Preparation of boron–doped diamond electrodes modified with copper–gold nanoparticles (CuAuNP) as oxygen sensors

A D Kurniawan, E Saepudin and T A Ivandini
Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok 16424, Indonesia
Corresponding author: ivandini.tri@sci.ui.ac.id

Abstract. Boron-doped diamond (BDD) electrodes are promising because they offer a wide electrochemical potential window, low background current, and good physical and chemical stability. In this study, to make them sensitive to dissolved oxygen, BDD electrodes were modified with copper–gold nanoparticles (CuAuNPs). A one-pot chemical reduction method was used to synthesize the CuAuNPs. Transmission electron microscopy revealed that the average diameter of the CuAuNPs was around 11 nm. The electrochemical behavior during oxygen reduction was characterized by cyclic voltammetry in a potential range from −1.0 to −1.5 V in a pH 7 phosphate-buffered saline solution containing various concentrations of the dissolved oxygen. The cyclic voltammograms showed that peaks corresponding to oxygen reduction occurred at −0.13 V. An approximately linear calibration curve was derived to correlate the peak current to the concentration of dissolved oxygen, indicating that the CuAuNP–BDD electrodes are promising for use as oxygen sensors. These electrodes can be readily applied to environmental monitoring, industrial safety, fuel cells, and automotive applications.

Keywords: Boron-doped diamond, surface modification, CuAuNP, oxygen sensors, cyclic voltammetry

1. Introduction
Over the years, the water quality in Indonesian rivers has degraded and the rivers are now classified as heavy polluted [1]. Thus, over the last 50 years, the detection of dissolved oxygen (DO) in water has been extensively studied because of its significant role to control the environmental, as well as to maintain safety in industry, in technology for fuel cell, and in the automotive industry [2].

Boron-doped diamond (BDD) is a carbon-based electrode that has many advantages over other electrodes, because of its wide electrochemical potential window, low background current, physical and chemical stability, and biocompatibility [3–5]. However, it does not provide catalytic activity for the reduction-oxidation reaction with oxygen.

Recently, nanomaterials have become integral to the development of sensors since their properties can be adjusted based on the size and shape of material and can be applied to various techniques. The use of nanoparticles, such as Au, Ag, and Cu nanoparticles, in sensors has been explored recently. Moreover, because of their optical, magnetic, and catalytic properties, a combination between multimetallic nanoparticles and an alloy or core-shell structures shows an interesting feature. Presently, advance trials are conducted to synthesis the nanoparticle alloys for applications in sensor, devices for photonic, and catalysis, because they often exhibit better catalytic properties than the monometallic forms of the metal itself do [6]. The BDD’s electrochemical characteristics can be upgraded through the modification of its surface by the metal nanoparticles deposition, to enhance the
activity of its electrocatalytic property, and thereupon, increase the process in terms of its sensitivity and selectivity.

This study focused on coating the surfaces of BDD electrodes with copper–gold nanoparticles (CuAuNPs) for this reason. Copper (Cu) is known to have a higher conductivity than gold and silver but is cheaper than both. Gold (Au) is known to have good sensitivity as an oxygen sensor since the introduction of the Clark electrode in the mid-1950s; in addition, it is favored because it is biocompatible, stable, and has high electrical and corrosion resistance [7].

We hypothesize that modifying the surfaces of BDD electrodes with shell-core CuAuNPs will provide better sensitivity to oxygen reduction. Thus, in this study, BDD electrodes modified with Au nanoparticles (AuNP–BDDN electrodes), copper nanoparticles (CuNP–BDD electrodes), and copper-gold nanoparticles (CuAuNP–BDD electrodes) were compared. Furthermore, the oxygen sensing capabilities of these electrodes were validated against measurements obtained using a conventional sensor designed for detecting DO in water.

2. Experimental

2.1. Materials and instruments
BDD was obtained from Keio University in Japan on a (1 0 0) silicon wafer template. The BDD and the silica had a total thickness of 1 mm and had a 0.1% boron/carbon content. Analytical-grade CuSO₄, HAuCl₄, KHPO₄, KHPPO₄, NaBH₄, L-ascorbic acid, citric acid, and other chemicals were obtained from Merck and WAKO.

