Modification of boron-doped diamond with gold-palladium nanoparticles for CO\textsubscript{2} electroreduction

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Abstract. Modification of boron-doped diamond (BDD) with gold-palladium nanoparticles (AuPdNPs) was performed for an application in electrochemical reduction of CO\textsubscript{2}. Preparation of the colloidal AuPdNPs involved two steps, including the synthesis of gold nanoparticles (AuNPs) and the growth of palladium on the surface of AuNPs. BDD, which had been terminated with allylamine under UV light irradiation for 6 h, then, was immersed in the colloidal AuPdNPs. Characterization of the nanoparticles by using Tunneling Electron Microscopy (TEM) showed flowers-like nanoparticles with an average size of 40 nm, while characterization of the modified BDD showed the Au and Pd surface coverage of 4.4 \% and 6.0 \%, respectively, on BDD surface. The electrochemical reduction of CO\textsubscript{2} at the modified BDD was performed in a two-compartment cell with 0.1 M NaCl solution in the cathode chamber and 0.1 M Na\textsubscript{2}SO\textsubscript{4} solution in the anode chamber. By applying the potential -0.9 V (vs. Ag/AgCl) in the system for 60 min, it showed the faradaic efficiency of the system at approximately 84.65 \% with acetic acid as one of the products.

Keywords: CO\textsubscript{2} electroreduction, gold-palladium, boron-doped diamond, surface modification.

1. Introduction

The increase of CO\textsubscript{2} concentration in atmosphere attracts the attention of scientists to convert CO\textsubscript{2} into value added products like CH\textsubscript{4}, HCOOH, \text{CH}_2\text{COOH} and CH\textsubscript{3}OH [1]. Boron-doped diamond (BDD) is one of the promising electrodes for CO\textsubscript{2} conversion, due to its wide range of working potential as well as chemically and mechanically high inertness [2]. Research on the electrochemical conversion of CO\textsubscript{2} was firstly reported by Hori et al. [3] who reported the conversion of CO\textsubscript{2} into formic acid using some types of working electrodes, such as lead, indium, cadmium and tin. Meanwhile, BDD had been applied for electroreduction of CO\textsubscript{2} to produce formaldehyde and formic acid with high Faradaic efficiency [4]. Furthermore, modification of BDD with some metals for electrochemical reduction of CO\textsubscript{2} had also been reported with some promising results [5,6].

On the other hand, metal nanoparticles are interesting due to their unique properties in optical, catalytic, electronic and magnetic characteristics. Among various nanostructures, flower is one of an attractive shape because it has an anisotropic structure, which not only provides optical capability but also serves as a catalyst where the activity and selectivity depend on its morphology [7-8]. Moreover, nanoparticles of bimetallic metals, such as AuPd, have been reported to provide a higher catalytic activity than both of its mono metals, i.e. Au and Pd nanoparticles [9]. AuPd nanoparticles were also reported as superior catalyst in trichloroethylene hydrodechlorination [10] as well as in the electrolytic study of CO\textsubscript{2} to produce hydrocarbons with C\textsubscript{2} to C\textsubscript{5} [11,12].

In this study, gold-palladium core-shell nanoparticles were prepared to modify the BDD electrode in order to study the catalytic effect of composite AuPd-modified BDD in electrochemical conversion of CO\textsubscript{2}.
2. Experimental section

2.1. Materials and instruments
BDD with a B:C ratio of 1:1000 was prepared by using microwave plasma-assisted chemical vapor deposition [13]. Both gold and palladium precursors (HAuCl$_4$·4H$_2$O and PdCl$_2$) were purchased from WAKO chemicals, Japan, while sodium citrate, ascorbic acid, sodium chloride, allylamine and other chemicals were purchased from Sigma-Aldrich.

Electrochemical parameters were conducted using a three-electrodes cell by using a potentiostat (EDAQ E-Corder 410). A platinum wire (Nilaco, Japan) was used as the counter electrode, while an Ag/AgCl system (BAS Inc., Japan) as the reference electrode. Some instruments were used to characterize the nanoparticles and the BDD surface, including UV-Vis spectrophotometry (Thermo Scientific Multisam Go), Transmission Electron Microscopy (TEM) (Microscope Tecnai 200 kV D2360 SuperTwin), and Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX) (JEOL/EO JCM-6000Plus, Japan).

2.2. Preparation of AuPd-modified BDD electrode
AuPd nanoparticles (AuPdNPs) was prepared through the gold seed mediated method as previously reported with some modification [14]. Briefly, 30 mL of colloidal AuNP was added into 15 mL of 1.0 mM H$_2$PdCl$_4$ and ultrapure water of 5 mL. The mixture was cooled at 4 °C in ice bath, then 6 mL of 10 mM ascorbic acid was added and stirred for around 15 min to obtain purple colloid [15]. Prior to modification, the BDD surface was changed into N-terminated BDD (N-BDD) by immersing in allylamine under UV light irradiation ($\lambda = 254$ nm) [16]. The N-BDD was then immersed in the prepared colloidal AuPdNPs for 12 h to attach the nanoparticles on the surface of BDD.

