In situ decomposition of bromine-substituted catechol to increase the activity of titanium dioxide catalyst for visible-light-induced aerobic conversion of toluene to benzaldehyde

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In situ decomposition of bromine-substituted catechol to increase the activity of titanium dioxide catalyst for visible-light-induced aerobic conversion of toluene to benzaldehyde

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Photocatalytic oxidation is an attractive approach for environmentally benign fine chemical synthesis. In addition, semiconductors have been intensively explored as photocatalysts for selective organic synthesis. In this study, we found that the photolysis of tetrabromocatechol on titanium dioxide produced surface-modified titanium dioxide, which showed higher activity than bare titanium dioxide in the aerobic conversion of toluene to benzaldehyde under visible light irradiation. When tetrabromocatechol was added to titanium dioxide dispersed in toluene, the titanium dioxide powder became orange in color due to the complex formation between tetrabromocatechol and titanium dioxide on the surface. The tetrabromocatechol was decomposed by visible light irradiation, and colorless titanium dioxide powder was obtained. We found that the apparent quantum yield of benzaldehyde formation determined by using the recycled colorless titanium dioxide powder at 450 nm was about eight times higher than that of bare titanium dioxide.

Introduction

Photocatalytic synthesis of valuable organic compounds using semiconductor catalysts has attracted significant attention because it proceeds under mild conditions, and semiconductors are generally more robust than organic- and metal-complex-based catalysts.[1-7] Benzaldehyde, which is one of the most important chemicals used as a raw material for the synthesis of other chemicals, is currently synthesized under high-temperature conditions using molecular oxygen in the presence of solid catalysts.[8] Therefore, it is desirable from a cost point of view to carry out this transformation under light irradiation at ambient temperature and pressure.[9,10] Many research groups have been developing visible-light-driven selective oxidation of toluene to benzaldehyde using photocatalysts, including narrow bandgap semiconductors as $BiVO_4$.[11-17]

Titanium dioxide (TiO_2) is one of the most studied semiconductor materials because it is non-toxic and cost-effective. TiO_2 is a wide bandgap semiconductor ($E_g > 3.2$ eV). Therefore, TiO_2 generates excitons (electron and hole pairs) only when irradiated with ultraviolet light. However, recent studies have demonstrated that selective oxidation of benzene proceeds on TiO_2 even under visible light irradiation.[18] Another wide-band-gap semiconductor, Nb_2O_5 (E_g = 3.2 eV), has also been reported to catalyse aerobic oxidation of aromatic hydrocarbons, including toluene, under visible light irradiation.[19] Such photocatalytic oxidation of aromatic hydrocarbons over TiO_2 and Nb_2O_5 is attributed to the charge transfer (CT) transition from the aromatic ring (donor) to the semiconductor surface (acceptor), which is located in the visible light region.[20] This CT mechanism has an attractive advantage for the selective oxidation of organic compounds because it avoids the generation of highly reactive OH radicals and allows selective one-electron oxidation of aromatic rings (Fig. 1a).

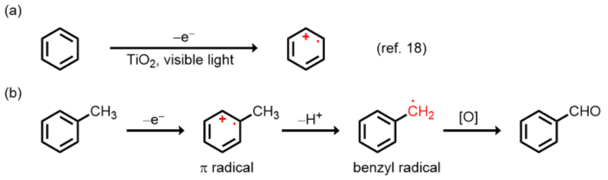

Fig. 1 (a) Visible-light-driven benzene oxidation over TiO_2. (b) Proposed scheme of toluene oxidation at the benzyl position.

The CT mechanism is expected to apply not only to benzene oxidation but also toluene oxidation. Since the proton at the benzyl position of the π radical cation of toluene is highly acidic (pK_a: −13 in CH_3CN),[21,22] the subsequent deprotonation should give highly reactive benzyl radical as shown in Figure 1b. As we expected, toluene was oxidized at the benzyl position, yielding

