

Electrochemical Vanillin Determination on Gold Nanoparticles Modified Multiwalled Carbon Nanotube Electrode

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Abstract: In this study, modified electrodes were prepared for Vanilline (VAN) determination. Multiwalled carbon nanotubes (MWCNT) were functionalized with acid treatment and then gold nanoparticles were electrodeposited on the MWCNTs by applying several repetitive scans in order to form gold nanoparticles modified multiwalled carbon nanotube glassy carbon electrode (Au-MWCNT/GCE) surface. The morphology and structure of electrode surfaces were characterized by scanning electron microscopy (SEM). The resulting Au-MWCNT/GC electrode showed efficient behavior to VAN electro-oxidation. The calibration graph consisted of two linear segments of 7.0×10^{-8} - 6.5×10^{-6} mol L⁻¹ and 7.0×10^{-6} - 7.5×10^{-5} mol L⁻¹ with a detection limit of 3.8×10^{-8} mol L⁻¹ that obtained from differential pulse studies. The practical applicability of the proposed modified electrode was tested for the determination of VAN in commercial ice cream and milk powder. The satisfactory results show that the Au-MWCNT/GCE has promising potential in sensor applications.

Altın Nanoparçacık Modifiye Çok Duvarlı Karbon Nanotüp Elektrotlarda Vanilin Tayini

Anahtar

Kelimeler

Vanilin,
Nano Parçacıklar,
Karbon Nanotüp.

Özet: Bu çalışmada, Vanilin(VAN) tayini için modifiye elektrotlar hazırlanmıştır. Çok duvarlı karbon nanotüpler (MWCNT) asit muamelesi ile foksiyonalize edilmiş ve ardından altın nanoparçacıklar ardışık tekrarlanan taramalar ile altın nanoparçacık modifiye çok duvarlı karbon nanotüp camımsı karbon elektrot (Au-MWCNT/GCE) oluşturmak üzere elektrokimyasal olarak biriktirilmiştir. Elektrot yüzey yapısı ve morfolojisi taramalı electron mikroskopu (SEM) ile karakterize edilmiştir. Elde edilen Au-MWCNT/GC elektrot VAN'nin yükseltgenmesine iyi bir yanıt vermiştir. Diferansiyel puls çalışmalarından elde edilen kalibrasyon eğrisi iki doğrusal aralık içerir ve bu aralıklar 7.0×10^{-8} - 6.5×10^{-6} mol L⁻¹ ve 7.0×10^{-6} - 7.5×10^{-5}

mol L⁻¹ dir ve belirtme alt sınırı ise 3.8x10⁻⁸ mol L⁻¹dir. Önerilen modifiye elektrodun pratik uygulaması ticari dondurma ve süt tozundaki VAN tayini ile test edilmiştir. Tatmin edici sonuçlar, Au-MWCNT/GCE nin sensör uygulamaları için umut vadeden potansiyele sahip olduğunu göstermiştir.

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1. Introduction

Vanillin (C₈H₈O₃), (4-hydroxy-3-methoxybenzaldehyde) is a phenolic aldehyde derived from vanilla bean e bean or pod of the tropical Vanilla plant that contains Vitamin-B, potassium, calcium, thiamin, riboflavin, and iron [1, 2].

Vanillin has been acting as an indispensable smell additive in most of the beverages and desserts such as candies, biscuits, cakes, pudding, chocolate, ice creams, wine which attract a large number of people, especially in the young ages [3, 4]. The overtaking of VAN can cause some undesirable effects to their consumers. The high dose of VAN can lead to severe side effects, including headaches, emesis, dyspnea, nausea and vomiting, and could damage liver and kidney functions [5, 6]. Due to the side effects of vanillin, it is forbidden in the infant food. Therefore, the quantitative determination of vanillin in foods and beverages has significant importance, especially for growing children [7].

Vanillin has been determined by various techniques such as; liquid chromatography-quadrupole linear ion trap mass spectrometry [8], capillary electrophoresis [9, 10], chemiluminescence [11, 12], chromatography [13-15] etc. These methods generally need multistep pretreatments which are time-consuming and also expensive. Among all, voltammetric techniques are suitable alternatives for determination of various organic and inorganic compounds due to their several advantages which are rapid,

simple, cheap, portable instrumentation, sensitive and selective [16-18]. Despite the advantages of electrochemical techniques, some limitations still need to be overcome such as high oxidation potentials and electrode fouling at conventional electrodes [19-21].

