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Photocatalysis of titanium dioxide modified by catechol-type interfacial surface complexes (ISC) with different substituted groups



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ABSTRACT

Visible-light responsive TiO₂ photocatalyst modified by catechol-type interfacial surface complexes (ISC) was designed by the reaction of Ti—OH moieties with catechol and such derivatives as 3-methoxycatechol involving electron-donating groups (EDG) and 3,4-dihydroxybenzonitrile involving electron-withdrawing groups (EWG). The visible-light response of the ISC is attributed to excitation from the donor levels created in the TiO₂ midband. The phenyl-ring-substituted groups strongly influence the electronic structures of the ISC: the catechols with substituted EWG induce an anodic shift of the donor levels accompanied by an enlargement of the energy gaps, compared with catechol without substituted groups. The photocatalytic activities for H₂ evolution from triethanolamine aqueous solutions were systematically investigated. It was confirmed that the more anodic the oxidative potentials of photoinduced holes in the ISC are, the higher the photocatalytic activities they exhibit.

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1. Introduction

TiO₂ photocatalysts are known to promote such photoreactions as decomposition of volatile organic compounds (VOC), H₂ production from aqueous solutions, and selective transformation of organic compounds [1–5]. In general, TiO₂ photocatalysts operate by band-gap excitation (3.0–3.2 eV or more) under UV irradiation, of which only a few percent reaches the earth's surface. Therefore, the development of visible-light-sensitive TiO₂ photocatalyst has been a great concern for efficient utilization of solar light [6–9]. Visible-light-responsive TiO₂ photocatalysts have been designed by several methods such as doping with nitrogen and other elements [10–14], organic dye sensitizer [15], plasmonic Au and Ag nanoparticles [16–19], and interfacial surface complexes (ISC) [20–30].

Recently, attention has been paid to photocatalysis due to the ISC formed by the interaction of TiO_2 surface with such colorless organic compounds as aromatic alcohols [20–25], amine [26,27], and phenolic compounds [28–30]. We previously reported the selective photocatalytic oxidation of benzyl alcohol into benzalde-hyde with high selectivity on TiO_2 under visible-light irradiation

[20–24] and theoretical studies on its reaction mechanisms by DFT calculations [25]. The visible-light response of the ISC formed by the interaction of benzyl alcohol with the TiO_2 surface is attributed to excitation from the donor levels in the TiO_2 midband, and the ISC is selectively converted into benzaldehyde.

Unlike the photocatalytic system employing the ISC as mentioned above, the binaphtol-modified and hydroxynaphthalenemodified TiO₂ photocatalysts exhibit hydrogen production from triethanolamine (TEA) aqueous solutions [29] and selective reduction of nitrobenzene into aminobenzene [30], respectively, under visible-light irradiation.

The ISC was extensively characterized by several spectroscopic techniques, such as UV–vis, FT-IR, Raman, as well as by theoretical calculations [31–33,28,34–39]. It is accepted that interaction between surface Ti—OH groups and phenolic groups of the catechol leads to the formation of catecholate species, which exhibit absorption in the visible-light region. In particular, it was reported that surface modification of nanocrystalline TiO₂ particles with different catechol-type derivatives was found to alter optical properties [31].

However, the photocatalytic activities using TiO_2 modified by catechol and its derivatives as simple aromatic molecules have not been systematically studied. Moreover, effects of phenyl ring substitution with electron-withdrawing groups (EWG) and



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electron-donating groups (EDG) on the optical properties of the ISC have yet to be clarified. In this study, we investigated the photocatalytic activities for H_2 evolution from aqueous TEA of TiO₂ modified by catechol and its derivatives substituted with EWG and EDG. In particular, relationships between electronic structures of the ISC and their photocatalytic activities have been clarified by the combination of electrochemical measurements and DFT calculations.

2. Experimental

Catechol (referred to as CA) and its derivatives such as 4-*tert*-butylcatechol (BC), 3-methoxycatechol (MC), 2,3-dihydroxybenzoic acid (BA), 3,4-dihydroxybenzonitrile (BN) and Tiron (TN), hydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆·6H₂O), acetonitrile, and triethanolamine (TEA) were purchased from Wako Co., Ltd. The derivatives of catechols were classified into two categories: BC and MC with substituted EDG and BA, BN, and TN with substituted EWG as shown in Fig. 1. Commercially available TiO₂ (anatase, 320 m² g⁻¹, ST-O1, Ishihara Co., Ltd.) was mainly used in this study. All chemicals were used without further purification.

