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Electrochemical oxidation of 2-mercapto ethanesulfonic acid by Cu nanoparticles-modified boron-doped diamond electrode

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ABSTRACT

Catalyst of *in-situ* Cu nanoparticles (CuNPs) is electrodeposited on boron-doped diamond electrode for a thiol compound of 2-mercapto ethanesulfonic acid (MCES) determination. The morphology of CuNPs was investigated by scanning electron microscopy (SEM). The SEM micrograph of CuNPs was shown spherical in shape and about 100 nm in diameter. Cyclic voltammetric, and square wave voltammetric results showed that the CuNPs acts as an efficient material for the electrocatalytic oxidation of MCES. According to the voltammetric studies, the MCES electrooxidation on the presented *in-situ* CuNPs electrode was occurred at lower potential than the absented CuNPs electrode and also the voltammogram was shown a well-defined oxidation peak. The *in-situ* CuNPs modified boron-doped diamond electrode was used as a sensor for determination of MCES with a good dynamic range of 100 to 1000 μM with a high sensitivity of 2.59 nA/μM and a low detection limit of 30 μM (S/N=3).

Keywords: Cu nanoparticles, electrochemistry, thiol conpound, boron-doped diamond electrode, 2-mercapto ethanesulfiic acid

INTRODUCTION

In recent years, much electrochemical sensor (electrode) development has concentrated on various miniature things: nanotubes, nanoballs, nanowires, and nanoparticles (Chen *et al*., 2002; Riley, 2002; He *et al*., 2004; Mazar, 2004; Li *et al*., 2005; Musameh *et al*., 2005; Wang and Musameh, 2005; Welch *et al*., 2005b; Zhang *et al*., 2005; Starowiez *et al*., 2006; Wang and Liu, 2006; Welch and Compton, 2006). This intense interest is due to their unique optical, magnetic, electronic and chemical properties, which differ greatly from those of the bulk material. The electroanalysis is one of the best methods for detecting species in solution due to its low cost, ease of use and reliability. With regards to electroanalysis, the main

advantages of nanoparticle-modified electrode over a macroelectrode or a film deposit are high effective mass transport, surface area, catalysis and control over local microenvironment (Welch *et al*., 2005a; Welch and Compton, 2006).

Nanoparticles, such as platinum, copper, and silver, is typical nanomaterials (Chen *et al*., 2002; Riley, 2002; He *et al*., 2004; Welch *et al*., 2005a; Zhang *et al*., 2005; Starowiez *et al*., 2006; Welch and Compton, 2006; Xu *et al*., 2006), have been used for development of sensors. These nanoparticles have possessed unique physical and chemical properties. For example, the electrocatalytic properties of copper surface towards nitrate reduction were explored (Welch *et al*., 2005a).

The boron-doped diamond electrode has emerged as a unique characteristics that make it particularly attractive for electrochemical applications (Yano *et al*., 1999; Aguilar *et al*., 2002; Fujishima *et al*., 2004; Honda *et al*., 2005; Ivandini *et al*., 2006a; Ivandini *et al*., 2006b; Preechaworapun *et al*., 2006; Treetepvijit *et al*., 2006; Watanabe *et al*., 2006; Preechaworapun *et al*., 2008), such as very low and stable voltammetric background current which results improvement in signal-to-background, long-term response stability as well as excellent activity towards any redox species without any pretreatment, low sensitivity to dissolved oxygen, a wide working potential window in aqueous solution, slight adsorption of polar organic molecules, and high resistance to deactivation. These material properties are the impetus for our interest in studying and developing diamond electrodes for electrochemical applications.

In this work, the nanomaterials for electrochemical sensors have been developed for the determination of 2-mercapto ethanesulfonic acid (MCES), one of vitamin, by copper nanoparticles-modified BDD electrode as an electrochemical sensor. MCES was prior determined in our group (Chailapakul *et al*., 2001) by electrochemical analysis, but the detection limit was very high and high oxidation potential. Therefore, MECS analysis has been developed based on the electrocatalytical properties of CuNPs and with one step of deposition. The proposed method provides a significantly low detection limit, high sensitivity and reproducible responses.

METHODOLOGY

All chemicals used were of analytical grade. Copper (II) sulfate pentahydrate and sodium sulfate were purchased from Merck (Germany). 2-Mercaptoethanesulfonic acid sodium (MCES) was obtained Sigma.

The BDD electrode (obtained from Associate Professor Yasuaki Einaga's laboratory) was grown on conductive Si substrate using microwave assisted chemical vapor deposition system. It was rinsed with isopropanol and deionized water prior to use, respectively. Before use as a working electrode, BDD film was rinsed followed by sonication with 2-propanol and high purity-water for 5 min prior to use in the electrochemical experiments.

