Modification of boron-doped diamond electrodes with platinum-iridium for carbon dioxide electroreduction

S R Atriardi, R K P Dewandaru, J Gunlazuardi 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) is reportedly a good electrode material for the electroreduction of CO₂ to produce formaldehyde with high Faradaic efficiency. In this study, BDD electrodes were modified with a platinum-iridium composite (Pt-Ir). Deposition of Pt-Ir on the surface of BDD was performed by two different methods. One method involved the modification of the BDD surface, wherein terminal-H atoms were substituted with N atoms. The N-terminal BDD was then immersed in a Pt–Ir nanoparticle solution to form Pt–Ir–BDD (1). The Pt–Ir nanoparticles were synthesized from a 3:4 molar ratio mixture of H₂PtCl₆ and K₂IrCl₆ by a hydrothermal method. Characterization of Pt–Ir nanoparticles by using UV-Vis spectrophotometry and Transmission Electron Microscopy (TEM) image showed an absorbance peak at 420 nm with an average particle size of 2.6±0.6 nm. In the second method, Pt-Ir was deposited onto BDD using chemically assisted electrodeposition by applying a reduction potential of −0.5 V (vs. Ag/AgCl) to form Pt–Ir–BDD (2). Scanning Electron Microscope (SEM) images showed that the second method provides better distribution of Pt–Ir on the BDD surface. Furthermore, cyclic voltammetry of CO₂, dissolved in 0.1 M NaCl showed a reduction potentials at 1.7, 1.3, and 1.2 V (vs. Ag/AgCl) at BDD, Pt–Ir–BDD (1) and Pt–Ir–BDD (2), respectively, indicating that modification with Pt-Ir allows the conversion of CO with higher Faradaic efficiency.

Keywords: Boron-doped diamond, iridium, platinum, surface modification, CO₂ electroreduction

1. Introduction
Global warming is caused by industrial emission of greenhouse gases (GHGs), such as COₓ, NOₓ, SOₓ, CFCs, and CH₄, and has many negative environmental effects. Carbon dioxide (CO₂) is the most abundant GHG in the atmosphere, accounting for ≈65% of total atmospheric GHGs [1]. Therefore, reducing atmospheric CO₂ levels is imperative if the impact of global warming is to be limited.

Electrochemical conversion is a promising technique for the removal of atmospheric CO₂. Furthermore, it can be used to produce a range of possible products. However, electrochemical reduction of CO₂ requires the development of suitable electrode materials. One such material is boron-doped diamond (BDD), which has many advantages over other electrode materials, including its extremely wide potential window and very low capacitance as well as its high chemically inertness and physical durability [2]. The use of BDD for CO₂ electroreduction in methanol solution has been reported to afford formaldehyde with a high faradic efficiency (74%) [3].

Platinum is known to be an excellent catalyst for a range of processes, largely owing to its large surface area. However, the catalytic effectiveness of platinum can be increased by compositing it with other metals to form platinum-based multimetallic composites (Pt-X, X = Cu, Au, Ag, etc.) [4]. These composites exhibit different optical, electronic, thermal, and catalytic characteristics to their...
monometallic counterparts. For example, platinum–iridium (Pt–Ir) provides significantly higher current density in comparison with that of Pt metal alone [5] and has been successfully applied to nitrate electroreduction, in which it exhibits higher activity than pure Pt or Ir metal [6]. Accordingly, in the current study, BDD electrodes were modified with Pt–Ir nanoparticles (NPs) as a means to improve their ability to convert CO to bulk products. Similar strategies involving the modification of BDD electrodes with Pt and IrO have proven to be effective previously [7,8].

2. Experimental

2.1. Materials and instruments

BDD electrodes with a B:C ratio of 1:1000 (i.e., 0.1% BDD) were fabricated using microwave plasma-assisted chemical vapor deposition at the Faculty of Science and Technology, Keio University, Japan. Hydrogen hexachloroplatinate (IV) (HPlCl), potassium hexachloroiridate (IV) (KIrCl), and sodium borohydride (NaBH) were purchased from Wako Pure Chemical Industries Ltd. Sodium hydroxide (NaOH), sodium chloride (NaCl), 2-propanol, and formaldehyde were purchased from Merck. Sulfuric acid (JT Baker), allylamine (Sigma Aldrich), CO, N, and ultra-pure deionized water from a Millipore Direct® Q5-UV with a resistivity of 18.2 MΩcm were also used.

