

Hydrophobic vitamin B₁₂. Part 18. † Preparation of a sol–gel modified electrode trapped with a vitamin B₁₂ derivative and its photoelectrochemical reactivity

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Received 2nd January 2003, Accepted 11th April 2003

First published as an Advance Article on the web 29th April 2003

A vitamin B₁₂ derivative, heptapropyl cobyrinate perchlorate, was readily trapped onto an indium tin oxide (ITO) electrode by a sol–gel reaction. The complex was physically retained in a silica gel film which is formed on an ITO electrode. The thickness of the film could be controlled by the withdrawing speed of the dip coating process. Formation of a sol–gel film was confirmed by SEM measurements, and the total amount of the complex in the film was determined by UV–VIS absorption spectra. The complex exhibits the Co^{II}/Co^I redox couple at -0.42 V vs. Ag–AgCl. The amount of the electroactive complex in the sol–gel film deduced from electrochemical measurements is 3.0×10^{-11} and 6.2×10^{-11} mol cm⁻² for thicknesses of 170 and 330 nm, respectively. This electroactive complex shows a high reactivity towards organic halides, and the controlled-potential electrolysis of benzyl bromide using the sol–gel modified electrode at -1.20 V vs. Ag–AgCl in aqueous solution containing 0.1 M KCl afforded dehalogenated products, bibenzyl and toluene, with a total turnover number of >1000 for 1 h.

Introduction

Vitamin B₁₂-dependent enzymes, involving a cobalt species as the catalytic center, mediate various reactions.¹ In order to simulate the catalytic functions of vitamin B₁₂ as exerted in the hydrophobic active sites of enzymes concerned, we have been dealing with hydrophobic vitamin B₁₂ derivatives which have ester groups in place of the peripheral amide moieties of the naturally occurring vitamin B₁₂,² and succeeded in performing various electroorganic reactions such as 1,2-migration of functional groups,^{3–10} asymmetric reactions,^{11–13} ring-expansion reactions,¹⁴ and synthesis of large-membered macrocyclic lactones¹⁵ using hydrophobic vitamin B₁₂ derivatives as a catalyst in organic solvents. In a recent development of electroorganic chemistry, it is considered that the immobilization of catalysts onto an electrode has many advantageous features such as utilization of small amounts of catalyst species, ready separation of products, and application to specific electro-organic syntheses.¹⁶ With this viewpoint, we and other groups reported some methods for immobilization of vitamin B₁₂ derivatives onto electrodes,^{17–22} and performed various electroorganic reactions. Unfortunately, all of these methods require a specific modification of the electrode surface so that a tedious procedure is needed for the preparation of the modified electrode. In contrast to these methods, the sol–gel method is a convenient technique for incorporation of various compounds into sol–gel films.^{23–26} There is no need for a pretreatment of the electrode, and it is easy to trap various compounds simply by co-mixing. In this paper, we report the incorporation of a vitamin B₁₂ derivative onto an indium tin oxide (ITO) electrode using the sol–gel method as shown in Fig. 1 and examine the catalytic activity for the dehalogenation of an organic halide.

Experimental

Materials

All solvents and chemicals used in the syntheses were of reagent grade and were used without further purification. Tetra-

ethoxysilane (TEOS, Shin-etsu Chemicals) was used after distillation under reduced pressure. Absolute ethanol was used after distillation. Heptamethyl cobyrinate perchlorate, [Cob(II)7C₁ester]ClO₄, and heptapropyl cobyrinate perchlorate, [Cob(II)7C₃ester]ClO₄, were synthesized by the previously reported method.^{2,27} The ITO-coated glass plates (5 × 50 mm) and the slide glass substrate were cleaned by sonication in 30% H₂O₂ aqueous solution for 30 min followed by sonication in ethanol for 1 h at 30 °C, and then dried with nitrogen gas.

Preparation of the sol–gel modified electrode

The silica gel films were prepared by hydrolysis and condensation of TEOS. A typical silica solution was prepared by mixing TEOS (0.62 g, 3.0 mmol), 0.1 M aq. HCl (0.22 g, 12 mmol), ethanol (1.11 g, 24 mmol) and [Cob(II)7C₃ester]ClO₄ (40.5 mg, 3.0×10^{-2} mmol) for 24 h at room temperature. The resulting solution was deposited on a freshly cleaned ITO electrode or a slide glass substrate (Matsunami Glass Industries) by dip coating at withdrawing speeds of 50 and 100 mm min⁻¹. The silica gel film formed on the substrate was dried (aged) for 12 h at 80 °C.

