Photocatalysis

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A Visible-Light-Harvesting Assembly with a Sulfocalixarene Linker between Dyes and a Pt-TiO_2 Photocatalyst**

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Semiconductor materials, which utilize light to drive unique reactions, have been investigated by many researchers.[1–6] Typical applications include degradation of organic contaminants in air and water, as well as hydrogen generation from water, alcohol, or aqueous ammonia.[4–10] Among semiconductor materials, TiO_2 photocatalysts are used for practical applications in everyday life. Functional coatings are studied extensively for the ability to perform multiple functions, such as self-cleaning properties and photoinduced surface hydrophilicity.[3,9–11] Unique photocatalytic reactions for the production of fine chemicals can also occur on TiO_2 under controlled reaction conditions.[12–16] The efficient utilization of visible light has been a great concern for energy usage and environmental reasons. A bare TiO_2 photocatalyst can only absorb UV light, which corresponds to about 3% of the energy of natural solar light. Therefore, the design of visible-light-sensitive TiO_2-based materials has been studied intensively using various approaches. Doping of heteroatoms, such as transition metals, carbon, nitrogen, and sulfur, into TiO_2 is a well-known method.[17–20] Anchoring of dye molecules and precious organometallic complexes (for example, derivatives of ruthenium bipyridyl complexes) on TiO_2 and other semiconductor materials are another promising method for achieving effective visible light harvest.[21–24] The TiO_2 is placed mainly in the direct path of photoformed electrons to the catalytically active site. Elaborate modifications of molecular structures, which can lead to unexpected physicochemical properties, are important for stable anchoring on a solid surface without adverse effects.

In contrast, the surface hydroxy groups of TiO_2 exhibit unique and specific reactivity with phenolic hydroxy or carboxylic groups of aromatic molecules, such as catechol and salicylic acid.[25–32] Through this reaction, colorless aromatic molecules are stably fixed onto the TiO_2 surface to form colored surface complexes. This visible light absorption originates from the direct electron transfer from coordinated aromatic molecules to the conduction band of TiO_2.[25–29] Unique visible light absorption of surface complexes has the potential to induce various photocatalytic reactions under controlled conditions,[29–32] while the absorption range and capacity of visible light remain limited and need to be improved.

Herein, a heterogeneous system sensitive to visible light was designed successfully by combining three components: Pt-TiO_2, 4-sulfocalix[4]arene (SCA[4]), and a cationic dye molecule (thiazole orange: TO; Figure 1). Sulfocalixarene, having both phenolic hydroxy groups and sulfonate moieties,

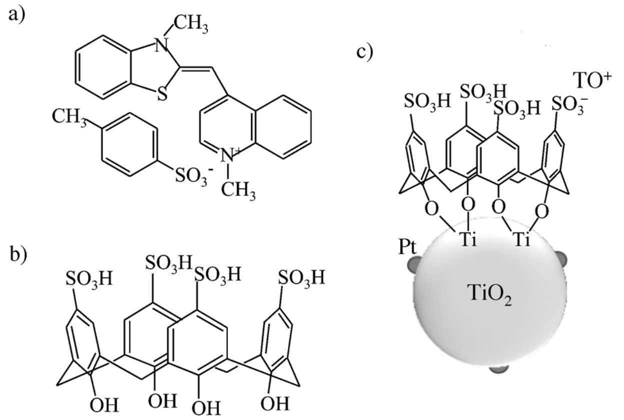

Figure 1. Structures and illustration of a) thiazole orange (TO^+) with *p*-toluenesulfonate, b) 4-sulfocalix[4]arene (SCA[4]), and c) TO-SCA[4]/Pt-TiO_2.

was used as a linker between Pt-TiO_2 and TO, which provides key properties for formation of surface complexes as well as ion exchange capacity. The photocatalytic performance for production of H_2 was also evaluated in the presence of a sacrificial reagent under visible light irradiation.

