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Visible light-induced heterogeneous Meerwein-Ponndorf-Verley-type reduction of an aldehyde group over an organically modified titanium dioxide photocatalyst

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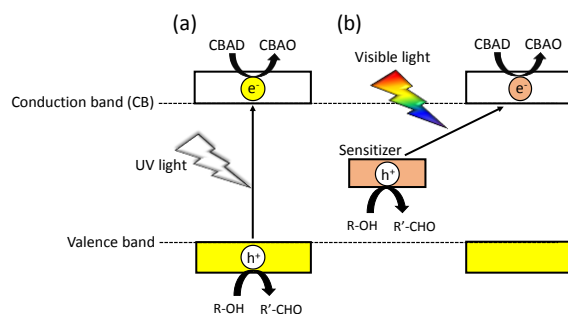
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An organically modified titanium dioxide photocatalyst prepared by a simple impregnation method chemoselectively and almost quantitatively converted benzaldehydes having other reducible functional groups to corresponding benzyl alcohols under visible light irradiation.

A titanium dioxide (TiO₂) photocatalyst exhibits high activity for water splitting and mineralization of organic compounds in water and air under irradiation of UV light¹⁻³. Recently, as the third application of TiO₂, photocatalytic conversion of organic compounds has attracted much attention because solar light can be used for the energy source (light and heat) and the reaction occurs at room temperature under atmospheric pressure. At an early stage of research on photocatalytic conversion of organic compounds, most of the studies were focused on either oxidation or reduction products⁴. Recently, new concepts for photocatalytic conversion has been proposed: 1) efficient utilization of both photogenerated electrons and positive holes, i.e., simultaneous formation of oxidized and reduced products with a high stoichiometry and 2) high chemoselectivity in which one functional group of the compound is oxidized or reduced with the other functional group(s) being preserved. Some results satisfying the above concepts have been reported, and such investigation will expand the applications of a TiO₂ photocatalyst. The next strategy for photocatalytic conversion of organic compounds is efficient utilization of visible light since sunlight consists of 5% of UV light, 50% of visible light and 45% of infrared light at the surface of the earth. In our previous study, we found that *p*-chlorobenzaldehyde (CBAD) was chemoselectively converted to *p*-chlorobenzyl alcohol (CBAO) in an alcoholic suspension of TiO₂ under UV light irradiation in which the chloro group was preserved⁵. Since solvent alcohols act as electron donors and hydrogen sources, this reaction can be regarded as a

heterogeneous Meerwein-Ponndorf-Verley-type reduction over a photocatalyst. This result indicates that photogenerated electrons in the conduction band (CB) of TiO₂ show a sharp selectivity for reduction of the aldehyde group (Scheme 1(a)).



Scheme 1 Heterogeneous Meerwein-Ponndorf-Verley-type reduction over a photocatalyst: (a) band-gap excitation of TiO₂ and (b) charge transfer from a sensitizer to the CB of TiO₂.

Therefore, the strategy for design of a photocatalytic system for chemoselective reduction of CBAD to CBAO under visible light irradiation is simple, as shown in Scheme 1(b), i.e., 1) utilization of photogenerated electrons in the CB of TiO₂ for reduction of CBAD to retain the high chemoselectivity of CBAO and 2) charge transfer from a sensitizer to the CB of TiO₂ under visible light irradiation. We chose 2,3-dihydroxynaphthalene (DHN)⁶ among various photosensitizers for TiO₂ because DHN is obtained easily and modification of TiO₂ with DHN is very easy without any special care (see experimental section in ESI†). Here we briefly report 1) chemoselective reduction of CBAD to CBAO over a DHN-modified TiO₂ (DHN/TiO₂) photocatalyst under visible light irradiation, 2) expandability of DHN/TiO₂ for chemoselective reduction of benzaldehydes having various functional groups and 3) a plausible reaction mechanism.

When TiO₂ powders were suspended in a methanol solution containing DHN, the color of TiO₂ immediately changed from white to pale yellow. The dried samples exhibited absorption of visible light with a wavelength of $\lambda >$

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400 nm and the photoabsorption in the visible light region gradually increased with increase in the amount of DHN (Figure S1). Figure 1 shows time courses of photocatalytic reduction of CBAD in an acetonitrile suspension of 0.3 wt%DHN/TiO₂ under irradiation of visible light from blue a LED under deaerated conditions. Material balance (MB) calculated by using Equation (1) is also shown in Figure 1.

$$MB = \frac{n(\text{CBAD})+n(\text{CBAO})+n(\text{BAD})+n(\text{BAO})}{n_0(\text{CBAD})}, \quad (1)$$

where $n(\text{CBAD})$, $n(\text{CBAO})$, $n(\text{BAD})$ and $n(\text{BAO})$ are the amounts of CBAD, CBAO, benzaldehyde (BAD) and benzyl alcohol (BAO) during the photocatalytic reaction, respectively, and $n_0(\text{CBAD})$ is the amount of CBAD before the photocatalytic reaction.