An EDAQ Potentiostat (from the Bioelectrochemistry main laboratory of Universitas Indonesia) was used to conduct electrochemical experiments. A three-electrode system was applied with Ag/AgCl as a reference and a Pt wire as the counter electrode. The working electrode was either a bulk–Au BDD electrode or an AuNP–BDD, CuNP–BDD, or CuAuNP–BDD electrode.

2.2. Preparation of AuNP–BDD and CuAuNP–BDD electrodes
Before modification with nanoparticles, the BDD was modified into nitrogen-terminated diamond based on an adaptation of a previously developed method [7,8]. Briefly, the BDD electrodes were ultrasonically washed for 15 min in isopropanol and followed by 15 min ultrasonic washing in ultrapure water. Then, they were dried with nitrogen gas. Next, the washed BDD electrodes were modified by a reaction with allylamine molecules under 254 nm ultraviolet light irradiation for 6–8 hours.

Gold nanoparticles (AuNPs) and copper–gold nanoparticles (CuAuNPs) were prepared based on an adaptation of the Zhang method [9] with a few adjustments. 100 μL of 0.1 M CuSO₄ and 150 μL of 0.1 M sodium citrate (Na.C.H.O.) were added to 20 mL of water at room temperature. Then, 1 mL of fresh NaBH₄ (3.8 mg in 4 mL water) was added to the solution under rapid stirring followed by continued stirring for 15 min. A 0.1 M HAuCl₄ solution was added to this mixture followed by stirring for 20 min. CuAuNPs were stored at room temperature (14 ± 2) for 24 h before use. The nanoparticles were characterized by UV–Vis spectroscopy and transmission electron microscopy (TEM). Then, the nanoparticles were deposited on the nitrogen-terminated BDD by immersing the BDD in a colloidal nanoparticle solution for 12 hours followed by drying.

2.3. Electrochemical studies using cyclic voltammetry
The bulk-Au electrode and CuAuNP–BDD electrodes were used as working electrodes, as the supporting electrode, Pt-spiral was employed, while for the reference electrode, Ag/AgCl (KCl–saturated) system was applied. The analysis was performed in 7 mL 0.1 M electrolyte solution of phosphate buffer solution (PBS) with 100 mV/s scan rate, within range of potential from −1.0 V to 1.5 V (vs. Ag/AgCl).

3. Results and discussion

3.1. Preparation and characterization of BDDN-CuAuNP electrodes
The preparation of CuAuNPs was based on a reduction reaction of AuCl₄ ions at Cu nanoparticles by the remaining NaBH₄, after the formation of CuNPs. The yellow CuNP solution did not exhibit a surface plasmon resonance (SPR) peak and the CuNPs had diameters of less than 2 nm. With the addition of HAuCl₄, the solution color changed to red wine, which indicates the growth of the Au shell.
on the Cu core. In addition, the increase in the SPR of the solution at 534 nm confirms the formation of AuNPs with a size increase of over 2 nm, which confirms that the formation of an Au shell on the Cu core [9]. The formed CuAuNPs were found to have diameters around 11 nm based on TEM observations. Moreover, the presence of the Cu core was confirmed by the EDX results, showing the presence of both Cu and Au (Figure 1).

Figure 2 shows a comparison of the UV-Vis spectra for the three nanoparticles. Whereas the CuNPs did not show any peak, the AuNPs and CuAuNPs exhibited SPR peaks around 522 and 534 nm, respectively. This slight shift of the peak indicates an interaction between the two metals in the nanoparticles. Furthermore, the stability of the CuAuNPs was characterized by UV-Vis spectrometer readings over 10 days; these results showed a decrease in the intensity, indicating agglomeration of the nanoparticles.