The change in light absorption properties before and after combination of each component, (that is, Pt-TiO_2, SCA[4], and TO) was investigated by UV/Vis spectroscopy. As shown in Figure 2a, Pt-TiO_2 exhibited a typical absorption band below 380 nm corresponding to the band-gap energy of TiO_2 with an anatase structure. After connection of SCA[4] on Pt-TiO_2 (SCA[4]/Pt-TiO_2), the powder color changed to yellowish gray, even though SCA[4] is a colorless compound and demonstrated no absorption in the visible light region (Figure 2b,d). Typical absorption of SCA[4] was observed only in the UV light region. This observation clearly indicates the successful connection of SCA[4] on Pt-TiO_2 by formation of surface complexes. Visible light absorption was also observed in PSA/Pt-TiO_2 and SCA[8]/Pt-TiO_2 prepared by treatment of Pt-TiO_2 with colorless *p*-phenolsulfonic acid (PSA) or 4-

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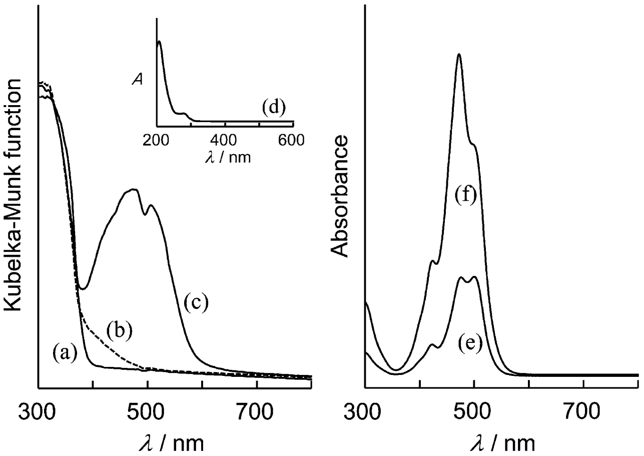

Figure 2. UV/Vis absorption spectra of a) Pt-TiO_2, b) SCA[4]/Pt-TiO_2, c) TO-SCA[4]/Pt-TiO_2, d) aq. SCA[4], and e,f) aq. TO with *p*-toluenesulfonate at e) 0.05 mmol L^{-1} and f) saturation.

sulfocalix[8]arene (SCA[8]; Supporting Information, Figure S1). Similar changes in light absorption have been reported by treatment of TiO_2 with aromatic molecules such as phenol and catechol.[25–28] These results clearly indicate that surface complexes were formed and stably fixed on TiO_2 through a similar process; that is, the dehydration reaction of phenolic hydroxy groups and surface hydroxy groups of TiO_2.[27–29]

After treatment of SCA[4]/Pt-TiO_2 with an aqueous TO solution (TO-SCA[4]/Pt-TiO_2), a typical absorption band was observed in the region from 400 to 700 nm (Figure 2c). A similar change was observed in TO-SCA[8]/Pt-TiO_2 (Supporting Information, Figure S1). The color of the aqueous TO solution immediately disappeared upon addition of SCA[*n*]/Pt-TiO_2. The shape of this absorption band was similar to that of the low-concentration aqueous TO solution (Figure 2e). For the saturated aqueous TO solution (Figure 2 f), an intense peak was observed ca. 470 nm. The two absorption peaks of TO at around 470 and 500 nm were assigned to the dimeric and monomeric form of TO, respectively.[32–34] These results suggest that TO was immobilized mainly on SCA[*n*]/Pt-TiO_2 in a monomeric form by interaction of the sulfonate moiety of SCA[*n*]. In fact, TO molecules were immobilized on SCA[*n*] through changes in the counter anion from *p*-toluenesulfonate to the sulfonate moiety of SCA[*n*] during stirring in aqueous TO solution. The TO molecules were hardly adsorbed on the TiO_2 surface directly without SCA[*n*] modification and were completely removed from the TiO_2 surface during the washing process.

However, even though PSA contains a sulfonate moiety, PSA/Pt-TiO_2 did not show any typical absorption bands after treatment in aqueous TO solution. This behavior was in contrast to that of SCA[*n*]/Pt-TiO_2. The sulfonate moieties of PSA were unable to separate spatially from the TiO_2 surface. The sulfonate moieties of PSA may interact with the TiO_2 surface because the formation of surface complexes does not affect the motion of PSA, which makes a large difference in these systems. For SCA[*n*], *p*-phenolsulfonic acid units are linked by methylene groups (Figure 1). The annulus rotations of *p*-phenolsulfonic acid units are strictly limited after connection of SCA[*n*] on Pt-TiO_2 by formation of surface complexes. The sulfonate moieties located on the upper rim of SCA[*n*] were at the outermost of SCA[*n*]/Pt-TiO_2, which has negative charges and can work effectively as ion-exchange sites. As a consequence, surface modification by SCA[*n*] resulted in the immobilization of TO on Pt-TiO_2, owing to the phenolic hydroxy groups and sulfonate moieties of SCA[*n*] acting as a linker for combination of these components.

