

Photochemical hydrogen evolution from aqueous triethanolamine solutions sensitized by binaphthol-modified titanium(IV) oxide under visible-light irradiation

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Abstract

Surface modification of titanium(IV) oxide (TiO₂) powders with 1,1'-binaphthalene-2,2'-diol (bn(OH)₂), having two phenolic hydroxyls and atropisomeric chirality, in refluxed ethanol led to the formation of a deep yellow-colored surface complex, giving visible-light absorption at a wavelength below ca. 550–600 nm. Quantitative analyses of the surface complex revealed that absorption intensity at 450 nm in diffuse reflection (DR) measurement was almost proportional to its amount and that its amount depended strongly on the amount of surface hydroxyl groups of TiO₂ but not on the crystal structure of TiO₂, anatase, and rutile. The bn(OH)₂ complexation was also applied to platinumized TiO₂ to drive photocatalytic molecular hydrogen (H₂) evolution from deaerated triethanolamine solutions under visible-light irradiation at a wavelength even longer than 540 nm. The photonic efficiency of the photocatalytic reaction at 450 nm was estimated to be 0.02% for bn(OH)₂-modified TiO₂ (JRC-TIO-3) loaded with 0.1 wt.% of platinum. On the basis of these experimental results, the reaction mechanism, which involves visible-light excitation of the surface complex, injection of electrons from the complex to TiO₂, and migration of the electrons to platinum deposits, where reduction of H⁺ takes place to give H₂, was elucidated.

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1. Introduction

It is generally of great importance to control the activity of TiO₂ photocatalysts by modification of their bulk and/or surface properties in compliance with different needs [1,2]. One of the intriguing subjects in both academic research and industrial research is development of new TiO₂-photocatalytic systems with enhanced activities under visible-light irradiation compared with the simply TiO₂-photocatalyzed processes, since bare TiO₂ can absorb light in the ultraviolet range, which corresponds to only ca. 3% of the energy of sunlight. Several strategies and methods for modifying the optical properties of TiO₂ particles, e.g. doping of a transition metal [3,4], plasma treatments, [5] and nitrogen doping [6,7], have been proposed, and photoactivity under visible-light irradiation has been proved in some limited reactions. Much interest has also been shown in surface modification of TiO₂ with transition metal complexes and/or organic dyes for construction of dye-sensitized pho-

tocatalytic systems that work under visible-light irradiation [8,9] as well as for improvement of the efficiency of dye-sensitized solar cells [10–12].

On the other hand, in order to clarify the reaction mechanism of the photocatalytic reaction of organic molecules, structural characteristics of these compounds adsorbed on TiO₂ surface have been extensively investigated using various spectroscopic techniques [13–19]. In the course of these studies, it was proved that colorless aromatic compounds having phenolic hydroxyls such as catechol and salicylic acid react with TiO₂ particles to form colored surface complexes [15–19]. Thus, it is expected that a novel visible-light-induced photocatalytic system can be developed by using the photoabsorption of surface complexes on TiO₂ particles. Recently, we have demonstrated that 1,1'-binaphthalene-2,2'-diol (bn(OH)₂), having two phenolic hydroxyls and atropisomeric chirality, reacts with TiO₂ and gives a colored surface complex, which works as catalyst for water reduction in the presence of a sacrificial donor under visible-light irradiation [20].

In this paper, we describe in detail the structural characteristics of the surface TiO₂-bn(OH)₂ complex and

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some mechanistic aspects of visible-light-induced photoactivity.

2. Experimental

2.1. Materials

Several kinds of titanium oxide (TiO₂) powders, those from commercial sources (Degussa P25, Degussa F281, Ishihara ST-01, Ishihara CR-EL, Hombikat UV-100, Showa Denko F-6, and Idemitsu UF), reference catalysts supplied from the Catalysis Society of Japan (TIO-2 and TIO-3), and powders synthesized by the HyCOM method [21,22] followed by calcination at 573 K under O₂, were used. The properties of these TiO₂ powders are summarized in Table 1. Ethanol (Wako), methanol (Wako), triethanolamine (2,2',2''-nitrioltrisethanol, TEOA; Wako), chloroplatinic acid (H₂PtCl₆·6H₂O, Wako), and 1,1'-binaphthalene-2,2'-diol (bn(OH)₂, racemate; Aldrich), were used without further purification.

