Modification of boron-doped diamond with gold nanoparticles and its preliminary study for electrosynthesis of vanillin

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Abstract. Vanillin is generally synthesized from coniferin, cresol, ferulic acid, guaiacol, lignosulphonates, and vanillyl mandelic acid using oxidation-reduction methods with various chemicals and consecutive stages. These methods are less environmentally friendly due to their use of harmful compounds and the ineffective multistage process. In this study, we investigated electrochemical oxidation of isoeugenol to vanillin. A boron-doped diamond (BDD) modified by gold nanoparticles (AuNPs) was prepared for use as the working electrode, with sulfuric acid used as the electrolyte. Peak oxidation and reduction of BDD-AuNPs occurred at 1.20 V and 0.40 V, respectively, and a voltammetric range of −1.50 V to 1.50 V was applied to determine the potential oxidation of isoeugenol. The results indicated that the optimal pH for electrooxidation was 8, with potential oxidation occurring at 0.50 V.

Keywords: boron-doped diamond, electrosynthesis, gold nanoparticles, isoeugenol, vanillin

1. Introduction

The growing demand for vanillin exceeds its availability. Sources of vanillin production worldwide originate from the petroleum industry and are nonedible, whereas the natural edible vanillin is derived from the extraction of vanilla plant seeds only (Vanilla planifolia). One extraction method involves the catechol pathways, which requires continuous oxidation stages and the use petroleum-based phenol [1].

Vanillin is the most abundant pure monoaromatic phenol currently produced at an industrial scale from lignin (at ~20,000 tons annually), with 3000 of those tons originating from lignin. Vanillin has many advantages as an aromatic compound, including its safety, and harbors two functional groups that can be modified chemically [2]. In addition, vanillin has potential as a difunctional feedstock for the preparation of thermoplastic polymers [1].

Alternative methods for vanillin conversion involve the use of lignin, guaiacol, coniferin, eugenol, and vanillyl mandelic acid [3], which utilize vanillyl alcohol oxidase from microorganisms, such as Bacillus subtilis, Pseudomonas sp., and Pseudomonas aeruginosa [4]. Adilina et al. [5] converted isoeugenol to vanillin using a cobalt(II) porphyrin heterogeneous catalyst, and electrochemical vanillin synthesis from lignin derivatives was reported by Reichert et al. [6]. Additionally, Mubarok et al. [7] performed vanillin electrosynthesis from isoeugenol using a platinum electrode in solvent.

In this study, we described the preparation of a gold-nanoparticle (AuNP)-modified boron-doped diamond (BDD-AuNPs) advantageous as a functional material because of its durability and catalytic characteristics [8,9]. We applied this material for a preliminary study of vanillin electrosynthesis from isoeugenol using pH variation.
2. Materials and methods

2.1. Materials and instruments

We used a mixture of cis- and trans-isoeugenol (98%; Wako Pure Chemical Co., Dalian, China), methanol p.a. (Sigma Aldrich, St. Louis, MO, USA), phosphoric acid, boric acid, acetic acid, tetrabutyl ammonium perchlorate (Tokyo Chemical Industries, Tokyo, Japan), allylamine (Wako Pure Chemical Co.), deionized ultrapure water (Merck Millipore, Billerica, MA, USA), tetrachloroauric(III) acid (Tokyo Chemical Industries), sulfuric acid p.a (Sigma Aldrich), and vanillin (Wako Pure Chemical Co.). The pH meter and potentiostat were obtained from (EDAQ Instrument Corp., Taipei, Taiwan), while the scanning electron microscopy (SEM) was from JEOL/EO JCM-6000Plus, Japan.

2.2. Experimental

2.2.1. Preparation of BDD–AuNPs. The BDD was cleaned by sonication in isopropanol and deionized ultrapure water for 5 min, respectively. Tetrachloroauric(III) acid diluted in sulfuric acid was used, as described previously [8]. Electrodeposition was conducted by amperometry at potential −200 mV (vs. Ag/AgCl) for 100 s. The results were characterized by SEM and cyclic voltammetry. Cyclic voltammetry of BDD–AuNPs was conducted in phosphate-buffered saline (PBS; pH 7) at a scan rate of 100 mV/s.

2.2.2. Electrochemical study of isoeugenol. Electrooxidation of isoeugenol was performed by cyclic voltammetry in one compartment. Variation of the pH was performed using Britton–Robinson (B–R) buffer solution as described previously [9], with slight modifications. The electrooxidation system contained a volumetric ratio of isoeugenol:tetrabutyl ammonium perchlorate: pH buffer (2:2:1, v/v) in a total volume of 5 mL, as described previously and with slight modifications [7]. Isoeugenol and tetrabutyl ammonium perchlorate (TBAP) were diluted in methanol to final concentrations of 0.1 M, and B–R buffer was diluted in ultrapure water.