Photocatalytic production of H_2 from an aqueous solution containing a sacrificial electron donor (triethanolamine: TEOA) was conducted as a test reaction under visible light irradiation using colored filters with different cutoff wavelengths. The aqueous TEOA was used without adjustment of pH, which was originally about 11. Time profiles of the amount of H_2 formed are shown in Figure 3.

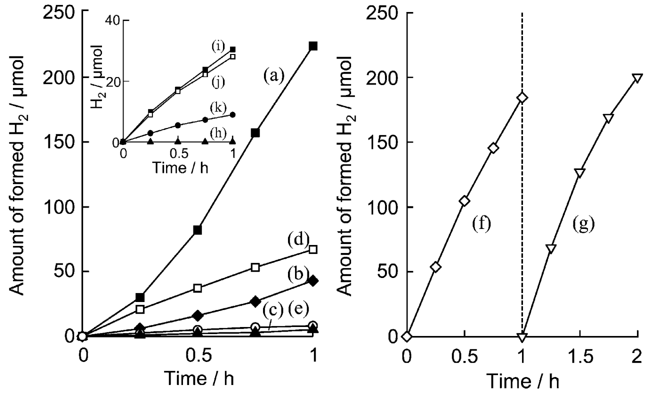

Figure 3. Time course of H_2 formation on a) TO-SCA[4]/Pt-TiO_2 ($\lambda > 450$ nm), b) TO-SCA[4]/Pt-TiO_2 ($\lambda > 500$ nm), c) TO-SCA[4]/Pt-TiO_2 ($\lambda > 550$ nm), d) TO-SCA[8]/Pt-TiO_2 ($\lambda > 450$ nm), and e) TO-SCA[4]/TiO_2 ($\lambda > 450$ nm) under visible light irradiation; and f,g) recycling tests after the f) second and g) third measurement of TO-SCA[4]/Pt-TiO_2 ($\lambda > 450$ nm). Inset: time courses of H_2 formation on h) Pt-TiO_2, i) SCA[4]/Pt-TiO_2, j) SCA[8]/Pt-TiO_2, and k) PSA/Pt-TiO_2 under visible light irradiation ($\lambda > 400$ nm).

The increase in the amount of H_2 formed from TO-SCA[*n*]/Pt-TiO_2 was directly proportion to irradiation time, while no H_2 formation was detected for Pt-TiO_2, as predicted by the light absorption property. The formation rate of H_2 on TO-SCA[4]/Pt-TiO_2 was approximately four-fold greater than that for TO-SCA[8]/Pt-TiO_2, although the amount of TO and number of *p*-phenolsulfonic acid moieties were similar in both samples. The amount of H_2 formed from the SCA[*n*]/Pt-TiO_2 and PSA/Pt-TiO_2 suspension was small even under visible light irradiation ($\lambda > 400$ nm) within this reaction timescale (Figure 3i–k), showing large differences after immobilization of TO. TO-SCA[4]/Pt-TiO_2 also produced H_2 even under irradiation at wavelengths longer than 550 nm, while the formation rate gradually decreased with the visible light absorption capacity of TO (Figure 3a–c). These results suggest that H_2 formation was due to photoexcitation of TO connected to the Pt-TiO_2 surface through SCA[4] as a linker. The apparent quantum yield was determined to be 10.4 % for SCA[4]/Pt-TiO_2 at 460 nm. The photocatalytic performance of TO-SCA[4]/Pt-TiO_2 was also repeatedly evaluated to confirm the stability in this reaction. As shown in Figure 3 a,f,g, TO-SCA[4]/Pt-TiO_2 was recyclable at least three times without a large decrease in photocatalytic performance for formation of H_2 under visible light irradiation ($\lambda >$ 450 nm). The turnover number calculated by the ratio of total amount of H_2 formed to TO content exceeded 600 after three cycles of reaction testing, indicating that this reaction proceeded photocatalytically.

