



Original Research Article

A gallic acid food electrochemical sensor based on amplification of paste electrode by CdO/CNTs nanocomposite and ionic liquid

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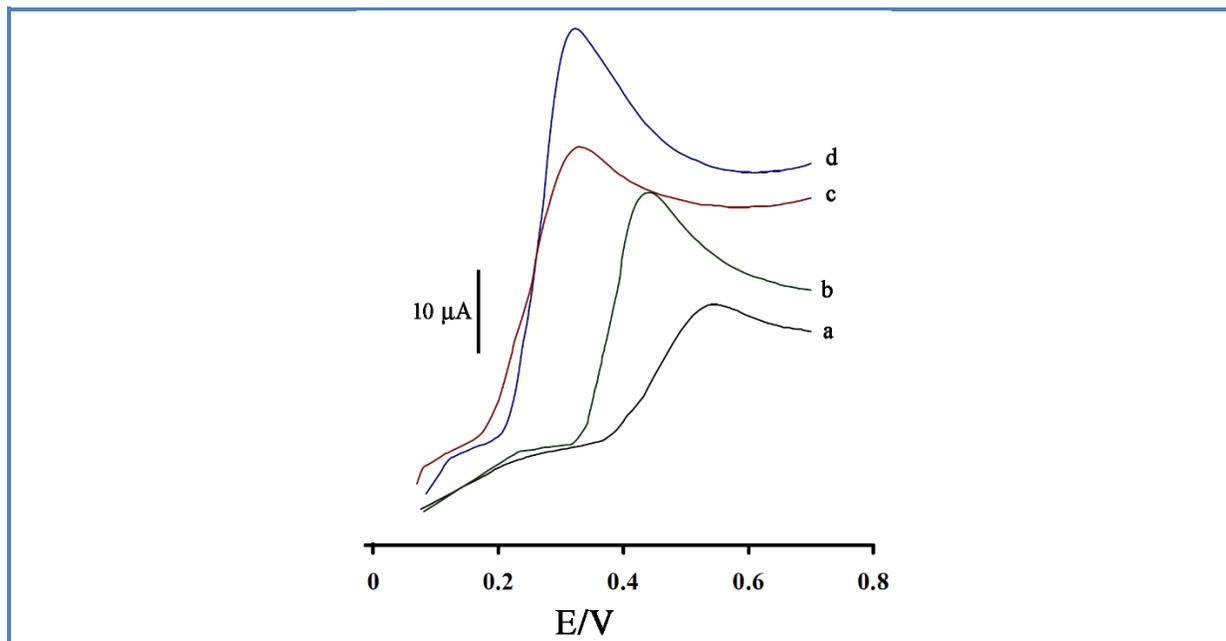
ABSTRACT

Gallic acid is one of the most abundant phytochemical in nature with anticancer activity against the prostate cancer. In this research work, carbon paste electrode (PE) modified with CdO/CNTs nanocomposite and 1-hexyl-3-methyl imidazolium bromide (HMIZBr) design and made-up for determination of gallic acid in food samples. Electrochemical behavior of gallic acid at the CdO/CNTs/HMIZBr/PE was investigated in aqueous solution using the voltammetric methods. The gallic acid oxidation signal was improved about 2.82 times on the surface of the CdO/CNTs/HMIZBr/PE compared with that of the PE. Using differential pulse voltammetric method as sensitive strategy, the CdO/CNTs/HMIZBr/PE showed linear dynamic range 0.004-500 μM with detection limit of 0.9 nM to determine the gallic acid. In addition, real sample analysis data showed the powerful ability of the CdO/CNTs/HMIZBr/PE to determine the gallic acid in white rice.