2.2. Preparation of bn(OH)₂-adsorbed TiO₂

In a typical experiment, 0.5 g of TiO₂ powder was suspended in an ethanolic solution of bn(OH)₂ (0.14 mol dm⁻³, 25 cm³), and the resulting suspension was refluxed for 8 h under an argon (Ar) atmosphere. The solid was collected by centrifugation (ca. 3500 rpm), washed twice with ca. 10 cm³ of ethanol, and dried under reduced pressure at ambient temperature. Ultraviolet and visible-light diffuse reflection (DR) spectra were obtained using Hamamatsu Photonics C7473-6 photonic multi-channel analyzer, and the data were converted to Kubelka–Munk (KM) function. Based on the contents of carbon and ash components quantified by elemental analysis, the amount of adsorbed bn(OH)₂ was estimated with assumption that the remaining ash was only composed of TiO₂. Since the carbon components in most of

the samples were less than 2 wt.% and the elemental analysis of organic compounds includes less than 0.3% of error, estimated amounts may include a large quantity of error. However, we could confirm reproducibility within 10% on some selected samples. Platinized TiO₂ powder, prepared by photoplatinization in deaerated aqueous methanol solution containing H₂PtCl₆·6H₂O [24], was also modified with bn(OH)₂ by the same procedure as that used for unplatinized TiO₂ powder.

2.3. Photoirradiation and product analysis

The bn(OH)₂-modified or bare TiO₂ powder (50 mg) and an aqueous TEOA (10 vol.%) or methanol (50 vol.%) solution (5 cm³) were placed in a glass tube (transparent at >300 nm, 18 mm in diameter and 180 mm in length), and the suspensions were photoirradiated under Ar at 298 K with vigorous magnetic stirring (1000 rpm). Photoirradiation was performed using a high-pressure mercury arc (Eiko-sha, 400 W) or a xenon arc (Ushio UXR-300DU, 300 W) with a Y-44, Y-50, O-55, or O-59 optical filter (Asahi Techno Glass) to cut out light of wavelength shorter than 430, 490, 540 or 580 nm, respectively. Liberated hydrogen (H₂) was analyzed using a gas chromatograph (GC, Shimadzu GC-8A) equipped with an MS-5A column (GL Sciences) and a TCD detector. Photonic efficiency, a molar ratio of product (twice the amount of H₂) to incident photons, was estimated at 450 nm using a JASCO CT-101T monochromator equipped with a xenon arc. The incident photon flux was estimated using a Moletron POWER MAX5200 laser power meter.

3. Results and discussion

3.1. Structure of TiO₂ modified with bn(OH)₂

Fig. 1 shows ultraviolet and visible DR spectra of Degussa P25, TIO-3, and TiO₂ powders treated with an ethanolic bn(OH)₂ solution. Untreated P25 and TIO-3 gave absorption in the ultraviolet region below ca. 400

Table 1
Properties of TiO₂ powders

Entry	Name/code	Supplier	Crystalline form ^a	S ^b (m ² g ⁻¹)
a	P25	Degussa	A(88)/R(12)	50
b	F281	Degussa	A	96
c	ST-01	Ishihara	A	320
d	CR-EL	Ishihara	A(0.5)/R(99.5)	3
e	UV-100	Hombikat	A	250
f	F-6	Showa Denko	A(83)/R(18)	102
g	UF	Idemitsu	am	115
h	TIO-2	CSJ ^c	A	18
i	TIO-3	CSJ ^c	R	40
j	HyCOM	Home made	A	133

^a A, anatase; R, rutile; am, amorphous. Figures shown in parentheses denote percent proportion of the most intense XRD peaks of anatase ((1 0 1), 2θ = 25.3°) and rutile ((1 1 0), 2θ = 27.5°) [23].

^b BET surface area measured by nitrogen adsorption at 77 K.

^c Reference catalysts from the Catalysis Society of Japan.