In contrast, the amount of H_2 formed from suspension of TO-SCA[4]/TiO_2 prepared without photodeposition of Pt nanoparticles on TiO_2 was less than 1/20 of that from suspension of TO-SCA[4]/Pt-TiO_2 under the same conditions, as shown in Figure 3 e. Considering the role of deposited Pt nanoparticles, the changes in fluorescence intensity were monitored by photoluminescence measurements. TO, having two conjugated aromatic rings connected by a vinyl bond, sometimes is used as a fluorescence marker because it produces intense fluorescence upon interaction with biological materials such as DNA and cancer cells.[33–35] However, the fluorescence of free TO is weak owing to nonradiative relaxation by rotation around the interconnecting bond.[33–35]

As shown in Figure 4, TO-SCA[4]/TiO_2 exhibited intense fluorescence in the region from 550 to 800 nm upon excitation of the absorption band. The peak position shifted to a lower wavelength compared to that of aqueous TO solution. A similar phenomenon related to the blue-shift of fluorescence was observed, resulting in binding of TO to DNA.[33,34] Meanwhile, TO-SCA[4]/Pt-TiO_2 only showed weak fluorescence in the same wavelength region. The photoluminescence of dye molecules can be quenched by the injection of photoformed electrons into semiconducting metal oxides.[36,37] The photoformed electrons efficiently move to Pt particles loaded in Pt/TiO_2 systems, preventing the formation of Ti^{3+} species and recombination.[38] The deposited Pt nanoparticles also act as H_2 formation sites by efficient migration of photoformed electrons upon excitation of TO and induce reduction of H^+, leading to higher photocatalytic performance compared to that on non-Pt-loaded systems.

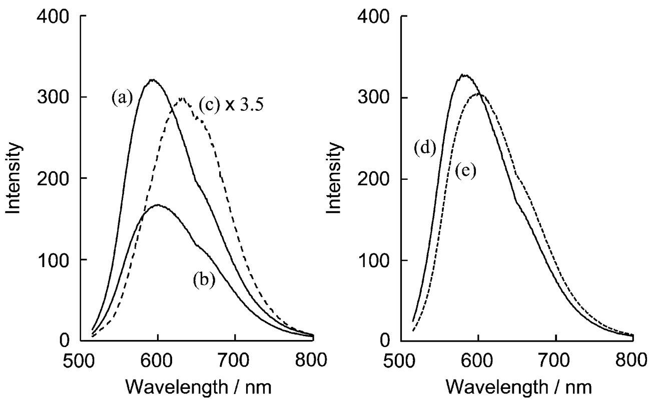

Figure 4. Photoluminescence spectra of a) TO-SCA[4]/TiO_2, b) TO-SCA[4]/Pt-TiO_2, c) aq. TO, d) TO-SCA[8]/TiO_2, and e) TO-SCA[8]/Pt-TiO_2 measured at 298 K (excitation: 450 nm).

Moreover, for TO-SCA[8]/TiO_2 and TO-SCA[8]/Pt-TiO_2 (Figure 4 d,e), a relatively small difference in photoluminescence intensity was observed compared to those of samples prepared using SCA[4] as a linker. This quenching in TO-SCA[4]/Pt-TiO_2 indicates the importance of SCA[4] as a linker for efficient transfer of photoformed electrons from TO into Pt-TiO_2. The different number of *p*-phenolsulfonic acid units linked by methylene groups, and their ring size, might affect the connection of SCA[*n*] on the TiO_2 surface, resulting in good photocatalytic performance of TO-SCA[4]/Pt-TiO_2 in the prepared samples.

In summary, TO-SCA[*n*]/Pt-TiO_2 was prepared successfully using SCA[*n*] as a linker between Pt-TiO_2 and TO. The unique properties of SCA[*n*] for formation of surface complexes on TiO_2 as well as immobilization of cationic compounds by ion exchange treatment play important roles for stable combination of these three components. TO-SCA[4]/Pt-TiO_2 exhibited photocatalytic performance for formation of H_2, even under irradiation at wavelengths longer than 550 nm, demonstrating a clear effect on immobilization of TO. The use of SCA[*n*] as a linker has potential for combining other types of cationic compounds for efficient visible light harvest without complicated procedures.