General analyses and measurements

The UV–VIS absorption spectra were measured on a Hitachi U-3300 spectrophotometer at room temperature, and a silica glass slide with undoped gel film was used as a reference. The EPR spectra were obtained on a JEOL JES-FE1G X-band spectrometer equipped with an Advantest TR-5213 microwave counter and an Echo Electronics EFM-200 NMR field meter. The sol solution containing [Cob(II)7C₃ester]ClO₄ was poured onto a glass plate, and the solvent was evaporated at 80 °C to form a red film. This film was dried under reduced pressure in the EPR cell, and the EPR spectrum was obtained at 77 K. The GLC analyses were carried out on a Shimadzu GC-9A apparatus equipped with a Shimadzu C-R6A Chromatopac. The GC-MS was obtained using a Shimadzu QP5050A. Scanning electron micrographs (SEMs) were recorded on a Hitachi S-5000 (HV = 25 kV) installed at the Centre of Advanced Instrumental Analysis, Kyushu University.

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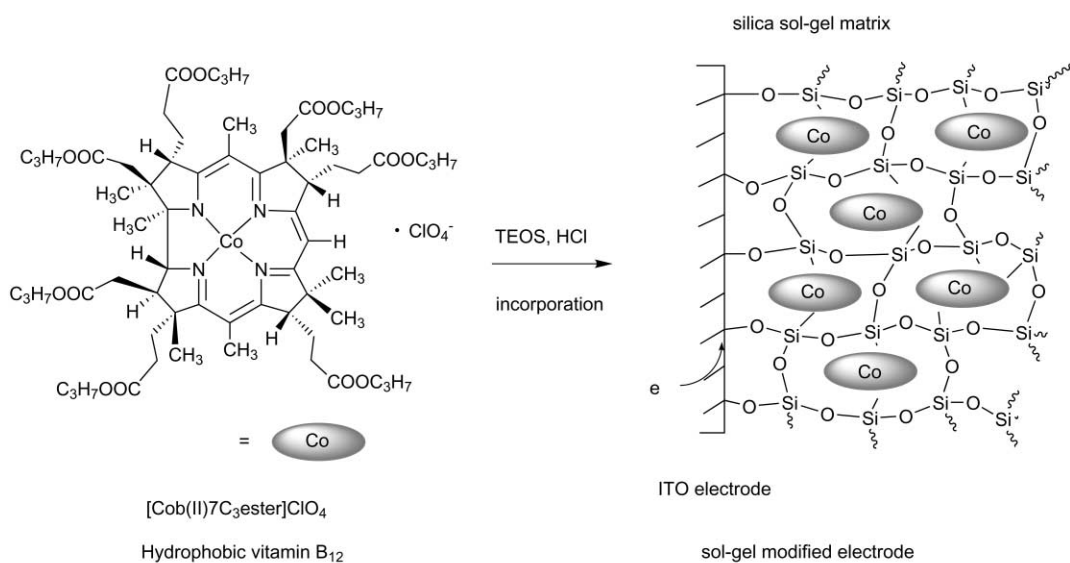


Fig. 1 Schematic representation for the preparation of a sol-gel modified electrode containing the trapped vitamin B₁₂ derivative [Cob(II)7C₃ester]ClO₄.

Cyclic voltammetry

Cyclic voltammograms (CVs) were obtained using a BAS CV 50W electrochemical analyzer. A three-electrode cell equipped with the sol-gel modified electrode and a platinum wire as the working and counter electrodes were used, respectively. An Ag-AgCl (3.0 M NaCl) electrode served as the reference. Aqueous solutions containing KCl (1.0 × 10⁻¹ M) were deaerated prior to each measurement, and the inside of the cell was maintained under an argon atmosphere throughout each measurement. All measurements were carried out at room temperature. The scan rate was varied over the range from 10 to 300 mV s⁻¹. The *E*_{1/2} value of the Fe^{II}/Fe^{III} redox couple for K₃[Fe^{III}(CN)₆] in aqueous solution was 0.21 V vs. Ag-AgCl with this setup.

