

## Self-Assembled Heterosupramolecular Visible Light Photocatalyst Consisting of Gold Nanoparticle-Loaded Titanium(IV) Dioxide and Surfactant

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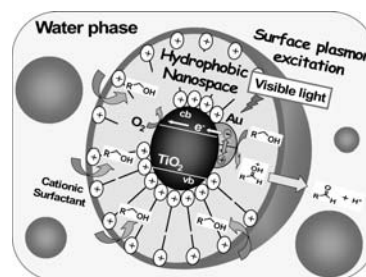
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“Heterosupramolecules” represented by dye-sensitized TiO<sub>2</sub> nanocrystalline films is a key material in intelligent nanodevices for the conversion of solar energy to electric and chemical energy.<sup>1,2</sup> We have previously reported a self-assembled heterosupramolecular photocatalyst consisting of TiO<sub>2</sub> and a cationic surfactant bilayer formed on the surface, the so-called admicelle, with a high level of activity for the degradation of 2-naphthol under UV light irradiation.<sup>3</sup> Similar enhancing effects by the addition of surfactants have also been reported in some other TiO<sub>2</sub>-photocatalyzed decompositions of organic substances for water purification.<sup>4–7</sup> However, there is no report on the application of the surfactant/TiO<sub>2</sub> system to oxidations as organic synthesis. This is mainly because the valence band holes of TiO<sub>2</sub> possess extremely strong oxidizing power,<sup>8</sup> and hence partially oxidized products are difficult to obtain selectively.<sup>9</sup> The greater fundamental drawback to the TiO<sub>2</sub> photocatalyst is that visible light is hardly utilized because of its wide band gap. Recently, the visible light excitation of the surface plasmon resonance (SPR) of Au nanoparticles (NPs) loaded on TiO<sub>2</sub> (Au/TiO<sub>2</sub>) has been found to cause the electron injection from Au to TiO<sub>2</sub>,<sup>10</sup> and the applications to the photovoltaic cell and biosensor have been reported.<sup>11</sup> The visible light-induced electron transfer endows Au NPs with mild oxidizing ability, allowing us to expect the application to oxidative organic synthesis. Such research has just begun with the oxidations of isopropanol to acetone<sup>12</sup> and thiol to disulfide;<sup>13</sup> however, the photocatalytic activity is low.

Here we report the Au/TiO<sub>2</sub> SPR-induced visible light photocatalytic chemoselective oxidation of alcohols to carbonyl compounds and a drastic enhancement of the oxidation by the addition of a cationic surfactant. To our knowledge, this is the first report on the visible light photocatalytic reaction in the heterosupramolecular system (Scheme 1). To vary Au particle size (*d*/nm) with its loading amount maintained constant, Au/TiO<sub>2</sub> was synthesized by the deposition–precipitation method where both heating temperature (*T<sub>c</sub>*) and time (*t<sub>c</sub>*) were altered.<sup>14,15</sup> The photocatalytic oxidation of alcohol was carried out as follows: Au/TiO<sub>2</sub> was added to a cinnamyl alcohol (Ph–C=C–CH<sub>2</sub>OH) solution (initial concentration, *C*<sub>0</sub> = 5 × 10<sup>−4</sup> mol dm<sup>−3</sup>), and light was irradiated under aerobic conditions. UV light irradiation to the suspension led to rapid nonselective Ph–C=C–CH<sub>2</sub>OH degradation. In contrast, visible light irradiation to the suspension yielded cinnamaldehyde (Ph–C=C–CHO) and cinnamic acid (Ph–C=C–COOH) as partially oxidized products in 90% and 10% selectivity, respectively, with 8% conversion at irradiation time (*t<sub>p</sub>*) = 24 h. The turnover number (TON = the molecule number of Ph–C=C–CHO gener-