Electrochemical measurements were conducted using an Electrochemical Analyzer (Model 1230A, CH Instruments) at room temperature in a conventional three-electrode electrochemical cell (2.0 mL), which was used for cyclic voltammetric experiments. They were carried out using a single compartment cell

with a silver/silver chloride (Ag/AgCl) with a salt bridge as the reference electrode and a platinum wire as the counter electrode. The BDD working electrode along with the conducting Si substrate was pressed against the bottom of the glass cell by a silicon rubber gasket (area 0.077 cm^2). The electrical contact for BDD was made through the backside of the scratched Si substrate by contacting the brass current collecting back plate. The BDD surface was electrodeposited by CuNPs through applied potential at -0.4 V for 5 seconds in 150 μM $CuSO_4$. The CuNPs modified BDD were characterized by the Scanning Electron Microscope (SEM; LEO, Model 1400VP).

RESULTS AND DISCUSSION

1. Cu nanoparticles (CuNPs) characterization

The characterization of CuNPs/BDD surface was shown in Figure 1. Figure 1A shows a typical SEM image of bare BDD surface and compared to the CuNPs/BDD surface in Figure 1B. The surface of bare BDD is clear while the surface of CuNPs/BDD were deposited by CuNPs which shown by a spherical shape (circle in Figure 1B) and spotted on the BDD. The average size of CuNPs is 100 nm.

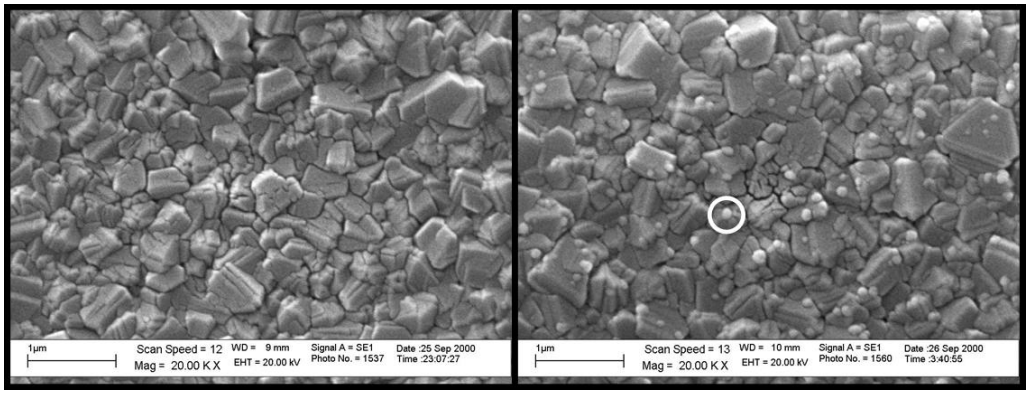

Figure 1 SEM images of (A) bare BDD and (B) CuNPs/BDD. The CuNPs deposited on BDD surface is marked by circle.

2. Optimized condition for MCES analysis

2.1 Electrochemical behaviors of MCES

Figure 2 shows the cyclic voltammograms of background electrolyte (0.1 M Na_2SO_4) (Figure 2a) and 300 μM MCES in 0.1 M Na_2SO_4 (Figure 2b and 2c) at the *in-situ* CuNPs/BDD and bare BDD electrodes, respectively. The *in-situ* CuNPs/BDD electrode was prepared by firstly electrodeposition at -0.4 V for 5 seconds with 150 μM $CuSO_4$ in 0.1 M Na_2SO_4 solution. Then the electrode and the same electrolyte solution were used for cyclic voltammetric analysis of MCES. The *in-situ* CuNPs/BDD exhibited a well-defined irreversible oxidation peak at 390 mV

versus Ag/AgCl, whereas the bare BDD electrode provided no peak in the +100 to +700 mV potential window. This phenomenon proved that the electrocatalytic properties of CuNPs toward MCES was obtained, the oxidation peak potential slightly shifted to lower value with the higher in peak current comparing to electrode without CuNPs.

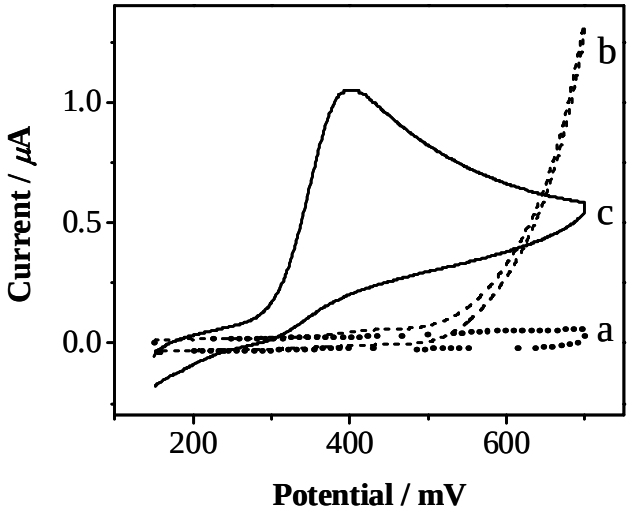

Figure 2 Electrocatalytic cyclic voltammograms of 0.1 M Na_2SO_4 electrolyte (a), and 300 μM MCES in 0.1 M Na_2SO_4 (b and c) at bare BDD electrode (a, b) and *in-situ* CuNPs/BDD electrode (c).