Electrolysis of benzyl bromide

The controlled-potential electrolysis at -1.20 V vs. Ag-AgCl was carried out in a one-compartment cell equipped with a sol-gel modified electrode as a cathode and a magnesium rod (diameter: 3 mm) as a sacrificial anode at room temperature under an argon atmosphere during irradiation with a 500-W tungsten lamp at a distance of 30 cm. The applied potential between the sol-gel modified and reference electrodes during the electrolysis was maintained constant with a Hokuto Denko HA-501 potentiostat/galvanostat, and the reaction was monitored on a Hokuto Denko HF-201 coulomb/ampere-hour meter. Initial concentrations: benzyl bromide, 1.0 × 10⁻² M; aqueous solution containing 0.1 M KCl. The products were analyzed by GC and GC-MS with a DB-1 capillary column (J&W Scientific; length 30 m; ID 0.25 mm, film 0.25 μm).

Results and discussion

Preparation and characterization of the sol-gel modified electrode

The sol-gel modified electrode on ITO was prepared from TEOS and [Cob(II)7C₃ester]ClO₄ in ethanol containing aqueous HCl as described in the Experimental section (see Fig. 1). After the dip coating of the silica gel solution containing the vitamin B₁₂ derivative, a homogeneous red gel film was formed on the ITO electrode. Formation of the gel film was also directly observed by SEM measurements as shown in Fig. 2. In a dip coating process, it is well known that the film thickness is regulated by the withdrawing speed of the substrate.²⁸

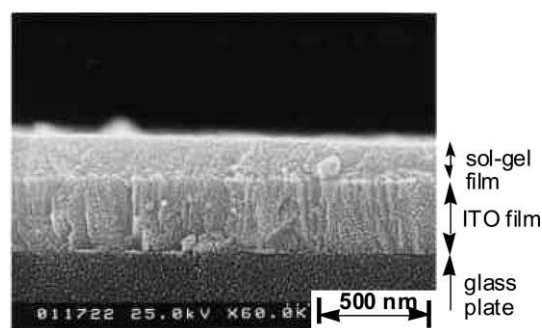


Fig. 2 Cross-sectional SEM photograph for the sol-gel modified ITO electrode containing the vitamin B₁₂ derivative [Cob(II)7C₃ester]ClO₄ at 50 mm min⁻¹ withdrawing speed for the dip coating.

The thicknesses of gel films for withdrawing speeds of 50 and 100 mm min⁻¹ were determined by SEM measurements to be 170 and 330 nm, respectively. We could prepare a sol-gel modified electrode containing [Cob(II)7C₁ester]ClO₄ in place of [Cob(II)7C₃ester]ClO₄, but the [Cob(II)7C₁ester]ClO₄ dissolved out slightly from the gel in aqueous solution. Therefore, we used the sol-gel modified electrode with [Cob(II)7C₃ester]ClO₄ in the electrochemical reactions.

The amounts of vitamin B₁₂ derivative in the gel films were determined by UV-VIS absorption spectra. Absorption spectra of a gel film were obtained by using a slide glass as substrate as shown in Fig. 3(a), since the ITO substrate has a weak absorption in the UV-VIS region. The absorption spectrum showed the intense α- and γ-bands of vitamin B₁₂ at 470 and 313 nm, respectively, and the spectrum is similar to that for [Cob(II)7C₃ester]ClO₄ in CH₂Cl₂ as shown in Fig. 3(b). These electronic spectra indicate that the structure of the vitamin B₁₂ derivative is not changed, at least to the limit of the sensitivity of the measurements. The total amounts of the B₁₂ complex were 1.0 × 10⁻⁹ and 3.7 × 10⁻⁹ mol cm⁻² for thicknesses of 170 and 330 nm, respectively. These values are comparable to that for the polymer-coated B₁₂ modified electrode we previously reported.¹⁸

The EPR spectra of [Cob(II)7C₃ester]ClO₄ were measured in the gel film, as a powder, and in a frozen solution of chloroform-benzene (2 : 1 v/v) at 77 K as shown in Fig. 4. The spectrum (Fig. 4(a)) in the gel film is very similar to that for powdered [Cob(II)7C₃ester]ClO₄ as shown in Fig. 4(b). This result indicates that [Cob(II)7C₃ester]ClO₄ is trapped into the gel film with high density. These spectra and the correspond-