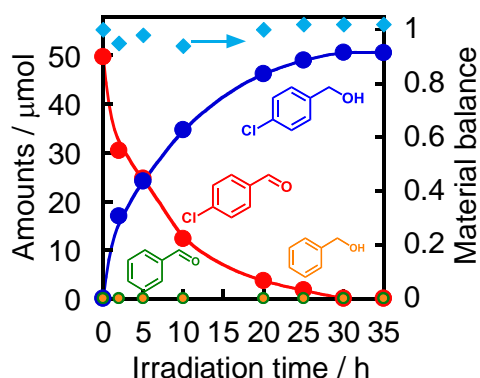


Figure 1 Time courses of amounts of CBAD, CBAO, BAD and BAO in photocatalytic reduction of CBAD in an acetonitrile suspension of 0.3 wt%DHN/TiO₂ under visible light irradiation.

The amount of CBAD monotonously decreased with photoirradiation, while CBAO as the reduced product of CBAD was formed corresponding to the conversion of CBAD. When CBAD had been almost completely consumed, CBAO was obtained almost quantitatively (>99% yield). The values of MB close to unity and the high yield of CBAO indicate that only reduction of the aldehyde group to a hydroxy group occurred and that no decomposition of CBAD or CBAO occurred. During the visible-light irradiation and even after consumption of CBAD, there was no formation of BAD or BAO, indicating that the DHN/TiO₂ photocatalyst system induced no dechlorination of CBAD and subsequent reduction of BAD to BAO, resulting in almost complete chemoselectivity. In the case of photocatalytic reduction of various organic and inorganic compounds over metal-loaded TiO₂, the metal species often acts as a co-catalyst for hydrogen (H₂) evolution (2H⁺ + 2e⁻ → H₂), which decreases the efficiency of electron utilization. Since the present photocatalyst system is metal-free, no H₂ was evolved, contributing to the high efficiency of electron utilization. There are several reports on MPV reduction over homogeneous⁷ and heterogeneous⁸ catalysts (Table S2). From the comparison with reactions using these catalysts, several advantages of photocatalytic reaction can be pointed out, i.e., photocatalytic reaction 1) occurs even at room temperature and under atmospheric pressure, 2) can be controlled by light

not by heat and 3) can be applied for conversions of UV-sensitive or thermosensitive substrates. DOI: 10.1039/C7CC00645D

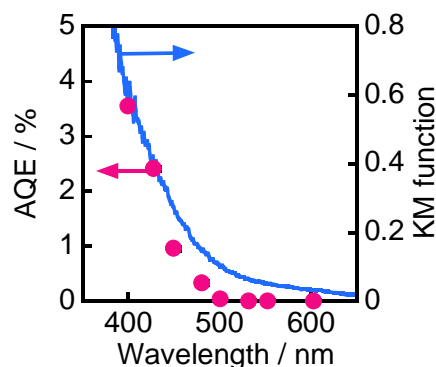


Figure 2 Action spectrum in the reduction of CBAD (ca. 50 μmol) to CBAO over DHN/TiO₂ (left axis) and absorption spectrum of DHN/TiO₂ (right axis).

The action spectrum is a powerful tool for determining whether an observed reaction occurs by a photoinduced or a thermocatalytic process. To obtain the action spectrum in this reaction system, chemoselective reduction of CBAD in acetonitrile suspensions of 0.3 wt%DHN/TiO₂ was carried out at 298 K under irradiation of monochromated visible light from an Xe lamp with a light width of ±7 nm using a multi-wavelength irradiation monochromator (MM-3PK, Bunkoukeiki Co., Ltd), and the light intensity was determined using a spectroradiometer (USR-45D, Ushio Inc.). The apparent quantum efficiency (AQE) at each centered wavelength of light was calculated from the ratio of the amount of CBAO and the amount of incident photons by using Equation (2).

The results are shown in Figure 2. The values of AQE

$$AQE = \frac{2 \times \text{amount of CBAO formed}}{\text{amount of incident photons}} \times 100, \quad (2)$$

determined at wavelengths of 400, 428, 450, 481 and 501 nm reached 3.5%, 2.4%, 0.96%, 0.33% and 0.038%, respectively. The tendency of the action spectrum was in agreement with the absorption spectrum of 0.3 wt%DHN/TiO₂, and the similarity clearly shows that reduction of CBAD in an acetonitrile suspension was induced by visible-light absorption of DHN-Ti species formed on the TiO₂ surface.

