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Heterosupramolecular photocatalysis: oxidation of organic compounds in nanospaces between surfactant bilayers formed on TiO_2†

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A heterosupramolecular photocatalyst consisting of TiO_2 and a cationic surfactant bilayer formed on the surface has achieved a very high level of activity in the oxidation of 2-naphthol through the cooperation of the inorganic and organic components.

'Heterosupramolecules' can be defined as artificial micro-devices that carry out advanced functions by cooperating with inorganic solids and organic molecules. Two of the limited number of heterosupramolecules developed so far include dye-sensitized solar cells based on nanocrystalline TiO_2 films[1] and a photosynthetic system using vesicles containing CdS particles.[2] Much attention has also been focused on TiO_2 as a photocatalyst for environmental purification, because of the great potential of holes to oxidize organic pollutants in water and air.[3–5] The strategy for increasing the photocatalytic activity of TiO_2 in most studies has been to optimize the balance between crystallinity and surface area.[6] However, the heterogeneous photocatalytic reaction generally proceeds *via* the Langmuir–Hinshelwood-type surface reaction mechanism. Thus, for practical dilute systems, it is more important to increase the surface concentration of substrates.[7,8] To our knowledge, this is the first report on the photocatalytic reaction of a heterosupramolecule consisting of TiO_2 particles and surfactant bilayers formed on the particle surfaces. Since 2-naphthol (2-NAP) and its analogs have been in wide use for the production of azo-dyes, it was selected as a model harmful substrate for the present study.

Anatase TiO_2 particles (BET surface area = 9.0 $m^2\ g^{-1}$) were supplied by TAYCA Co. (JA-1) and used without further activation. The adsorption isotherm of trimethylstearylammonium chloride ($C_{18}TAC$) on TiO_2 particles was obtained by measuring the concentrations in solutions before and after adsorption. All suspensions (0.1 g of TiO_2/10 mL) in the presence of 10 mM NaCl were equilibrated for 24 h at 25 °C. After equilibration, the solids were separated by centrifugation and the supernatant was analyzed using a dye method.[9] The ζ-potential and adsolubilization measurements were carried out in the same manner as described in the previous paper.[10] TiO_2 particles (0.5 g) were added to a 0.6 mM solution of $C_{18}TAC$ (50 mL), and the mixture was kept at 25 °C for 24 h. To this suspension, 50 mL of a 0.4 mM 2-NAP solution (solvent: H_2O–acetonitrile = 99/1 v/v) was added and stirred further in the dark for 24 h. Irradiation of this suspension in a reaction vessel was carried out with a 400 W high-pressure mercury arc. The light intensity integrated from 320 to 400 nm was measured to be 2.6 mW cm^{-2}. To determine the total amount of 2-NAP left or the amount of phthalic acid generated after irradiation, the 2-NAP or phthalic acid in the adsorbed bilayer was extracted into the liquid phase by adding 400 mL of methanol to the suspension (100 mL). After filtration with a syringe filter, the filtrate was analyzed by electronic absorption spectroscopy. The solvent of the filtrate (100 mL) was completely removed by evaporation, and then 10 mL of a mixed solvent (H_2O–acetonitrile = 7/3 v/v) was added; the solvent contained phosphoric acid to control the pH at 2.5. The solution was then subjected to high-performance liquid chromatography (HPLC) analysis. *This analysis confirmed that the pre-irradiation amount of 2-NAP agreed with the initially added amount to within an experimental margin of error of ±3.5%.* The amount of 2-NAP or phthalic acid present in the water phase after reaction was determined by analyzing the filtrate after the irradiated suspension was filtered without the addition of methanol.

The adsorption of $C_{18}TAC$ on TiO_2 particles was examined. Adsorption isotherm (a) in Fig. 1A shows that the adsorption amount (Γ) sharply rises at the equilibrium concentration (C_{eq}) < 0.01 mM, then increases slowly to reach a constant value at $C_{eq} > 0.13$ mM. Plot (b) shows the ζ-potential of the TiO_2 particles as a function of C_{eq}. The ζ-potential is −45.8 mV in the absence of $C_{18}TAC$. The polarity of the surface charge is inverted by the addition of a small amount of $C_{18}TAC$, and the ζ-potential is almost constant (45 ± 5 mV) at $C_{eq} > 0.13$ mM. In this concentration range, the dispersibility of the TiO_2 suspension was significantly improved, and the particles were barely sedimented after the suspension had been allowed to stand overnight. The cross-sectional area occupied by one $C_{18}TAC$ molecule in the saturated adsorption state was calculated to be 0.23 nm^2 $molecule^{-1}$, which is approximately half the value of dodecyltrimethylammonium bromide with the same head group in a close-packed monolayer (0.49 nm^2 $molecule^{-1}$).[10] From these results, we concluded that a close-packed bilayer of $C_{18}TAC$ was formed on the surface of TiO_2 ($C_{18}TAC/TiO_2$) at $C_{eq} > 0.13$ mM.

