Photocatalytic Decomposition of Trichlorobenzene Using TiO2 Supported on Nickel-Poly(tetrafluoroethylene) Composite Plate

Hiroyuki Uchida,* Shinobu Katoh, and Masahiro Watanabe
Laboratory of Electrochemical Energy Conversion, Faculty of Engineering, Yamanashi University, Takeda 4-3-11, Kofu 400

(Received December 21, 1994)

Using TiO_2 photocatalysts supported on nickel–poly(tetrafluoroethylene), Ni–PTFE, composite plate, a rapid and complete degradation of trichlorobenzene in dilute aqueous solution was performed. The Ni–PTFE substrate enhanced the decomposition rate of pollutants, since electrons photogenerated in TiO_2 were efficiently consumed in the reduction of dissolved oxygen as a reaction coupled with the oxidative degradation.

Recently, photocatalytic degradation processes of organic pollutants in water have been extensively studied.[1] Many studies have shown that an illumination of semiconductor powders such as colloidal TiO_2 suspended in aqueous solutions containing organic compounds and oxygen induces an oxidative mineralization of organics to carbon dioxide, sulfate, nitrate, *etc.*, accompanied by the reduction of O_2 dissolved in the solution. It has been demonstrated that the quantum efficiency on TiO_2 for the photodegradation of organic pollutants in water is limited by the reduction kinetics of dissolved O_2.[2] The photodecomposition rate of organic compounds is greatly accelerated by attaching metal particles such as Pd or Pt on the TiO_2 surface, because metal particles act as electron–accepting sites for the effective charge separation and as electrocatalysts for the oxygen reduction.[2, 3] From practical view points such as a recovery of used photocatalyst particles from the solution, it is desirable to support them on immobilized substrates rather than colloids. However, the mass transport of both organic compounds and dissolved oxygen to the supported photocatalysts becomes generally worse.

In this research, we examine to enhance the photodecomposition rate of trichlorobenzene, a typical toxic chlroaromatic, by accelerating the O_2 reduction with use of new films with immobilized photocatalysts shown in Figure 1. Microcrystalline TiO_2 particles are supported on nickel–poly(tetrafluoroethylene), Ni–PTFE, composite plate. Using similar Ni–PTFE electrodes in organic or inorganic electrolysis, some unique electrochemical behaviors attributed to their ultrahydrophobicity have been reported.[4] We expect for PTFE particles to enrich oxygen around Ni particles contacted with TiO_2 in the film by the hydrophobic property. It is expected also for Ni particles to reduce the concentrated O_2 effectively by collecting electrons photogenerated in TiO_2 particles and by the catalytic action for the electrochemical reduction of O_2 with the electrons.

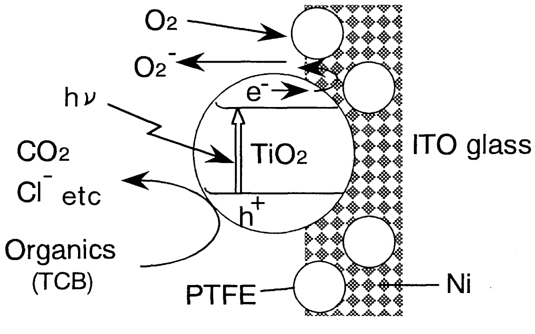

Figure 1. Schematic illustration of a new photocatalyst film. TiO_2 microcrystals are supported on Ni–PTFE substrate.

Nickel–PTFE composite film was deposited on an ITO (indium–doped tin oxide)–glass substrate (active area: 5 cm^2, 6~8 Ω cm^2, Yoneda Glass Co.) in a similar manner as in Ref. 4. The plating was carried out galvanostatically at a current density of 50 mA/cm^2 by passing 50 C of charge at 45°C in a magnetically stirred Ni–sulfamate bath containing 60 g/dm^3 PTFE particles (Teflon oligomer, Cefralrub–I, average size: 4 μm, Central Glass Co.) and 0.6 g/dm^3 cationic surfactant (MEGAFACK, DIC). Microcrystalline TiO_2 colloid was prepared by controlled hydrolysis of titanium tetraisopropoxide in 2–propanol.[5] The TiO_2 microcrystals were deposited on the Ni–PTFE film formed on ITO glass by an electrophoresis.[5] Transparent TiO_2 layer with a thickness of *ca.* 50 μm was produced on the Ni–PTFE. For the comparison with this, the TiO_2 layers were formed on Ni–plated ITO or on naked ITO under the same conditions. Three kinds of photocatalyst plates, prepared on the same ITO–substrate, will be denoted as TiO_2/Ni–PTFE, TiO_2/Ni, and normal–TiO_2, respectively.