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Graphical Abstract



Introduction

Gallic acid with antioxidant activity showed great effect against the cancer cells, which confirmed importance of the gallic acid in human body [1]. Gallic acid with phenolic structure is a trihydroxybenzoic acid that is found in sumac, witch hazel, gallnuts, tealeaves, and oak bark many types of plants [2, 3]. This compound has attracted a great deal of attention due to its application as antioxidant [4-10]. Gallic acid is useful in food industries such as the chocolate and the wine industry [11, 12]. Due to the aforementioned points, many analytical sensors were suggested to determine the gallic acid in food and pharmaceutical formulation [13-15].

Among the analytical methods, electrochemical methods revealed more advantages for determination of food and pharmaceutical compounds due to its fast response [16-18]. On the other hand, for easy determination of food and pharmaceutical compounds, researchers need to portable systems such as electrochemical sensors [20-

23]. To improve the electrochemical sensor ability, researchers modified them by conductive mediators such as ionic liquids and nanomaterials. Nanotechnology is a new approach to science and especially analytical sensors [24-26]. Due to high surface area of nanomaterials, they showed good advantages to modify the electrochemical sensors for electroactive compounds analysis [27]. Ionic liquids are another class of high-conductivity modifiers that have been widely used in recent years to modify the electrochemical sensors [28-32]. They are a suitable alternative binder for paraffin oil in fabrication of carbon paste modified electrodes.

In this research, a two-fold amplified sensor was designed and fabricated (CdO/CNTs/HMIZBr/PE) to determine the gallic acid in food samples. The oxidation signal of gallic acid was selected as analytical issue to determine antioxidant in food samples. Results showed that the CdO/CNTs/HMIZBr/PE is a good analytical sensor to determine the gallic acid in food samples.

Experimental

Reagents and Apparatus

The gallic acid (97%), 1-hexyl-3-methylimidazolium bromide, phosphoric acid, graphite powder, SWCNTs-COOH, sodium hydroxide, cadmium (II) acetate anhydrous and paraffin oil were purchased from the Merck and Sigma-Aldrich Company. CdO/CNTs were synthesized by reported procedure [33]. A μ -Autolab system (Netherlands with NOVA software) was used to record the electrochemical signals. Ag/AgCl/KCl_{sat} was used as reference electrode.

Preparation of CdO/CNTs/HMIZBr/PE

The CdO/CNTs/HMIZBr/PE was fabricated by mixing 0.06 g CdO/CNTs nanocomposite+0.94 g graphite powder and using paraffin oil+HMIZBr as binders with ratio 80:20 v:v. The mixture was converted to a paste using hand mixing.

Real Samples Preparation

White rice samples were used to study the ability of the sensor in real sample analysis. 4.0 g of rice was powdered and then ultrasonic in 50% ethanol solution for 2 h. After filtering the sample, it was used for analysis of gallic acid using standard addition method.

Result and Discussion

Voltammetric Examination

Electro-oxidation of the gallic acid was evaluated at different pH of phosphate buffer solution (PBS) using CdO/CNTs/HMIZBr/PE. Cyclic voltammograms of 300 μ M gallic acid in the pH range 5.0-8.0 are presented in Figure 1 inset. A negative shift with slope 63.3 mV/pH (plot of E-pH) was observed for electro-oxidation of the gallic acid, confirming the equal value of electron and proton in redox mechanism of this antioxidant compound (Figure 1).