The amount of 2-NAP dissolved into the $C_{18}TAC$ adsorbed bilayer (adsolubilization amount, Γ_{sol}) was determined as a function of the initial $C_{18}TAC$ concentration (C^0). Fig. 1(B), plot (a) shows that the Γ_{sol} value goes through a maximum at $C^0 \cong 1$ mM. This C^0 corresponds to the C_{eq} value of 0.48 mM, which is near the critical micelle concentration of $C_{18}TAC$ (0.34 mM).[11] At $C^0 < 1$ mM, 2-NAP is effectively incorporated into the hydrophobic spaces between the adsorbed bilayer, whereas a part of 2-NAP is probably dissolved into the micelles at $C^0 > 1$ mM. As shown in Fig. 1(B), plot (b) the partition coefficient, K, defined as the ratio of the amount of 2-NAP in the bilayer to that in the bulk, is 2.6 at $C^0 \cong 1$ mM. The uptake of 2-NAP into the bilayer reaches 72% of the total.

Irradiation ($\lambda_{ex} > 300$ nm) in the presence of TiO_2 leads to a slow decrease in the concentration of 2-NAP (Fig. 2(a)); t_p denotes irradiation time. Both TiO_2 and O_2 (air) were needed in order for 2-NAP to photodecompose. *Upon the addition of $C_{18}TAC$, the rate of decomposition is drastically increased.*

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† Electronic supplementary information available: further characterization data and experimental details. See http://www.rsc.org/suppdata/cc/b2/b204593a/

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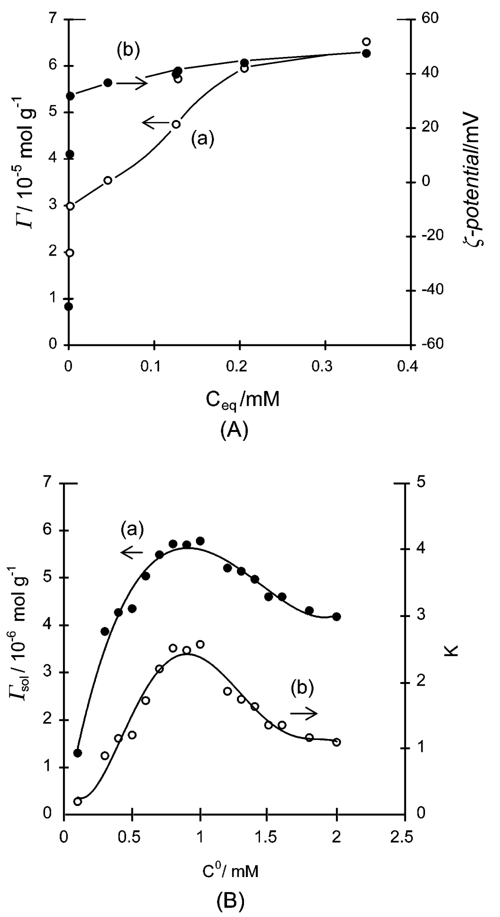

Fig. 1 (A) Adsorption isotherm of C_{18}TAC on TiO_2 particles (a) and ζ-potential of the TiO_2 particles (b) as a function of C_{eq}. (B) 2-NAP uptake into the C_{18}TAC adsorbed bilayer (a) and the partition coefficient, K, (b) as a function of C^0. All the measurements were carried out at 25 °C and pH ≅6.5.