Metal nanoparticles have been extensively used as an electrode modifier in electrochemical studies due to their higher electron transfer rate, catalytic activity, and increased electrode surface area compared to the other conventional electrodes [22-25]. Besides their advantages, metal nanoparticles need a supporting material for stability on electrode surface in solutions. Carbon nanotubes (CNTs) are great substrates for this purpose. They possess many special properties, such as high chemical stability, surface area, enhanced mass transport capability and good electrical conductivity [26-29].

In this study, electrochemically synthesized gold nanoparticles modified on multiwall carbon nanotubes in order to prepare a sensitive electrochemical sensor for VAN determination. This modified electrode was successively applied to real sample detection of food products.

2. Experimental Study

2.1. Materials and Method

Multi-walled carbon nanotubes (MWCNTs, purity > 95% diameter 110–170 nm, length 9 μm) were purchased from Aldrich. N,N Dimethyl Formamide (DMF), HNO₃ and HCl were all in ultrapure grade, purchased from Merck.

Au solution was obtained by dissolving Au wire (99.999% in purity, Tanaka Kikinzoku Kogyo Co., Ltd.). All solutions were prepared using ultrapure water (Milli-Q 18.2 MX cm, Millipore System Inc.).

Voltammetric measurements were carried out by using a BAS 100B/W voltammetric analyzer (Bioanalytical Systems, Inc.) with a three electrode system consisting of a working electrode (bare GCE with a diameter of 3 mm, 0.0707 cm² geometric area, MWCNT/GCE and Au-MWCNT/GCE), a platinum wire counter electrode, and an Ag/AgCl (sat. KCl) reference electrode. The pH measurements were made with a WTW handheld 330i ion analyzer meter. The surface morphology of the modified electrode was examined using a Philips XL 30 SFEG scanning electron microscopy.

2.2. Preparation of Modified Electrodes

Before modification, GCE was activated by polishing with a different grade of Al₂O₃ slurry (0.05–3 μm) on a synthetic cloth, then rinsing with pure water and ultrasonication for 3 min in an ultrapure water and ethanol mixture.

Multiwall carbon nanotube, as received, was pretreated with concentrated HNO₃ for purification and activation of nanotubes as follows: appropriate amount of MWCNT was boiled in concentrated HNO₃ for few minutes and then washed several times with ultrapure water. The acid-treated MWCNT was dispersed in DMF to get a black suspension. A 10 μL sample of MWCNT suspension was dropped on the pre-conditioned bare GCE surface and then the DMF of the suspension on the GCE surface was evaporated at 60 °C for one hour to fabricate the MWCNT/GCE.

The electrochemical Au nanoparticles deposition was performed by using the electrochemical reduction of 1 mmol L⁻¹ HAuCl₄ on the MWCNT/GCE in 0.1 mol L⁻¹ HCl solution. It was performed by consecutive cyclic voltammograms in the potential range between -1.0 V and 0.6 V.

3. Results

3.1. Characterization of Electrodes

Figure 1. shows the SEM micrographs of modified electrodes. The SEM image of acid-treated MWCNT (Figure 1.a) revealed that the distribution of carbon nanotubes on the GCE surface was rather uniform with a smooth surface. Figure 1.b shows that there was nano Au formation as bright, round-shaped, homogeneously dispersed particles adhering to the MWCNT/GC electrode surface. In the backscattered image, due to higher molecular weight of Au, Au nanoparticles were seen bright. The average particle size of Au on MWCNT/GCE was calculated as 200 nm. In Figure 1.c energy dispersive X-ray spectroscopy (EDX) measurements confirmed that Au nanoparticles were successfully electrodeposited on MWCNT/GCE. The weight gain of the MWCNTs due to the Au loading was about 4.81%.