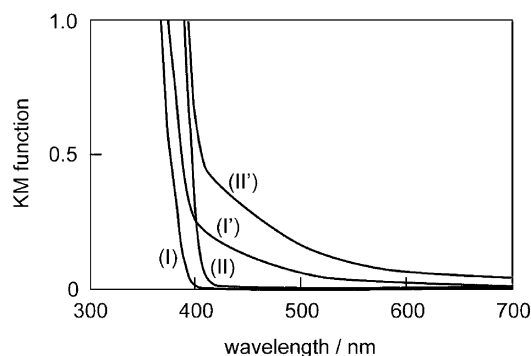


Fig. 1. Ultraviolet and visible light DR spectra of (I) P25, (II) TIO-3, (I') bn(OH)₂-modified P25, and (II') bn(OH)₂-modified TIO-3.

and 410 nm, respectively, corresponding to their band-gap photoabsorption. The gaps were reported to be ca. 3.0 eV (410 nm) for rutile (TIO-3) and 3.2 eV (390 nm) for anatase [25], and P25, a mixture of anatase and rutile, might give an intermediate spectrum. Treatment of the colorless compound $\text{bn}(\text{OH})_2$ induced striking changes in the spectral features of these TiO_2 powders: the color of the powders became deep yellow after $\text{bn}(\text{OH})_2$ treatment, giving visible-light absorption below ca. 550–600 nm. Due to the overlap of the fundamental band-gap photoabsorption of TiO_2 , the exact position of the peak, if present, of newly appearing visible-light absorption could not be determined. However, the shapes in the visible range and the absorption edge positions of the two $\text{bn}(\text{OH})_2$ -treated TiO_2 powders were quite similar; there seemed to be no significant dependence on the crystal form, anatase, and rutile of TiO_2 .

To identify the surface species, the amounts of $\text{bn}(\text{OH})_2$ attached to several TiO_2 powders were quantified by elemental analysis of carbon and ash components. Fig. 2 shows plots of absorption intensity at 450 nm of $\text{bn}(\text{OH})_2$ -treated TiO_2 powder (I_{450}) and its BET surface area (S) as a function of the amount of adsorbed $\text{bn}(\text{OH})_2$ per unit weight of TiO_2 (M_{bn}). It is clear from this figure that there is an almost linear relation between M_{bn} and I_{450} of several TiO_2 powders. This suggests that the $\text{bn}(\text{OH})_2$ species adsorbed on TiO_2 give visible-light absorption, independent of the

kind of bare TiO_2 powder. Since I_{450} was measured in KM function which contains a term of light scattering as well as that of absorption and thus it depends on the light scattering properties of bare TiO_2 powders, deviation of a plot (g) higher from a linear line might be caused by the scattering properties of these TiO_2 powders (consisting of amorphous) which seem a different from the ordinary crystalline powders. It is also noted that a plot (e) seems to slightly deviate lower from a linear line. Although there is no clear basis at present, this might be due to the presence of another type of a surface complex on the sample (e), having lower absorption coefficient than that on other ordinal TiO_2 powders (see below). A linear relationship was also observed between M_{bn} and S for all TiO_2 powders except for the amorphous TiO_2 (Idemitsu UF), which showed a relatively high density of $\text{bn}(\text{OH})_2$ adsorption and as is discussed in the following section.

As already reported by several workers [15–19], white TiO_2 particles and colloids turn yellow upon immersion in a solution containing phenols such as salicylic acid and catechol. The development of the yellow color is a clear indication of the formation of surface TiO_2 -salicylate and TiO_2 -catechol complexes, and the absorption bands in the visible range were assigned to intramolecular ligand-to-metal charge transfer transition [18,19]. Thus, the observed visible-light absorption in the present experiment is attributable to the formation of a surface TiO_2 - $\text{bn}(\text{OH})_2$ complex. According to previous reports on TiO_2 -salicylate and TiO_2 -catechol surface complexes [16–19], there appears to be two different structures of the complex. One structure is formed by chelation of a surface titanium atom with two hydroxyl groups in a $\text{bn}(\text{OH})_2$ molecule (“chelation”, a 1:2 adduct) and the other is formed by binding of each phenolic hydroxyl group in $\text{bn}(\text{OH})_2$ to the surface titanium atom (“esterification”, a 2:2 adduct), both of which are induced by intermolecular dehydration of surface and phenolic hydroxyls, as shown in Scheme 1. Although there

