Reductive Molecular Transformations on Vitamin B_{12} Modified Electrode

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Functionalization of electrode surface has stimulated continuing interest in a wide range of chemical areas because of its significance utilities for catalyst, sensor, and microelectronic devices. Especially modification with metal complex provided a good catalyst for electroorganic syntheses. Such modified electrodes are generally considered to hold many advantages, such as utilization of small amounts of catalyst species, readily separation of products, and performance of specific electroorganic syntheses. Previously, we reported the some methods for immobilization of vitamin B_{12} derivatives[1] onto electrode surface.[2, 3] Unfortunately, in these methods a stability of modified electrode is not so high because of noncovalently weak interaction between complex and electrode. Such problem abets us to prepare covalently bounded B_{12} modified electrode for practical use. In this paper, we report the synthesis of a new hydrophobic vitamin B_{12} derivative which has a trimethoxysilyl group at a peripheral position, and the complex was covalently immobilized onto platinum electrode surface.

A hydrophobic vitamin B_{12} derivative (**1**) was synthesized by the reaction between a hydrophobic vitamin B_{12} having monocarboxylic acid and 3-(trimethoxysilyl)propylamine. Immobilization of **1** onto Pt electrode was carried out as follows. (see Fig. 1) An anodization of bared Pt plate (area 1 cm^2) in 0.5 M H_2SO_4 at +1.9 V vs. Ag/AgCl for 5 min give platinum oxide layer. Thus formed plate was immersed into a 5 mM solution of **1** in dry toluene for 30 min under nitrogen atmosphere. After the plate was taken from the solution, it was rinsed with toluene (2 times), dichloromethane (2 times), and ethanol (2 times) to remove any physisorbed material. The modified electrode was dried (aged) for 12 h at 80 °C.

The electrode surface was characterized by X-ray photoelectron spectroscopy (XPS) experiments. The XPS peaks at 153.5, 284.8, 398.8, 531.8, and 779.8 eV were observed, which could be attributed to Si, C, N, O, and Co, respectively. The distribution of these atoms is coincided with that for **1**. This XPS result indicated clearly that the hydrophobic vitamin B_{12} was successfully immobilized onto the Pt plate.

The Co(II) species of hydrophobic vitamin B_{12} is electrochemically active and exhibits reversible Co(II)/Co(I) redox couple at −0.72 V vs. Ag/AgCl in DMF as shown in Fig. 2. The corresponding redox potential for heptamethylcobyrinate perchlorate in DMF is −0.62 V vs. Ag/AgCl. The apparent coverage of the surface with the immobilized **1** was evaluated by the charge under the reductive Co(II)/Co(I) wave in cyclic voltammetry; 1.60×10^{-10} mol cm^{-2}. The Co(I) form of hydrophobic vitamin B_{12} is supernucleophile and reacts with various organic halides. The controlled-potential electrolysis of phenetyl bromide was carried out using the B_{12} modified electrode in DMF at −1.4 V vs. Ag/AgCl, and the products were analyzed by GC-MS. After the electrical charge passed 1 F/mol based on the initial concentration of substrate, 56 % of styrene was selectively formed. Turnover number based on B_{12} catalyst immobilized onto the electrode was over 15,000. Of course, the reaction did not proceed when we used a bared Pt electrode under the same conditions.

In summary, hydrophobic vitamin B_{12} derivative is covalently bounded onto Pt electrode efficiently, and the complex maintained the electrochemical activity. Some organic halides are known as environmental pollutants, therefore the degradation of such compounds is important in the viewpoint of green chemistry.

References

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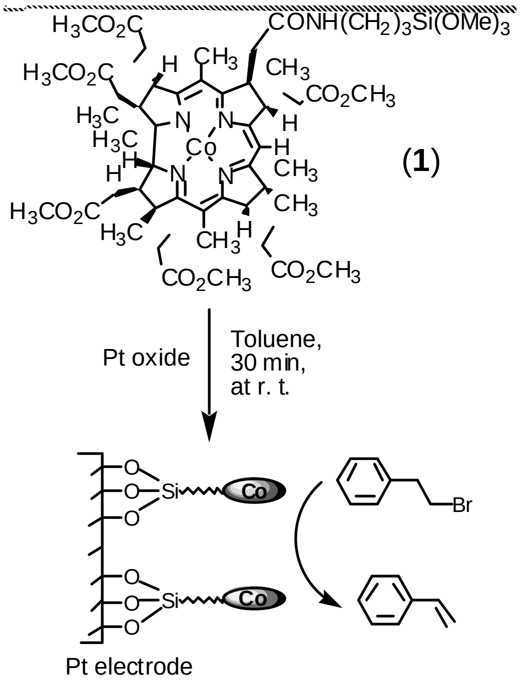

Figure 1. Preparation of B_{12} modified electrode and the molecular transformation on the electrode.

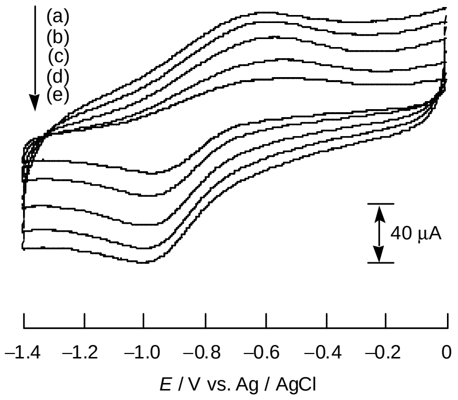

Figure 2. Cyclic voltammograms of **1** immobilized Pt electrode in DMF containing of 0.1 M $n\mathrm{Bu}_4\mathrm{ClO}_4$ at different scanning rates. Scan rate (a) 400, (b) 300, (c) 200, (d) 100, (e) 50 mV s^{-1}.