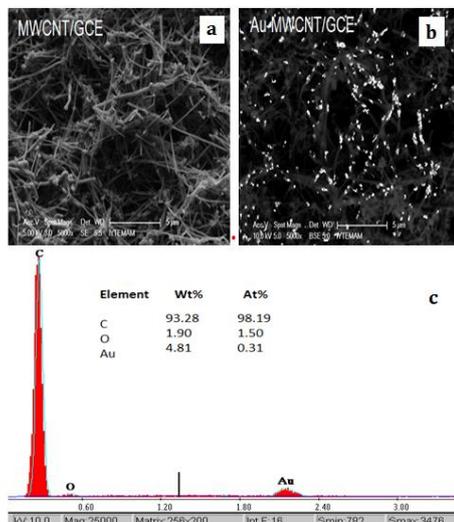


Figure 1. SEM images of a) MWCNT/GCE, b) Au-MWCNT/GCE, c) EDX spectrum of Au-MWCNT/GCE.

3.2. Electrochemical Behavior of Vanillin

The electrochemical behavior of VAN was investigated by cyclic voltammetric technique with bare and modified electrodes. Figure 2 showed the comparison of bare GCE, MWCNT/GCE and Au-MWCNT/GCE towards VAN oxidation in PBS. A small and broad oxidation peak was observed for 10^{-4} mol L^{-1} vanillin at 0.056 V on the bare GCE surface. After MWCNT deposition, the peak current shifted to the more negative values with increasing current value. The best catalytic activity in terms of peak current and peak potential was observed at Au-MWCNT/GC electrode. The peak current was found 14 times higher than bare electrode. In addition, VAN was oxidized at more negative potentials (40 mV) as compared to the GCE. This improved characteristic can be attributed to the synergistic effect of both gold nanoparticles and carbon nanotubes.

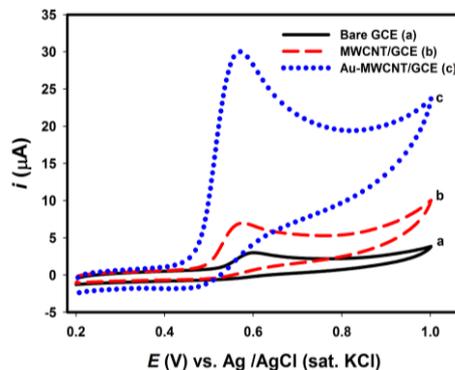


Figure 2. Cyclic voltammograms of 10^{-4} mol L^{-1} Vanillin oxidation on a) Bare GCE (and inset), b) MWCNT/GCE and c) Au-MWCNT/GCE

The effect of electrolyte solution pH on the electrochemistry of VAN oxidation was studied in the PBS with the pH range 2.0–8.0 (figure not shown). The dependence of peak potential on solution pH was represented in Figure 3a. The peak potential of VAN shifted to more negative potential values with increasing pH values which proved that protons were directly involved in the VAN electro-oxidation. The peak potential linearly depends on pH in the range of 2.0–8.0 according to following equation: E_p (V) = -0.06 pH + 1.0272 with $R^2 = 0.9956$. The slope of -60.0 mV pH^{-1} indicates that the electron transfer is accompanied by an equal number of protons and electrons in the electrochemical oxidation reaction of VAN on Au-MWCNT/GCE. The high oxidation peak current at relatively negative potentials was obtained at pH:7.15 PBS that chosen as an optimum pH for further studies.

The gold nanoparticles modified MWCNT/GC electrodes were prepared with different coverage by changing the cycle numbers to obtain the most appropriate surface for VAN oxidation. Cycle numbers varies between 1 and 20 that carried out in 1 mmol L^{-1} $H AuCl_4$ containing 0.1 mol L^{-1} HCl solution. 5 successive cycles of gold deposition on

the MWCNT/GCE surface, provide the desirable change in peak characteristics in terms of peak current (Figure 3b).