**Scheme 1.** Self-Assembled Heterosupramolecular Visible Light Photocatalyst



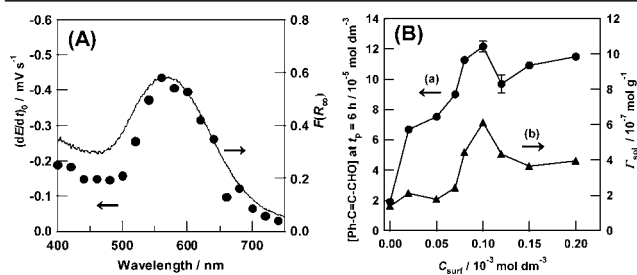
ated/the number of Au surface atoms) at *t<sub>p</sub>* = 24 h exceeding 10 is evidence for the oxidation to progress catalytically. The photonic efficiency ( $\Phi$ , molecules produced/incident photons) at the light wavelength ( $\lambda$ ) = 555 ± 15 nm was calculated to be 3.3 × 10<sup>−4</sup> by assuming a two-electron process for the oxidation. No reaction occurred in the Au/TiO<sub>2</sub> system under anaerobic conditions and in the TiO<sub>2</sub> system under aerobic conditions. Although Au NPs are known to exhibit thermal catalytic activity for the oxidation of alcohols,<sup>16</sup> the conversion was very low in the dark (1.4% at *t<sub>p</sub>* = 24 h). Further, Au NP-loaded zirconium(IV) dioxide (Au/ZrO<sub>2</sub>) showed no visible light photocatalytic activity. This is probably because the conduction band edge of ZrO<sub>2</sub> is too high for the electron transfer from Au NPs to occur.<sup>17</sup> Consequently, the visible light-induced electron transfer from Au NPs to TiO<sub>2</sub> mainly contributes to the Ph–C=C–CH<sub>2</sub>OH oxidation, and O<sub>2</sub> acts as an acceptor for the electrons injected to TiO<sub>2</sub> to complete the catalytic cycle.

To clarify the origin for the reaction, Au NP-loaded mesoporous TiO<sub>2</sub> nanocrystalline films (Au/mp-TiO<sub>2</sub>) were formed on the surfaces of fluorine-doped SnO<sub>2</sub> electrodes, and the electrode potential (*E*) change induced by irradiation of monochromatic light was examined in a Ph–C=C–CH<sub>2</sub>OH solution containing 0.1 mol dm<sup>−3</sup> Na<sub>2</sub>SO<sub>4</sub> as a supporting electrolyte.<sup>18,19</sup> Visible light irradiation in the presence of Ph–C=C–CH<sub>2</sub>OH gave rise to the cathodic shift of *E*. The potential upward shift can be considered as corresponding to the net electron transfer from Ph–C=C–CH<sub>2</sub>OH to TiO<sub>2</sub> mediated by the SPR-excited Au NPs. Figure 1A compares the action spectrum of the initial rate (*dE/dt*)<sub>0</sub> (solid circles) and the electronic absorption spectrum of Au/mp-TiO<sub>2</sub> (solid line): (*F*(*R<sub>∞</sub>*)) denotes the Kubelka–Munk function. The good resemblance of the profiles clearly indicates that the excitation of the Au NP-SPR is the driving force for the Ph–C=C–CH<sub>2</sub>OH oxidation. The increases in both the TON and the absorption intensity of Au NP-SPR with increasing *d* further supported this conclusion (data not shown).<sup>20</sup>

In view of the idea of “reasonable delivery photocatalytic reaction systems”,<sup>21</sup> the sufficient supply of the alcohol to the oxidation

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**Figure 1.** (A) Action spectrum of  $(dE/dt)_0$  (solid circles) and diffuse reflectance UV-vis spectrum of Au/mp-TiO<sub>2</sub> (solid line). (B) Plots of Ph-C=C-CHO concentrations at  $t_p = 6$  h:  $C_0 = 5 \times 10^{-4}$  mol dm<sup>-3</sup> (a) and adsolubilization amounts of Ph-C=C-CH<sub>2</sub>OH (b) vs C<sub>18</sub>TAC concentration.