Previous study showed the better affinity of the nitrogen–modified BDD toward AuNPs compared to the one modified with oxygen or hydrogen [7,8]. Because the surfaces of the CuAuNPs were shown to be covered with an Au shell, these nanoparticles were expected to interact strongly with the nitrogen-terminated BDD. Thus, before modification with nanoparticles, the BDD surfaces were pretreated via a photochemical reaction under ultraviolet light ($\lambda = 254$ nm) with allylamine dropped at the surface; by this process, the allylamine’s double bonds will be broken to form a new covalent bond between the allylamine’s C ions and BDD’s C ions [7,8]. This process induced nitrogen termination to facilitate the deposition of the nanoparticles. Figure 3 shows an SEM image of the CuAuNP–BDD.
Figure 2. (a) UV-VIS spectra of (i) CuNPs, (ii) AuNPs and (iii) CuAuNPs and (b) CuAuNP stability over 10 days.

Figure 3. SEM image of CuAuNP–BDD.

Figure 4. (a) Cyclic voltammograms obtained with the CuAuNP–BDD electrode for 0.1 M PBS (pH 7) with different DO concentrations and (b) a linear curve representing the relationship between the peak oxygen reduction current and the DO concentration.

The observed white spots covering the BDD surface indicate that the BDD was modified with CuAuNPs successfully.

3.2. Electrochemical properties of oxygen at CuAuNP–BDD electrode

Cyclic voltammetry was used to examine the electrochemical behavior of the electrodes in the presence of oxygen. Figure 4 shows cyclic voltammograms obtained with the CuAuNP–BDD
electrode in 0.1 M PBS (pH 7) with different DO concentrations. The results show a reduction peak at −0.13 V (vs. Ag/AgCl). The voltammograms obtained with the bulk-Au electrode were similar to those obtained with the CuAuNP–BDD electrode, indicating that the gold shell influences the electrode properties and the reduction peak in the CuAuNP–BDD electrode. The peak current associated with the oxygen reduction increased linearly as the DO concentration increased. Based on the results, the limit of detection was estimated to be 0.168 ppm, indicating that the proposed electrodes can be used as oxygen sensors.

4. Conclusions
In this study, a one-pot chemical reduction method was used to synthesize CuAuNPs were successfully. Nitrogen-terminated BDD surfaces were modified with CuAuNPs successfully as confirmed by the SEM image. The obtained CuAu–BDD electrodes resulted in similar voltammograms to those obtained using a bulk-Au electrode, indicating that the gold shell affects the CuAu–BDD electrode properties in terms of the reduction peak. In addition, the electrochemical results showed that the reduction peak current increased as the oxygen concentration increased, suggesting that the CuAu–BDD electrodes are promising for applications in oxygen sensing.

Acknowledgements
This research was supported by PITTA Grant Universitas Indonesia, Contract No. 1822/UN2.R3.1/PPM.00.01/2017. The authors would like to thank Einago (www.einago.com) for the English language review.

References
[1] Ministry of Environment and Forestry 2014 Ministry of Environment and Forest Statistic 2014 pp 1–418.
[2] Hutton L, Newton M E, Unwin P R and Macpherson J V 2009 Anal. Chem. 81 1023–32.
[3] Macpherson J V 2015 Phys. Chem. Chem. Phys. 17 2935–49.
[4] Ivandini T A and Einaga Y 2012 Chem. Comm. 53 1338–47.
[5] Medina-Sánchez M, Mayorga-Martinez C C, Watanabe T, Ivandini T A, Honda Y, Pino F, Nakata K, Fujishima A, Einaga Y and Merkoçi A 2016 Biosens. Bioelectron. 75 365–74.
[6] Lou T, Qiang H and Chen Z 2017 Talanta 163 132–9.
[7] Tian R H and Zhi J F 2007 Electrochem. Commun. 9 1120–6.
[8] Ivandini T A, Saepudin E and Einaga Y 2015 Anal. Sci. 31 643–9.
[9] Zhang J, Xu X, Yang C, Yang F and Yang X 2011 Anal. Chem., 83 3911–7.