In a typical surface modification of TiO₂, 1 g of TiO₂ (ST-01) was added to aqueous solutions (30 mL) involving CA and its derivatives (40–200 µmol), and the suspension was stirred at 298 K for 3 h vigorously under N₂ bubbling in the dark. To determine amounts of modifiers loaded onto the TiO₂, concentrations of the modifiers in solutions were analyzed by HPLC (Shimadzu LC10ATVP, UV–vis detector, column: Chemcopak, mobile phase: a mixture of acetonitrile and 1.0 vol% aq. HCOOH in a volume ratio of 3:7) after separation of the solids by a centrifuge. It was observed that no surface modifiers remained in the solutions; i.e., all the modifiers were confirmed to anchor on the TiO₂ surface. The photocatalyst was referred to as *x*-XX/TiO₂, where XX and *x* stand for kinds of modifiers and amounts (µmol) adsorbed onto TiO₂ (1 g), respectively.

UV–vis spectra were obtained by a diffuse reflection method with a spectrometer (UV-3100PC, Shimadzu). The reflectance spectra were converted into a Kubelka–Munk function. The IR spectra of samples were measured with a FT-IR (IRPrestige-21, Shimadzu) with MIRacle A (ZnSe ATR accessory) and measured with 100 scans at resolution 4 cm^{-1} .

Photocatalytic activities were evaluated by the evolution of H_2 from aqueous TEA. The aqueous TEA (10 vol%, 10 mL) suspended with photocatalyst (50 mg) and desired amounts of aqueous



Fig. 1. Molecular structures of catechol and its derivatives with substituted EDG and EWG.

H₂PtCl₆ (Pt/Ti: 0.1–2.0 atomic%) as co-catalyst was introduced into a Pyrex cell under purging with N₂. It was then irradiated by blue LED lamps adjusted to 25,000 lux (λ_{max} = 460 nm, ca. 10 mW/cm²). The photoproduced H₂ was quantitatively analyzed by GC-TCD (Model 802, Ohkura; column: Molecular Sieve 5A).

To evaluate apparent quantum yields (AQY), photoirradiation was carried out by a 100 W Xenon lamp (Lax Cute II, Asahi Spectra Co., Ltd.) through several bandpath filters with a FWHM of 10 ± 2 nm (Asahi Spectra). The AQY at each centered wavelength of light was calculated using the following Eq. (1):

AQY (%) =
$$\frac{(\text{amounts of H}_2 \text{ formed}) \times 2}{(\text{amounts of photons irradiated})} \times 100$$
 (1)

The flux of incident photons was measured by a power meter (Ophir, ORION/PD), and photoirradiation was conducted in the range of 7.24×10^{18} – 1.03×10^{19} photons h⁻¹.

Photoelectrochemical measurements were carried out in a three-electrode cell using a potentiostat/galvanostat (HABF5001, HOKUTO DENKO). Photoirradiation was performed through a low-cutoff filter (Y-45, Asahi Technoglass Co. Ltd.) transmitting light with $\lambda > 420$ nm. Aqueous LiClO₄ (0.1 M) involving TEA (10 vol%) was used as the electrolyte solution. The electrolyte was bubbled vigorously with N₂ for 30 min prior to measurements. TiO₂ film was used for the working electrode, Pt wires for the auxiliary electrode, and Ag/AgCl for the reference electrode. The TiO₂ film was prepared as follows: 2.85 g of TiO₂ powder (Degussa, P-25) and 0.15 g of ST-01 was well dispersed in 5 mL of dilute HNO₃ (pH 3) involving 0.3 g of polyethylene glycol ($H_w = 20,000$) and 0.3 mL of Triton X-405. The paste was then spread onto transparent and conductive ITO-coated glass (10 Ω cm⁻², Geomatec Co. Ltd.) by spin coating, followed by heat treatment in air at 673 K for 1 h. This process was repeated twice and the film thickness was adjusted to ca. 15 μ m. Then the BN/TiO₂ and BC/TiO₂ films were prepared by immersing TiO₂ films for 3 h in aqueous BN and BC (5 mM), respectively.