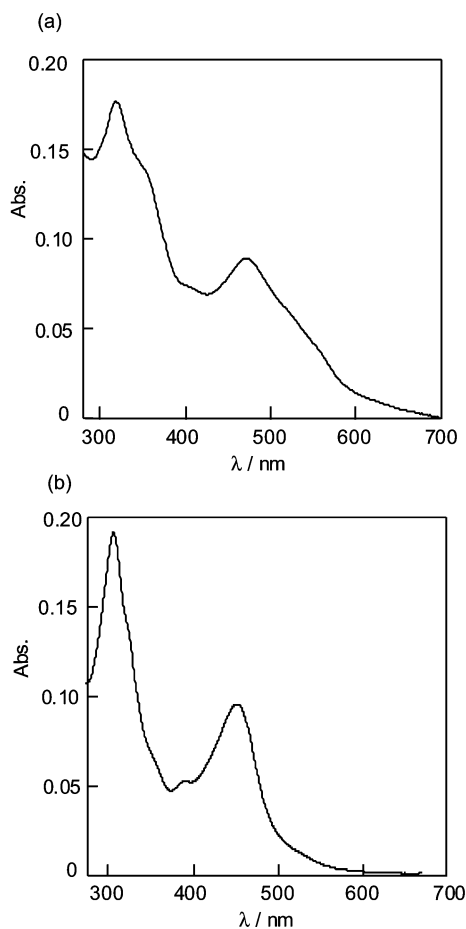


Fig. 3 Electronic spectra of (a) a sol-gel modified glass plate containing the vitamin B₁₂ derivative [Cob(II)7C₃ester]ClO₄ and (b) 5.0×10^{-4} M [Cob(II)7C₃ester]ClO₄ in CH₂Cl₂.

ing spin Hamiltonian parameters are comparable to those of vitamin B₁₂ derivatives.^{2,29} These EPR and electronic spectra clearly indicate that the cobalt(II) state was maintained even after the sol-gel process.

It is noted that the B₁₂ complex containing hydrophobic peripheral substituents within the gel film was quite stable and was not dissolved out when the electrode was immersed in water. Thus, the sol-gel method readily trapped a large amount of the B₁₂ complex to give a film with stable electrochemical activity as described below.

Electrochemistry of sol-gel modified electrodes

Before the electrochemical measurements, the sol-gel modified electrode was immersed in an aqueous solution containing 0.1 M KCl in order to incorporate the electrolyte into the gel, since the silica gel film has poor conductivity. The B₁₂ complex in the film exhibited the Co^{II}/Co^I redox couple at -0.42 V vs. Ag-AgCl as shown in Fig. 5. The corresponding potential of heptamethyl cobyrinate perchlorate [Cob(II)7C₁ester]ClO₄ in aqueous solution is -0.54 V vs. Ag-AgCl. The value of the voltammetric peak current (i_p) depends on the square root of the scan rate (ν). Therefore, it is likely that the electron transfer of the B₁₂ complex in the gel film is a diffusion-driven process. The anodic and cathodic peaks are expected to be at the same voltage for a rigidly surface-immobilized species. The cyclic voltammogram exhibited the behaviour seen for diffusion controlled reactions because the B₁₂ complex can move in the gel. The amount of electroactive catalysts in the films was estimated by integrating the Co^{II} reduction peaks and by applying Faraday's law, yielding a surface concentration Γ_0 of B₁₂ of 3.0×10^{-11} mol cm⁻² (thickness: 170 nm) and 6.2×10^{-11} mol cm⁻²