2.3. Electroreduction of CO
The electrochemical experiments were carried out in a cell with two compartments with the AuPdNPs-modified BDD was used as the working electrode. Chronoamperometric method was applied. The electrolytes in the anodic chamber (0.1 M Na$_2$SO$_4$) and in the cathodic chamber (0.1 M NaCl) were saturated with N, for 30 min. Then, the one in the cathodic chamber was bubbled with CO, for 60 min. The applied potential of -0.9 V (V vs. Ag/AgCl) was conducted. The products were then analyzed using HPLC and GC.

3. Results and Discussion

3.1. Synthesis of AuPdNPs
AuPdNPs were synthesized using seeds mediated growth method, in which gold nanoparticles (AuNPs) were used as the core for palladium growth. Solution of H$_2$PdCl$_4$ was used as the precursor of Pd. When NaBH$_4$ solution was added, PdCl$_2$ ions were reduced to form PdNPs. Figure 1a shows UV-
Figure 2. SEM images (with 2000 times magnification) (a) BDD and (b) AuPd-BDD

Vis spectra of the colloidal of AuNPs, palladium nanoparticles (PdNPs), and AuPdNPs. The figure shows that AuNPs has a typical absorption in the visible region of 552 nm, reflecting the surface plasmon resonance of AuNPs [15]. This peak was not found in the spectrum of PdNPs nor at AuPdNPs. Therefore, the formation of AuPdNPs was predicted due to the covering of PdNPs at the AuNPs core. The results in figure 1b showed flowers-like AuPdNPs, confirming that the synthesized AuPdNPs was core-shell nanoparticles, with Au as the core and Pd as the shell.

Meanwhile, the TEM characterization of AuPdNPs was applied to determine the size and shape of the particles. Figure 1b shows the enriched palladium clusters attached onto the seeds of gold surface, forming a core-shell AuPd nanoparticle in flower-like shape. The average particle size of AuPdNPs was around 40 nm.

3.2. Characterization of AuPd-modified BDD by using SEM-EDS

SEM-EDS characterization of AuPd-BDD was performed to study its morphology. Figure 2a shows typical of unmodified crystal grains of BDD. The average size of the crystal grain of BDD was approximately 8.2 μm. After immersing the BDD in the colloidal AuNPs (figure 2b), distribution of other conductive particles was clearly shown by the presence of brighter particles on the BDD surface, indicating that AuPdNPs could be deposited on the BDD surface.

Further characterization of the modified BDD using EDS confirmed that the surface of the modified BDD composed of carbon (65.25 %), oxygen (16.28 %), nitrogen (7.97 %), gold (4.42 %) and palladium (6.09 %), confirmed that the AuPd nanoparticles was successfully deposited on the BDD surface.

3.3. Electroreduction of CO

Cyclic voltammetry of BDD and AuPd-modified BDD in 0.5 M HSO₄ was performed; figure 3a shows the difference between BDD and AuPd-modified BDD. While on the unmodified BDD surface it shows neither oxidation nor a well-defined reduction peak in the potential range of -2.0 to +1.0 V (vs. Ag/AgCl), a typical oxidation peak of gold was observed at around 0.0 V at AuPd-modified BDD. In addition, a reduction peak at around -1.3 V was also observed at AuPd-modified BDD, which probably due to the reduction of oxygen [16].

In order to study the electrochemical behavior of CO₂, cyclic voltammetry of CO₂ in 0.1 M NaCl solution was investigated at AuPd-modified electrode. Prior to the measurement, N₂ was bubbled into the solution to remove other possible impurity gas. Then, CO₂ was dissolved into the solution. Figure 3b shows the cyclic voltammograms (CVs) of the solutions with and without the presence of CO₂. The CVs with the presence of CO₂ showed a typical sharp reduction peak at around -1.5 V. This peak increased with the increase of the bubbling time of CO₂, indicating a strong relation of the peak with electrochemical reduction of CO₂. Further, the optimum time CO₂ bubbling of 60 min was fixed for the next measurements as it generates maximum current response. Investigation in various pHs was also conducted and showed that the optimum pH was 3.7 (data was not shown).
Figure 3. CVs of (a) 0.5 M H₂SO₄ at unmodified BDD electrode (black line) in comparison with at AuPd-modified BDD (red line) and (b) 0.1 M NaCl solutions in the presence of dissolved CO₂ with various bubbling times.

The electrochemical reduction of CO₂ was performed in an electrochemical cell with two compartments separated by Nafion® membrane. A solution of 0.1 M NaCl was placed in the cathode chamber, while 0.1 M Na₂SO₄ solution was in the anode chamber. Electrochemical reductions were conducted by using chronoamperometric technique at the potential of -0.9 V in order to perform direct CO₂ reduction on the electrode surface. The liquid products were characterized by using HPLC, while the gas products were analysed by gas chromatography. The results showed that although the products mostly contained hydrogen gas, acetic acid and formic acid can be produced at around 9.77% and 41.23% of faradaic efficiency (FE), indicating that the AuPd-modified BDD is promising for an application in CO₂ reduction.

4. Conclusions

Boron-doped diamond (BDD) was successfully modified with gold-palladium nanoparticles (AuPdNPs) by immersing a nitrogen-modified BDD in colloidal AuPdNPs with surface composition of 65.25% carbon, 16.28% oxygen, 7.97% nitrogen, 4.42% gold, and 6.09% palladium. The AuPdNPs modified BDD can electrochemically convert the CO₂ at -0.9 V into acetic acid and formic acid with the faradaic efficiency of 9.77% and 41.23%, respectively.

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