Electrochemical Response of Diamond Electrode to Methylene Blue in Aqueous Solution

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The boron-doped diamond electrode with carrier density of \(5.5 \times 10^{19}/\text{cm}^3\) showed high electrochemical response to methylene blue in aqueous solution. The cathodic and anodic current peaks due to leuco-methylene blue / methylene blue redox system were observed clearly on the diamond electrode in the solution containing methylene blue with lower concentration than 10 \(\mu\text{M}\). It was also possible to detect methylene blue in the coexistence of another dye, brilliant blue FCF by using diamond electrode.

**Keywords**: Diamond Electrode, Methylene Blue, Amperometric Detection

1. Introduction

Boron-doped diamond (BDD) is actively used as functional electrode material because of its unique characteristics of wide potential window, low background current and high chemical stability. There are various reports concerning application of BDD electrode to detection of chemical species (\(^{11-15}\)), water treatment (\(^{16-20}\)), and ozone formation (\(^{21-25}\)).

In the present work, we are investigating on electrochemical monitoring and treatment of aqueous solution for the purpose of water purification. Dyes are included in commodities of food, medicine, clothes and cosmetics. Since they may cause pollution in water environment such as coloring and COD increasing, it is necessary to detect and analyze them in aqueous solution. As examination dye, we have chosen methylene blue which is widely used as reagent for medicine, coloring, redox reaction and photocatalytic ability test. Although concentration of methylene blue in water is usually estimated by absorption spectrum, it is not obtainable easily in the case of mixture of other dyes. The wavelength of maximum absorbance of brilliant blue FCF aqueous solution, 629 nm, is close to that of methylene blue solution, 665 nm. Therefore, it seems to be difficult to distinguish these dyes by spectroscopic method. In this case, electrochemical method based on amperometric technique may be expected for detection of methylene blue. We carried out detection of low concentration of methylene blue by using BDD electrode in order to know its utility in analysis of dyes in water.

2. Experimental

We used BDD film (PERMELEC ELECTRODE) deposited on silicon substrate by CVD. This film had the thickness of 2 \(\mu\text{m}\) and amount of boron doping of 1300 ppm. The film attached to a lead wire through gold ohmic contact was used as a BDD working electrode (surface area: 0.5 and 0.9 \(\text{cm}^2\)). A counter and a reference electrodes were a platinum and Ag/AgCl electrodes, respectively. The surface of BDD electrode was polished with alumina powder and washed with pure water in an ultrasonic bath before electrolysis. The temperature of electrolytic solution (volume: 30 mL) was kept at 25 \(\degree\text{C}\). Electrochemical measurement was based on cyclic voltammetry by a potentiostat-galvanostat (Hokuto, HA-151) equipped with a function generator (Hokuto, HB-105). The capacitance of BDD / electrolyte interface was measured by an LCR meter (Hioki, 3532 LCR HiTESTER) with frequency of 1 kHz. The absorption spectra of dye solution was measured by a UV-visible spectrophotometer (Shimazu, UV-1700).

3. Results and Discussion

From the measurement of Raman spectrum of BDD used here, the strong peak due to diamond structure at 1333 cm\(^{-1}\) was clearly observed and the peak due to non-diamond structure at 1530 cm\(^{-1}\) did not appear.

**Fig. 1** shows the relation between \(1/C^2\) and \(E\) for BDD electrode in 1.0 M KCl aqueous solution. \(C\) is the capacitance of BDD electrode / this electrolyte interface and \(E\) is electrode potential of BDD. The linear relation of Mott-Schottky plot that is shown as equation (1) was confirmed.

![Fig. 1](image_url) Relation between \(1/C^2\) and \(E\) of the BDD electrode in 1 M KCl aqueous solution.

\(C\): capacitance of the BDD electrode / electrolyte interface. \(E\): electrode potential of the BDD electrode.

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Note

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![Fig. 1](image_url) Relation between \(1/C^2\) and \(E\) of the BDD electrode in 1 M KCl aqueous solution.

\(C\): capacitance of the BDD electrode / electrolyte interface. \(E\): electrode potential of the BDD electrode.

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\[ \frac{1}{C^2} = \frac{2}{eNdd^2} (E - E_a) \]

\( e \) is quantity of charge on the electron, \( N \) carrier density, \( d \) dielectric constant of electrode material, \( d^2 \) permittivity of free space and \( E_a \) flat-band potential.

From the negative slope of the linear portion indicating the interface of p-type semiconductor electrode / electrolyte in Fig. 2, the value of \( N \) was estimated to be \( 5.5 \times 10^{19} / \text{cm}^3 \) by adopting dielectric constant of diamond of 5.7. This value was about 1/4 of 2.2 \( \times 10^{20} / \text{cm}^3 \) which was derived from the ratio of number of B atom to number of C atom equaling to 1300 : 10^6 in raw material. The value of flat-band potential in this case was 2.63 V vs. Ag/AgCl by extrapolating of the linear portion to potential axis. The more positive flat-band potential than 3.0 V vs. Ag/AgCl was reported on the BDD electrode treated anodically\(^{30}\). Pleskov et al. reported on the positive value of flat-band potential reflecting the oxidation state of the surface of BDD electrode\(^{37}\).

