Supporting Information

Are You Still Using Organic Dyes? Colorimetric Formaldehyde Analysis for True Photocatalytic-activity Evaluation

Fitri Rizki Amalia[a], Mai Takashima[a,b†]* and Bunsho Ohtani[a,b††]

[a]*Graduate School of Environmental Science, Hokkaido University, Sapporo 060-0810, Japan.*
[b]*Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan.*
† Present address: Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan.
††Present address: Present address: Nonprofitable Organization touche NPO, 1-6-414, North 4, West 14, Chuo-ku, Sapporo, 060-0004, Japan

* Corresponding author: Takashima.m@cat.hokudai.ac.jp

1. Experimental Section for Summary of Three Photocatalytic Systems

To prepare assembly of photoinduced reaction under UV and green LED in three photocatalytic systems (see **Fig. 1**), Hamamatsu Photonics L11921-400 (HMP) high-intensity 365-nm UV-LEDs and visible-light (green) LED (Aitec system TSPA22X8-57G-4) equipped with a power supply (Aitec system TPDC2-0510NCW) were used as a light source. The power was set to 100 mW by adjusting the controllers and was checked by Hioki 3664 power meter with a 9742 optical sensor.

There were two main instruments that were used for the detection of substrate consumption or product liberation. The gas product was measured by a gas chromatography (GC; Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD) and a column of molecular sieve 5A (MS-5A) and Porapak-Q for hydrogen (H_2) and carbon dioxide (CO_2) detection, respectively. Meanwhile, for colorimetric formaldehyde (HCHO) and rhodamine B (RhB) analyses, the measurement was conducted by a spectrophotometer (Shimadzu MPS-2450, UV-vis multipurpose spectrophotometer).

A non visible light-absorbing titania, ST-G1, was supplied from Showa Denko Ceramics. This titania is predominantly rutile with a small portion of anatase with specific surface area of ca. 6 m^2 g^{-1}. For the two VR absorbing titanias, Sample A and Sample B, their production process and all structural characteristics are not disclosed (see "**4. Visible-light Active Titania Photocatalyst** " in this ESI). Titania samples used for the analyses shown in **Figs. 3 and 4** were listed in **Table S1**.[1]

Table S1 Structural characteristics of titania samples shown in **Fig. 4**

number	name	supplier	SSA/ m^2 mg^{-1}	particle size/ nm	crystalline ratio/ %		
					anatase	rutile	noncrystalline
1	ST-01	Ishihara Sangyo	344	4	79.9	0.0	20.1
2	ST-157	Tayca	81	19	81.2	0.0	18.8
3	Fluka	Fluka	9	167	93.3	3.3	3.4
4	Merck	Merck	12	126	93.2	4.4	2.4
5	FP-6	Showa Denko Ceramics	104	14	82.9	8.4	8.7
6	P25	Nippon Aerosil	58	26	81.7	15.4	3.0
7	634662	Aldrich	14	104	20.2	74.0	5.8
8	MT-150A	Tayca	114	13	0.0	81.9	18.1
9	ST-G2	Showa Denko Ceramics	4	348	3.0	94.8	2.2
10	ST-G1	Showa Denko Ceramics	7	231	0.2	96.8	2.9

1.1 Methanol dehydrogenation ($CH_3OH \rightarrow HCHO + H_2$)

A 50 mg of a photocatalyst was suspended in 5 mL of aqueous 50vol% methanol as a sacrificial electron donor in a 15-mL test tube. Chloroplatinic acid (H_2PtCl_6) solution was added to obtain 2wt% of platinum on a photocatalyst. Bubbling with argon was conducted to remove air prior to photoirradiation. Under 100-mW UV LED, the suspension was irradiated for total 4 h at a 1-h interval. Meanwhile, under 100-mW green LED, firstly, photodeposition of platinum on titania samples (2wt%) was conducted by an in-situ method. The titania suspension in aqueous 50vol% methanol with the chloroplatinic-acid solution was irradiated by the UV LED for up to 25 min. After the irradiation, H_2 gas evolved during photodeposition was purged by argon stream prior to visible-light photoirradiation. The photocatalytic activity was evaluated under photoirradiation by the green LED and the product was measured at t = 0, 2, 4, 6, 8 and 24 h. The evolved H_2 gas was measured by gas chromatography. Meanwhile, the suspension was taken regularly for analysis of HCHO evolution. Separation of the powder and solution was conducted