To determine the oxidative potentials (E_A) of organic compounds, cyclic voltammograms were obtained using three electrodes: a glassy carbon electrode with active surface area of 7.1 mm² (BAS Inc.) for the working electrode, Pt wires for the auxiliary electrode, and Ag/AgCl for the reference electrode.

3. Results and discussion

3.1. Surface characterization of TiO_2 modified by catecholate-type complexes

Fig. 2a and a' shows FT-IR ATR spectra of free CA and 80-CA/TiO₂, respectively. The CA exhibits IR bands at 1514 and 1470 cm⁻¹ assigned to the stretching ν (C–C) or ν (C=C) vibrations of the aromatic ring, 1365 cm^{-1} to the $\delta(O-H)$, 1096 and 1040 cm⁻¹ to the bending δ (C–H), and 1300–1150 cm⁻¹ to the stretching ν (C–O) or bending δ (C–O) vibrations [31,34,37,40]. On the other hand, the 80-CA/TiO₂ exhibits bands at ca. 1480 cm⁻¹ assigned to ν (C–C) or ν (C=C), and at ca. 1250 cm⁻¹ to ν (C–O) and/or δ (C–O), while that at ca. 1365 cm⁻¹ assigned to δ (O–H) has completely disappeared. These results indicate that the catecholate species is formed by linkage of the surface Ti-OH groups with CA. Moreover, the IR bands of 80-BC/TiO₂ and 80-BN/TiO₂ photocatalysts are also shown in Fig. 2. It was observed that the characteristic bands at ca. 1365 cm⁻¹ due to the δ (O–H) of free BC and BN disappeared on 80-BC/TiO₂ and 80-BN/TiO₂, suggesting that the linkage of the surface Ti-OH groups with BC and BN forms corresponding catecholate species [41].

 TiO_2 photocatalysts modified by CA and its derivatives (BC, MC, BN, and TN) exhibit absorption with lower energy than 3 eV,



Fig. 2. FT-IR ATR spectra of free (a) CA, (b) BC, (c) BN and (a') 80-CA/TiO₂, (b') 80-BC/TiO₂ and (c') 80-BN/TiO₂.

although TiO₂ by itself exhibits little absorption in the visible-light regions, as shown in Fig. 3. It should be noted that the modifiers in aqueous solutions showed absorption in the UV region with energy higher than 4 eV, as shown in Fig. SI 1 in the Supporting Information. These results indicate that the interactions of colorless catechol and its derivatives with the TiO₂ surface exhibit strong visible-light absorption, which originates with the electronic transitions in the ISC [32,36]. Furthermore, the energy gaps were determined from UV–vis spectra, and results are listed in Table 1. It was observed that BC/TiO₂ (2.28 eV) and MC/TiO₂ (2.32 eV) with substituted EDG exhibit smaller energy gaps than CA/TiO₂ (2.40 eV), while BN/TiO₂ (2.52 eV) and TN/TiO₂ (2.57 eV) with substituted EWG exhibit larger energy gaps. That is, the energy gaps of the ISC enlarged as the electron-withdrawing ability in the substituted groups increased.

The oxidative potentials (E_A) of CA, its derivatives (BC, MC, BA, BN, TN), and TEA were determined from the cyclic voltammogram and results are listed in Table 2. It was found that the E_A increases as follows: BC \approx MC < (TEA) < CA < BA < BN < TN. From these results, it was clearly indicated that the E_A of BC and MC with substituted EDG are more cathodic than that of TEA, while those of CA and BA, BN, and TN with substituted EWG are more anodic.



Fig. 3. UV-vis spectra of (a) TiO_2 , (b) 80-BC/ TiO_2 , (c) 80-MC/ TiO_2 , (d) 80-CA/ TiO_2 , (e) 80-BN/ TiO_2 , and (f) 80-TN/ TiO_2 .