sites on the Au NP surface and the prompt separation of the product from the reaction field are clues to achieving high activity and selectivity. First, the additive effect of trimethylstearylammmonium chloride (C<sub>18</sub>TAC) with varying concentrations impacting the reaction rate was examined. Figure 1B(a) shows plots of the concentration of Ph-C=C-CHO produced at  $t_p = 6$  h vs C<sub>18</sub>TAC concentration ( $C_{\text{surf}}$ ). Surprisingly, the reaction is drastically enhanced at  $C_{\text{surf}} = 0.10$  mmol dm<sup>-3</sup> near the critical admicelle concentration (CAMC),<sup>3</sup> while no decomposition of C<sub>18</sub>TAC occurred. Ph-C=C-CHO was generated in 95.3% selectivity (4.7% Ph-C=C-COOH) with 24% conversion at  $t_p = 6$  h. The  $\Phi$  value increased to  $2.0 \times 10^{-3}$  at  $C_{\text{surf}} = 0.10$  mmol dm<sup>-3</sup>, which should be further increased by optimizing the particle size and loading amount of Au NPs.<sup>12</sup> Also, the thermal conversion was 3.4 times increased by the addition of the surfactant. The Ph-C=C-CHO concentration sharply increases in the region of  $C_{\text{surf}}$  from 0.02 to 0.10 mmol dm<sup>-3</sup>, decreasing at  $C_{\text{surf}} > 0.10$  mmol dm<sup>-3</sup>. The amount of Ph-C=C-CH<sub>2</sub>OH dissolved into the admicelle (adsolubilization amount per amount of TiO<sub>2</sub>,  $\Gamma_{\text{sol}}$ ) from the bulk solution was determined as a function of  $C_{\text{surf}}$  (Figure 1B(b)). The  $\Gamma_{\text{sol}}$  also reaches a maximum at  $C_{\text{surf}} = 0.10$  mmol dm<sup>-3</sup>, and at  $C_{\text{surf}} > 0.10$  mmol dm<sup>-3</sup>, the competitive Ph-C=C-CH<sub>2</sub>OH incorporation into the micelles in the bulk solution decreases the value. At  $C_{\text{surf}} = 0.10$  mmol dm<sup>-3</sup>, the ratio of the Ph-C=C-CH<sub>2</sub>OH concentration in the admicelle to that in the bulk solution is estimated to reach as much as 6000 by assuming that the admicelle thickness is approximately 5 nm. The positive correlation between the reaction rate and  $\Gamma_{\text{sol}}$  indicates that the effect of the admicelle concentrating Ph-C=C-CH<sub>2</sub>OH in the vicinity of the Au surfaces greatly accelerates its oxidation. Another intriguing point is that the amount of Ph-C=C-CHO produced at  $t_p = 6$  h ( $2.4 \times 10^{-5}$  mol at  $C_{\text{surf}} = 0.1$  mmol dm<sup>-3</sup>) is larger than that of Ph-C=C-CH<sub>2</sub>OH adsolubilized before reaction ( $1.2 \times 10^{-7}$  mol at  $C_{\text{surf}} = 0.1$  mmol dm<sup>-3</sup>) by a factor of ca. 200. Second, an application of the heterosupramolecular system for several alcohols was studied (Table 1). The remarkable acceleration of the chemoselective oxidations with selectivities > 99% for all the alcohols tested shows the wide effectiveness of this methodology. The Hammett plot for the carbonyl compound formation showed a linear correlation excepting 4-HO-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OH,<sup>22</sup> for which an extraordinary enhancement is observed, although the reason remains unknown presently.

On the basis of these results, we can summarize the essential mechanism for this heterosupramolecular visible light photocatalytic reaction as follows (Scheme 1): The C<sub>18</sub>TAC admicelle is formed on the Au/TiO<sub>2</sub> surfaces at CAMC, and alcohol is incorporated into the hydrophobic nanospace of the admicelle from the water

**Table 1.** Results of Alcohol Oxidation with and without Surfactant

Alcohol <sup>a</sup>	Carbonyl compound formation <sup>b</sup>		Ratio <sup>d</sup>
	with C <sub>18</sub> TAC <sup>c</sup>	without	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	2.74	0.83	3.3
4-HO-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	6.22	0.21	29.6
4-MeO-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	4.30	1.21	3.6
4-Cl-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	1.89	0.33	5.7
PhCH(OH)Me	3.12	0.93	3.4

<sup>a</sup>  $C_0 = 5 \times 10^{-4}$  mol dm<sup>-3</sup>. <sup>b</sup>  $\times 10^{-5}$  mol dm<sup>-3</sup> at  $t_p = 6$  h. <sup>c</sup>  $C_{\text{surf}} = 0.1$  mmol dm<sup>-3</sup>. <sup>d</sup> Enhancement ratio by the addition of C<sub>18</sub>TAC.