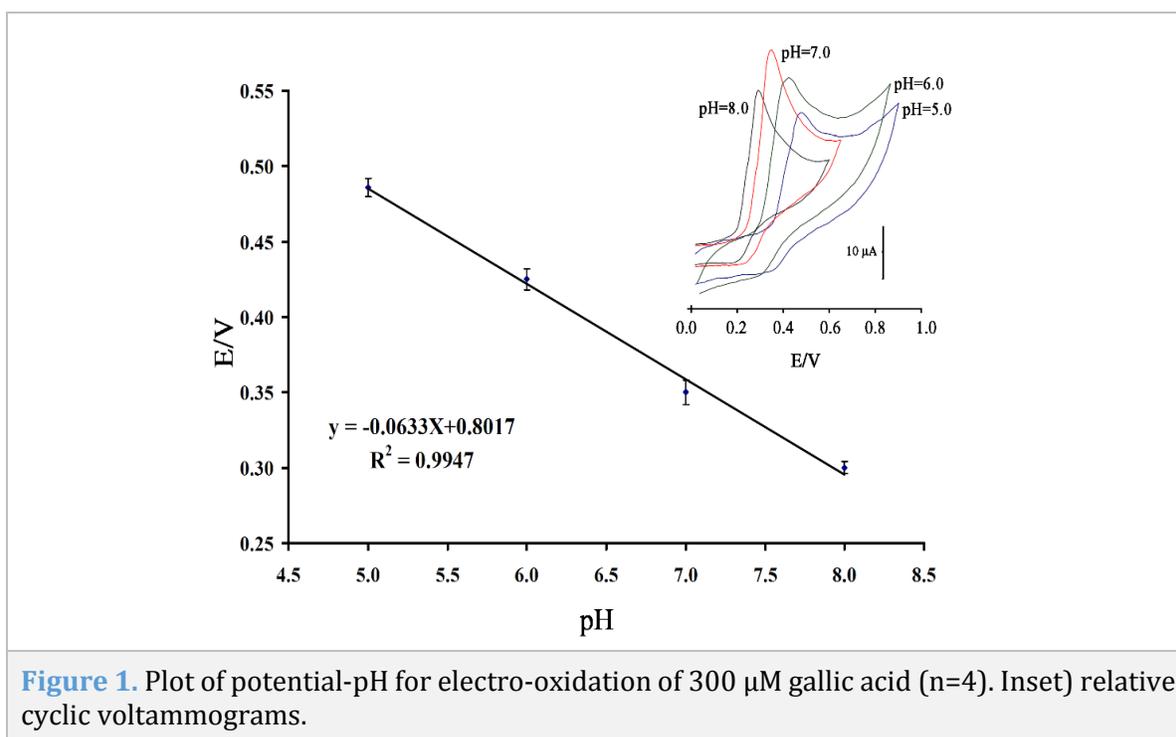
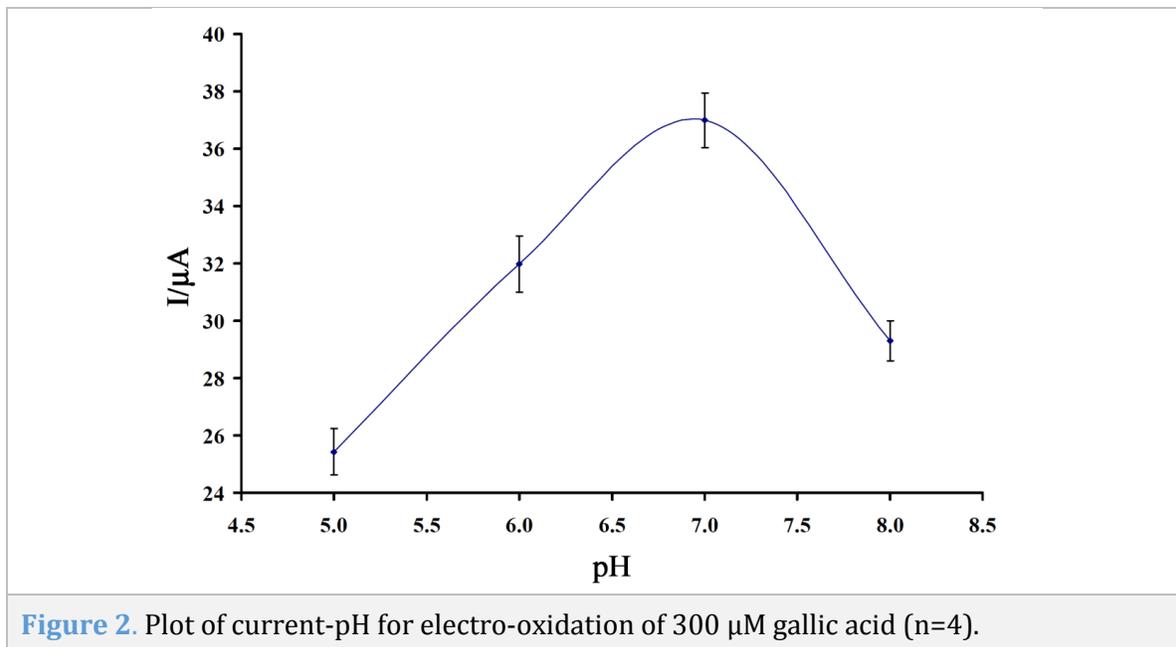