by centrifugal filtration, i.e., the suspension was put in inner filter cup (Shimadzu C4506-045) which was put inside the outer sample cap (Shimadzu C4504-97), and the solution was made to pass through a membrane and transferred to the outer sample cup during centrifugation (13,000 rpm for 5 min). Then, the obtained filtrate was diluted, if necessary. Nash reagent, a mixed aqueous solution of ammonium acetate (2.0 mol L^{-1}), acetic acid (5×10^{-2} mol L^{-1}) and acetylacetone (2×10^{-2} mol L^{-1}), was used to analyze the HCHO amount.[2] For HCHO analysis, 1.00 mL of Nash reagent was mixed with 1.00 mL of the diluted HCHO-containing solution and heated by a blower. The resultant diacetyldihydrolutidine (DDL) in a yellow solution was then extracted by chloroform and its amount was measured by a spectrophotometer (λ_{max} = 394 nm).

1.2 Formaldehyde oxidative decomposition ($HCHO + O_2 \rightarrow CO_2 + H_2O$)

A 50 mg of a photocatalyst was suspended in 5 mL of 1.25×10^{-2} mol L^{-1} aqueous HCHO solution, prepared by dissolving paraformaldehyde powder in water, in a 15-mL test tube. Since formalin, commercial aqueous formaldehyde, contains methanol as a stabilizer, paraformaldehyde was used as a source of formaldehyde. The suspension was stirred in the dark for 1 h to achieve adsorption equilibrium prior to irradiation by the100-mW UV LED. The liberated CO_2 gas was detected by GC along with suspension sampling for HCHO analysis at 1, 2, 3, and 4-h irradiation. Under green LED (100 mW) irradiation, the suspension was irradiated and the liberated CO_2 and consumption of HCHO were analyzed at t = 2, 4, 6, 8, and 24 h. The procedure for HCHO measurement was similar with that of the methanol dehydrogenation system.

1.3 Rhodamine B decoloration

A 45-mg portion of a photocatalyst was suspended in a 90-mL aqueous RhB solution (1×10^{-5} mol L^{-1}). The dark stirring was conducted for 1 h followed by photoirradiation by the UV LED or green LED. Under UV-LED irradiation, the concentration of RhB was analyzed at t = 0, 30, 60, 90, and 120 min. On the other hand, under green-LED irradiation, the concentration was measured at t = 0, 2, 4, 6, 8, and 24 h. Sampling was conducted by taking ca. 2.5 mL of suspension by an autopipette, followed by centrifugation (13,000 rpm for 5 min). A 2-mL portion of the obtained supernatant was taken by an autopipette and then analyzed by a spectrophotometer.

2. Action-spectrum Analysis

Action-spectrum analysis is a method to evaluate the origin of photoinduced reaction in an action spectrum, i.e., wavelength dependence of apparent quantum efficiency (AQE) by comparing

to the diffuse-reflectance (DR) spectra of a photocatalyst.[3] In this work, a diffraction grating-type multiwavelength illuminator (Jasco CRM-FD) equipped with 300-W xenon lamp (Hamamatsu Photonics C2578-02). The intensity of irradiation was measured by a Hioki 3664 power meter equipped with a 9742 optical sensor. The apparent quantum efficiency (AQE) was calculated as follows:

$$\text{AQE} = (\text{number of electron/hole transfer}) \times (\text{rate of product formation/mol s}^{-1}) / (\text{rate of incident photons} = \text{light flux/mol s}^{-1})$$

Here n, the number of electron/hole, is defined for each product liberation or substrate consumption. For example, eight-electrons transfer (n = 8) are assumed for carbon-dioxide liberation by the photocatalytic oxidative decomposition of 1 molecule of acetic acid,[4] though it is impossible to evaluate the true number of n based on the experimental results. For the oxidative decomposition of HCHO, measured by the consumption of HCHO, n can be 4 or 2 if the following stoichiometry, $HCHO + O_2 = CO_2 + H_2O$ or $HCHO + 1/2\ O_2 = HCOOH$, is assumed.[5] It should be noted that for dye decoloration, number of n cannot be defined since no stoichiometry has been clarified,[6] and thereby, we have to use n = 1 for convenience in this study.