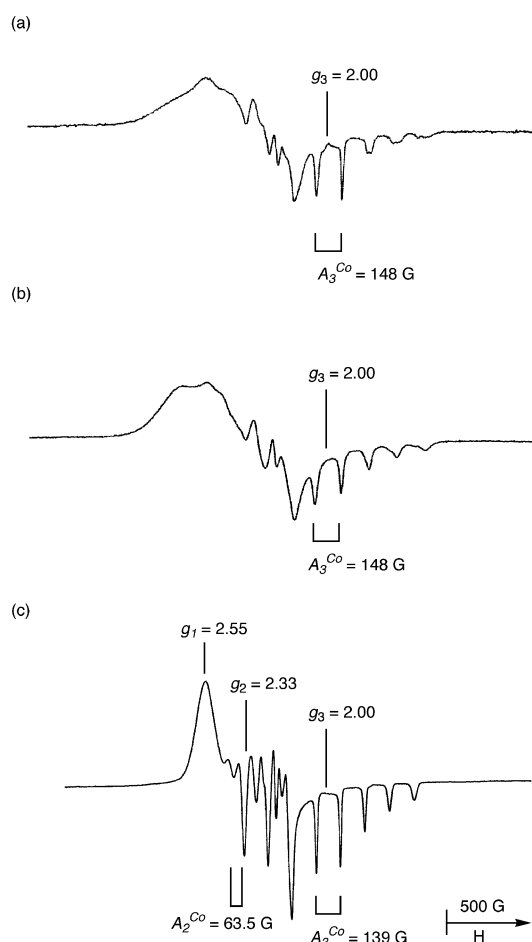


Fig. 4 EPR spectra of (a) [Cob(II)7C₃ester]ClO₄ in the gel film, (b) powdered [Cob(II)7C₃ester]ClO₄ and (c) 6.3×10^{-3} M [Cob(II)7C₃ester]ClO₄ in CHCl₃-C₆H₆ (2 : 1 v/v) at 77 K.

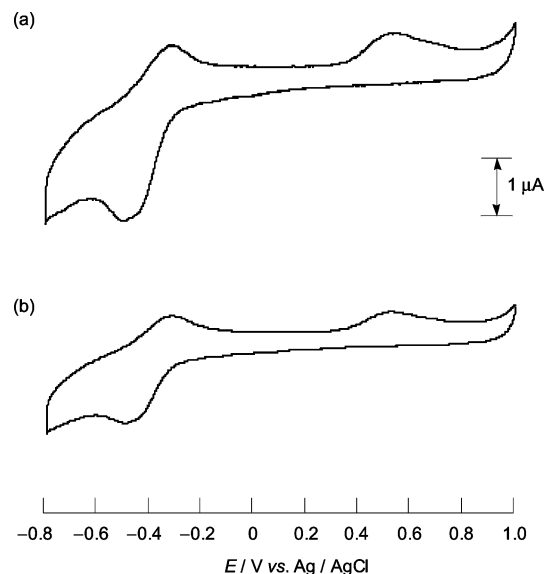


Fig. 5 Cyclic voltammograms of the sol-gel modified electrode containing the vitamin B₁₂ derivative [Cob(II)7C₃ester]ClO₄ in aqueous solution containing 0.1 M KCl. Scan rate is 10 mV s⁻¹: (a) film thickness: 330 nm, (b) film thickness: 170 nm.

(thickness: 330 nm). The total amounts of B₁₂ on ITO determined by UV-VIS spectroscopy were 1.0×10^{-9} and 3.7×10^{-9} mol cm⁻² for thicknesses of 170 and 330 nm, respectively. This experimental result shows that only a small percentage of the B₁₂ complex on ITO is active for the electrolysis.

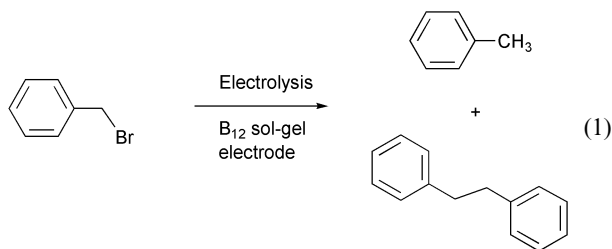
Table 1 Product analyses for the controlled-potential electrolyses of benzyl bromide using the modified electrode^a

Dopant in sol-gel electrode	Electrolysis conditions			Product ratio ^d		Total turnover number ^e	
	$h\nu^b$	Charge ^c /F mol ⁻¹	Time/h	Conversion (%)	Toluene		Bibenzyl
[Cob(II)7C ₃ ester]ClO ₄	Irradiation	0.1	2	8.5	6	94	2260
[Cob(II)7C ₃ ester]ClO ₄	In the dark	0.015	2	0	0	0	–
None	Irradiation	0.019	2	0	0	0	–

^a Controlled-potential electrolyses were carried out in aqueous solution at -1.20 V vs. Ag–AgCl under an argon atmosphere. Initial concentration: benzyl bromide, 1.0×10^{-2} M; KCl, 0.1 M. ^b Under irradiation using a 500-W tungsten lamp at a distance of 30 cm. ^c Electrical charge passed per mol of benzyl bromide. ^d Products were analyzed by GC and GC-MS. ^e Total turnover number was estimated from the total amount of [Cob(II)7C₃-ester]ClO₄ in the sol-gel modified electrode, 3.7×10^{-9} mol cm⁻².

