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Supplementary information for

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

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Experimental section

DHN/TiO_2 samples were prepared by a simple impregnation method. A TiO_2 sample (ST-01, Ishihara) was suspended in a methanol solution containing DHN in an evaporating dish, and methanol was vapored over a water bath at 313 K until the powder was dried, and DHN/TiO_2 was obtained. Diffuse reflectance spectra were obtained with a UV−vis spectrometer (UV-2400, Shimadzu, Kyoto) equipped with a diffuse reflectance measurement unit (ISR-2000, Shimadzu). In a typical run, prepared DHN/TiO_2 (50 mg) was suspended in an acetonitrile solution (5 cm^3) containing *p*-chlorobenzaldehyde (CBAD, *ca.* 50 μmol) and triethanolamine (100 μmol) as a sacrificial reagent in a test tube, which was sealed with a rubber septum under argon, and then photoirradiated with visible light of the two sets of a blue LED (420-530 nm, 8.7 and 13.7 mW cm^{-2}, Hayashi Watch Works, Tokyo) from two directions with magnetic stirring at 298 K. The emission spectra of light from two blue LEDs are shown in Figure S1(b). After the suspension had been filtered to remove the powder, the amounts of CBAD unreacted and corresponding *p*-chlorobenzyl alcohol (CBAO) formed in the liquid phase were determined with an FID-type gas chromatograph (GC-2025, Shimadzu, Kyoto) equipped with a DB-1 column. Chlorobenzene was used as an internal standard sample. The internal standard reagent (5 mm^3) was added to the reaction solution (2 cm^3). After the mixture had been stirred for 10 min, CBAD and CBAO in the mixture were analyzed. The amounts of CBAD and CBAO were determined from the ratios of the peak areas of CBAD and CBAO to the peak area of chlorobenzene.

Photoabsorption properties

Figure S1(a) shows a transmission spectrum of DHN dissolved in a methanol solution. DHN exhibited strong absorption in the region of UV light with a wavelength of $\lambda < 400$ nm, probably due to its conjugation, but did not absorb visible light. When TiO_2 powder was suspended in a methanol solution containing DHN, the color of TiO_2 immediately changed from white to pale yellow. After removal of methanol in a water bath kept at 313 K, the color of the dried powder was still yellow. Figure S1(b) shows diffuse reflection spectra of TiO_2 samples umodified and modified with DHN. TiO_2 showed strong absorption only in the region of UV light because of the large band gap (ca. 3.1 eV). As expected from the color change of TiO_2 immersed in DHN solution, this sample exhibited absorption of visible light with a wavelength of $\lambda > 400$ nm and the photoabsorption in the visible light region gradually increased with increase in the amount of DHN. In studies on sensitization of TiO_2[S1], formation of a diol-Ti complex by strong interaction between the diol portion of dihydroxy compounds and Ti atoms of TiO_2 was observed by Fourier transform infrared spectroscopy (FT-IR), and formation of the diol-Ti complex resulted in photoabsorption in the region of visible light.

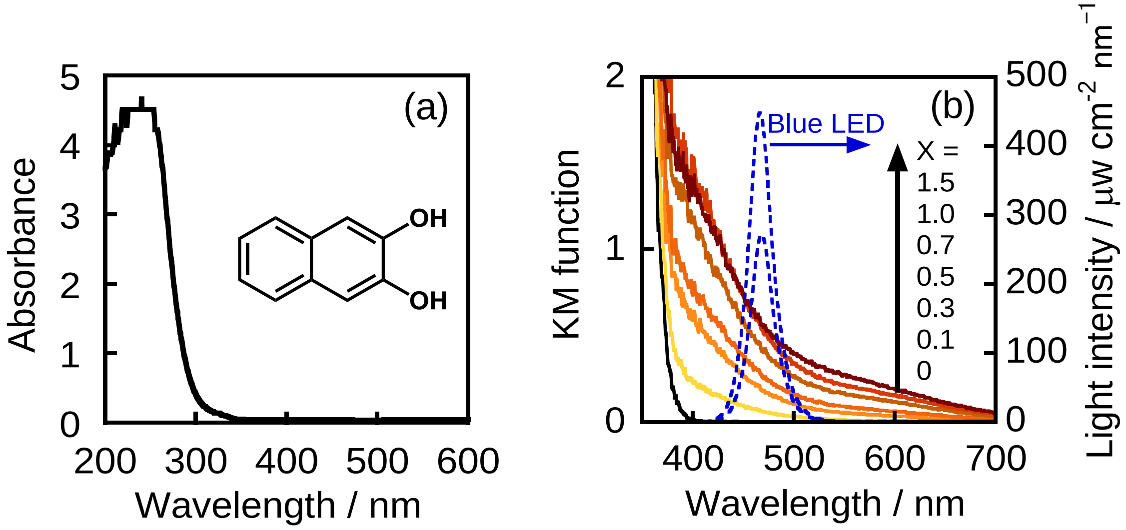

Figure S1 (a) Transmission spectrum of DHN dissolved in a methanol solution and (b) diffuse reflectance spectra of TiO_2 and X wt%DHN/TiO_2 (left axis) and emission spectrum of the blue LED used as the light source for photocatalytic reactions (right axis).