Electrochemical measurements were performed using a three-electrode cell (eDAQ e-corder 410). A platinum wire and an Ag/AgCl reference electrode were used in a saturated KCl solution as the counter and the reference electrodes, respectively. Other techniques used in this research were UV-Vis spectrophotometry (Thermo Scientific Multiscan Go), a transmission electron microscopy (TEM) (Tecnai 200kV D2360 SuperTwin), scanning electron microscopy (SEM) (JEOL/EO JCM-6000Plus, Japan), and energy dispersive X-ray analysis (EDX).

2.2. Preparation of Pt–Ir-BDD electrodes

2.2.1. Synthesis of platinum-iridium NPs and preparation of Pt–Ir–BDD (1). Synthesis of platinum-iridium nanoparticles (Pt–Ir NPs) was conducted using a hydrothermal method as previously described [5] with some modifications. Briefly, 1 mM HPlCl (15 mL) and 1 mM KIrCl (20 mL) were mixed and boiled with stirring until the volume of the mixture was reduced to 10 mL. Then, the mixture was transferred to an autoclave containing 5% formaldehyde (0.5 mL) and heated at 180°C for 10 h. Separately, a BDD electrode was converted into an N-terminated BDD electrode by the addition of allylamine to the BDD surface under illumination with a UV lamp (λ = 254 nm) [9,10]. Pt–Ir–BDD (1) was prepared by the immersion of the N-terminated BDD into a Pt–Ir NP solution for 12 h.

2.2.2. Preparation of Pt–Ir–BDD (2). The deposition of Pt–Ir NPs onto the BDD surface involved two steps: (1) wet-chemical deposition of uniformly distributed Pt–Ir seeds and (2) electrochemical overgrowth of the Pt–Ir seeds [11]. First, a solution of 1.0 M NaBH, in 0.1 M NaOH (10 μL) was dropped at the BDD surface to allow the adsorption of BH ions. The formation of Pt–Ir seeds was performed by then adding a drop (40 μL) of 1 mM HPlCl:KIrCl (3:4 molar ratio) solution onto the adsorbed NaBH. The electrode was then rinsed with water and dried under flowing N. Repeating this process three times resulted in the generation of bigger Pt–Ir seeds and higher surface coverage. Electrochemical overgrowth of these Pt–Ir seeds was conducted at a constant applied potential of −0.5 V (vs. Ag/AgCl) for 10 min in 1 mM HPlCl:KIrCl solution (3:4 molar ratio).

2.3. CO electroreduction

Electrochemical reduction of CO, was performed in a three-electrode cell. A solution of 0.1 M NaCl was used as the electrolyte. BDD, Pt–Ir–BDD (1), or Pt–Ir–BDD (2) was used as the working electrode, while Ag/AgCl and Pt spiral wire was used as the reference and the counter electrodes, respectively. Then, the electrolyte solution was aerated with N, for 15 min to remove other gases, followed by CO aeration. Then, the electrochemical reduction of CO, was assessed using cyclic voltammetry (CV) analysis over the potential range 1.0–2.0 V (vs. Ag/AgCl).
3. Results and Discussion

3.1. Synthesis of Pt–Ir NPs
Pt–Ir NPs were successfully synthesized from 1 mM H₂PtCl₆·K₂IrCl₆ (3:4) precursor solutions using a hydrothermal method. The addition of formaldehyde was employed to reduce Pt(IV) to Pt(0) and Ir(VI) to Ir(0). The process is expressed by the following reactions [5]:

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\begin{align*}
H_2PtCl_6 + HCHO + H_2O &\rightarrow Pt + CO_2 + 6H^+ + 6Cl^- \\
K_2IrCl_6 + HCHO + H_2O &\rightarrow Ir + CO_2 + 4H^+ + 2K^+ + 6Cl^- 
\end{align*}
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Figure 1a shows the results of UV-Vis characterization for different NPs, with the absorbance peak for the Pt–Ir NPs visible at 420 nm. However, Pt NPs do not present peaks and Ir NPs present a peak at 405 nm. The optical properties of these NPs are highly dependent on their diameters [12]. The TEM image of the Pt–Ir NPs shows that they are well distributed and sometimes agglomerated (figure 1b). The average particle size of the Pt–Ir NPs is 2.6 ± 0.6 nm (figure 1c).

