.0	7.3	3.8	1.8
Fruit juice	---	<LOD	<LOD	---	---	---	---	---
	5.00	5.22±0.66	4.95±0.33	104.4	19.0	8.1	3.8	2.1

Conclusions

The carbon paste modified CdO/SWCNTs/PE electrode was successfully used for sensing of caffeic acid in the concentration range of 0.02 to 200 µM with detection limit 9.0 nM. The real sample analysis data confirm the ability of CdO/SWCNTs/PE to measure caffeic acid in fruit juice and different wine samples with recovery range 97.96 to 104.4 % that is acceptable value to a new food sensor.

Conflict of interest: *This paper is free of conflict of interest.*

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