Communication

Photohydrogenation of Acetophenone Using Coumarin Dye-Sensitized Titanium Dioxide under Visible Light Irradiation

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Abstract: The use of coumarin dyes adsorbed on titanium dioxide (TiO_2, P25) successfully extended the photocatalytic UV response of TiO_2 toward visible light region. The hydrogenation of acetophenone (AP) using TiO_2 modified with coumarin dyes proceeded with good chemical efficiencies under visible light irradiation. The role of sacrificial reagents on this dye-sensitized system is also reported.

Keywords: dye-sensitized photocatalyst; coumarin dyes; titanium dioxide; photohydrogenation; acetophenone; sacrificial reagents

1. Introduction

Dye-sensitization on semiconductor particles has recently attracted extensive attention related to dye-sensitized solar cells (DSSCs) [1–6], water splitting [7–11], CO_2 fixation [12,13] and organic chemistry [14–17]. In the dye-sensitization, the electron injection occurs from excited dyes (dye*) into conduction band (CB) of semiconductor particles to generate an oxidized form of dye (dye$^{•+}$), which is

further reduced by an electron donor to regenerate a neutral form of dye (Figure 1). Thus, it is essential for successful catalytic transformations to choose an appropriate electron donor, because the efficient electron transfer prevents self-oxidation (degradation) of the dyes.
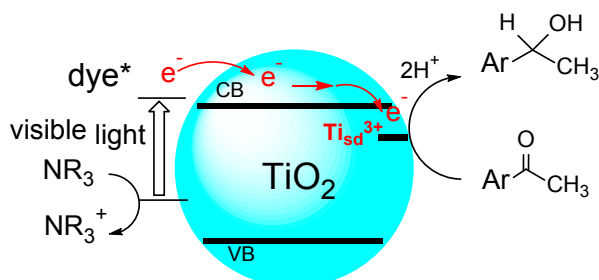
Figure 1. Photohydrogenation of acetophenone derivatives on dye-sensitized TiO2.

Recently, we have reported the photohydrogenation of acetophenone (AP) derivatives on titanium dioxide (TiO2, P25) modified with fluorescein or rhodamine B as a metal-free organic dye [17]. Although the use of these dyes successfully extended the UV response of TiO2 [18–20] toward visible light region, the reaction rate was slower than the direct hydrogenation using UV excitation of non-modified TiO2. Therefore, we focus our attention on the improvement of chemical efficiency. In this paper, we report the utility of sterically less hindered and stable coumarin dyes effectively bounding to TiO2 (Figure 2). We also report the role of sacrificial electron donors in this system.
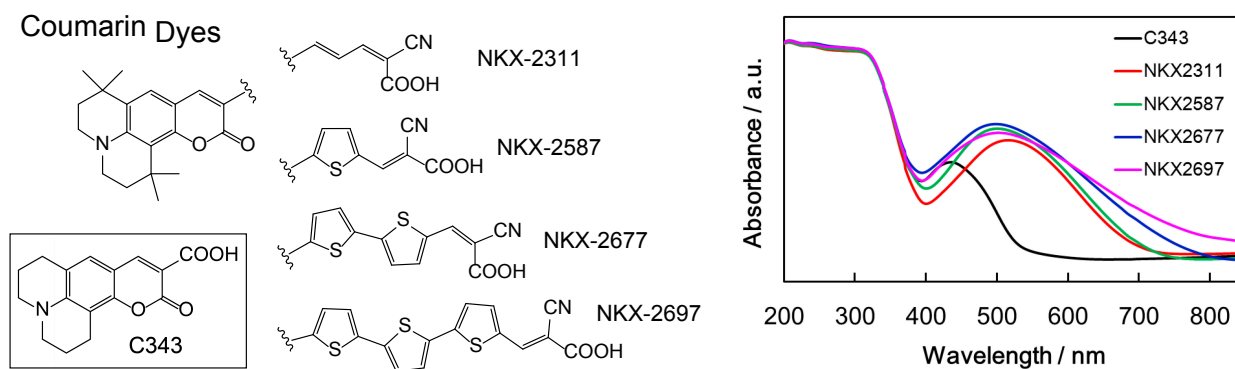
Figure 2. Coumarin dyes and diffuse reflectance spectra of coumarin-TiO2 powders.