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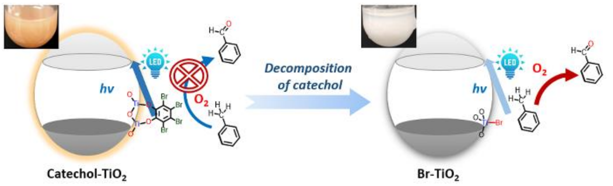
benzaldehyde when blue light (> 420 nm) was irradiated to the toluene suspension of titanium oxide under aerobic conditions. In order to enhance the activity of TiO_2 in the aerobic conversion of toluene to benzaldehyde under visible light irradiation, we focused on the surface halogenation of TiO_2. Surface chlorination and fluorination of TiO_2 has been reported to enhance the photocatalytic activity of TiO_2.[23-31] Although surface bromination of TiO_2 has never been reported, it has been reported that modification of a $[Ti_6O_8(OH_2)_{20}]^{8+}$ cluster with bromide ion improved the selective conversion of toluene and benzyl alcohol to benzaldehyde under visible light irradiation with high efficiency.[32] Herein, we investigated the effect of bromine-containing compounds as additives on the TiO_2-catalysed aerobic conversion of toluene to benzaldehyde under visible light irradiation**.** As a result, we found that tetrabromocatechol (Br_4Cat) effectively enhances the activity of titanium dioxide in the aerobic conversion of toluene to benzaldehyde under visible light irradiation. Our experimental results indicate that TiO_2 modified with Br_4Cat has no activity for the photocatalytic oxidation of toluene, but that Br_4Cat becomes a precursor for generating surface-modified TiO_2 that shows better activity than bare TiO_2 in selective converting toluene to benzaldehyde under visible light irradiation (Scheme 1).



Scheme 1 Generation of surface-modified TiO_2 that shows better activity than bare TiO_2 in photocatalytic selective conversion of toluene to benzaldehyde through the photo-decomposition of Br_4Cat.

Experimental

Materials

TiO_2 powder (JRC-TIO-17, average diameter: 21 nm, identical to Degussa P25) was supplied from the Catalysis Society of Japan. All reagents and organic solvents were purchased from Wako Pure Chemical Industries and used without further purification except for toluene and tetrabromocatechol. Toluene was purified by distillation. Tetrabromocatechol was purchased from Sigma-Aldrich, although it can be prepared by the bromination reaction of pyrocatechol with bromine in acetic acid.[33]

Physical measurements

X-ray photoelectron spectroscopy (XPS) was performed with a hemispherical electron energy analyzer (R4000, Scienta Omicron) and a monochromatized Al K_α X-ray source ($h\nu$ = 1486.7 eV, MX-650, Scienta Omicron). The total energy resolution of the XPS experiments was estimated to be 0.59 eV. The samples were fixed on copper sample holders using conductive carbon tape. The binding energies were referenced to the Fermi edge of metallic Au foil. The obtained XPS spectra were fitted by the Voigt functions with the Tougaard background. Diffuse reflectance (DR) UV-vis spectroscopy was carried out using a JASCO V-570 spectrophotometer. Raman spectra were measured with a Horiba Labram HR Evolution Raman microscope with an excitation light of 532 nm and a 100× focusing lens. Product analysis was carried out with gas chromatography (GC) using a Shimadzu GC-2014 and GCMS-QP2020 instruments equipped with a GL-Science InertCap 1701 column (60 m).

Photocatalytic reaction using bromine-containing compounds as an in-situ additive

The photo-oxidation of toluene was carried out according to the reported procedure.[11] TiO_2 (10 mg) was dispersed in purified toluene (1 mL) in a Hungate-type anaerobic tube containing a small stirring bar. A bromine-containing compound was added to the suspension of TiO_2. After oxygen gas was introduced through a butyl rubber stopper, the tube attached with an oxygen balloon was placed into a homemade 3D-printed merry-go-round system, whose temperature was controlled to 25 °C by a water circulator. The light was irradiated from the side of reactors by two blue LED lamps (Kessil, A160WE Tuna Blue) fitted with a filter (> 420 nm). After the reaction, a dimethyl sulfone solution in acetonitrile (0.1 M, 1 mL, 0.1 mmol) was added to the reaction mixture as a standard, followed by membrane filtration and GC analysis. The results were summarized in Table 1.

Catechol-modified TiO_2 powder, Br_4Cat-TiO_2

The following method was carried out to prepare catechol-modified TiO_2. To Br_4Cat (1.0 µmol, 10 µmol, or 1.0 mmol) was suspended and sonicated in acetone (100 mL) for 5 min. TiO_2 (100 mg) was added to the suspension, and the mixture was sonicated for 12 hours in the dark. The resultant orange-coloured powder was separated by filtration, washed with acetone (10 mL), and dried in vacuo. The sample was used for toluene oxidation, and DR, Raman, and XPS spectra measurements. Toluene oxidation was conducted using catechol-modified TiO_2 (10 mg) in toluene (1 mL) under light irradiation using the LED lamps.