Photocatalytic degradation of 1,2,4–trichlorobenzene (TCB), written by Eq. (1), was carried out on the plates.

$$C_6H_3Cl_3 + 6\ O_2 \xrightarrow{h\nu\ (TiO_2)} 6\ CO_2 + 3\ HCl \qquad (1)$$

A Pyrex glass test tube was used as the reaction cell. The photocatalyst plate was immersed in 8 cm^3 of air–saturated aqueous solution containing 5 x 10^{-5} M (1 M = 1 mol dm^{-3}) TCB. The cell in a thermostat bath at 25°C was illuminated with 500 W Xe–lamp which provided an irradiance of 135 mW cm^{-2}. Changes in the concentration of TCB were monitored by measuring the optical absorption spectrum (peaked at 227 nm) of the solution. The degradation products, Cl^- ion and dissolved CO_2, were analyzed by a Cl^- selective electrode (Horiba, 8002–06T) and a CO_2 specific electrode (TOA, CE–235), respectively.

The contents of Ni and TiO_2 in the film were determined by ICP and by a colorimetry using Tiron as a complexing reagent, respectively. The PTFE content was determined as the remainder of the film. Analytical results are summarized in Table 1. Nickel particles with uniform diameter of *ca.* 0.7 μm or less were observed by scanning electron microscope(SEM) on the surface of the layer deposited on ITO substrate; the surface was not smooth in microscopic scale. The SEM observation of Ni–PTFE composite film showed that PTFE particles (dia. = *ca.* 5 μm) were incorporated in the Ni layer uniformly. The content of PTFE particles in the film was only 1.5 wt%, but their occupancy at the surface was large due to the small density. Hence, the uniformly–distributed PTFE particles made the film so hydrophobic that the contact angle between a water droplet and the surface was 145°, while that for Ni without PTFE was

Table 1. Compositions of photocatalyst plates prepared

	Weight / mg cm^{-2}		
	TiO_2	Ni	PTFE
normal-TiO_2	0.77	-	-
TiO_2/Ni	0.96	2.98	-
TiO_2/Ni-PTFE	1.01	2.64	0.04

only 60°. The content of TiO_2 in films ranged from 0.77 to 1.01 mg cm^{-2}, slightly depending on the roughness of the surface.

Figure 2 (a) shows time courses of Cl^- production during photocatalytic degradation of TCB over various photocatalyst plates. The amount of Cl^- released, $[Cl^-]$, increases almost linearly with time on TiO_2/Ni and that after 90 min is 5 times higher than that on normal-TiO_2. The production rate of Cl^- is accelerated further for TiO_2/Ni-PTFE, where $[Cl^-]$ after 90 min is 10 times higher than that on normal-TiO_2 and close to that released from every TCB molecules in the solution. Consistent with most results with single-ring chloroaromatics,[1] the extraction of Cl^- from TCB proceeds to the complete degradation (CO_2 evolution) of the residual framework as shown in Figure 2 (b). The amount of CO_2 evolved, $[CO_2]$, increases linearly with time on TiO_2/Ni-PTFE, and the complete mineralization of TCB into CO_2 was done after 3 h. However, that on TiO_2/Ni exhibits slow-down in the same level on normal-TiO_2 after 60 min, probably due to insufficient O_2 supply. In fact, TCB was scarcely photodegraded even on TiO_2/Ni-PTFE in the absence of dissolved O_2. A series of blank experiments, such as an illumination of TiO_2/Ni-PTFE in pure water, a photochemical reaction of TCB on Ni-PTFE without TiO_2, or a contact between TCB and TiO_2/Ni-PTFE in the dark, showed no production of Cl^- and CO_2. Hence, it is obvious that the TiO_2 particles played an important role in efficient complete photodegradation of TCB in the cooperation with Ni and PTFE.