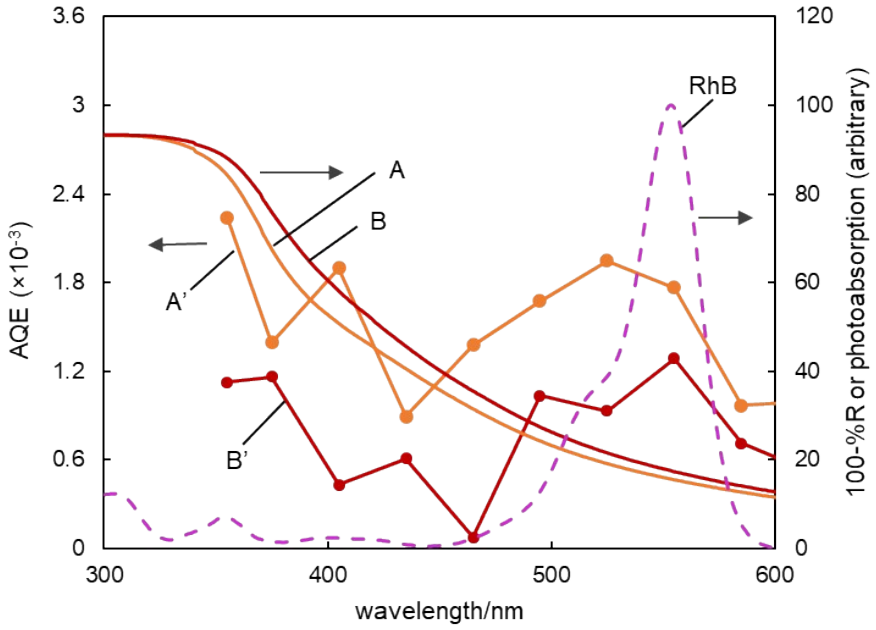

Figure S1. DR spectra of (A) Sample A and (B) Sample B, action spectra of RhB decoloration (measured by absorbance) on (A') Sample A and (B') Sample B, and (RhB) photoabsorption spectra of aqueous RhB solution.

2.1 Rhodamine B decoloration on Sample A and Sample B

For action spectrum of RhB decoloration, 3.0 mL of an aqueous RhB solution (1×10^{-5} mol L^{-1}; pH 3 adjusted by 0.1-mol L^{-1} hydrochloric acid) was added to a cuvette cell containing a 30-mg photocatalyst (Sample A or Sample B). Dark stirring for 1 h was performed to achieve adsorption equilibrium, followed by photoirradiation for 5 min. The decreased amount of RhB by irradiation was used to calculate the AQE. **Figure S1** shows the action spectrum analysis of RhB decoloration by Sample A and Sample B. Even though the action-spectrum plots for both samples were scattered, which probably due to the different light intensity depending on the wavelength and possible non-linear light-intensity dependence (The above-mentioned AQE equation is derived by assuming linear light-intensity dependence.), we could see the tendency that the photoinduced RhB decoloration was increased at ca. 555 nm of photoirradiation wavelength, which was close to the photoabsorption maximum of RhB in its solution (but not in a real suspension), even though there were no enhancement of DR spectra of both samples in those regions. Therefore, the origin of the photoinduced decolorization of RhB in those regions was due to the photoabsorption of RhB, which led to the self-sensitized RhB decolorization, i.e., not true