3. Results and discussion

SEM images revealed the differences between the surfaces of BDD (figure 1a) and BDD–AuNPs (figure 1b). AuNPs electrodeposited on the surface of the BDD enables increases in surface activity as a catalytic site of chemical reactions. In addition to the BDD, AuNPs improve the formation of hydroxyl radical and chemically absorb and substrates with d-orbitals, which are preserved. Therefore, AuNPs increase electron conductivity to increase the reaction rate and selectivity based on the natural affinity of AuNPs. Electrodeposition of AuNPs onto the BDD was performed at molecular ratio of tetrachloroauric(III) acid as a gold precursor and sulfuric acid as an electrolyte of 1:100, respectively [8]. A constant potential at 200 mV for 100 s allowed the formation of AuNPs ordered with nucleation, which continued with increasing layers of AuNPs. This process is affected by the applied potential, programmed step deposition, deposition time, mass transport of the electrolyte, pH system, and handling material [10]. In this work (figure 1b), the distribution size of the nanoparticles on the BDD surface was quite uniform.
Figure 2. Cyclic voltammogram of BDD and BDD-AuNPs in PBS (pH 7).

(a) (b) (c)

Figure 3. Cyclic voltammogram in the (a) absence and (b) presence of isoeugenol (c) magnification of the result in the presence of isoeugenol at an oxidation range of 0 mV to 1000 mV. The experiment was performed at room temperature without stirring and at a scan rate of 100 mV/s.

Cyclic voltammograms from experiments in PBS (pH 7) containing BDD–AuNPs showed three peaks representing peak Au oxidation at 1115 mV and 1231 mV along with a reduction peak at 408 mV. The reduction peak indicated the acquisition of Au(0) from Au(III). Figure 2 shows that the reaction initiated at oxidation and continued through reduction [11]:

\[
\text{Au}^0_{(s)} \rightarrow \text{Au}^{3+}_{(aq)} + e^- \quad (1)
\]
\[
\text{Au}^0_{(s)} \rightarrow \text{Au}^{3+}_{(aq)} + 3e^- \quad (2)
\]
\[
\text{Au}^{3+}_{(aq)} + 3e^- \rightarrow \text{Au}^0_{(s)} \quad (3)
\]
\[
\text{O}_2_{(aq)} + 2\text{H}_2\text{O}_{(aq)} + 4e^- \rightarrow 4\text{OH}^-_{(aq)} \quad (4)
\]

This reaction sequence describes the electrochemical behavior of AuNPs in the presence of isoeugenol.
Table 1. Potential oxidation and current-based oxidation of isoeugenol with pH variation.

| pH | Potential oxidation (vs. Ag/AgCl) | Current oxidation (µA) |
|----|----------------------------------|------------------------|
| 3  | Unidentified                      | 324                    |
| 5  | 322                               | 45.21                  |
| 6  | 428                               | 23.03                  |
| 7  | 500                               | 177.94                 |
| 8  | 282                               | 45.58                  |
| 12 |                                  |                        |

Figure 4. Resonance of radical isoeugenol

Figure 3 shows a cyclic voltammogram for an experiment using blank solvent in the presence and absence of isoeugenol, which resulted in different oxidation and reduction peaks. B–R buffer contains boric acid (HBO\textsubscript{3}), acetic acid (CH\textsubscript{3}COOH), phosphoric acid (H\textsubscript{3}PO\textsubscript{4}), and sodium hydroxide (NaOH), which are suitable in an electrochemical system, especially one involving polarography, to stabilize ionic strength in solvent [12,13].

The pKa of vanillin 7.4 affects its stability in product solutions [14]. The pH values of isoeugenol and TBAP in methanol are 6.6 and 7.0, respectively. The reactivity of isoeugenol and vanillin under extreme alkaline conditions caused more rapid deprotonation of the phenolic substituent. In a more acidic system, isoeugenol became less electroactive, because the solvent began losing its ability to facilitate formation of the phenolic transition state [7,15,16].

The resonance of the phenolic transition state was initiated by the homolytic proton from the hydroxyl group [7,17]. Therefore, electron nonpairing freely mobilized around four possible transition states, representing the majority transition state in for this species (1). This transition state represented the rate-determining step of the formation of various products.

4. Conclusions
A BDD-AuNP electrode was successfully prepared using electrodeposition methods and sulfuric acid as an electrolyte at −200 mV for 100 s. Electrooxidation of isoeugenol was optimized at pH 8 with a potential oxidation of 500 mV. These results demonstrated the potential for vanillin electrosynthesis using an AuNP electrode with isoeugenol in methanol.

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