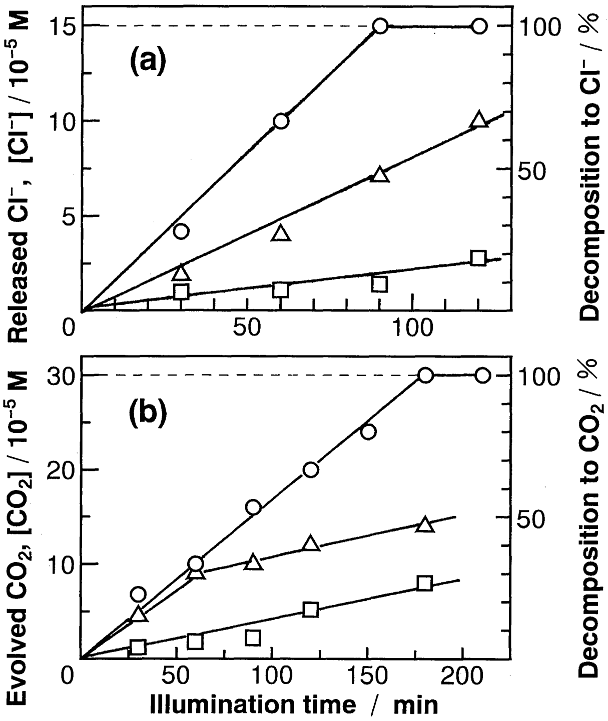

Figure 2. Time courses of Cl^- ion (a) and CO_2 (b) production during photodegradation of TCB (50 μM) over normal-TiO_2 (□), TiO_2/Ni (△), and TiO_2/Ni-PTFE (○). Concentrations corresponding to the complete decomposition of 50 μM TCB ($[Cl^-]$: 150 μM, $[CO_2]$: 300 μM) are shown by dotted lines.

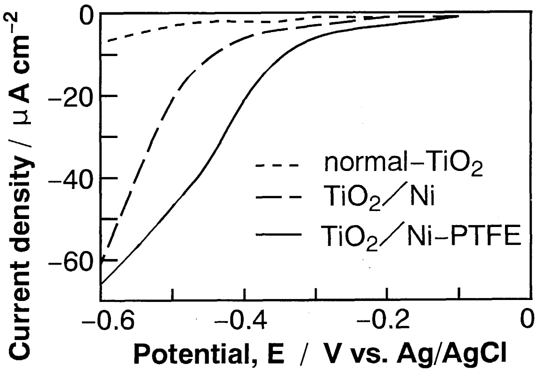

Figure 3. Voltammograms on three kinds of TiO_2 plates in air-saturated 0.1 M $NaClO_4$ for O_2 reduction measured in the dark with potential sweep rate of 10 mV/s.

A possible reason why Ni and PTFE particles around TiO_2 photocatalysts enhance the overall photocatalytic reaction rate is probably ascribed to the enhanced consumption of excited electrons on Ni particles contacted with TiO_2 for the oxygen electroreduction. This prevents the waste of holes through the recombination with electrons, resulting in the accelerated extraction of Cl^- and degradation of residual framework. In order to evaluate the activity for O_2 reduction on various photocatalyst plates, the cathodic polarization properties of them were examined in air-saturated 0.1 M $NaClO_4$ electrolyte solution in the dark (Figure 3). Oxygen reduction current increases in the order, normal-TiO_2 < TiO_2/Ni < TiO_2/Ni-PTFE; the highest reduction current was obtained in the presence of both Ni and PTFE, supporting our consideration described above.

The performance of the TiO_2/Ni-PTFE is certainly improved by more uniform distribution of each constituent particles. Also, the amount of metal electrocatalysts such as Ni can be greatly reduced by attaching metal microcrystals directly on TiO_2 particles. Such efforts are under progress.

References and Notes

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