2. Results and Discussion

The coumarin-TiO2 powders were prepared according to our reported method [17]. At first, we measured UV/vis absorption spectra of coumarin-TiO2 powders (Figure 2). The absorption spectrum of C343-TiO2 exhibited absorption band in 400–550 nm region [21]. It is important to note that absorption spectra of four NKX coumarin-TiO2 powders were observed in longer-wavelength region covering the whole range of visible light (400–800 nm), which were much broader than those of fluorescein-TiO2 and rhodamine B-TiO2 [17]. In particular, TiO2 adsorbed with NKX-2697 having three thiophene rings exhibited the broadest absorption band with slight absorption in near infrared region (>800 nm).

The amounts of dyes adsorbed on TiO2 were estimated by measuring the concentration of dyes entirely desorbed from TiO2 [17]. The amounts for C343 and NKX2311 were obtained to be 3.2 and 0.92 μmol g^{-1}, respectively. As expected, these values were higher than those of fluorescein (0.10 μmol g^{-1}) and rhodamine B (0.27 μmol g^{-1}) [17]. C343 and NKX2311 should be of greater advantage over fluorescein and rhodamine B having a sterically hindered xanthene ring. Other three coumarins (NKX2587, NKX2677 and NKX2697) have thiophene moieties as an additional functional group. Since strong intermolecular π-π stacking interaction between the thiophene moieties enhanced adsorption ability onto the TiO2 surface [22], the entire desorption of these NKX coumarins could not be achieved by the hydrolysis using NaOH solution. However, we can assume that almost similar amounts of dyes would be adsorbed on TiO2, because the molar extinction coefficient of NKX2587, NKX2677 and NKX2697 (54,300, 64,300 and 73,300 L mol^{-1} cm^{-1} in *tert*-butanol/acetonitrile 1:1, respectively) [22] is the same order of magnitude with that of NKX2311 (51,900 L mol^{-1} cm^{-1} in methanol) [23].

We next studied the hydrogenation of AP using coumarin-TiO2 powders. The conversions after 24 h or 48 h irradiation are summarized in Table 1. At first, the reactions were carried out in the presence of triethylamine (TEA) as a sacrificial electron donor. As expected, C343-TiO2 and NKX2311-TiO2 showed the better catalytic activities than fluorescein-TiO2 and rhodamine B-TiO2 [17], although the conversions using NKX2587-TiO2, NKX2677-TiO2 and NKX2697-TiO2 were low. It should be noted that the catalytic activities of NKX2587-TiO2, NKX2677-TiO2 and NKX2697-TiO2 having thiophene moieties were improved by using diisopropylethylamine (DIPEA) as the alternative sacrificial reagent. The role of sacrificial reagents will be discussed later. When C343-TiO2 and NKX2311-TiO2 were employed, the replacement of the electron donor from TEA to DIPEA led the slight decreases in the conversions (Table 1), though this reason has been unclarified at present. On the other hand, the photohydrogenation of AP did not proceed when all coumarins modified on silica gel or alumina powder (inert solids) were employed in acetonitrile containing TEA as well as DIPEA. Furthermore, the photoreaction did not occur for all of the free coumarins homogeneously dissolved in acetonitrile solution (0.1 mmol/L) containing the sacrificial reagents. It is thus concluded that the hydrogenation is never induced by the direct electron transfer from the excited coumarins to AP.

The role of sacrificial reagents can be explained by considering the relationship between HOMO levels of dyes corresponding to oxidation potentials (E_{ox}: dye$^{•+}$/dye) listed in Table 2 and the oxidation potential of TEA (TEA$^{•+}$/TEA) [24] or DIPEA (DIPEA$^{•+}$/DIPEA) [25]. In the case of C343 and NKX2311, the electron transfer from TEA to dye$^{•+}$ can smoothly proceed, because these HOMO levels (+1.18 V and +1.28 V *vs.* standard hydrogen electrode (SHE)) are comparable or more positive than that of TEA (+1.20 V *vs.* SHE) (Figure 3a). In contrast, the HOMO levels of NKX2587, NKX2677 and NKX2697 are more negative than the oxidation potential of TEA, thereby diminishing the electron transfer efficiency (Figure 3b). The electron transfer efficiency is increased by the use of DIPEA (+0.92 V *vs.* SHE) comparable or negatively positioned compared to E_{ox} (dye$^{•+}$/dye). On the other hand, electron injection from the excited dyes (dye*) into the CB of TiO2 would efficiently occurred in all dye-sensitized systems, since all LUMO levels of dyes corresponding to ($E_{ox} - E_{0-0}$) listed in Table 2 are more negative than the CB edge of TiO2 (*ca.* −0.5 V *vs.* SHE) [5,22,23]. Thus, the hydrogenation is mainly influenced by HOMO levels of dyes rather than LUMO levels of dyes. The similar trend was reported in a dye-sensitized H2 production, where energy gap between HOMO

