Ag(core)–AgCl(shell) standard microelectrode-loaded TiO$_2$

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Micrometer-sized Ag(core)–AgCl(shell) composite crystals have been formed on TiO$_2$ thin films by a two-step electrochemical method to provide information on the thermodynamic condition for efficient photoinduced interfacial electron transfer.

Under the present circumstances, in which environmental pollution has become a serious problem, metal-oxide semiconductor photocatalysts represented by TiO$_2$ having a photoinduced oxidation power strong enough to completely mineralize all organic pollutants have attracted much interest as "eco-materials" for water purification.[1–3] A major challenge in semiconductor photocatalysis is to increase the reaction efficiency by restricting the recombination of the charge carriers. The coupling of semiconductor photocatalysts with metal nanoparticles,[4,5] different semiconductors,[6–9] and both[10] is a promising approach to improve the charge separation efficiency through interfacial electron transfer. However, the thermodynamic condition, which is the basis for designing the coupling systems, is not necessarily clarified.

Here we report a two-step method consisting of electrochemical reduction (ER)/electrochemical oxidation (EO) for preparing Ag(core)–AgCl(shell) composite crystal-loaded TiO$_2$ to obtain thermodynamic information on the photoinduced interfacial electron transfer.† Fig. 1A shows X-ray diffraction (XRD) patterns of various samples. In pattern (a) of a TiO$_2$ film formed on a SnO$_2$ film-coated glass substrate (TiO$_2$/SnO$_2$), several peaks due to the diffraction from (110), (101), (200), (211), (310) and (301) planes of tetragonal SnO$_2$ are observed at 2θ = 26.5, 33.7, 37.8, 51.5, 61.6 and 65.5°, respectively. The film thickness of TiO$_2$ (ca. 60 nm) is too small for its diffraction peaks to be observed; however, a 5 times-coated sample gave the (101) diffraction peak of anatase TiO$_2$. Also, from the Tauc plots, the band gap of a 1 time-coated sample was determined to be 3.2 eV, which is in agreement with the value reported for anatase TiO$_2$.[11] Pattern (b) of the sample after the ER process (Ag/TiO$_2$/SnO$_2$) yields peaks at 2θ = 38.1, 44.3 and 64.4°, which can be assigned to the diffraction from (111), (200) and (220) planes of Ag crystals, respectively. Pattern (c) of Ag/TiO$_2$/SnO$_2$ subjected to electrolytic oxidation gives diffraction peaks at 2θ = 27.8, 32.2, 46.2 and 57.5° due to the (111), (200), (220) and (222) planes of AgCl crystals, respectively, while the Ag diffraction peaks weaken.

Figs. 1B and C show scanning electron microscopic (SEM) images (left) and size distribution (right) of Ag particles and

Ag–AgCl composite particles on the TiO$_2$/SnO$_2$ surface, respectively. The ER process yields Ag particles with a mean size of 1.0 μm on TiO$_2$. The inset shows the presence of a step on the (111) plane, suggesting that Ag crystals preferentially grow along the (111) plane with a lower surface energy.[12] The subsequent 1.5-h EO process changes the Ag crystals into AgCl polycrystals with a mean size of 1.2 μm. An SEM image of a Ag–AgCl particle
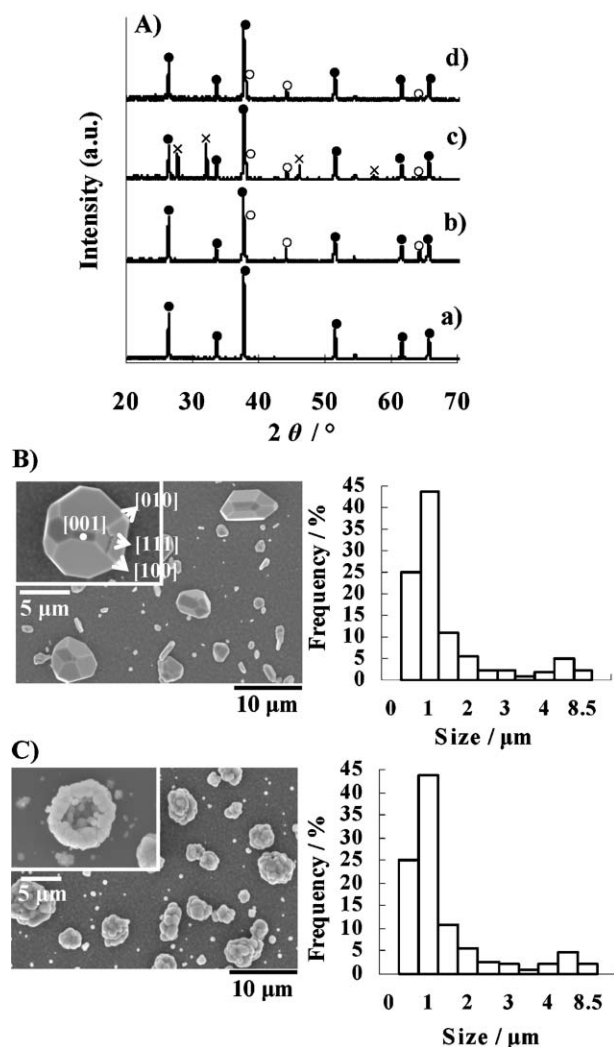