According to the previous report, the ISC is likely to form through bidentate binuclear (bridging) complexes being more energetically favorable than five-membered ring coordination [31,35]. Such coordination bonds help to induce intramolecular ligand-to-titanium charge transfer transitions within the ISC [36]. DFT calculations for ISC with different substituted groups clearly demonstrated that the donor levels in the TiO₂ midband are mainly constructed by the orbitals of the catecholate species hybridized with lattice oxygen. The donor levels and energy gaps obtained

Table 1

Energy gaps of TiO_2 modified with catechol and its derivatives estimated by UV-vis spectroscopy and DFT calculations.

| Photocatalyst | Energy gaps (eV) ^a | Energy gaps (eV) ^b | Donor level (eV) ^c |
|---------------------|-------------------------------|-------------------------------|-------------------------------|
| BC/TiO ₂ | 2.28 | 2.39 | 0.43 |
| MC/TiO ₂ | 2.32 | 2.43 | 0.37 |
| CA/TiO ₂ | 2.40 | 2.48 | 0.33 |
| BN/TiO ₂ | 2.52 | 2.51 | 0.31 |
| TN/TiO ₂ | 2.57 | - | - |

^a Energy gaps were estimated by UV-vis spectroscopy.

^b Details in computational methods and Figs. SI 2–7 are shown in the Supporting Information. Energy gaps were determined from the differences between the donor level and conduction band minimum of TiO₂ by DFT calculations.

^c Donor level indicates the difference above the valence band maximum of TiO₂ by DFT calculations.

| Table 2 | |
|-----------|--|
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Oxidative potentials (E_A) of organic compounds.^a

| Organic compounds | $E_{\rm A}$ (V) vs. Ag/AgCl |
|-------------------|-----------------------------|
| BC | 1.08 |
| MC | 1.12 |
| CA | 1.18 |
| BA | 1.36 |
| BN | 1.44 |
| TN | 1.47 |
| TEA | 1.14 |

^a E_A was determined from an anodic peak in the voltammogram of the organic compounds (5 mM, 0.1 M aqueous LiClO₄). Details are shown in Fig. SI 10 in the Supporting Information.



Fig. 4. Photocatalytic H₂ evolution [I] from aqueous TEA (10 vol%) on (a) 80-BC/TiO₂, (b) 80-MC/TiO₂, (c) 80-CA/TiO₂, (d) 80-BA/TiO₂, (e) 80-BN/TiO₂, and (f) 80-TN/TiO₂; catalytic recycling property [II] on the 80-BN/TiO₂.



Fig. 5. Photocatalytic activity of (a) 80-BC/TiO₂, (b) 80-MC/TiO₂, (c) 80-CA/TiO₂, (d) 80-BA/TiO₂, (e) 80-BN/TiO₂ and (f) 80-TN/TiO₂ as a function of the E_A of each modifier. The arrow represents the E_A of TEA.

from DFT calculations are listed in Table 2. It was observed that an increase of electron-withdrawing ability of the substituted groups induces anodic shift of the donor levels, accompanied by an enlargement of the energy gaps. These results correspond to energy gaps measured by UV–vis spectroscopy (see Table 2) and clearly demonstrate the electronic effects due to the substituted groups.

3.2. H_2 evolution from aqueous TEA on several ISC photocatalysts under visible-light irradiation

The activities on several ISC photocatalysts were evaluated by H₂ evolution from aqueous TEA through in situ photodeposition of Pt under visible-light irradiation. As shown in Fig. 4[I], the photocatalytic activity strongly depends on the substituted groups: $80\text{-BC/TiO}_2 \approx 80\text{-MC/TiO}_2 < 80\text{-CA/TiO}_2 \ll 80\text{-BA/TiO}_2 < 80\text{-BN/TiO}_2 \approx 80\text{-TN/TiO}_2$. By optimizing amounts of the modifier and Pt co-catalyst loaded, the preferable photocatalyst was 80-BN/TiO_2 (Pt/Ti: 0.50 atomic%) (details are shown in Figs. SI 8 and 9 in the Supporting Information). The photocatalytic activity



Fig. 6. AQY (a) for H_2 evolution from aqueous TEA (10 vol%) and (b) absorption spectrum of 80-BN/TiO_2.

on the 80-BN/TiO₂ (Pt/Ti: 0.5 atomic%) exhibited a turnover number (TON), i.e., a total number of the photoformed H_2 per BN-complex, of ca. 15 for 5 h, indicating that this reaction proceeds photocatalytically. The photocatalytic performance of 80-BN/TiO₂ (Pt/Ti: 0.5 atomic%) was repeatedly evaluated to confirm the stability of the ISC in this reaction. This photocatalyst was recyclable at least three times without drastic decrease of H_2 evolution after consecutive evacuations (see Fig. 4[II]).