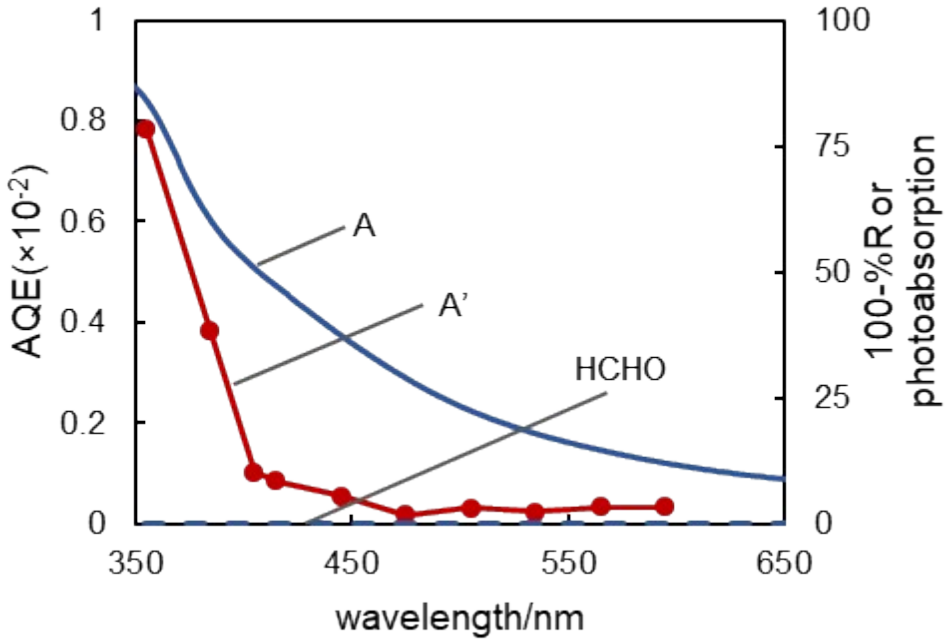

Figure S2. (A) DR spectra of Sample A, (A') action spectra of HCHO consumption on Sample A and (HCHO) photoabsorption spectra of HCHO solution with 5-10% methanol as stabilizer.

photocatalytic activity.[7,8]

2.2 Formaldehyde consumption on Sample A

For taking an action spectrum of HCHO consumption, a suspension of a 3.00-mL solution of HCHO (5×10^{-4} mol L^{-1}) and 30 mg of Sample A was placed in a long-necked cuvette cell. The suspension was stirred in the dark for 1 h followed by monochromatic irradiation for 2 h at each wavelength. The suspension was centrifuged (13,000 rpm for 5 min) and 1.00 mL of the supernatant was taken (without dilution) and mixed with 1.00 mL of Nash reagent. The solution was heated for 5 min, followed by keeping in a standing position for 10 min and the liberated DDL was extracted by 4-mL chloroform. The consumption amount of HCHO after irradiation was used to calculate the AQE for the plot of action spectra. **Figure S2**, the action spectra of HCHO-consumption on Sample A, shows that photocatalytic activity of HCHO consumption was observed at wavelength 400-600 nm solely due to photoabsorption of the photocatalyst since HCHO cannot absorb light in this wavelength range. This result suggested that the photoinduced HCHO-consumption may show the true photocatalytic activity of Sample A.

2.3 Previous Results on Titania Photocatalysis

In the previous studies on action-spectrum analysis on photocatalytic methanol dehydrogenation and oxidative decomposition of acetic acid, it has been found that the observed action spectra for the former reaction resembled the photoabsorption spectrum of titania and almost no light-intensity dependence suggesting that loaded platinum does not affect the photoabsorption.[4(17 in the text)].

3. Experimental Section for Chemical Balance Study in Methanol Dehydrogenation and Formaldehyde Oxidative Decomposition

For this study, a 400-W high-pressure mercury-arc lamp (Eiko-sha 400, $\lambda > 290$ nm, roughly estimated light flux at 365 nm = 1 μmol s^{-1}) was used as the light source equipped with a merry-go-round apparatus and magnetic stirrers. For product analysis, a spectrophotometer (Shimadzu MPS-2450, UV-vis multipurpose spectrophotometer) and high-performance liquid chromatography (HPLC: Shimadzu LC-20AD, equipped with a Shimadzu CDD-10A vp detector and a Shimadzu Shim-pack SCR-102H column) were used for the analysis of HCHO and formic acid (HCOOH), respectively. For the analysis of gas products, a GC was used to detect the production of H_2 and CO_2 gas with MS-5A and Porapak-Q columns, respectively. For the detection

of carbon monoxide (CO), Shimadzu GC 2014 with TCD detector and MS-13X column were utilized.

3.1 Methanol Dehydrogenation

A 50 mg of a commercial titania sample was suspended in 5.00 mL of aqueous 50vol% methanol in a 35-mL test tube. The chloroplatinic acid solution was added to obtain 2wt% of platinum deposition on a titania photocatalyst, and stirring was conducted to enhance the distribution of platinum on titania particles. Air was purged from the headspace of the test tube by argon bubbling (ca. 5 min) and the test tube was sealed with a rubber septum to prevent gas leakage from the test tube. The suspension was irradiated by the mercury-arc lamp for 1 h under vigorous magnetic stirring (ca. 1000 rpm). After photoirradiation, gaseous products, i.e., H_2, CO_2 and CO, were analyzed by GCs. Before the analysis of liquid products, the photocatalyst was separated from the suspension by centrifugal filtration (13,000 rpm for 5 min). For HCOOH analysis, the solution was measured by HPLC (mobile phase: gradient flow of (A) 5 mmol L^{-1} *p*-toluene sulfonic acid monohydrate and (B) a mixture of 20-mmol L^{-1} bis (2-hydroxyethyl) iminotris (hydroxymethyl) methane, 5-mmol L^{-1} *p*-toluene sulfonic acid monohydrate and 100-μmol L^{-1} ethylene diamine tetraacetic acid (EDTA)). For HCHO analysis, the colorimetric analysis was conducted by the above-mentioned method using Nash reagent.