**Fig. 2** shows the cyclic voltammograms (first scan) of BDD (surface area: 0.5 cm\(^2\)), glassy carbon (surface area: 1.0 cm\(^2\)) and platinum (surface area: 0.8 cm\(^2\)) electrodes, respectively, in 0.01 M KCl aqueous solution containing 10 \( \mu \text{M} \) methylene blue. On the BDD electrode, the cathodic current peak and corresponding anodic peak were observed. These peaks are interpreted by the following reaction\(^ {20, 29}\):

\[ \text{C}_6\text{H}_5\text{SnNa}^- + \text{H}^+ + 2e^- \rightarrow \text{C}_6\text{H}_5\text{Sn} \]  \hspace{1cm} (2)

On both glassy carbon and platinum electrodes, the distinct current peaks did not appear. It seems to be difficult to detect low concentration of methylene blue by bare glassy carbon and platinum electrodes because of high background current on these electrodes. The much lower background current on BDD electrode might be due to the property of p-type semiconductor of BDD electrode in aqueous solution. The appearance of current peaks due to leuco-methylene blue / methylene blue system has been reported on glassy carbon electrode in the concentration of 50 \( \mu \text{M} \)\(^{30}\) and also on nanogold electrode in the concentration of 10 \( \mu \text{M} \)\(^{15}\).

**Fig. 3** shows the cyclic voltammograms of BDD electrode in 0.01 M KCl aqueous solution containing different concentration of 2, 4 and 6 \( \mu \text{M} \) methylene blue. The current peaks due to leuco-methylene blue / methylene blue system were observed in each solution. It has been reported that the gold electrode modified with 1-decanethiol could show this redox current peaks in the solution containing 3 \( \mu \text{M} \) methylene blue\(^ {32}\).

This figure also shows the relationship between cathodic current peak and concentration of methylene blue determined by using BDD electrode. It was possible to detect current peak with the magnitude below 1 \( \mu \text{A} \) on BDD electrode without necessity of chemical modification of the surface. This linear relation reflects possibility for amperometric determination of concentration of methylene blue in the range of 0-10 \( \mu \text{M} \). The plots of anodic current peak against concentration of methylene blue was not clear in linear relationship.

In order to check the utility of BDD electrode in detection of methylene blue, we examined the electrochemical response in aqueous solution containing mixture of methylene blue and brilliant blue FCF.

**Fig. 4** a and b show the absorption spectra of 0.01 M KCl aqueous solution containing different concentration of methylene blue in the absence and presence of 10 \( \mu \text{M} \) brilliant blue FCF, respectively. Since these dyes have similar absorption spectra, it may be difficult to distinguish methylene blue easily.

**Fig. 5** shows the voltammograms of BDD electrode (surface area: 0.9 cm\(^2\)) in 0.01 M KCl aqueous solution containing different concentration of 2, 6 and 10 \( \mu \text{M} \) of methylene blue and 10 \( \mu \text{M} \) brilliant blue FCF. The current peaks due to leuco-methylene blue / methylene blue system was observed in each solution and a linear relation between the cathodic peak and concentration of methylene blue was confirmed as shown in this figure. It was also possible to detect methylene blue in the solution of dye mixture of methylene blue and crystal violet by using BDD electrode.
5. Summary

The cathodic and anodic current peaks at the potential of $-0.16 \text{ V}$ and $-0.11 \text{ V}$ vs. Ag/AgCl, respectively, due to leuco-
methylene blue / methylene blue redox process could be detected
on BDD electrode in aqueous solution containing methylene blue with lower concentration than $10 \mu \text{ M}$. The BDD electrode
showed the clear electrochemical response to methylene blue in the
case of coexistence of brilliant blue FCF. In aqueous solution
containing Eosin Y, we have also obtained the results of linear
dependence of anodic current peak at $+0.90 \text{ V}$ vs. Ag/AgCl
upon dye concentration. A simple and rapid detection of dyes in
water based on electrochemical technique will be expected by
further understanding of anodic and cathodic processes of vari-
os dyes on BDD electrode.

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Fig. 4 Absorption spectra of 0.01 M KCl aqueous solution containing
different concentration of 2, 6 and $10 \mu \text{ M}$ of methylene blue in the
absence (a) and presence (b) of $10 \mu \text{ M}$ brilliant blue FCF

Fig. 5 Cyclic voltammograms (first scan) of BDD electrode in 0.01 M
KCl aqueous solution containing different concentration of 2 $\mu \text{ M}$,
6 $\mu \text{ M}$ and $10 \mu \text{ M}$ of methylene blue and $10 \mu \text{ M}$ brilliant blue FCF
and relation between cathodic current peak and concentration of
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Scan rate: 10 mV/s.
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