levels of dyes and I_3^-/I^- redox potential dominates the overall reaction efficiency [21]. Additionally, the sacrificial reagents such as TEA and DIPEA may also act as a proton source giving AP-OH, because an oxidative dealkylation of TEA and DIPEA *via* cation radical intermediates (NR_3^+) proceeds to give a proton [26].

Table 1. Dye-sensitized photohydrogenation of acetophenone (AP) [a].
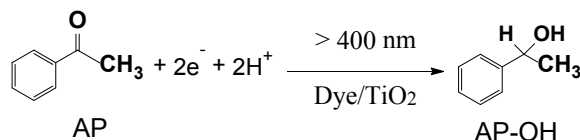
| Dye-TiO₂ Photocatalyst	In the Presence of TEA		In the Presence of DIPEA	
	Conversion [b] (%) after 24 h	Conversion [b] (%) after 48 h	Conversion [b] (%) after 24 h	Conversion [b] (%) after 48 h
C343-TiO₂	74	100	54	92
NKX2311-TiO₂	76	96	56	84
NKX2587-TiO₂	27	39	74	84
NKX2677-TiO₂	18	29	62	75
NKX2697-TiO₂	22	30	54	79
fluorescein-TiO₂ [17]	56	80	-	-
rhodamine B-TiO₂ [17]	63	82	-	-

[a] Carried out for a mixture of AP (3 mmol) and photocatalyt (0.10 g) in the presence of TEA or DIPEA (3 mL) in deaerated CH_3CN (total volume: 30 mL) under visible light (>400 nm) at 32 °C. [b] Determined by GC analysis.

Table 2. Properties of coumarin dyes.

Coumarin Dye	E_{0-0} [a]/eV	E_{ox}: dye$^{•+}$/dye/V *vs.* SHE	($E_{ox} - E_{0-0}$)/V *vs.* SHE
C343	+2.4	+1.18 [b]	−1.2
NKX2311	+1.8	+1.28 [b]	−0.5
NKX2587	+1.8	+1.01 [c]	−0.8
NKX2677	+1.6	+0.93 [c]	−0.7
NKX2697	+1.5	+0.91 [c]	−0.6

[a] 0-0 energies of the dyes adsorbed on the P25 TiO₂ estimated from the onset of absorption spectra (Figure 2).
[b] In DMF from Ref. [23]. [c] In CH₃CN from Ref. [22].
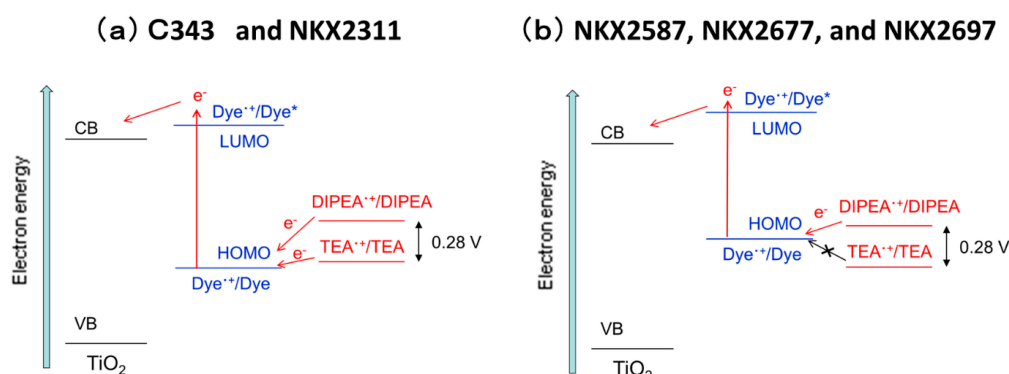
Figure 3. Energetics and electron transfer processes occurring on the dye-sensitized TiO₂.