Colour-faded TiO_2 powder, re-Br_4Cat-TiO_2

After irradiating a toluene suspension of Br_4Cat-TiO_2 with blue light for 15 hours, the resulting colour-faded TiO_2 powder was collected by filtration and washing with toluene. The recycled TiO_2, denoted as re-Br_4Cat-TiO_2, was used for toluene oxidation, DR and XPS spectra measurements, and for the determination of apparent quantum yield (AQY). The AQY was determined according to the reported procedure.[11] The toluene filtrate was also irradiated using the LED lamps for 15 hours under identical conditions. The amounts of the product were quantified by GC before and after the light irradiation.

Results and discussion

Photocatalytic toluene oxidation

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Table 1 Effect of additive on the toluene oxidation in the presence of TiO_2 [a]

entry	additive	Product /μmol	
		benzaldehyde	benzyl alcohol
1	none	3	N.D.
2	Br_4Cat^b	45	N.D.
3	$Br_2{}^c$	15	N.D.
4	$AcBr^d$	23	N.D.
5	NH_4Br^b	9	N.D.
6	KBr^e	6	N.D.
7	$KBr^{e,f}$	3	N.D.

[a] Reaction conditions: catalyst 10 mg, toluene 1 mL, irradiation time: 15 h, reaction temperature: 25 °C, 1 atm oxygen, blue LED light (> 420 nm). [b] 1 μmol [c] 2 μmol [d] 4 μmol [e] 0.1 mmol [f] TiO_2 powder was obtained by drying an aqueous suspension of TiO_2 containing KBr, and used.

The activity of TiO_2 to aerobically oxidize toluene under blue-light irradiation was examined in the presence of several bromine-containing compounds, and the results are summarized in Table 1. The addition of Br_4Cat, Br_2, and acetyl bromide (AcBr) (4 μmol based on Br) afforded significantly higher amounts of benzaldehyde than bare TiO_2 (Table 1, entries 1 to 4). The product amounts observed using Br_4Cat, Br_2, and AcBr are 15-, 5- and 7.7-fold higher than that obtained with bare TiO_2, respectively. These activities are higher than those reported with bismuth oxide-based semiconductors without metal co-catalysts under blue light irradiation.[11,15,16] The addition of NH_4Br or KBr afforded only a low amount of benzaldehyde (Table 1, entries 5 and 6), probably due to their low solubility in toluene. Therefore, we prepared the suspension of TiO_2 in KBr aqueous solution and dried it overnight. The TiO_2 powder obtained from the KBr solution showed only comparable activity to that of bare TiO_2 (Table 1, entry 7). These results indicate that the addition of bromine-containing compounds soluble in toluene enhances the activity of TiO_2 in aerobic oxidation of toluene to benzaldehyde under blue-light irradiation. Among bromine-containing compounds tested in this study, Br_4Cat showed the highest amount of benzaldehyde. Benzyl bromide has been reported to form as a by-product of the photocatalytic aerobic oxidation of toluene to benzaldehyde using a $[Ti_6O_8(OH_2)_{20}]^{8+}$ cluster with bromide ion as a catalyst.[32] However, benzyl bromide was not observed in our system using Br_4Cat and TiO_2. Interestingly, when Br_4Cat was added to the TiO_2 suspension in toluene, the TiO_2 powder turned orange. However, the orange colour gradually faded away during the blue light irradiation, as shown in the upper in Fig. 2).

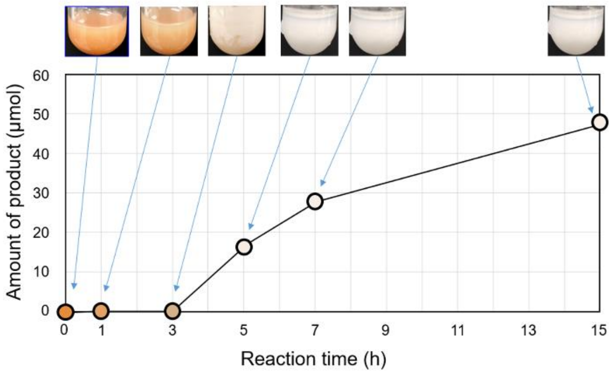

Fig. 2 Photographs of the colour change of the reaction tubes in the toluene oxidation over $Br_4Cat\text{-}TiO_2$ (upper). Time course of photocatalytic product formation in the toluene oxidation over $Br_4Cat\text{-}TiO_2$ (lower). Reaction conditions: catalyst 10 mg, toluene 1 mL, reaction temperature: 25 °C, 1 atm oxygen, blue LED light (> 420 nm).