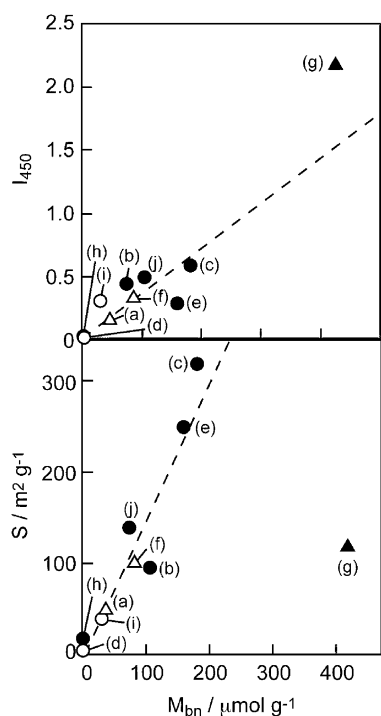
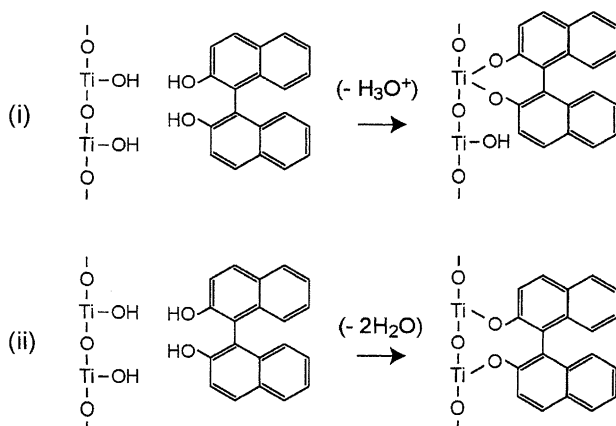


Fig. 2. Relations between M_{bn} and I_{450} (upper) or S (lower) for (a) Degussa P25, (b) Degussa F281, (c) Ishihara ST-01, (d) Ishihara CR-EL, (e) Hombikat UV-100, (f) Showa Denko F-6, (g) Idemitsu UF, (h) TIO-2, (i) TIO-3, and (j) HyCOM. Open circles, filled circles, open triangles, and filled triangles denote rutile, anatase, their mixtures, and amorphous, respectively.



Scheme 1. Schematic illustration of the reactions between Ti-OH and phenolic hydroxyl group in $\text{bn}(\text{OH})_2$ through (i) chelation (a 1:2 adduct) and (ii) esterification (a 2:2 adduct), both of which are accompanied by the liberation of water.

is no experimental method for discriminating these two possible structures of the surface complex in the samples, the fact that a yellow-colored powder giving a similar absorption spectrum in the visible light range below ca. 550 nm was also obtained by the reaction of TiO_2 with 2-naphthol, which has only one phenolic hydroxyl group (data not shown), suggested that the latter structure (“esterification”) could interpret the present results of $\text{bn}(\text{OH})_2$, but did not exclude the former structure (“chelation”). Further studies for clarification of the structure are now underway.