Fig. 5 shows activity for H₂ evolution on several ISC photocatalysts as a function of E_A of corresponding modifiers. It was observed that the BC-TiO₂ and MC-TiO₂ with substituted EDG exhibited little activity (Fig. 5a and b), while CA-TiO₂; BA-TiO₂, BN-TiO₂, and TN-TiO₂ with substituted EWG exhibit photocatalytic activities (Fig. 5c–f). It was confirmed that the more anodic the E_A of catechols with substituted groups are, the higher the activities of the ISC photocatalyst become. Furthermore, photocatalytic activities can be explained by the correlation of oxidative potentials of modifiers with that of TEA. Meanwhile, when methanol was employed instead of TEA as a sacrificial hole scavenger, the photocatalytic reaction did not proceed on the BN/TiO₂. This result suggests that the photoinduced hole on the BN/TiO₂ do not have enough oxidizability of methanol.

To clarify photoresponsive sites, the apparent quantum yields (AQY) on the 80-BN/TiO₂ were measured, and results are shown in Fig. 6. The AQY for H₂ evolution was estimated to be 0.8% under monochromatic photoirradiation at 510 nm, 12.5% at 450 nm, and 32% at 420 nm; i.e., the action spectrum that is formed by the AQY plots fits the absorption of 80-BN/TiO₂. These results suggest that the photoexcitation of the ISC plays a significant role in the photocatalytic reaction.



Fig. 7. $I_{ph}-E$ curve on (a) BN/TiO₂ and (b) BC/TiO₂ electrodes, and (inset) typical photoresponse on BN/TiO₂ in aqueous LiClO₄ (0.1 M) involving TEA (10 vol%) at -0.6 V vs. Ag/AgCl under visible-light illumination (λ > 420 nm).



Fig. 8. Possible processes for BN/TiO2-catalyzed H2 evolution from aqueous TEA solutions in the presence of Pt co-catalyst under visible-light irradiation.

3.3. Understanding reaction mechanisms in the photocatalytic system

Fig. 7 (inset) shows a stable and photosensitive current at -0.6 V vs. Ag/AgCl (pH 10). The photocurrent (I_{ph})-voltage (E) characteristics of the BN/TiO₂ film under visible-light irradiation $(\lambda > 420 \text{ nm})$ are shown in Fig. 7a. As the cathodic bias is applied to the BN/TiO₂ photoelectrode, the photocurrent gradually decreases, and the onset potential was estimated to be $-0.94\,V$ vs. Ag/AgCl. On the other hand, the BC/TiO₂ exhibited little photocurrent (see Fig. 7b). These results indicate that the TEA can be oxidized by the photoinduced holes on the BN/TiO₂, not on the BC/TiO₂, since the E_A of BN is more anodic and that of BC is more cathodic than that of TEA, as shown in Table 1. It was thus confirmed that the influence of the electronic structures of the ISC with EWG and EDG on the photocurrent efficiency has been clearly demonstrated by the combination of the photo-electrochemical properties.

Fig. 8 shows the reaction mechanism for photocatalytic H_2 production from aqueous TEA on BN/TiO₂ under visible-light irradiation. From the results of the energy gap and onset potential for the photoresponse on BN/TiO₂, the donor level is determined to be located at 0.68 eV above the valence band of TiO₂. The donor levels can be tuned by the electronic effects of the substituted groups. The photocatalytic activity strongly depends on the relationships between the donor levels and oxidative potentials of the TEA. Visible-light irradiation of the BN/TiO₂ photocatalyst induces the charge carrier (hole and electron) separation. The photoinduced holes localized in the ISC can oxidize the TEA. On the other hand, the photoexcited electrons participate in the reduction of protons to form H₂ on the conduction band through the Pt co-catalyst, since the onset potential at -0.94 V is more cathodic than the redox potential $E(H^+/H_2)$ at -0.80 V.

4. Conclusions

A visible-light-sensitive photocatalyst for H₂ evolution from aqueous TEA in the presence of Pt co-catalyst was successfully designed by surface modification of the TiO₂ with catechol and

its derivatives. TiO₂ with such modifiers as BN and TN with EWG was found to exhibit high photocatalytic activity, while BC and MC with EDG do not induce activity. The photocatalytic activity is significantly influenced by the electronic structures of the substituted groups, which can tune the donor levels. Understanding the electronic effects of the substituted groups in the aromatics helps us to further design new photocatalytic systems.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2015.05.010.

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