3. Experimental Section

C343 (dye content 97%) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. The coumarin dyes of NKX2311, NKX2587, NKX2677 and NKX2697 shown in Figure 2 were gifted from Dr. Hara and Dr. Koumura, AIST Japan. Polycrystalline TiO_2 powder (Degussa P25, specific surface area: *ca.* 50 m^2 g^{-1}) was used after previously heated at 120 °C in air for 2 h to remove adsorbed water on the TiO_2 surface. The dyes were adsorbed onto the pre-heated TiO_2 powder by immersing 1.0 g of the powder into the coumarin dye solution (0.3 mol L^{-1}) containing acetonitrile/*tert*-butanol (50 vol. %) overnight at room temperature in the dark. After repeating centrifugation and washing with ethanol at least six times, the TiO_2 powders modified with the coumarin dyes (dye-TiO_2) were dried overnight at 40 °C and kept in the dark. The amounts of dyes adsorbed on the P25 TiO_2 powders were estimated by measuring the concentration of the dyes entirely desorbed from the TiO_2 powder, which was attained by immersing 0.20 g of the dye-TiO_2 samples into 2.0 mL of 0.1 mol L^{-1} NaOH solution as reported by Jang *et al.* [15]. After centrifugation, the absorbance of supernatant for C343 was measured at maximum wavelength of 400 nm. In order to determine the amount of NKX2311 desorbed from TiO_2, the supernatant was once neutralized by adding a few drops of 0.5 mol L^{-1} HCl aqueous solution, followed by extracted with five portions of 10 mL diethylether. The ether layer was dried over anhydrous $MgSO_4$ and then filtered. Removal of diethyl ether under reduced pressure provided a red residue (NKX2311) which was then dissolved in 20 mL of methanol. The amount of NKX2311 was determined using the molar extinction coefficient of 51,900 L mol^{-1} cm^{-1} [23] and absorbance at maximum wavelength (503 nm) in the methanol solution.

Irradiation experiments were carried out for a mixture of AP and the dye-TiO_2 powder in the presence of sacrificial electron donor (10 vol. %) of TEA or DIPEA in deaerated acetonitrile solution at 32 °C. The solution was placed in a cylindrical glass cell (40 mm × 45 mm i.d.) and sealed with a rubber septum. Argon gas (99.99%) was passed into the solution through the rubber septum for 30 min. The degassed solution was stirred in a water bath for 30 min to attain thermal equilibrium at 32 °C in the dark. The suspended solution was irradiated with visible light (wavelength > 400 nm) from a 300 W xenon arc lamp (ILC Technology, CERMAX LX300, Fremont, CA, USA) through a dichroic mirror and a cut-off filter (Toshiba L42). Light intensity was measured to be 360 mW cm^{-2} by the use of thermopile sensor (Coherent 210, Santa Clara, CA, USA). After appropriate irradiation times, 0.2 cm^3 of sample solution was withdrawn and centrifuged to remove the catalyst powders. Concentrations of the substrates and products in supernatants were determined by using a gas chromatograph (Shimadzu GC-14A, Kyoto, Japan) equipped with a capillary column (GL Science Inert-Cap Pure-WAX, Tokyo, Japan, 30 m ×0.25 mm i.d., 0.25 μm film thickness), a flame-ionization detector (FID), and an auto injector (Shimadzu AOC-17, Kyoto, Japan). The GC analytical conditions were described in the previous report [17].

4. Conclusions

We have developed the P25 TiO_2 powders modified with coumarin dyes based on coumarin 343 (C343) framework. Some of these catalysts effectively hydrogenated acetophenone under visible light

irradiation. The low catalytic activities of NKX2587-TiO$_2$, NKX2677-TiO$_2$ and NKX2697-TiO$_2$ containing thiophene rings were improved by replacing a sacrificial reagent of TEA with DIPEA, which was attributable to the negative shift (*ca.* 0.3 V) of the oxidation potential of sacrificial reagent. It is thus demonstrated that the dye-sensitized photohydrogenation is affected by the HOMO levels of dyes in comparison with the oxidation potential of sacrificial reagents.

Acknowledgments

Author Contributions

S. Kohtani contributed to design of the study and manuscript writing. M. Mori performed experiments and analyzed the data. E. Yoshioka carried out part of the data analysis and experiments. H. Miyabe designed and coordinated throughout this study.

Conflicts of Interest

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