3.2 Formaldehyde Oxidative Decomposition

A 50 mg of a photocatalyst was suspended in a 5-mL freshly prepared HCHO solution (5×10^{-2} mol L^{-1}; from paraformaldehyde) in a 35-mL test tube. The test tube was sealed off by a rubber septum and parafilm prior to irradiation. The photoirradiation was conducted for 1 h, and the gas and liquid products, i.e., CO_2, CO, and HCOOH, were analyzed by the GCs and HPLC, while the consumption of HCHO was analyzed by a spectrophotometer using the above-mentioned method. A 1-mL portion of hydrochloric acid (5 mol L^{-1}) was injected into the test tube prior to CO_2 analysis to release the dissolved CO_2 from the suspension.

4. Visible-light Active Titania Photocatalyst

There have been reported two strategies to make UV-absorbing titania active under VR irradiation by narrowing the bandgap. One is to raise the valence-band top (VBT) position keeping

the conduction-band bottom (CBB) unchanged by, e.g., doping nitrogen, sulfur or the other element.[9] Since the VBT of titania seems low enough (anodic) for the oxidation of organic compounds by positive holes, a little raise of VBT may not give overall activity changes. The other strategy is to make CBB lower (anodic) while keeping the VBT position. In the application of photocatalysis for the organics decomposition, oxygen is reduced by photoexcited electron at CBB as a counter reaction of oxidation by positive holes. Since the CBB of titania (both anatase and rutile) is reported to be just above the potential of one-electron reduction of titania, lowering the CBB position must accompany the modification of titania to make possible to reduce oxygen by two-electron transfer process.[10] In such a case, CBB position must be lower than the standard hydrogen potential and thereby no hydrogen evolution proceeds even under UV irradiation.

The two commercial visible-light active titanias used, Sample A and Sample B, showed visible-light absorption as shown in **Fig. 2** probably through one of the above-mentioned strategies (or both), though the process and additives for narrowing the bandgap is not disclosed by the supplier. Judging from the results under the visible-light (green LED) irradiation shown in **Fig. 1**, i.e., no hydrogen evolution from aqueous methanol and appreciable formaldehyde oxidation, it is suggested that those visible-light active titanias were prepared by lowering their CBB position.

References

(1) A. Nitta, M. Takashima, M. Takase and B. Ohtani, *Catal. Today*, 2019, **321-322**, 2–8.

(2) T. Nash, *Biochem. J.* 1953, **55**, 416–421.

(3) T. Torimoto, N. Nakamura, S. Ikeda and B. Ohtani, *Phys. Chem. Chem. Phys.,* 2002, **4**, 5910–5914.

(4) T. Torimoto, Y. Aburakawa, Y. Kawahara, S. Ikeda and B. Ohtani, *Chem. Phys. Lett*. 2004, **392**, 220–224.

(5) A. Nikolenko and B. Melnykov, *Chem. Chem. Technol.* 2010, **4**, 311–315.

(6) I. N. Reddy, C.V. Reddy, J. Shim, B. Akkinepally, M. Cho K., Yoo and D. Kim, *Catal. Today,* 2020, **340**, 277–285.

(7) X. Yan, T. Ohno, K. Nishijima, R. Abe and B. Ohtani, *Chem. Phys. Lett.,* 2006, **429**, 606–610.

(8) G. Q. Li, N. Yang, X. L. Yang, W. L. Wang and W. F. Zhang, *J. Phys. Chem. C,* 2011, **115**, 13734–13738.

(9) For example: R. Asahi, T. Morikawa, T. Ohwaki and Y. Taga, *Science*, 2002, **293**, 269–271.

(10) For example: M. Endo-Kimura, B. Karabiyik, K. Wang, Z. Wei, B. Ohtani, A. Markowska-Szczupak and E. Kowalska, *Catalysts*, 2020, **10**, 1194.