Figure 1. Plot of potential-pH for electro-oxidation of 300 μ M gallic acid (n=4). Inset) relative cyclic voltammograms.

On the other hand and using comparing cyclic voltammograms currents (Figure 2), maximum oxidation current for electro-oxidation of 300 μM gallic acid using CdO/CNTs/HMIZBr/PE as

sensor was observed at pH=7.0 and this condition was used for the next steps of investigation.



To evaluate the type movement of gallic acid of this reaction, linear sweep voltammograms (LSV) of 250 μM gallic acid was recorded at the scan rate ranging from 10 to 100 mV/s using the CdO/CNTs/HMIZBr/PE as electrochemical sensor (Figure 3). In continuous, the plot of current vs. $v^{1/2}$ was draw (Figure 3) and results confirmed the linear relation with equation $I=2.8189 v^{1/2}+3.2131$ ($R^2=0.9933$) for this investigation. This result confirmed a diffusion process for electro-oxidation of gallic acid on the surface of the CdO/CNTs/HMIZBr/PE.

In addition, LSV of 400 μM gallic acid was recorded on the surface of CPE (curve a), CdO/CNTs/PE (curve b), HMIZBr/PE (curve c) and CdO/CNTs/HMIZBr/PE (curve d). By moving from CPE to CdO/CNTs/HMIZBr/PE oxidation current of gallic acid was improved from 16.86 μA to 47.6 μA , confirming the positive role of the CdO/CNTs and HMIZBr in modification of CPE.