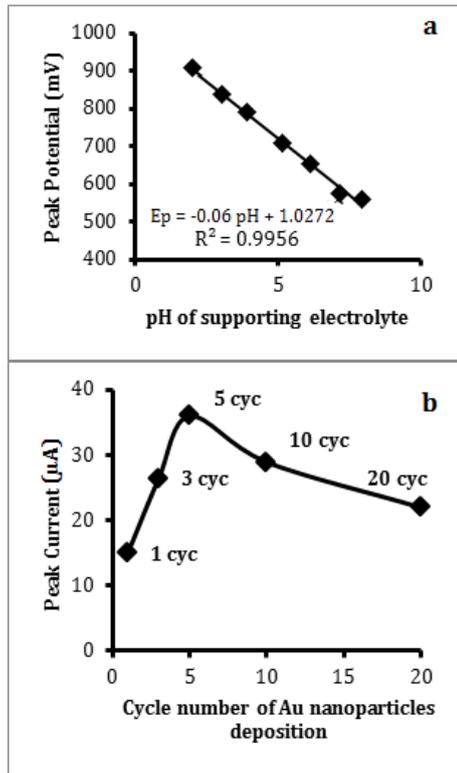


Figure 3. Influence of the pH of supporting electrolyte on the peak potential of VAN oxidation at MWCNT/GCE and b) Effect of the cycle number of Au deposition on MWCNT/GCE on oxidation peak of 10^{-4} M VAN in pH 7.15 PBS.

In Figure 4, the effect of scan rate on peak current of vanillin oxidation was also determined in VAN containing PBS. The oxidation peak current of VAN at Au-MWCNT/GCE was proportional to the square root of the scan rate in the range of 10–200 mV s^{-1} which suggests a diffusion-controlled electrode process takes place on the electrode surface. The oxidation peak potential of VAN was shifted positive values with increasing the scan rate that the electron transfer was quasi-reversible (not shown here).

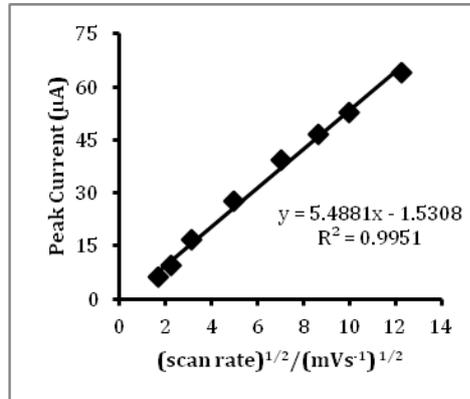


Figure 4. Dependence of scan rate on peak current of 1.0×10^{-4} mol L^{-1} VAN oxidation at Au-MWCNT/GCE in 0.1 M pH 7.15 PBS.

3.3. DPV Determination of VAN

To evaluate linear range, LOD, and sensitivity of the Au-MWCNT/GCE, DPV studies were carried out for different concentrations of VAN. Figure 5 depicts the DPV curves of Au-MWCNT/GCE in N_2 saturated pH 7.15 PBS containing different concentration of VAN ranging from 7.0×10^{-8} mol L^{-1} to 7.5×10^{-5} . The two linear calibration curves were obtained in the region of 7.0×10^{-8} – 6.5×10^{-6} mol L^{-1} and 7.0×10^{-6} – 7.5×10^{-5} mol L^{-1} . The linear regression equation for lower concentration was obtained as $i_p (\mu\text{A}) = 1.2605 C_{\text{VAN}} (\mu\text{mol L}^{-1}) + 0.4525$, with correlation coefficient $R = 0.9974$. The linear regression equation for upper concentration was obtained as $i_p (\mu\text{A}) = 0.2463 C_{\text{VAN}} (\mu\text{mol L}^{-1}) + 7.9892$, with correlation coefficient $R = 0.9956$. The limit of detection (LOD) was calculated using the equation $\text{LOD} = 3.3\sigma/m$, where the σ is the standard deviation of the response for blank solution, m is the slope of the calibration graph. The LOD value of VAN on Au-MWCNT/GCE was calculated as 3.8×10^{-8} mol L^{-1} .

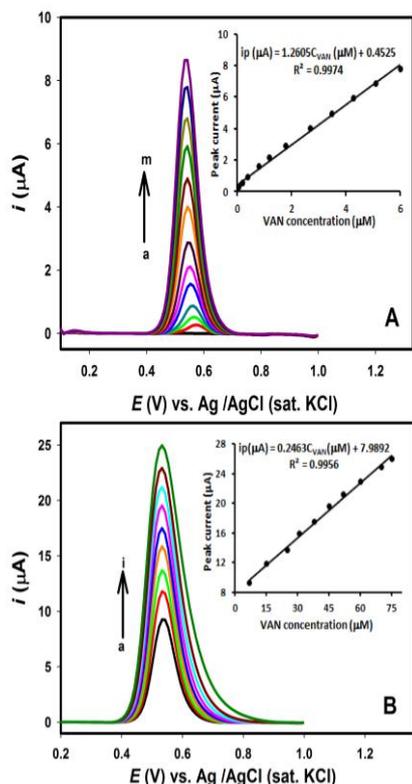


Figure 5. DPVs of Au-MWCNT/GCE in different concentrations of vanillin solutions in pH 7.15 buffer solution. (A) a-m: blank solution and 7.0×10^{-8} – 6.5×10^{-6} mol L⁻¹ inset: calibration curve for lower concentrations of VAN (B) a-i: 7.0×10^{-6} – 7.5×10^{-5} mol L⁻¹ inset: calibration curve.