phase to be concentrated near the Au NP surfaces. Visible light excitation of the Au NP-SPR of Au/TiO<sub>2</sub> triggers the electron transfer from Au to TiO<sub>2</sub>. Au NPs with lowered Fermi energy oxidize alcohol on their surfaces, while O<sub>2</sub> is reduced by the electrons accumulated in TiO<sub>2</sub>. The resulting hydrophilic intermediates like R-C=O<sup>+</sup>H are spontaneously transported into the water phase to yield a carbonyl compound. As a result of the consumption of the alcohol in the reaction field, it is further supplied from the water phase.

In summary, we have shown that a heterosupramolecular photocatalyst consisting of Au/TiO<sub>2</sub> and a cationic surfactant admicelle exhibits a very high level of activity for the chemoselective oxidation of alcohols to carbonyl compounds under visible light irradiation. This study would expand the highly efficient and selective organic synthesis using sunlight as an energy source.

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**Supporting Information Available:** Experimental details; catalyst characterization (Figure S1); PCP curves (Figure S2); Hammett plots (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- Grätzel, M. *Nature* **2001**, *414*, 338.
- Youngblood, W. J.; Lee, S. A.; Maeda, K.; Mallouk, T. *Acc. Chem. Res.* **2009**, *42*, 1966.
- Tada, H.; Matsui, H.; Shiota, F.; Nomura, M.; Ito, S.; Yoshihara, M.; Esumi, K. *Chem. Commun.* **2002**, 1678.
- Marcì, G.; Addamo, M.; Augugliaro, V.; Coluccia, S.; López, E.-G.; Loddo, V.; Martra, G.; Palmisano, L.; Schiavello, M. *J. Photochem. Photobiol., A* **2003**, *160*, 105.
- Cho, Y.; Kyung, H.; Choi, W. *Appl. Catal., B* **2004**, *52*, 23.
- Fabrizi, D.; Crime, A.; Davezza, M.; Medana, C.; Baiocchi, C.; Bianco, P.; Pramauro, E. *Appl. Catal., B* **2009**, *92*, 318.
- Yamada, K.; Mukaihata, N.; Kawahara, T.; Tada, H. *Langmuir* **2007**, *23*, 8593.
- Choi, W. *Catal. Surv. Asia* **2006**, *10*, 16.
- (a) Palmisano, G.; Augugliaro, V.; Pagliaro, M.; Palmisano, L. *Chem. Commun.* **2007**, 3425. (b) Augugliaro, V.; Kisch, H.; Loddo, V.; Lopez-Munoz, M. J.; Marquez-Alvarez, C.; Palmisano, G.; Palmisano, L.; Parrino, F.; Yurdakal, S. *Appl. Catal., A* **2008**, *349*, 182.
- Tian, Y.; Tatsuma, T. *J. Am. Chem. Soc.* **2005**, *127*, 7632.
- Tian, Y.; Shi, X.; Lu, C.; Wang, X.; Wang, S. *Electrochem. Commun.* **2009**, *1603*.
- Kowalska, E.; Abe, R.; Ohtani, B. *Chem. Commun.* **2009**, 241.
- Naya, S.; Teranishi, M.; Isobe, T.; Tada, H. *Chem. Commun.* **2010**, 815.
- Kiyonaga, T.; Mitsui, T.; Torikoshi, M.; Takekawa, M.; Soejima, T.; Tada, H. *J. Phys. Chem. B* **2006**, *110*, 10771.
- Catalyst characterizations are contained in the Supporting Information (Figure S1).
- Mallat, T.; Baiker, A. *Chem. Rev.* **2004**, *104*, 3037.
- Furube, A.; Du, L.; Hara, K.; Katoh, R.; Tachiya, M. *J. Am. Chem. Soc.* **2007**, *129*, 14852.
- Takahashi, Y.; Tatsuma, T. *Electrochem. Commun.* **2008**, *10*, 1404.
- The data are contained in the Supporting Information (Figure S2).
- Link, S.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 8410.
- Tada, H.; Kiyonaga, T.; Naya, S. *Chem. Soc. Rev.* **2009**, *38*, 1849.
- The data are contained in the Supporting Information (Figure S3).

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