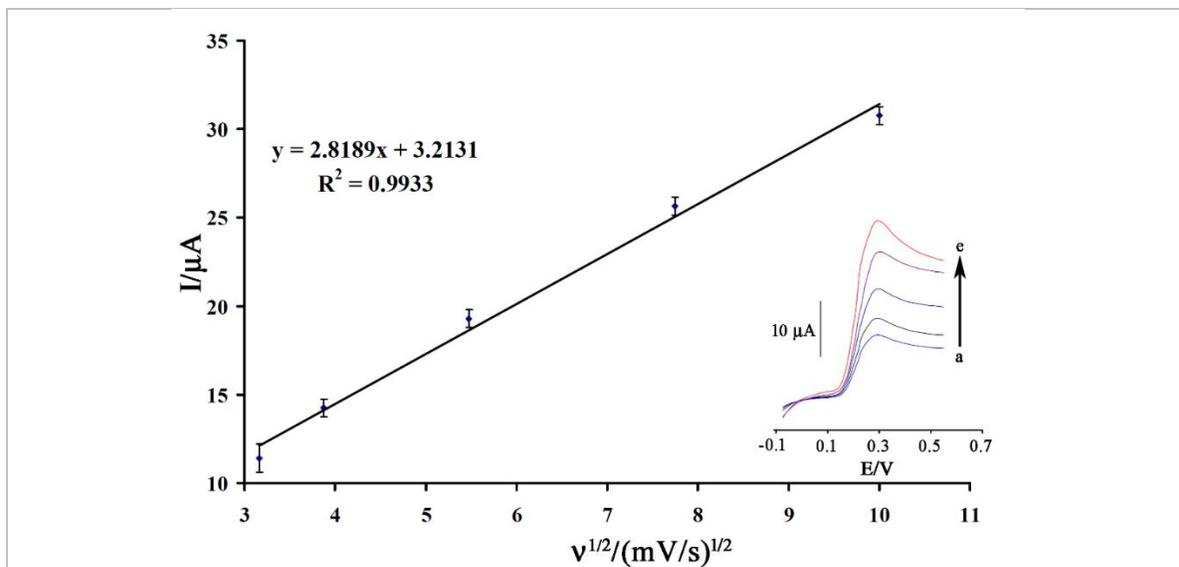


Figure 3. Plot of current- $v^{1/2}$ for electro-oxidation of 250 μM gallic acid ($n=4$). Inset) LSV of 250 μM gallic acid at scan rates a) 10; b) 15; c) 30; d) 60 and e) 100 mV/s.

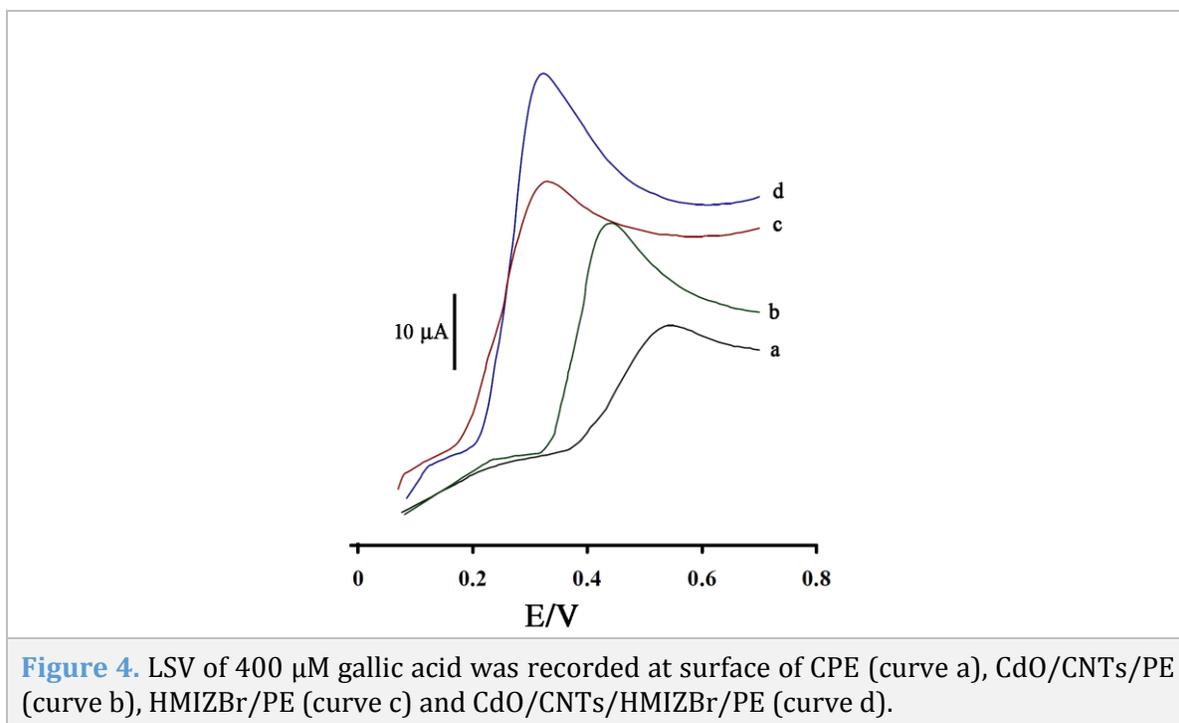


Figure 4. LSV of 400 μM gallic acid was recorded at surface of CPE (curve a), CdO/CNTs/PE (curve b), HMIZBr/PE (curve c) and CdO/CNTs/HMIZBr/PE (curve d).