3.4. Stability, Repeatability and Reproducibility Study

The repeatability of the modified electrode was also evaluated by DPV using the same electrode, while the ten measurements of 5.0×10^{-6} mol L⁻¹ VAN yielded a RSD of 2%. The investigation of reproducibility was evaluated by comparing the DPV responses of ten Au-MWCNT/GCEs prepared under the same conditions. The RSD for the resulting signals of 5.0×10^{-6} mol L⁻¹ VAN was 3.8%. Additionally, the stability of Au-MWCNT/GCE was also studied. The peak current retained 96% of its original when

the modified electrode was stored in 0.1 M PBS at room temperature for 10 days.

3.5. Interference study

The influence of potentially interfering compounds on the determination of vanillin was studied by DPV under the optimum conditions.

The interfering organic and inorganic compounds were chosen from the group of substances generally coexisted with vanillin in food products. The tolerance limit was defined as the maximum concentration of the interfering compound that caused an error of less than 5% for the determination of 5.0×10^{-6} mol L⁻¹ vanillin. It was observed that the 1000 fold of glucose, sucrose, benzoic acid, caffeic acid, tartaric acid, citric acid, oxalic acid Fe³⁺, Al³⁺, Zn²⁺, Mg²⁺, Pb²⁺, K⁺, Na⁺, SO₄²⁻ Cl⁻, and NO₃⁻ showed no obvious interference effect to VAN determination.

3.6. Analysis of Real Example

To investigate the performance of Au-MWCNT/GCE by practical analytical applications, VAN determination was carried out in ice cream and milk powder. The samples were prepared regarding to section 2.3. 1.0 mL of each pre-treated sample solution was transferred to a voltammetric cell containing 10.0 mL supporting electrolyte and analyzed in the same day. The content of VAN was determined by standard addition method and results were listed in Table 1. The amount of VAN was calculated as 0.78 mg/g and 15.96 μg/g for ice cream and milk powder, respectively. The recovery experiments were also performed that were in the range of 92.81–103.94%. These results indicated that the modified electrode has good analytical performance and it can be accurately used for the VAN determination in commercial food samples.

Table 1. VAN Determination on Au-MWCNT/GCE in different food samples (n=3)

Samples	Added ($\mu\text{mol L}^{-1}$)	Found ($\mu\text{mol L}^{-1}$)	Recovery (%)	RSD (%)
Ice cream	-	5.2	-	3.1
	8.0	13.5	102.27	2.5
	10.0	15.8	103.94	3.4
	15.0	20.1	99.50	4.0
Milk powder	-	2.1	-	2.2
	4.0	5.9	96.72	3.6
	8.0	12.9	92.81	4.1
	15.0	16.8	98.24	3.7

4. Discussion and Conclusion

In this paper, gold nanoparticles modified glassy carbon electrode was prepared by the electrochemical method. The modified electrode shows improved electrocatalytic activity towards the oxidation of VAN due to the synergistic effect of carbon nanotubes and metal nanoparticles that have increasing electronic conductivity and effective surface area. The developed electrode can be easily fabricated and has a high reproducibility, repeatability and long-term stability. The scanning electron microscopy images confirmed the morphological difference of surface before and after gold nanoparticles deposition on MWCNT/GCE. The differential pulse voltammograms showed that under optimized conditions, the peak currents increased linearly within the two linear ranges. These ranges found as 7.0×10^{-8} - 6.5×10^{-6} mol L⁻¹ and 7.0×10^{-6} - 7.5×10^{-5} mol L⁻¹. The detection limit was also calculated as 3.8×10^{-8} mol L⁻¹. In conclusion, the prepared modified electrode can be successively used for the voltammetric determination of vanillin in synthetic and real sample analysis with excellent sensitivity and anti-fouling properties.

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