The EDX spectrum of the Pt–Ir NPs is given in figure 2, showing peaks corresponding to the investigated sample (Pt, Ir), clearly demonstrating that Pt–Ir NPs were successfully synthesized, as well as signals from the carbon-coated cooper TEM grid (C, Cu) and impurities from the nanoparticle synthesis (O).

3.2. Modification of BDD with Pt-Ir and its characterization
Pt–Ir–BDD (1) was prepared by immersing the N-terminated BDD surface into a Pt–Ir NP solution. Conversely, Pt–Ir–BDD (2) was prepared using a seeding technique with NaBH₄ as a reducing agent.
Figure 2. EDX spectrum of Pt–Ir NPs.

(a) (b) (c)

Figure 3. SEM Images (2000× magnification) of (a) BDD, (b) Pt–Ir–BDD (1), and (c) Pt–Ir–BDD (2).

Figure 4. CV characterization of BDD, Pt–Ir–BDD (1), and Pt–Ir–BDD (2) in 0.5 M HSO₄.

Figure 5. The influence of the aeration time of CO₂ into 0.1 M NaCl solutions on the pH values.

[11]. The Pt–Ir NP seeds deposited by this process were then enlarged using electrodeposition by applying a potential of −0.5 V. Figure 3 shows the surface morphologies of the BDD, Pt–Ir–BDD (1), and Pt–Ir–BDD (2) electrodes. Pt–Ir particles on BDD surface are observed with the white point on BDD surface. It can be seen that the Pt–Ir NPs prepared by the seeding method are more evenly distributed than those deposited by the immersion method.
CV analysis of the BDD electrodes in 0.5 M H₂SO₄ in figure 4 shows that they were successfully modified with Pt–Ir. A scan rate of 100 mV/s was applied throughout this study. The CV characteristics of Pt–Ir–BDD (1) and Pt–Ir–BDD (2) are similar, exhibiting hydrogen evolution at −0.3 V (vs. Ag/AgCl) and oxygen evolution at +1.5 V (vs. Ag/AgCl), as well as reduction-oxidation peaks for Pt and Ir (figure 4).

3.3. Preliminary study of CO₂ electroreduction
To reduce CO₂, it was dissolved in 0.1 M NaCl solution. The bubbling of CO₂ was conducted for 15, 30, and 60 min. to identify the optimum CO₂ aeration time. The optimum aeration time of CO₂ was found to be 15 min, providing a solution pH of 3.8 (figure 5).

Furthermore, CV analysis of the CO₂ solutions at the different electrodes revealed reduction peaks at approximately −1.7 V (vs. Ag/AgCl) for BDD, −1.3 V (vs. Ag/AgCl) for Pt–Ir–BDD (1), and −1.2 V (vs. Ag/AgCl) for Pt–Ir–BDD (2) as shown in figure 6. The results indicated that the direct electrochemical reduction of CO₂ in 0.1 M NaCl solution is promising to be conducted at similar potentials using a chronoamperometric technique.

4. Conclusions
Pt-Ir NPs with an average size of 2.6 ± 0.6 nm were successfully synthesized using a hydrothermal method. Pt-Ir-BDD electrodes were successfully prepared by immersion in this Pt-Ir NP solution (Pt-Ir-BDD (1)) or by chemical seeding followed by electrodeposition (Pt-Ir-BDD (2)). However, the seeding method was found to provide a better distribution of nanoparticles than the immersion method. The potentials observed for CO electroreduction were −1.7 V (vs. Ag/AgCl) for BDD, −1.3 V (vs. Ag/AgCl) for Pt-Ir-BDD (1), and −1.2 V (vs. Ag/AgCl) for Pt-Ir-BDD (2).
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