Experimental Section

Materials: Anatase-type TiO_2 (Ishihara Sangyo, Ltd., ST-01) was supplied from the Catalysis Society of Japan as a reference catalyst. Hydrogen hexachloroplatinate(IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) was purchased from Nacalai Tesque, Inc. Thiazole orange (TO) with *p*-toluenesulfonate as the counterion, *p*-phenolsulfonic acid (PSA), and triethanolamine (TEOA) were obtained from Sigma–Aldrich Co. The 4-sulfocalix[*n*]arene (SCA[*n*], with *n* describing the number of *p*-phenolsulfonic acid moieties linked by methylene units: $n = 4$ and 8) was purchased from Tokyo Kasei Kogyo Co., Ltd. All chemicals were used without further purification.

Synthesis of SCA[*n*]/Pt-TiO_2: The photodeposition of Pt nanoparticles on TiO_2 was conducted using a de-aerated aqueous methanol solution of $H_2PtCl_6 \cdot 6H_2O$ under UV light irradiation ($\lambda > 290$ nm). The Pt content of the sample (Pt-TiO_2) obtained was 0.2 wt% by inductively coupled plasma (ICP) analysis. For connection of SCA[*n*] to the TiO_2 surface by formation of surface complexes, a given amount of SCA[*n*] was physically mixed with TiO_2 or Pt-TiO_2, washed with ion-exchanged water, and then dried under vacuum at 298 K. Samples obtained were denoted as SCA[*n*]/TiO_2 and SCA[*n*]/Pt-TiO_2, respectively. The content of SCA[4] and SCA[8] was adjusted to 0.05 and 0.025 mmol g^{-1}, respectively. The connection of PSA on the TiO_2 surface was also conducted in a similar manner and the sample obtained was denoted as PSA/Pt-TiO_2 (content of PSA: 0.2 mmol g^{-1}). In each sample, the surface density of *p*-phenolsulfonic acid moieties linked by methylene units was equivalent to ca. 0.50 nm^{-2}.

Synthesis of TO-SCA[*n*]/Pt-TiO_2: The immobilization of TO on SCA[*n*]- and PSA-connected samples was conducted using an ion-exchange method. The changes of the counter anion of TO from *p*-toluenesulfonate to the sulfonate moiety of SCA[*n*] occurred during stirring in aqueous TO. The ratio of TO/sulfonate moiety was adjusted to 0.25. Samples were recovered by washing with ion-exchanged water repeatedly followed by centrifugation. An illustration of the Pt-TiO_2, SCA[*n*], and TO combined system (TO-SCA[4]/TiO_2) is shown in Figure 1.

Each sample was characterized using the following methods. Diffuse reflectance UV/Vis spectra were recorded at 298 K with a Shimadzu UV-2450A double-beam digital spectrophotometer; photoluminescence spectra were measured using a Spex Fluorolog-3 spectrophotometer after sample degassing under vacuum at 298 K.

The photocatalytic performance of prepared samples was evaluated by the production of H_2 in the presence of TEOA as a sacrificial reagent under visible light irradiation. Fixed amounts of the sample (20 mg) and aqueous TEOA (0.2 mol L^{-1}; 5 mL) were placed into a Pyrex reaction vessel. After bubbling argon gas into the solution for 30 min, visible light irradiation was performed using a 500 W Xe arc lamp through a colored filter (HOYA; L-40, L-45, Y-50, and Y-55). The amount of H_2 formed in the gas phase was measured using a gas chromatograph (Shimadzu GC-14B) equipped with a MS-5A column and TCD detector. The solid catalyst was recovered by centrifugation, washed three times with deionized water, dried under vacuum at 298 K, and subjected to the next photocatalytic reaction in recycle tests. The apparent quantum yield (AQY) was measured using a band-pass filter ($\lambda_{max} = 460$ nm, half width: 10 nm) and was estimated as follows:

$$\mathrm{AQY}(\%) = 100 \times (2R/I)$$

where R and I represent the amount of H_2 formed and number of incident photons, respectively. The flux of incident photons was measured using potassium trioxalatoferrate(III) trihydrate ($K_3Fe(C_2O_4)_3 \cdot 3H_2O$) as a chemical actinometer to be about 6.51×10^{15} photons s^{-1}.

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