Previous studies on the quantification of surface hydroxyls (Ti–OH) on TiO_2 by sodium hydroxide titration [26] have shown that the density of Ti–OH is almost constant, ca. 2.5 hydroxyls nm^{-2} , among several polycrystalline TiO_2 powders except for amorphous samples, which have a relatively high density of Ti–OH, ca. 16 hydroxyls nm^{-2} [27]. Assuming surface complexation through dehydration between Ti–OH with the hydroxyl groups in $\text{bn}(\text{OH})_2$ as discussed above and uniform and similar chemical properties of Ti–OH in TiO_2 samples, a linear relationship between M_{bn} and S , as shown in Fig. 2, seems quite reasonable for the samples of TiO_2 having almost the same Ti–OH surface density. Deviation of the Idemitsu UF ((g) in Fig. 2) is thought to be due to its higher density of surface Ti–OH. From the reciprocal slope of Fig. 2 (lower), the surface density of $\text{bn}(\text{OH})_2$ on the ordinary polycrystalline samples was estimated to be 0.8 $\mu\text{mol m}^{-2}$ or 0.48 molecules nm^{-2} . The density was ca. 1/5 of the above estimated Ti–OH density, and approximately half (or little less) of Ti–OH was used for surface complexation when the 2:2 adduct was presumed. This estimation of surface coverage is consistent with the estimated coverage, half or a little less, using the cross-sectional area of a $\text{bn}(\text{OH})_2$ molecule (ca. 1 nm^2) in the surface structure shown in Scheme 1. It is reasonable to assume that the loosely packed arrangement of $\text{bn}(\text{OH})_2$ is caused by its large molecular size and a mismatching of the Ti–OH spatial arrangement to anchor $\text{bn}(\text{OH})_2$. On the other hand, the higher density of $\text{bn}(\text{OH})_2$ on Idemitsu UF was attributed to the sufficiently high density of Ti–OH to allow close packing of $\text{bn}(\text{OH})_2$ on the surface. The estimated density of $\text{bn}(\text{OH})_2$ on UF, ca. 2.8 molecules nm^{-2} , was three-times larger than that estimated from the cross-sectional area. This might be caused, at least partly, by underestimation of its BET surface area; surface adsorption of nitrogen was measured after evacuation at 383 K, which was >100 K lower than that for the other TiO_2 samples, to minimize the thermal effect on its structure [28] and at the same time to allow water to remain on the surface.

Thus, a part of the surface of $\text{bn}(\text{OH})_2$ -modified TiO_2 particles remains uncovered with $\text{bn}(\text{OH})_2$, and it is therefore expected that photoinduced reactions can be driven by $\text{bn}(\text{OH})_2$ -modified TiO_2 with photoabsorption by surface complexes and with redox reactions by photoexcited electrons (or holes) on the unmodified bare surface.

3.2. Photoreactivity of platinized TiO_2 modified with $\text{bn}(\text{OH})_2$

Photoinduced reduction of water to produce H_2 from an aqueous solution containing a sacrificial electron donor, methanol or TEOA, was conducted as a test reaction of photoactivity of the $\text{bn}(\text{OH})_2$ -modified TiO_2 . Preliminary experiments revealed the requirement of platinization to make active sites on the surface for H_2 production. Therefore, before the photoactivity test, a small amount of platinum (Pt) particles was deposited on TiO_2 (0.05–2 wt.%, corresponding to ca. 0.2–5% of surface coverage [29]) followed by modification with $\text{bn}(\text{OH})_2$. Consistent with this small coverage of Pt particles on TiO_2 , M_{bn} on platinized (2 wt.%) TIO-3 (40 $\mu\text{mol g}^{-1}$) was comparable or even larger than that on bare TIO-3 (32 $\mu\text{mol g}^{-1}$). One possible explanation for this small increment is attachment of $\text{bn}(\text{OH})_2$ to the surface of Pt particles. We tried to obtain the absorption spectrum of $\text{bn}(\text{OH})_2$ complex on platinized TiO_2 but failed due to interference by gray-colored Pt particles. Another possible explanation is an increase in Ti–OH during the Pt photodeposition process; the formation of Ti–OH induced by band-gap excitation of TiO_2 has been reported in relation with a phenomenon of photoinduced super hydrophilicity [30].

Fig. 3 shows H_2 liberation from aqueous methanol and TEOA solutions under ultraviolet light irradiation (>300 nm) over $\text{bn}(\text{OH})_2$ -modified and -unmodified TiO_2 (TIO-3). In all the experimental runs, a linear increase in the molar amount of H_2 was observed. Due to the lower solubility of TEOA in water, the concentrations of these two electron donors were different (50 and 10 vol.% for methanol and TEOA, respectively), and pH of an aqueous TEOA solution (originally ca. 11) was not adjusted to be neutral. The electron-donating ability, therefore, cannot be discussed on