Fig. 1 A, XRD patterns of TiO$_2$/SnO$_2$ (a), Ag/TiO$_2$/SnO$_2$ (b), Ag–AgCl/TiO$_2$/SnO$_2$ (c) and sample (c) after 90-min irradiation in a 1.0 × 10^{-5} M 2-NAP solution (d). B, SEM images of Ag particles electrodeposited on TiO$_2$/SnO$_2$ (left, t_d = 1 h) and the size distribution (right). The inset shows a single Ag crystal grown on the TiO$_2$ surface. C, Ag–AgCl particles on TiO$_2$/SnO$_2$ (left, t_o = 1.5 h) and the size distribution (right).

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detached from the TiO$_2$ film by treatment with a 4 M HNO$_3$ solution is shown in the inset of Fig. 1C. Since Ag is easily dissolved into the concentrated HNO$_3$ solution, only AgCl is left as a solid. This demonstrates that the AgCl part of the Ag–AgCl composite particle has a bowl shape with a fairly uniform thickness. Evidently, the oxidation of Ag proceeds from its surface to yield Ag(core)–AgCl(shell) type micro-composite crystals on the TiO$_2$ surface (Ag@AgCl/TiO$_2$/SnO$_2$).

2-Naphthol (2-NAP), which is widely used as a raw material, shows time courses for photoinduced decomposition in the presence of TiO$_2$/SnO$_2$ (a), Ag/TiO$_2$/SnO$_2$ (b), and Ag@AgCl/TiO$_2$/SnO$_2$ (c): t_p denotes irradiation time.† Under these conditions, self-decomposition of 2-NAP was below 5% at t_p = 1.5 h. In the presence of O$_2$ (A), TiO$_2$ photocatalytic decomposition of 2-NAP (a) is enhanced somewhat with the Ag loading (b), and Ag@AgCl/TiO$_2$/SnO$_2$ (c) exhibits a high photoreactivity far exceeding those of TiO$_2$/SnO$_2$ and Ag/TiO$_2$/SnO$_2$. Even without O$_2$ (B), the high activity of Ag@AgCl/TiO$_2$/SnO$_2$ is maintained, whereas TiO$_2$/SnO$_2$ and Ag/TiO$_2$/SnO$_2$, which need O$_2$ as an electron acceptor, are almost inactive. In the dark, no reaction occurred in any system, and the adsorption amount was negligibly small. After the reaction, the diffraction peaks of Ag intensified concurrently with the disappearance of the diffraction peaks of AgCl (Fig. 1A-d). The solution pH decreased from 5.8 to 4.3, and $(2.1 \pm 0.2) \times 10^{-6}$ mol of Cl$^-$ ions (equimolar amount of AgCl before reaction) was detected in the solution. AgCl is an n-type semiconductor with a band gap of 3.1 eV. It is also known to show a photoreactivity for the oxidation of water in the presence of excess Ag$^+$ ions in the solution;[13–15] however, irradiation of an AgCl particle suspension (0.5 mg/50 mL) led to hardly any decomposition of 2-NAP under the present conditions. This indicates that the photoreactivity of Ag@AgCl/TiO$_2$/SnO$_2$ is caused by excitation of not AgCl but TiO$_2$. As seen in Figs. 2A and B, the photoreactivity of Ag@AgCl/TiO$_2$/SnO$_2$ decreases as the reduction of AgCl to Ag proceeds. However, a reactivity comparable with that of Ag/TiO$_2$/SnO$_2$ is maintained in the presence of O$_2$, and further, approximately 75% of the initial photoreactivity was restored by electrochemically reoxidizing Ag generated after reaction. The improvement of the adhesion between Ag@AgCl crystals and TiO$_2$ would enable its repeated use without deterioration.

