

Preparation and Reactivity of Vitamin B₁₂–TiO₂ Hybrid Catalyst Immobilized on a Glass Plate

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The vitamin B₁₂–TiO₂ hybrid catalyst was effectively immobilized on a glass plate, and the immobilized catalyst shows an efficient reactivity for various molecular transformations, such as the 1,2-migration of a phenyl group and dechlorination of perchloroethylene during irradiation by UV light.

Immobilized catalyst is generally considered to hold many advantages, such as utilization of small amounts of catalyst, usable in various media, and ready separation of products and catalyst.¹ The catalyst can be recovered and recycled resulting in reducing waste generated. Cobalt complexes, i.e. vitamin B₁₂ derivatives (B₁₂), are good catalysts for several molecular transformations,² and efforts toward immobilization of vitamin B₁₂ derivatives on various supports have been achieved by several groups.³ Utilizing the property of B₁₂ derivative to react with various organic halides by dehalogenation in the Co(I) state, an efficient dehalogenation system has been constructed.⁴ Furthermore, cleavage of the cobalt–carbon bond of the intermediately formed alkylated complex should afford radical species which can be utilized for radical-mediated organic reactions.⁵ Recently, we reported the construction of a B₁₂ catalytic system utilizing titanium dioxide as a photosensitizer.⁶ The UV light irradiation of the hybrid catalyst composed of the B₁₂ derivative (cyanoaquacobyrinic acid) and TiO₂ promoted several molecular transformations such as the dechlorination of 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) and 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (DDD), the 1,2-migration of a phenyl group, and ring-expansion reactions.⁶ In this catalyst, immobilized B₁₂ on TiO₂ was reductively activated by band gap excitation of TiO₂ with UV light irradiation. The present study further advanced this B₁₂–TiO₂ hybrid catalytic system from the viewpoint of green chemistry. The previous powdered B₁₂–TiO₂ system requires filtration during the work-up procedure. During filtration, some powdered catalyst was

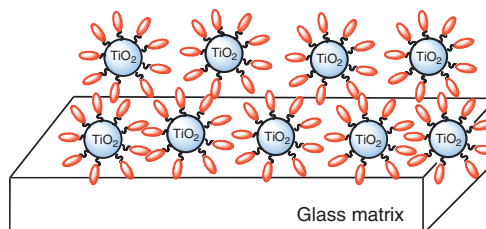
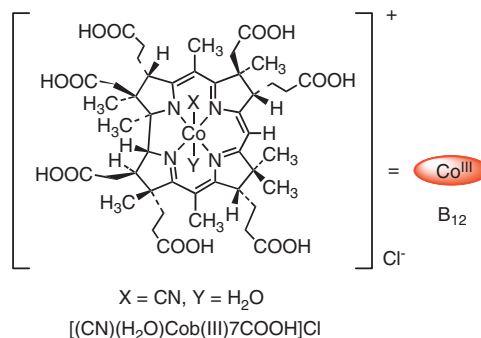


Figure 1. Schematic representation of B₁₂–TiO₂ glass plate.

lost and contaminated the product solution. To improve this step, the B₁₂–TiO₂ hybrid catalyst was immobilized on a glass plate as shown in Figure 1 since one of the merits of the TiO₂ particle is that it is easily attached to the surface of various substrates, such as glass.⁷

The B₁₂–TiO₂-coated glass plate was prepared by the following procedure. A TiO₂ sol solution was deposited on a freshly cleaned slide glass substrate by dip coating, and then the glass plate was immersed in a 10 mM aqueous solution of the B₁₂ derivative. The glass plate was dried at room temperature. The prepared hybrid glass plate was characterized by UV–vis, XPS, XRD, and SEM. From the UV–vis absorption spectrum, the characteristic absorption maxima of B₁₂ were observed at 352, 455, 498, and 529 nm, and the apparent surface coverage of B₁₂ was determined to be 2.5×10^{-9} mol cm⁻². From the SEM image, growth of a porous film containing B₁₂–TiO₂ nanoparticles was clearly observed as shown in Figure 2. The thickness of the TiO₂ film was ca. 300 nm, which is controlled by changing the rate of the dip-coating. Due to this porous structure, the substrate can access the B₁₂ catalytic center within the film.