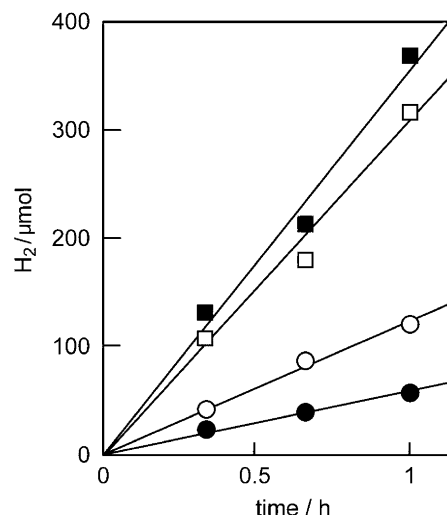


Fig. 3. Time courses of H_2 liberation by unmodified (open symbols) and $\text{bn}(\text{OH})_2$ -modified (closed symbols) TIO-3 (2 wt.% Pt) suspended in a deaerated aqueous methanol (squares) or TEOA (circles) solution under ultraviolet-light (>300 nm) irradiation.

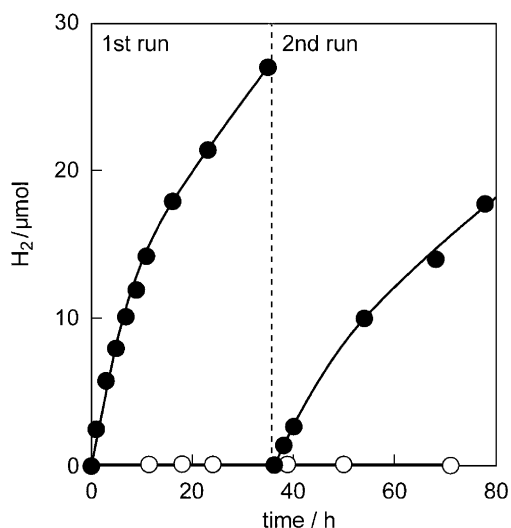


Fig. 4. Time courses of H_2 liberation by unmodified (open circles) and $bn(OH)_2$ -modified (closed circles) TiO_2-3 (1 wt.% Pt) suspended in a deaerated aqueous TEOA solution under visible-light (>430 nm) irradiation.

the basis of these results. It is notable that $bn(OH)_2$ -modified TiO_2 showed almost the same or an even slightly higher rate than that of unmodified TiO_2 in the aqueous methanol suspension, suggesting negligible or at most only partial coverage of the surface of Pt particles by $bn(OH)_2$. On the other hand, when TEOA was used as a sacrificial electron donor, the H_2 -liberation rate was halved by the $bn(OH)_2$ modification. It was presumed that access of TEOA, the size of which is much larger than that of methanol, to the bare (not covered with $bn(OH)_2$) surface was restricted. In a TiO_2 -photocatalyzed reaction using photoexcited electrons and positive holes in TiO_2 , adsorption of a reaction substrate such as TEOA on bare TiO_2 is required.

Fig. 4 shows the time courses of H_2 liberation from unmodified and $bn(OH)_2$ -modified TiO_2 (TiO_2-3) from an aqueous TEOA solution under visible-light irradiation (>430 nm). H_2 liberation from the $bn(OH)_2$ -modified TiO_2 suspension was observed, while, as predicted from the negligible photoabsorption of bare TiO_2 in the visible region (Fig. 1), no appreciable liberation of H_2 from unmodified TiO_2 was detected [20]. The total amount of evolved H_2 after 80 h of irradiation reached more than 40 μmol . Since the amount of $bn(OH)_2$ on 50 mg of TiO_2-3 was estimated to be 2 μmol (corresponding to 24 μmol of H atoms based on the assumption of the structure shown in Scheme 1), the total H_2 yield was 20-times greater than the molar amount of $bn(OH)_2$, indicating that the photoinduced reaction proceeded catalytically. It is also notable that the rate of H_2 production decreased gradually. This may be due to decomposition or leaching of the surface complex during the reaction. At present, however, there is no experimental evidence to elucidate the decrease of adsorbed $bn(OH)_2$, mainly because of the interference by Pt deposits, which causes greatly reduced DR and difficulty in evaluating DR spectra with high accuracy and reproducibility. In the sec-