The linear dynamic range and limit of detection for determination of gallic acid using CdO/CNTs/HMIZBr/PE was recorded in this step. So, differential pulse voltammetric method was used (Figure 5). The signals confirmed a

linear dynamic range 0.004-500 μM with detection limit of 0.9 nM for determining the gallic acid using CdO/CNTs/HMIZBr/PE (Figure 5).

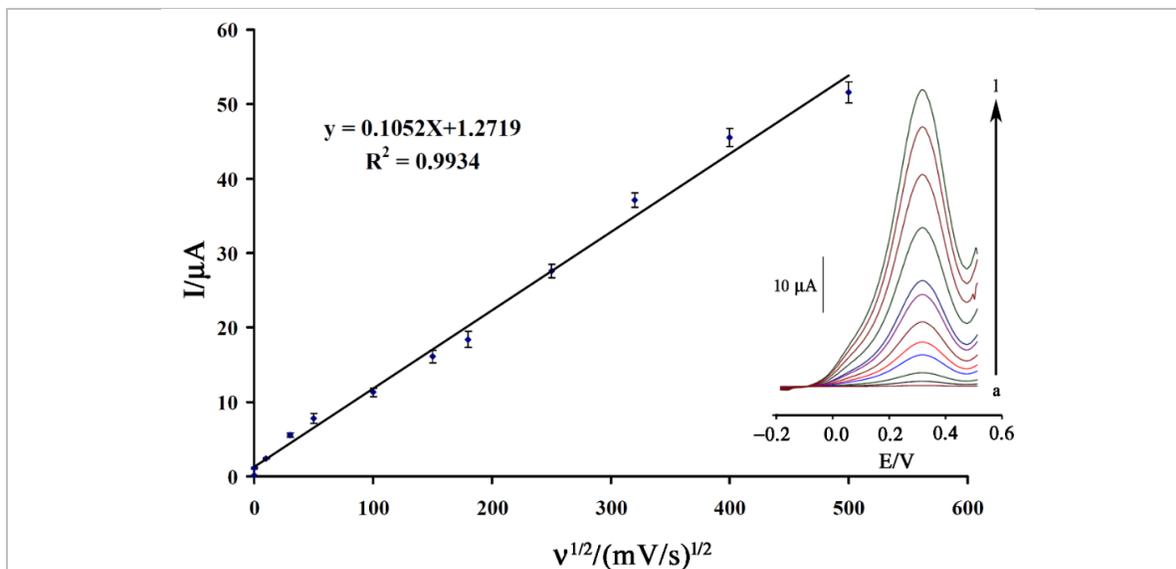


Figure 5. Plot of current- gallic acid concentration recorded at surface of CdO/CNTs/HMIZBr/PE (n=4). Inset) DP voltammograms of a) 0.004; b) 0.1; c) 10; d) 30; e) 50; f) 100; g) 150; h) 180; i) 250; j) 320; k) 400 and l) 500 μM gallic acid.

After identifying and optimizing the conditions of analysis, the ability of CdO/CNTs/HMIZBr/PE determine the gallic acid in real sample was checked. Obtained data

are demonstrated in Table 1. The recovery data confirmed the ability of the CdO/CNTs/HMIZBr/PE determine the gallic acid in real sample.

Table 1. Determination of gallic acid in food samples (n=3).

samples	Added gallic acid (μM)	Expected gallic acid (μM)	Founded gallic acid (μM)	Recovery %
White rice	---	---	<LOD	---
	10.00	10.00	10.32 \pm 0.48	103.2
	20.00	20.00	19.78 \pm 0.56	98.9

Conclusion

An electrochemical strategy was selected as analytical approach to determine the gallic acid. The CdO/CNTs/HMIZBr/PE was selected as working electrode in an electrochemical system. The CdO/CNTs/HMIZBr/PE showed high performance ability for determination of gallic acid with detection limit 0.9 nM. In addition, CdO/CNTs/HMIZBr/PE was used to determine the gallic acid in white rice as real sample. Real sample analysis data showed a recovery range 98.9-102.2% that is sufficient for a new and high quality food sensor.

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