Electrolysis of benzyl bromide

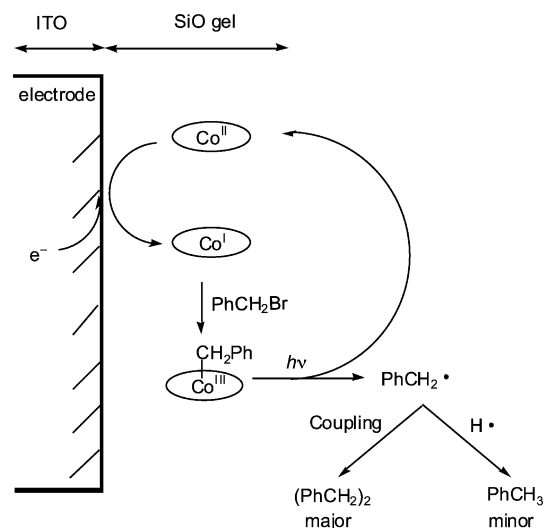
Monovalent cobalt in reduced B₁₂ derivatives is a strong nucleophile and reacts with various organic halides to give organocobalt complexes with cobalt–carbon bonds.³⁰ A compound with a cobalt–carbon bond is homolytically cleaved by photolysis, electrolysis or thermolysis to form the corresponding radical species.³¹ In order to examine the catalytic activity of the B₁₂ modified electrode (thickness, 330 nm; 6.2×10^{-11} mol cm⁻²), the electrolysis of benzyl bromide was carried out in aqueous solution. The electrolysis of benzyl bromide was performed at -1.20 V vs. Ag–AgCl under the irradiation of visible light, and the products were analyzed by GC-MS. Product analyses under various conditions are shown in Table 1. After an electrical charge of 0.1 F mol⁻¹ was passed based on the initial concentration of benzyl bromide, bibenzyl and toluene were detected as products (eqn. (1)).



The major product was bibenzyl, and total turnover number was 2260 for 2 h estimated from the total amount of vitamin B₁₂ derivative in the sol-gel electrode. Products were not obtained in the dark as shown in Table 1. This reaction did not proceed when we used a B₁₂ undoped sol-gel ITO electrode or a bare ITO electrode under the same conditions. Therefore, the trapped complex catalyzes the electrolysis of organic halides under irradiation with visible light.

The electrolysis of benzyl bromide was also investigated upon the addition of a spin-trapping reagent, 5,5'-dimethylpyrroline *N*-oxide (DMPO). Upon the addition of DMPO, the formation of bibenzyl and toluene was completely inhibited. This result indicates that radical species are generated as electrolysis intermediates under the present conditions and a possible mechanism is shown in Fig. 6. The reaction is initiated by the electrochemical reduction of Co(II) to Co(I) species. The Co(I) species, which is a strong nucleophile, reacts with benzyl bromide to yield the benzyl–cobalt complex. The cobalt–carbon bond of the complex then homolytically cleaves to form a benzyl radical upon irradiation with visible light. The benzyl radicals are efficiently coupled to form bibenzyl on the modified electrode before they diffuse out. It was reported that the electrolysis of benzyl bromide mediated by vitamin B₁₂ at -1.20 V vs. SCE gave bibenzyl as a major product in DMF or a bicontinuous microemulsion *via* radical coupling reactions.^{32,33} Such previous reports support our proposed mechanism.

In conclusion, the silica gel films doped with the vitamin B₁₂ derivative, heptapropyl cobyrinate perchlorate [Cob(II)7C₃-ester]ClO₄, were successfully prepared by the sol-gel method

**Fig. 6** Proposed mechanism for the electrolysis of benzyl bromide mediated by the vitamin B₁₂ derivative [Cob(II)7C₃ester]ClO₄ in a sol-gel film.

and deposited on an ITO electrode. The B₁₂ complex held in gel on the electrode possesses electrochemical activity and exhibits high reactivity for dehalogenation of an organic halide. It has been reported that certain bacteria can use tetrachloroethane as an electron acceptor by reducing it to *cis*-dichloroethane, and this enzyme, *reductive dehalogenase*, contains a vitamin B₁₂ as cofactor.³⁴ Therefore, the application of the B₁₂ complex to catalytic dehalogenation reactions of various organic halides is quite interesting from the viewpoint of green electrochemistry.³⁵

Acknowledgements

We thank Prof. N. Kimizuka and Mr. K. Kuroiwa, Kyushu University, for help in measuring the SEM. We also thank Prof. A. Matsuda, Osaka Prefecture University, for supply of the ITO-coated glass plates. The present work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. The authors are also grateful for financial supports from the Showa Shell Sekiyu Foundation and Tokuyama Science Foundation.

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