A plausible reaction mechanism in the Ag@AgCl/TiO$_2$/SnO$_2$ system is summarized in Scheme 1: the conduction band (cb) and valence band (vb) edges are approximately −1.2 and +2.1 V $vs.$ SHE, respectively.[16] Electron–hole pairs are generated by the band gap excitation of TiO$_2$. In this case, the excitation of SnO$_2$ can be neglected because SnO$_2$-film coated glass was used as a cut-off filter.† The cb-electrons [flat band potential, E_{fb} = −0.46 V $vs.$ SHE at pH 5.8][17] escaping from the recombination move into Ag@AgCl with a standard electrode potential ($E°$) of +0.22 V $vs.$ SHE.[18] Fig. 2C shows current–potential curves of Ag/TiO$_2$/SnO$_2$ in the presence (a) and absence (b) of O$_2$, and Ag@AgCl/TiO$_2$/SnO$_2$ with O$_2$ (c). In Ag/TiO$_2$/SnO$_2$, a small current in curve (a) at U < −135 mV, which is not observed in curve (b), arises from the O$_2$ reduction. On the other hand, in Ag@AgCl/TiO$_2$/SnO$_2$ (c), a large current starts to flow at U ($vs.$ Ag/AgCl) < +75 mV, which corresponds to the AgCl reduction. This ideal non-polarization character means that the electrons flowing into Ag@AgCl are rapidly removed into the water as Cl$^-$ ions. Thus,
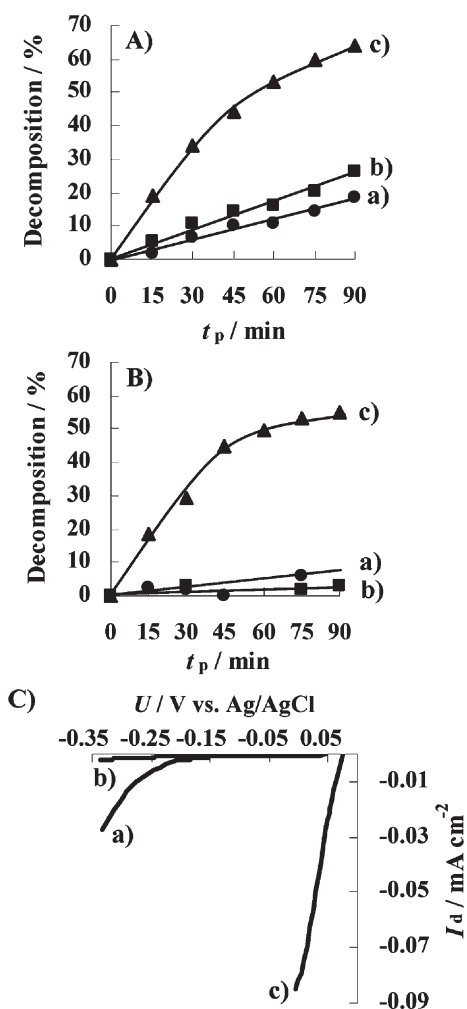

Fig. 2 Time courses for photocatalytic decomposition of 2-NAP with (A) and without (B) O$_2$: (a) TiO$_2$/SnO$_2$; (b) Ag/TiO$_2$/SnO$_2$; (c) Ag@AgCl/TiO$_2$/SnO$_2$. (C) Polarization curves for Ag/TiO$_2$/SnO$_2$ before (a) and after (b) 30-min argon bubbling and Ag@AgCl/TiO$_2$/SnO$_2$ without argon bubbling (c) in a 0.2 M KCl aqueous solution.