To confirm this, axial ligation of the cobalt center of B₁₂ was monitored by UV–vis. As the hybrid glass plate was immersed in an imidazole methanol solution, the spectrum changed to one with absorption maxima at 359, 465, 518, and 554 nm as shown in Figure 3. This spectrum was identified as the imidazole-coordinated B₁₂ complex.⁸ Therefore, it is obvious that the substrate molecules could access the B₁₂ catalytic center, and all of the immobilized B₁₂ is expected to participate in the catalytic reaction.

A catalytic reaction using the B₁₂–TiO₂ glass plate was carried out as shown in Table 1. The diethyl 2-bromomethyl-2-phenylmalonate (**1**) substrate was converted to products, and the phenyl-migrated product **2** was formed along with the formation of the simply reduced product **3** in ethanol as expressed by eq 1. The reaction did not proceed when we used the B₁₂-unmodified TiO₂ or in the dark as shown by Entries 4

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GC-mass spectra were obtained using a Shimadzu GCMS-QP5050A equipped with a J&W Scientific DB-1 column (length 30 m; ID 0.25 mm, film 0.25 μ m). Volatile organic compounds (PCE, TCE, and DCE) were analyzed with a Shimadzu GCMS-QP2010SPG equipped with a Perkin-Elmer Turbo Matrix HS16 using a J&W Scientific DB-624 column (length 60 m; ID 0.32 mm, film 1.80 μ m). The UV-vis absorption spectra were measured with a Hitachi U-3300 spectrophotometer at room temperature. Scanning electron micrographs (SEMs) were recorded on a Hitachi S-5000 (HV = 25 kV). The X-ray photoelectron spectroscopy (XPS) experiments were performed with a Physical Electronics XPS 5800. The X-ray diffraction (XRD) analyses were measured with a MacScience Micro-focus X-ray M18XHF diffractometer (CuK α , λ = 1.54056 Å). Dip coatings were performed by an Eintesla MD-408 micro dip-coater.

Chemicals. All solvents and chemicals used in the syntheses were of reagent grade, and were used without further purification. A corrinoid compound (B₁₂), cyanoaquacobyrinic acid ([[(CN)-(H₂O)Co(III)7COOH]Cl]), was synthesized using a reported method.^{6a} The titanium dioxide sol solution (TS-S4110, anatase) was kindly supplied by Sumitomo Chemical. The diethyl 2-bromomethyl-2-phenylmalonate (**1**) substrate and authentic sample of diethyl 2-methyl-2-phenylmalonate (**3**) were synthesized from diethyl phenylmalonate.^{6b} The phenyl-migrated product, diethyl benzylmalonate (**2**), was purchased from Aldrich. Perchloroethylene (PCE) was purchased from GL Science as a methanol solution (5000 μ g mL⁻¹).

Preparations of B₁₂-TiO₂ Glass Plate. The TiO₂ sol solution (TS-S4110) was deposited on a freshly cleaned slide glass substrate (Matsunami Glass Industries) by dip coating at withdrawing speeds of 50 mm min⁻¹. The TiO₂ film formed on the substrate was dried for 24 h at room temperature. The obtained glass plate coated with the TiO₂ film was immersed in a 1 mM solution of cyanoaquacobyrinic acid (B₁₂) in H₂O for 30 min. The B₁₂ content on the glass plate was determined by UV-vis; B₁₂ content: 2.5×10^{-9} mol cm⁻². UV-vis λ /nm: 352, 455, 498, 529. XPS *E*/eV: 780.4 (Co2p), 458.6 (Ti2p), 398.8 eV (N1s). XRD 2θ /°: 25.2, 37.8, 48.0, 53.8, 55.0, 62.6 (anatase).

Catalytic Reaction of B₁₂-TiO₂ Glass Plate (General Procedure). The B₁₂-TiO₂ glass plate (area: 2.5×5.5 cm² $\times$ 2 (both sides), B₁₂: 6.9×10^{-8} mol) was immersed in a 10 mL ethanol solution of a diethyl 2-bromomethyl-2-phenylmalonate (3.0×10^{-5} mol, 3.0 mM) under nitrogen gas atmosphere. The solution was stirred at room temperature under irradiation with 365 nm UV light (1.76 mW cm⁻² at 12 cm distance). The product was directly analyzed by GC-MS. Diphenyl was used as the internal standard.

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