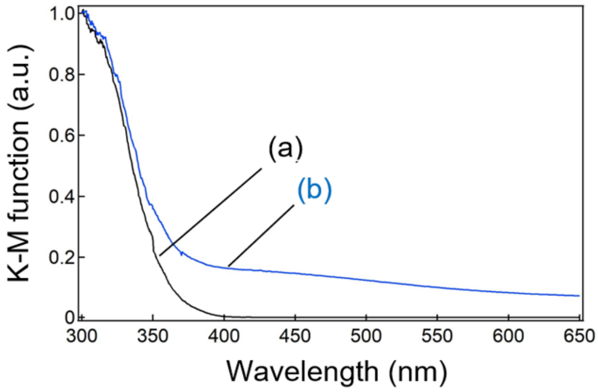

Fig. 3 DR UV-vis spectra of bare TiO_2 (a, black) and $Br_4Cat\text{-}TiO_2$ (b, blue). The samples were diluted with $BaSO_4$ by a factor of 100. The spectra were normalized to one at 300 nm.

In order to provide insights into the relationship between the orange colour and the toluene oxidation, we prepared Br_4Cat-modified TiO_2 ($Br_4Cat\text{-}TiO_2$) using 1.0 mmol of Br_4Cat and 100 mg of TiO_2 to monitor the progress of the product formation in the photocatalytic toluene oxidation over time (Fig. 2). Before the reaction, $Br_4Cat\text{-}TiO_2$ has orange in colour. The DR spectrum showed a broad absorption band at around 400 nm (Fig. 3), which is assignable to charge transfer transition from $Br_4Cat\text{-}TiO_2$ to the valence band of TiO_2.[34] No products were detected until 3 hours after the start of the reaction, and after this induction period, the product amount gradually increased, showing a saturated curve around 15 hours.

We also monitored the colour change of TiO_2 powders in the reaction tubes during the reaction mentioned above, as shown in Fig. 2 (upper). The orange colour, characteristic of catechol modified TiO_2, gradually decreased during the induction period and faded away after 5 hours. The results clearly show that $Br_4Cat\text{-}TiO_2$ has no activity for the toluene oxidation, and that the vital catalyst for the benzaldehyde formation is a newly formed catalyst through the photolysis of Br_4Cat.

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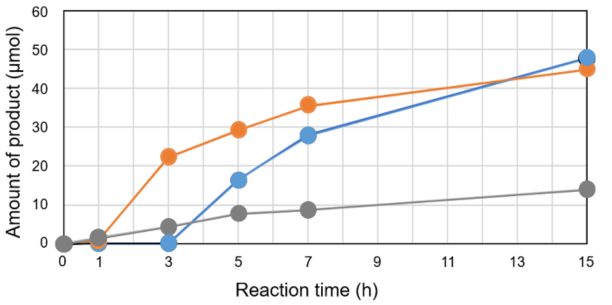

Fig. 4 Time course of photocatalytic product formation in the toluene oxidation over Br_4Cat-TiO_2 (blue), $Br_4Cat/100$-TiO_2 (orange), and $Br_4Cat/1000$-TiO_2 (grey). Reaction conditions: catalyst 10 mg, toluene 1 mL, reaction temperature: 25 °C, 1 atm oxygen, blue LED light (> 420 nm). Br_4Cat-TiO_2, $Br_4Cat/100$-TiO_2, and $Br_4Cat/1000$-TiO_2 were prepared by adding 1 mmol, 10 μmol, and 1 μmol of Br_4Cat to a suspension of 100 mg of TiO_2 in acetone, respectively.

To investigate the effect of the Br_4Cat amount on the induction period, we prepared additional Br_4Cat-modified TiO_2 powders by reacting 1 or 10 μmol of Br_4Cat with 100 mg of TiO_2 ($Br_4Cat/1000$-TiO_2 and $Br_4Cat/100$-TiO_2). As shown in Fig. 4, the three Br_4Cat/TiO_2 catalysts showed distinctly different time course curves. When the amount of Br_4Cat was reduced by 100-fold, the induction period was shortened to 1 hour. When Br_4Cat was further reduced by a factor of 10, no induction period was observed. Thus, the induction period became longer as the amount of Br_4Cat was increased. These results suggest that Br_4Cat-TiO_2 is converted to a vital catalyst during the photolysis of Br_4Cat.