2.2 $CuSO_4$ concentration for catalytic of MCES

Since the electrocatalytic properties of CuNPs/BDD electrode toward electrocatalytic oxidation of MCES is based on the amount of CuNPs on the BDD surface, the various $CuSO_4$ concentrations were determined by cyclic voltammetry, which the results was shown in Figure 3A. The average anodic peak current (n=3) of each $CuSO_4$ concentration were plotted versus $CuSO_4$ concentration as in Figure 3B. The highest peak current was observed for 150 μM $CuSO_4$.

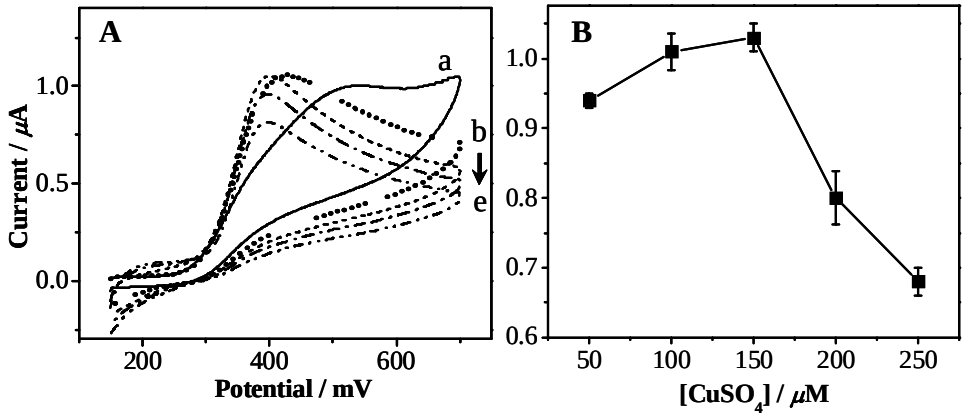

Figure 3 (A) Cyclic voltammogram of various concentration of $CuSO_4$ (50 μM (a), 100 μM (b), 150 μM (c), and 200 μM (d)) in 0.3 μM MCES solution. (B) The relationship between $CuSO_4$ concentration and average peak current responses (n=3) from (A).

3. Calibration and detection limit

Figure 4 shows the cyclic voltammograms of CuNPs/BDD based electrode tested under fixed $CuSO_4$ solution and various MCES concentrations. The calibration characteristic is shown in Figure 4 (inset). A linear dependence between the catalytic peak current and the concentration of MCES was obtained in the range 100 – 1000 μM. The linear regression equation was *y = 0.00259 x + 0.24134*, with a correlation coefficient of 0.99876. Its detection limit was 30 μM (3σ) with a sensitivity of 0.00259 μA μM^{-1} MCES and its limit of quantitation was 100 μM (10σ). This value was comparble with those reported by our research groups (Chailapakul *et al*., 2001).

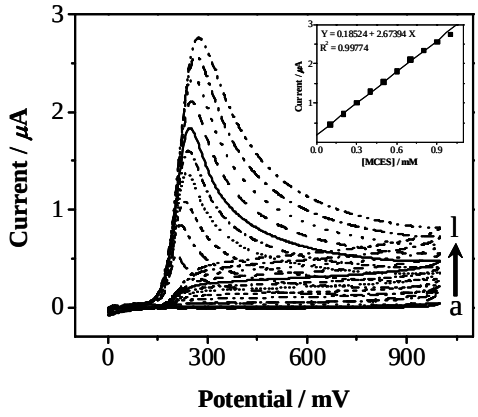

Figure 4. Cyclic voltammograms of 0.1 M Na_2SO_4 (a), 0.1 M Na_2SO_4 added with 150 μM $CuSO_4$ (b) and various MCES concentrations (from 100 to 1000 μM (c to l)). The inset showed a calibration plot of peak current versus MCES concentration.

CONCLUSION

This work demonstrates the electrocatalytic of CuNPs and its application for the determination of MCES. Therefore, to combine the *in-situ* CuNPs on the BDD electrode surface with the catalytic reaction of the MCES by *in-situ* CuNPs. The good results showed a low detection limit 30 μM, sensitivity as 2.59 *n*A/μM and linear range as 100 to 1000 μM. This proposed method will be applied to determine the contents of thiol compounds in food and anti-microbial drugs in the feature.

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