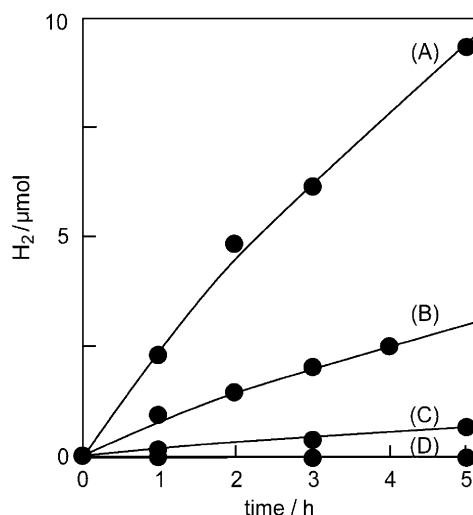


Fig. 5. Dependence of rate of H_2 liberation by $bn(OH)_2$ -modified TiO_2-3 loaded with 0.5 wt.% of Pt on wavelength of photoirradiated light of (A) >430, (B) >490, (C) >540, and (D) >580 nm.

ond run of irradiation after Ar bubbling to purge liberated H_2 and other volatile compounds such as ammonia, the initial rate ($0.65 \mu\text{mol h}^{-1}$) was less than half of that in the first run ($1.7 \mu\text{mol h}^{-1}$) but was more than 30% higher than the rate in the final stage of the first run ($0.48 \mu\text{mol h}^{-1}$). These facts indicate that accumulation of a volatile by-product(s) accounts at least partly for the deactivation during the course of irradiation. Under visible-light irradiation, negligible H_2 liberation was observed when methanol was used as a sacrificial electron donor instead of TEOA even at high pH (similar to the TEOA solution), though methanol worked efficiently when TiO_2 was photoexcited under ultraviolet-light irradiation (see Fig. 3).

Fig. 5 shows dependence of the rate of H_2 liberation on the wavelength of irradiated light for $bn(OH)_2$ -modified TiO_2 (TiO_2-3) loaded with 0.5 wt.% of Pt. The H_2 liberation required irradiation at a wavelength of <580 nm; no H_2 was produced under photoirradiation at a wavelength longer than 580 nm. This wavelength dependence corresponded to photoabsorption of TiO_2 - $bn(OH)_2$ complexes shown in Fig. 1, i.e. the observed visible-light-induced H_2 liberation was derived from photoexcitation of the surface $bn(OH)_2$ complex on TiO_2 .

Fig. 6 shows dependence of the rate of H_2 liberation on the amount of Pt deposits for $bn(OH)_2$ -modified TiO_2 (TiO_2-3). No H_2 liberation was observed in the absence of loaded Pt. The highest activity of ca. $7 \mu\text{mol h}^{-1}$ was observed when 0.1 wt.% of Pt was deposited on TiO_2 (TiO_2-3), and the photonic efficiency of this powder was estimated to be ca. 0.02% [20]. Further loading reduced the activity, presumably due to reduction of photoabsorption by the $bn(OH)_2$ surface complex and/or enhanced deactivation of the photoexcited complex. A previous study on characterization of Pt deposits on P25 TiO_2 powder [29] revealed that the optimum Pt deposition for P25 (0.1 wt.%), the surface area of which is

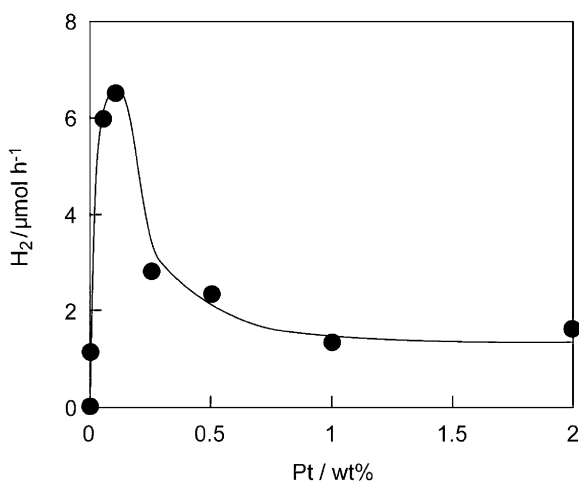
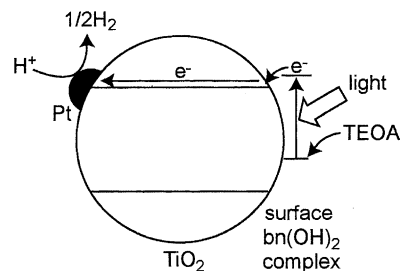