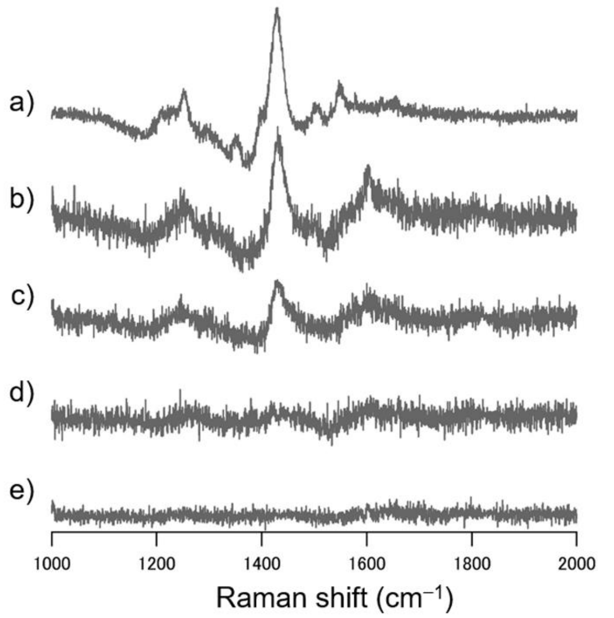

Fig. 5 Raman spectra of Br_4Cat-TiO_2 (a) and TiO_2 powders that were obtained after 1 (b), 3 (c), 7 (d), and 15 hours (e) of the reaction.

To further elucidate what took place in conjugation with the colour change of Br_4Cat-TiO_2, we performed toluene oxidation in four reaction tubes under identical conditions and isolated TiO_2 powders after 1, 3, 7, and 15 hours of blue light irradiation to measure the Raman spectra of these samples. The Raman spectra of the TiO_2 powders were shown in Fig. 5, together with those of Br_4Cat-TiO_2 before the reaction and bare TiO_2. The TiO_2 sample showed peaks at 144, 399, 519, and 639 cm^{-1} (Fig. S1), known to be the typical Raman peaks of anatase TiO_2.[35] Br_4Cat-TiO_2 powder before the reaction showed a peak at 1430 cm^{-1}, assignable to the catechol ring modes (Fig. 5).[36] The peak at 1430 cm^{-1} was observed until 3 hours after the start of the reaction. After 7 hours, there were no Raman peaks attributed to organic compounds. These results show that Br_4Cat is decomposed on TiO_2 under blue light irradiation, consistent with the disappearance of the orange colour at the initial stage of the reaction. It should be noted that the orange colour of Br_4Cat-TiO_2 was retained in toluene under argon even after 15 hours of irradiation with blue light. This result indicates that Br_4Cat is aerobically decomposed on TiO_2 under blue light irradiation.

Characterization of a recycled catalyst

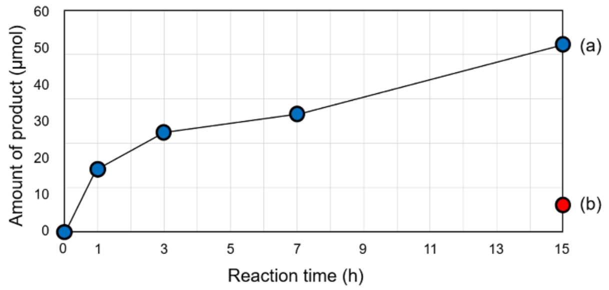

Fig. 6 Time course of photocatalytic product formation in the toluene oxidation over re-Br_4Cat-TiO_2 (a, blue) and bare TiO_2 (b, red). Reaction conditions: catalyst 10 mg, toluene 1 mL, reaction temperature: 25 °C, 1 atm oxygen, blue LED light (> 420 nm).