This is apparent in Fig. 2(b), in which the signs (●) and (○) express the 2-NAP concentrations determined by absorption spectroscopy and HPLC, respectively. The first-order rate constant for system (b) in Fig. 2 (1.0 h^{-1}) was greater than that for system (a) (0.026 h^{-1}) by a factor of *ca.* 40. Comparable accelerating effects were obtained over a wide pH range (3 < pH < 9). The amount of 2-NAP decomposed at $t_p = 5$ h was *ca.* 75% of the total, which is almost in agreement with the amount incorporated into the C_{18}TAC adsorbed bilayer before irradiation. Thus, the increase in the reaction rate with the addition of C_{18}TAC is caused mainly by the concentration of 2-NAP in the vicinity of the TiO_2 surface. Liquid chromatography-mass spectrometry (LC-MS) analysis confirmed the formation of phthalic acid with a yield of 2.6% at $t_p = 5$ h [MS: m/z = 165 (M^-), 121 ($C_6H_5COO^-$)] and several intermediates (unidentified). The population ratio of phthalic acid outside to inside the bilayer was 0.86 at $t_p = 5$ h.

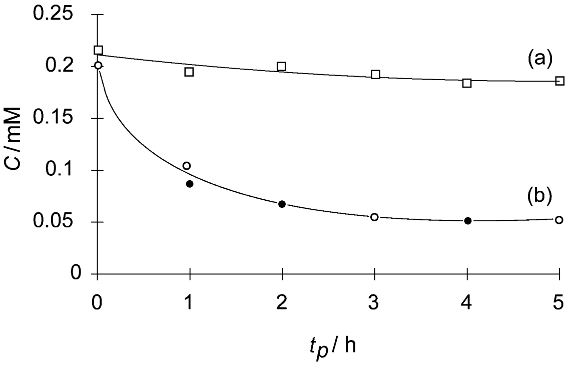

Fig. 2 Time courses for the photocatalyzed decomposition of 2-NAP in the absence (a) and presence (b) of C_{18}TAC. The temperature was kept at 30 ±1 °C and the initial pH was 6.3.

Diffuse reflectance Fourier transform infrared (DRIFT) spectra of the $C_{18}TAC/TiO_2$ particles recovered after irradiation without 2-NAP and with it were measured. In the spectrum at $t_p = 0$, the absorption peaks at 2924 and 2855 cm^{-1} were assignable to the CH_2 antisymmetric and symmetric stretching vibrations of C_{18}TAC, respectively. The C_{18}TAC molecules on the TiO_2 surface remained intact at $t_p = 2$ h in the presence of 2-NAP, whereas the absorption peaks of C_{18}TAC almost disappeared at $t_p = 1$ h in the absence of 2-NAP. This finding indicates that 2-NAP is oxidized more easily than C_{18}TAC. The frontier orbital energies of C_{18}TAC were obtained by *ab initio* calculations: E(HOMO) = −12.305 and E(LUMO) = −1.516 eV.[12] For comparison, the energies for sodium dodecylsulfate, a typical anionic surfactant, were also calculated: E(HOMO) = −6.349 and E(LUMO) = +3.181 eV. The positive charge on the head group of C_{18}TAC significantly lowers its frontier orbital energies. Spin-trapping ESR experiments revealed that the activated species in this reaction is the $OH^\cdot$ radical. Since the $OH^\cdot$ radical is an electrophilic strong oxidant, 2-NAP with a HOMO energy (−7.807 eV) much higher than that of C_{18}TAC may be more susceptible to its attack.

The essential reaction mechanism is summarized as follows. In the dark, C_{18}TAC molecules form a close-packed adsorbed bilayer on the surface of TiO_2. 2-NAP is effectively incorporated into the hydrophobic nanospaces between the adsorbed bilayer. Upon irradiation, the holes generated in the valence band of TiO_2 oxidize Ti_s-OH groups and/or H_2O_{ad} to produce $OH^\cdot$ radical. This powerful oxidant preferentially attacks 2-NAP rather than C_{18}TAC to oxidize it to phthalic acid. A portion of the resulting oxidized products is transported from the hydrophobic reaction field to the water phase. On the other hand, adsorbed O_2 acts as an acceptor for excited electrons in the conduction band.[5,13] The O_2 consumed in the adsorbed bilayer will be consumed by the diffusion from the water phase. In conclusion, the effect of the adsorbed bilayer can be attributed to both the concentration of the substrate near the TiO_2 surface and the increase in the effective reaction surface area with the improvement of the particle dispersibility.

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