Anodic stripping voltammetry of nickel ions and nickel hydroxide nanoparticles at boron-doped diamond electrodes

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Abstract. Anodic stripping voltammetry (ASV) of nickel ions in phosphate buffer solution (PBS) have been investigated at boron-doped diamond (BDD) electrodes. The deposition potential at 0.1 V (vs. Ag/AgCl) for 300 s in 0.1 M PBS pH 3 was found as the optimum condition. The condition was applied for the determination of nickel contained in nickel hydroxide nanoparticles. A linear calibration curve can be achieved of Ni(OH)₂-NPs in the concentration range of x to x mM with an estimated limit of detection (LOD) of 5.73 x 10⁻⁶ mol/L.

Keywords: Boron-doped diamond, melamine, Ni(OH)₂ nanoparticles, strip test immunokromatografi

1. Introduction
Anodic stripping voltammetry (ASV) using boron-doped diamond (BDD) electrodes have been reported as a superior technique for trace metals detection, including metal ions and metal nanoparticles. The stability of BDD with its sp³ carbon contributes to the high reproducibility of the measurements [1-5]. On the other hand, the development of sensor and biosensor employing metal nanoparticles as the probe is growing fast because of the excellence of this material, including the possibility to miniaturize the devices as well as the high sensitivity of optical and electrochemical signals, which induces to the high precision and accuracy of measurements [6-8].

In this study, ASV of nickel ions and nickel nanoparticles has been studied. Ni(OH)₂ is widely applied in electrochemistry due to its earth-abundant nature and its catalytic activity [9]. However, its application for a probe in sensors and biosensors are very limited. Meanwhile, synthesis of Ni(OH)₂ nanoparticles was reported [10]. ASV of nickel ions and nanoparticles showed that selective detection can be performed, indicated the possibility to apply the nanoparticles for a probe in sensors and biosensors.

2. Materials and methods
2.1. Anodic stripping voltammetry (ASV) of Ni(NO₃)₂ using BDD electrode
ASV of Ni(NO₃)₂ was performed in 0.1 M phosphate buffer solution (PBS) with a BDD films as the working electrode. Pt wire and Ag/AgCl system were used as the counter and the reference electrodes,
respectively. Parameters of pH, potential deposition and deposition times were investigated. Linear calibration curves were performed in a concentration range from 5 to 200 mM.

2.2. Preparation of Ni(OH)$_2$ nanoparticles
Ni(OH)$_2$ nanoparticles were synthesized by complexation-precipitation method on hydrothermal condition. Mechanism reaction was estimated to occur through the formation of nickel-citrate complex, followed by disassociation of the complex in the presence of NaOH solution to form Ni(OH)$_2$-NPs in hydrothermal condition [10].

2.3. Synthesis Ni(OH)$_2$ nanoparticles (Ni(OH)$_2$-NPs)
Ni(OH)$_2$-NPs was synthesized based on the previous study [10]. Briefly, a volume of 10 mL Ni(NO$_3$)$_2$ solution was mixed with 10 mL of 2.86 x 10$^{-2}$ M NaBH$_4$ solution, then added by 5.71 x 10$^{-1}$ M C$_6$H$_5$NaO$_7$. The mixture was stirred at 35°C for 10 h. Then, 5 mL of NaOH solution was added and continuously stirred for 5 min. Subsequently, the mixture was put into an autoclave and heated at a temperature of 120°C for 24 h. The synthesized Ni(OH)$_2$-NPs were characterized using UV-Vis spectrophotometer, FTIR, and TEM.

3. Results and discussion

3.1. Anodic stripping voltammetry of Ni(NO$_3$)$_2$
ASV is basically performed in two steps, including the pre-concentration and the stripping steps of the metal analytes. At the pre-concentration step, Ni$^{2+}$ was expected to be Ni$^0$, while Ni$^0$ can be oxidized to be Ni$^+$ or Ni$^{2+}$ at the stripping step. Therefore, ASV of Ni$^{2+}$ at BDD electrodes was investigated at pH 3, 4, and 5 because Ni$^0$ can be immediately oxidized and produce sufficient oxidation current responses in acidic condition. Two oxidation peaks at around +0.4 V and +1.1 V (vs. Ag/AgCl), attributed to the oxidation of Ni$^0$ to Ni$^+$ and Ni$^{2+}$, respectively, were observed at all pHs of 3, 4, and 5. The peak at +1.1 V and pH 3 was selected since it generates the highest current. Furthermore, potential depositions were varied from 0 to -700 mV for 60 s with a scan rate of 100 mV/s, suggested the optimum condition at -100 mV. The deposition times were varied from 0 to 300 s at deposition potential of -100 mV, suggested the optimum time at 300 s. In addition, scan rate dependence was also investigated, which revealed that 100 mV/s was the optimum scan rate. Based on the result, a linear calibration curve can be achieved in the concentration range of 5-200 mM in the optimum condition (figure 1).

UV-Vis spectrum of Ni(OH)$_2$-NPs in figure 2a reflects a peak at 220-230 nm, which conforms the criteria of Ni(OH)$_2$-NPs characteristic [10]. This absorption peak shifted from those of Ni(NO$_3$)$_2$

![Figure 1](image-url)
solution, indicated that Ni^{2+} ions has changed. Investigation of FTIR spectra (figure 2b) shows a broad absorption at the wavenumber around 3600 cm^{-1} and a strong peak at 1650 cm^{-1}, indicated the vibration stretching of O-H and asymmetrical stretching of carbonyl functional group (C=O), respectively. In addition, symmetrical stretching C=O was also observed as a results of the trisodium citrate excess in the sample. Furthermore, TEM image shows that the Ni(OH)$_2$-NPs were hexagonal crystals with an average size of 14 nm (figure 2c).

3.2. Anodic stripping voltammetry of Ni(OH)$_2$ nanoparticles

Determination of the nanoparticles was performed using the optimum condition described in section 3.1. Solution of 0.1 M PBS pH 3 was used as the electrolyte. A deposition potential of -100 mV was applied for 300 s with the scan rate of 100 mV/s. Figure 3a shows the voltammograms of various concentrations of Ni(OH)$_2$ nanoparticles with the linear calibration curve in figure 3b. High linearity (R$^2$ = 0.99) with an estimated LOD of 0.057 mM could be achieved, indicating that the method can be applied for the detection method employing Ni(OH)$_2$ nanoparticles as a probe.

4. Conclusions

Anodic stripping voltammetry of nickel at boron-doped diamond electrodes have been investigated. A deposition potential of -100 mV for 300 s with a scan rate of 100 mV/s applied in a solution of 0.1 M PBS pH 3 was found to be optimum condition. The method was successfully applied for the determination of Ni(OH)$_2$ nanoparticles, indicating that application of this nanoparticles is promising for a probe in sensors and biosensors.
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