We collected colour-faded TiO_2 powder by filtration after 15 hours of the reaction using Br_4Cat-TiO_2, denoted as re-Br_4Cat-TiO_2, to examine the time dependence of toluene oxidation shown with open circles in Fig. 6 (a, blue). The recycled TiO_2 powder showed higher activity in toluene oxidation than bare TiO_2, and in this case, no induction period was observed. On the other hand, the filtrate showed negligible activity for the toluene oxidation to benzaldehyde under identical conditions. The amount of benzaldehyde was less than 1 μmol after 15 hours, which is even lower than that observed with bare TiO_2. These results clearly show that homogenous catalysts are not significantly responsible for this photocatalytic reaction.

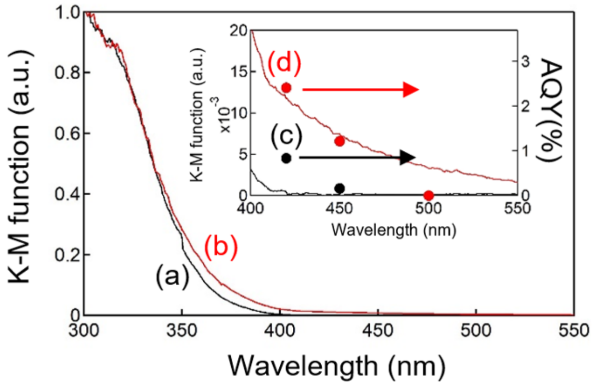

Fig. 7 DR UV-vis spectra of bare TiO_2 (a, black) and re-Br_4Cat-TiO_2 (b, red). The samples were diluted with $BaSO_4$ by a factor of 100. The spectra were normalized to one at 300 nm. The inset shows the apparent quantum yield (AQY) of benzaldehyde production by

bare TiO_2 (c, black) and re-Br_4Cat-TiO_2 (d, red) determined at 420, 450 and 500 nm, together with a zoom of the DR vis spectra.

The absorption of re-Br_4Cat-TiO_2 in DR UV-vis spectrum is slightly extended to the visible region (Fig. 7). A similar red-shifted band has been reported with Br-doped TiO_2 hollow spheres.[37] Gao and co-workers proposed that Br would bind to Ti and form Ti–Br bond producing a defect band between conduction and valence bands of TiO_2, consequently increasing the response to visible light.[38]

Next, we determined the apparent quantum yield (AQY) for the benzaldehyde formation by the irradiation of monochromatic light at 420, 450 and 500 nm. The quantum yields determined using re-Br_4Cat-TiO_2 were 2.4 and 1.2% at 420 and 450 nm, respectively, shown in the inset of Fig. 7. These values are 2.9- and 7.7-fold higher than those obtained with bare TiO_2. In both TiO_2 powder, no product was detected when irradiated at 500 nm. This result shows that bare TiO_2 is capable of catalysing aerobic conversion of toluene to benzaldehyde under visible light irradiation at least up to 450 nm wavelength. Considering no significant absorption in the DR spectrum of bare TiO_2, the toluene oxidation using bare TiO_2 as a catalyst should procced through the CT mechanism as proposed for visible-light driven benzene oxidation over TiO_2.[18] Importantly, re-Br_4Cat-TiO_2 exhibited higher AQY values in this reaction than bare TiO_2. The AQY values at 420 nm and 450 nm are in good match with the DR spectrum of re-Br_4Cat-TiO_2. This result suggests that the red shift in the absorption of re-Br_4Cat-TiO_2 may contribute to the toluene oxidation over re-Br_4Cat-TiO_2 under blue light irradiation. However, the AQY value at 500 nm does not correlate with the absorption in the DR spectrum of re-Br_4Cat-TiO_2. Therefore, the other factors should be considered to explain the higher AQY values observed for re-Br_4Cat-TiO_2: the toluene oxidation on re-Br_4Cat-TiO_2 may proceed through the CT mechanism in the same way as on bare TiO_2. However, the detailed mechanism, such as the contribution rate of the red shifted absorption and the enhanced CT mechanism to the improvement of the AQY values of re-Br_4Cat-TiO_2, is unclear at present.

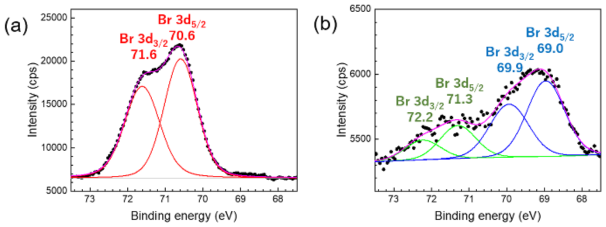

Fig. 8 XPS spectra of (a) Br_4Cat-TiO_2 and (b) re-Br_4Cat-TiO_2.