Effect(s) of various factors on photocatalytic reduction of CBAD

We investigated reduction of CBAD to CBAO in an acetonitrile suspension of DHN/TiO_2 under various reaction conditions to clarify the effect(s) of various factors on photocatalytic reduction of CBAD over DHN/TiO_2, and the results are shown in Table S1. First, several blank tests were carried out under the conditions of the presence or absence of a catalyst and blue light irradiated from a blue LED as shown in Entries 12-14. In the absence of the blue light or a catalyst, or in the absence of both, reduction of CBAD to CBAO did not proceed at all. Therefore, it is clear that this reaction is a photocatalytic reaction requiring both light and a catalyst. Second, various X wt%DHN/TiO_2 samples exhibiting photoabsorption in visible light (Figure S1(b)) were used to evaluate the effect of the amount of DHN loaded on the surface of TiO_2 (Entries 1-6). The amount of DHN showed a weak effect on the CBAO yield in the range from 0.3 to 1.0 wt%, although photoabsorption of these samples in the range of visible light monotonously increased with increase in the amount of DHN. Since photoabsorption in the visible region gradually increased with increase in the amount of DHN as shown in Figure S1(b), the amount of photons absorbed by DHN/TiO_2 would increase. In our previous study, we found that there was a linear correlation between the reaction rate and amount of adsorption of the substrate in photocatalytic reduction of nitrobenzenes to corresponding aminobenzenes in an aqueous suspension of TiO_2 under UV light irradiation[S2], indicating that adsorption ability toward the substrate is also a decisive factor for photocatalytic reaction. From the viewpoint of adsorption of the substrate on the surface of the photocatalyst, the increase in the amount of DHN decreases the open surface for adsorption of CBAD. Therefore, an increase in the amount of DHN has both positive and negative effects on the photocatalytic activity, resulting in the highest performance with moderate loading (0.3 to 1.0 wt%) of DHN. We then examined the effects of metals on reduction of CBAD (Entries 7-11). The metals were loaded on 1.0 wt%DHN/TiO_2 by using the photodeposition method. When Ag and Cu were loaded, the samples showed CBAO yields slightly smaller than that of metal-free DHN/TiO_2, indicating that these metals were inert for this reaction. When Au, Pd and Pt were loaded, much smaller CBAO yields were obtained and side reactions such as hydrogen production and dechlorination of the chloro group preferentially proceeded. From these results, no positive effect of these metals was observed, and metal-free DHN/TiO_2 was best for this reaction, which is also ideal from the viewpoint of simple chemistry and environmentally friendly chemistry.

Table S1 Effects of various reaction conditions on photocatalytic reduction of CBAD to CBAO in acetonitrile suspensions of DHN/TiO_2.[a]

Entry	Photocatalyst	Metal co-catalyst	Blue light	Yield / %
1	0.1 wt%DHN/TiO_2	-	Yes	28
2	0.3 wt%DHN/TiO_2	-	Yes	34
3	0.5 wt%DHN/TiO_2	-	Yes	32
4	0.7 wt%DHN/TiO_2	-	Yes	33
5	1.0 wt%DHN/TiO_2	-	Yes	32
6	1.5 wt%DHN/TiO_2	-	Yes	16
7	1.0 wt%DHN/TiO_2	Ag	Yes	29
8	1.0 wt%DHN/TiO_2	Cu	Yes	26
9	1.0 wt%DHN/TiO_2	Au	Yes	6
10	1.0 wt%DHN/TiO_2	Pd	Yes	0
11	1.0 wt%DHN/TiO_2	Pt	Yes	1
12	0.3 wt%DHN/TiO_2	-	No	-
13	-	-	Yes	-
14	-	-	No	-

[a] TiO_2: ST-01, CBAD: 50 μmol, Acetonitrile: 5 cm^3, Reaction temperature: 298 K, Time: 2 h.

Table S2 Comparison of experimental data over various catalysts for the MPV reduction under several conditions.

Catalyst		Condition	Time / h	Yield / μmol	Sel. / %	Ref.
Homogeneous catalyst	$Al(O^iPr)_3$	273 K	12	15	>99	7(a)
	Al calix[4] arene	298 K	12	900	>99	7(b)
	$B(O^iPr)_3$	353 K	15	26,000	98	S3
	$B(OEt)_3$	353 K	15	26,000	98	S3
Heterogeneous catalyst	ZrO_2	393 K	2	130	>99	8(a)
	Zr-*β*-zeolite	355 K	6	4,900	>99	8(b)
	$B(O^iPr)_3$-MCM-41	353 K	8	26,000	>99	S3
	Ir/H-MoO_x	373 K, H_2(2 MPa)	2	1,900	93	S4
	Cu/MgAlO	423 K, H_2(4 MPa)	3	5,000	>99	S5
Photocatalyst	DHN/TiO_2	298 K	30	50	>99	This study
	TiO_2	293 K	0.2	45	98	5

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