To check the high chemoselectivity of DHN/TiO₂ for reduction of the aldehyde group to a hydroxy group, intermolecular selective reaction of BAD and chlorobenzene (CB) was further investigated under irradiation of visible light. In photocatalytic reduction of an equimolar mixture of BAD and CB in acetonitrile suspensions as shown in Figure 3, we found that DHN/TiO₂ gave only BAO as the product from BAD, while no benzene formed by dechlorination of CB was detected. Even when excess irradiation of light was carried out, the chloro group was not eliminated. Also in the intermolecular selective reduction between BAD and CB, the aldehyde group was chemoselectively reduced to a hydroxy group over DHN/TiO₂. We previously reported that Pd-loaded TiO₂ cleaved the carbon-chloro bond (C-Cl) in the CB under

irradiation of UV light, whereas metal-free TiO₂ was inert to dechlorination of the CB because the photo-generated electrons in the conduction band have no ability to cleave C-Cl.⁹ In fact, in Entry 10 of Table S1, DHN/TiO₂ having Pd as a co-catalyst reductively cleaved C-Cl of CBAD, resulting in the formation of BAD after 2 h.

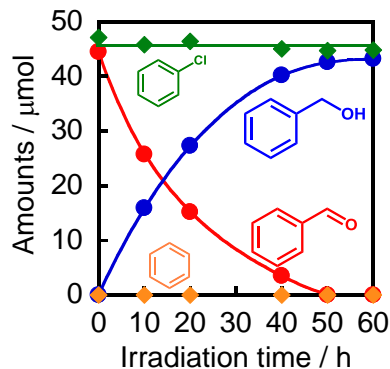


Figure 3 Intermolecular competitive reduction of BAD and CB in an acetonitrile suspension of DHN/TiO₂ under irradiation of visible light.

In order to demonstrate high chemoselectivity for reduction of a carbonyl group over DHN/TiO₂ under visible-light irradiation, aromatic aldehydes substituted by various other functional groups such as bromo, iodo, unsaturated bond and methyl groups were used as substrates, and the results are shown in Table 1. First, we chose *p*-bromobenzaldehyde and *p*-iodobenzaldehyde having more reducible groups than a chloro group (Entries 2, 3). Despite the above nature of bromo and iodo groups, no debromination or deiodination of *p*-bromobenzaldehyde and *p*-iodobenzaldehyde occurred, and only the aldehyde group of two benzaldehydes was reduced to a hydroxy group with high conversion and high selectivity. These results indicate that DHN/TiO₂ was inert for the reductive cleavage reaction of carbon-bromo (C-Br) and carbon-iodo (C-I) bonds. Moreover, in order to confirm the high chemoselectivity of DHN/TiO₂ for a carbonyl group, aromatic aldehydes having unsaturated carbon-carbon and carbon-nitrogen bonds were used as substrates. In previous studies, we found that benzonitrile and phenylacetylene can be reduced to benzylamine and styrene over a TiO₂ photocatalyst having palladium and copper co-catalysts, respectively¹⁰, but not over metal-free TiO₂. As expected, aldehyde groups bound to phenylacetylene and benzonitrile at para and meta positions, respectively, and were reduced to hydroxy groups with unsaturated carbon-carbon and carbon-nitrogen bonds being preserved (Entries 4, 5). Cinnamaldehyde was not selectively reduced to cinnamyl alcohol probably because of the photochemical reaction driven by blue light (Entry 6). Benzaldehydes having electron-donating groups such as a methyl group at para position were also chemoselectively reduced, although complete conversion (>99%) was not achieved (Entry 8). As far as we know, this is the first report about visible light-induced MPV-type reduction of aromatic aldehydes under irradiation of visible light. 4-

Pentenal was not reduced to corresponding alcohol, indicating that this photocatalytic reduction system is limited to the reduction of aromatic aldehyde compounds.

Table 1 Chemoselective reduction of aromatic aldehydes having various functional groups in an acetonitrile suspension of DHN/TiO₂ under visible-light irradiation.

Entry	Substrate	Product	Time / h	Conv. / %	Sel. / %
1			30	>99	>99
2			24	>99	>99
3			40	>99	93
4			40	>99	>99
5			20	>99	>99
6			46	78	43
7			40	>99	>99
8			60	81	81

The effects of functional groups on the reaction rate shown in Table 1 suggest that the electron state of other functional groups controls the activation state of the intermediate(s) in this reaction. Therefore, the rate of reduction of benzaldehydes having various electron-withdrawing and electron-donating groups to corresponding benzyl alcohols was determined. The formation rate of benzaldehyde having a cyano group was largest and the rate decreased linearly in the order: chloro > H > methyl > methoxy, i.e., reduction of the aldehyde group to a hydroxy group is accelerated by the electron-withdrawing groups. This result suggests that the aldehyde group can more easily receive electrons from DHN/TiO₂ under visible light irradiation due to the decrease in electron density of the aromatic ring by the induction effect of substituted electron-withdrawing groups.