In the EDS spectra, we observed that Br is distributed not only over Br_4Cat-TiO_2 but also over re-Br_4Cat-TiO_2 (Fig. S2). Therefore, we determined the chemical states of Br before and after blue light irradiation by XPS (Fig. 8 and Fig. S3). In the XPS spectra of Br_4Cat-TiO_2 and re-Br_4Cat-TiO_2, signals characteristic of TiO_2 were observed at 459.5 eV (Ti $2p_{3/2}$), 465.1 eV (Ti $2p_{1/2}$), and 530.7eV (O 1s), which were also observed for bare TiO_2. In the XPS spectrum of Br_4Cat-TiO_2, doublet peaks were observed at around 71.6 eV (Br $3d_{3/2}$) and 70.6 eV (Br $3d_{5/2}$), which have been reported to correspond to bromine bonded to aromatic carbon.[39] On the other hand, re-Br_4Cat-TiO_2 exhibited two doublet peaks for Br $3d_{3/2}$ and $3d_{5/2}$. These peaks were deconvoluted into a weaker doublet peak located at 72.2 eV (Br $3d_{3/2}$) and 71.3 eV (Br $3d_{5/2}$) and a doublet peak located at 69.9 eV (Br $3d_{3/2}$) and 69.0 eV (Br $3d_{5/2}$). Since the former doublet peak has larger binding energy than the Br doublet peak observed with Br_4Cat-TiO_2, the weaker doublet peak should be attributed to bromine bonded to the carbon of oxidized species derived from Br_4Cat. The more intense doublet peak shifted to lower binding energy than those observed with bromine bonded carbon, indicating the bromide anion bound to a metal centre. For example, $CdBr_2$ shows a Br $3d_{5/2}$ signal at 69.2 eV,[40] while CH_3Br shows at 71.0 eV.[41] Thus, bromide anion possibly exists as Ti–Br bond. Since it has been reported that the photocatalytic activity of TiO_2 is enhanced by doping halogen on the surface of TiO_2,[23,42] surface Ti–Br species should have a main contribution to the activity of re-Br_4Cat-TiO_2. However, since the activity of re-Br_4Cat-TiO_2 is higher than that of TiO_2 in the presence of Br_2 additive, the positive effect of the carbon–Br species cannot be excluded. The contribution of the carbon–Br species will be investigated in the future.

Conclusions

In summary, even unmodified titanium dioxide catalyzes aerobic oxidation of toluene to benzaldehyde under visible light irradiation. The apparent quantum yield is ca. 1% at 420 nm. Thus, bare TiO2 is not highly active, but the usage of visible light for the toluene oxidation to benzaldehyde on bare TiO2 was first demonstrated in this study. We also found that catechol-modified TiO_2, Br_4Cat-TiO_2, is not active for the aerobic conversion of toluene to benzaldehyde under blue light irradiation. However, through the photolysis of Br_4Cat on TiO_2, Br_4Cat-TiO_2 was converted to surface-brominated TiO_2 (Br-TiO_2), which showed higher catalytic activity than bare TiO_2 in the aerobic oxidation of toluene to benzaldehyde under blue light irradiation.

Various visible light-responsive TiO_2 catalysts have been developed, but most of them require special procedures for preparation or at least heat treatment at high temperatures for the preparation. We believe that if visible light responsivity could be achieved by simply adding appropriate additives to a toluene suspension of TiO_2, it would be useful in practical application because it allows a one-pot reaction from the generation of the active catalyst to the catalytic reaction using the prepared catalyst. Surprisingly such one-pot reactions have been rarely examined. Br-doped TiO_2 co-doped with Cl,[43] N,[44] and Sm[38] have been studied. These Br-doped TiO_2 samples have been prepared by hydrothermal method using Ti precursors and bromine donors such as NH_4Br,[45] and thus, Br should be mainly located inside the TiO_2. Thus, using Br_4Cat as a precursor additive is an efficient way to produce surface brominated TiO_2, which shows higher activity than bare TiO_2 in the blue-light-mediated aerobic conversion of toluene to benzaldehyde with high selectivity. Surface modification of TiO_2 as described in this paper may be a promising strategy for more efficient photocatalytic conversion of organic compounds using TiO_2 under visible light irradiation.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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