Fig. 6. Dependence of rate of H₂ liberation by bn(OH)₂-modified TiO₂ on amount of Pt deposits. Rate of H₂ liberation was estimated from the slope of the time course curve in the initial 2 h of photoirradiation.

similar to that of TiO₂-3, corresponds to the minimum amount of Pt loading required to distribute at least one Pt deposit (ca. 2 nm) on each TiO₂ particle. The Pt deposits act as active sites for H₂ liberation through reduction of H⁺ with photoexcited electrons of the surface bn(OH)₂ complex that have migrated presumably via TiO₂.

The TiO₂ powders such as Ishihara ST-01 and HyCOM, both of which consist of anatase crystallites, also produced H₂ under the visible-light irradiation at >430 nm. The rates of H₂ liberation were 0.5 μmol h⁻¹ for ST-01 with 2 wt.% of Pt and 3.7 μmol h⁻¹ for HyCOM with 1 wt.% of Pt [20]. Although the activity of these samples is thought to depend on the amount of Pt loading, similar to that in Fig. 6, and although the amount of Pt deposits for these samples has not been optimized, a comparison of the trends in H₂ liberation rates for the three samples with those of M_{bn} (Fig. 2) indicates that there are no simple proportional relations between them. The relatively lower activity of ST-01, consisting of less crystallized anatase particles, i.e. having a larger number of defects, in spite of larger M_{bn}, suggested the importance of crystallinity of TiO₂, as has been reported for the photocatalytic activity of platinumized TiO₂ for dehydrogenation of alcohol [22]. In the presumed mechanism, as discussed in the following section, photoexcited electrons in the surface bn(OH)₂ complex are injected into TiO₂, and it migrate into TiO₂ to reach the Pt deposit. The crystallinity governs the efficiency of the electron migration. Anyway, highly active photocatalytic systems are to be constructed by selection of suitable TiO₂.

As suggested in the preliminary paper [20], visible-light-induced H₂ evolution is thought to proceed through a sensitizing mechanism initiated by excitation of the surface complex by visible light followed by electron injection into the conduction band of TiO₂. Such a surface charge transfer has been studied and has been confirmed for a TiO₂-catechol surface complex system [17]. The injected electrons in the



Scheme 2. Proposed model for overall reaction of visible-light-induced photocatalytic H₂ evolution by bn(OH)₂-modified TiO₂ loaded with platinum.

TiO₂ particles migrate to the platinum deposits, where reduction of H⁺ takes place to give H₂. TEOA must work as a sacrificial electron donor to reduce the oxidized form of the surface complex. A schematic model of the overall reaction is shown in Scheme 2. Judging from the wavelength of the bn(OH)₂ complex absorption edge, ca. 580 nm (ca. 2.1 eV), and the fact that the complex in an excited state can inject electrons into the conduction band of TiO₂, the ground-state electronic level of the complex should be ca. 1 V negative from the upper edge of the valence band in TiO₂. Methanol could inject electrons into the ground state, but negligible H₂ was liberated as described above. The difference in the adsorption abilities of a bn(OH)₂-modified surface, but not a bare TiO₂ surface, and/or in the reactivity of the oxidized form of bn(OH)₂ complex toward TEOA and methanol might cause the distinction of these sacrificial donors.

4. Conclusions

The present study has shown that derivatization of a semiconductor surface with a simple aromatic compound as a complexation reagent can induce a visible-light-induced photocatalytic ability. Although, a similar photosensitized water reduction system, which includes a surface complex between TiO₂ and 8-hydroxyquinoline, has been demonstrated [31], the present system, proved to drive a photocatalytic reaction under visible-light irradiation, can be further extended. In the present study, we used only a racemate of bn(OH)₂, but when optically active (*R*)- and (*S*)-bn(OH)₂'s are used as complexing agents, we can expect stereoselective photocatalytic reactions (for example, phenylethylamine having a chiral carbon center, which has been confirmed to work as an electron donor in the present system) through chiral modification. Further studies along this line are now under way.

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