The reaction rates were analyzed in detail using the Hammett equation as an empirical rule. The Hammett constants reported in the literature¹¹ were used, and the results are shown in Figure 4. Formation rates of benzyl alcohols showed a reasonably linear Hammett correlation and a Hammett ρ value larger than zero (0.63, $r^2 = 0.98$) was obtained, indicating that reduction of the aldehyde group to a hydroxy group proceeds via an anionic intermediate. In the photocatalytic selective oxidation of alcohol over visible light-responding photocatalysts¹², a reaction that is a reverse reaction to that in this study, the reaction rate was enhanced by an electron-donating group and the Hammett ρ value was smaller than zero. Therefore, the results of benzaldehyde reduction and alcohol oxidation support each other.

This result is different from ordinary MPV reduction because it proceeds in a hydride reductive manner through the six-membered transition state formed among carbonyl compound, alcohol and catalyst as the rate-determining step as reported by Komanoya *et al.*^{8a}. They demonstrated the presence of the six-membered transition state based on the kinetic isotope effect using various deuterated 2-propanol as sacrificial alcohol in addition to FT-IR analysis. In the case of (CH₃)₂CHOD, no kinetic isotope effect was observed ($k_H/k_D = 1.1$), whereas (CH₃)₂CDOH gave a large k_H/k_D of 1.9. The result indicates the β -H elimination of 2-propanol participated in the reduction of carbonyl compound.

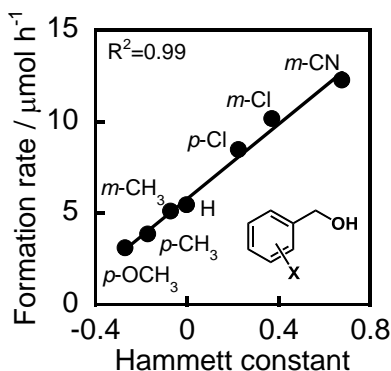


Figure 4 Hammett correlation study for photocatalytic reduction of various aromatic aldehydes to corresponding aromatic alcohols in an acetonitrile suspension of DHN/TiO₂ under irradiation of visible light.

Based on the results of the action spectrum and the linear Hammett correlation described above, we can consider the mechanism of chemoselective reduction of an aldehyde group over DHN/TiO₂ under irradiation of visible light as shown in Figure 5. First, the surface complex species formed by DHN and TiO₂ functions as a site for absorbing visible light, and the generated electrons are injected into the conduction band of TiO₂. These electrons are used for reduction of the aldehyde group of benzaldehydes adsorbed on the TiO₂ surface. Detailed analysis using the Hammett equation indicated that an anionic intermediate was formed during reduction of the aldehyde group. It is expected that the generated anionic species is stabilized by protons (H⁺) formed by oxidation of triethanolamine used as a hole scavenger.

In summary, we succeeded in visible light-induced Meerwein-Ponndorf-Verley-type reduction of various benzaldehydes having other reducible functional groups to corresponding benzyl alcohols over an organically modified TiO₂ (OMT) photocatalyst prepared by a simple impregnation method without any special care. This is the first report of chemoselective reduction of an aldehyde group under irradiation of visible light. The results obtained in this study satisfy three important requisites in material transformation, i.e., 1) catalyst preparation based on an element strategy that uses abundant elements, 2) environmental friendliness that uses no harmful chemicals and 3) efficient utilization of sunlight. This paper provides a new concept for an

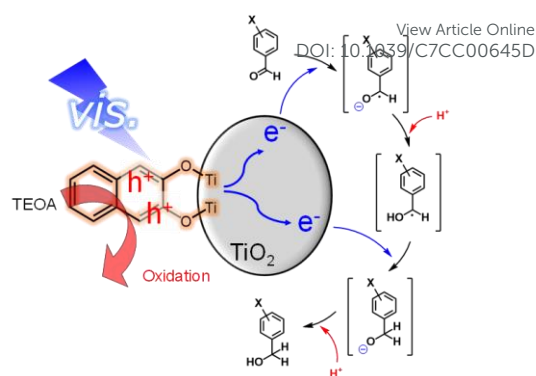


Figure 5 Proposed photocatalytic mechanism over DHN/TiO₂ for reduction of an aldehyde group.

environmentally-friendly material transformation system working under sunlight. Since the reaction rate is still small compared with the reaction rates over homogeneous and heterogeneous thermocatalysts (Table S2), engineering approaches such as efficient light irradiation to the photocatalyst system are also important.

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