thermodynamically and kinetically, Ag@AgCl can be an excellent electron acceptor as compared to O$_2$ ($E°$ = −0.284 V $vs.$ SHE). Consequently, the holes left in the valence band of TiO$_2$ are used
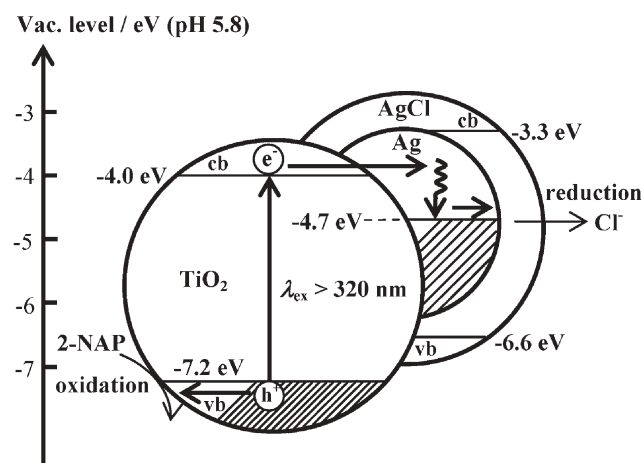
Scheme 1 Energy diagram in the Ag@AgCl/TiO$_2$ photoreaction system.
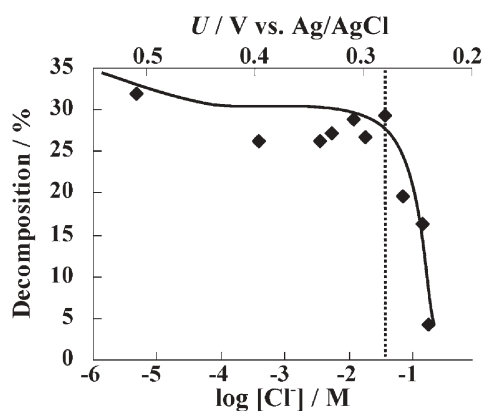
Fig. 3 Plots of the decomposition ratio of 2-NAP *vs.* Cl⁻ concentration. The Ag/AgCl electrode potential shown in the second abscissa corresponds to the Cl⁻ concentration in the first abscissa.

exclusively for the direct or indirect oxidation of 2-NAP because they hardly oxidize Cl⁻ ions.[19] Further, although the involvement of Cl· radicals formed by the excitation of AgCl cannot be ruled out completely,[20] the possibility seems to be small in such an electron rich state of AgCl. Product analyses by ¹H-NMR and FT-IR spectroscopy confirmed that the product mixture contains CH_3, CH_2, and $C=O$ groups. One can infer that the naphthalene ring of 2-NAP undergoes oxidative cleavage during the reaction, and phthalic acid was previously detected as a product.[21]

Ag/AgCl is a typical standard electrode, and Ag@AgCl loaded on TiO_2 can be regarded as standard microelectrodes.

Fig. 3 shows the ratio of 2-NAP decomposed after 1-h irradiation as a function of Cl⁻ concentration: the Ag/AgCl electrode potential shown in the second abscissa was calculated from the Nernst equation. The decomposed ratio abruptly decreases at $U < 0.28$ V, while it is almost constant in the more anodic potential region. The electrode potential shifts cathodically by 59 mV with a one-order increase in the Cl⁻ concentration, whereas the conduction band edge of TiO_2 remains constant. This finding suggests that an energy gap of more than 0.7 eV is necessary between the cb-edge of TiO_2 and the redox potential of Ag@AgCl for efficient one-directional interfacial electron transfer.

Ag@AgCl micro-composite crystal-loaded TiO_2 has been prepared by a two-step electrochemical method, showing that an energy gap of more than 0.7 eV is needed for efficient charge separation. This study provides useful information for the design of semiconductor-based coupling photocatalysts.

Notes and references

† Anatase TiO_2 films with a thickness of 40 ± 5 nm were formed on SnO_2 film-coated glass substrates [conductivity = (6.5 ± 1.0) × 10² S cm⁻¹, Asahi Glass Co.] using the same sol–gel method as previously reported (TiO_2/SnO_2).[22] By applying 1.0 V between a TiO_2/SnO_2 cathode (35 mm × 25 mm) and a Pt anode (40 mm × 20 mm), Ag of 85.3 μg cm⁻² was electrodeposited on the cathode from a 2 mM $AgClO_4$ solution containing a 0.2 M $NaClO_4$ electrolyte (Ag/TiO_2/SnO_2): the electrodeposition time (t_d) was fixed at 1 h. The Ag was oxidized in a 0.2 M KCl electrolyte solution by flowing current between an Ag/TiO_2/SnO_2 anode (35 mm × 12.5 mm) and a Pt cathode (40 mm × 20 mm) with a density of +0.2 mA cm⁻²: the electrolytic oxidation time (t_o) was varied from 1 to 120 min. The surface morphology of the samples was observed to determine the particle size distribution using a scanning electron microscope (SEM, Hitachi, S-4000). X-ray diffraction (XRD) analysis was carried out using Rigaku, RINT2500 (Cu-Kα light source, 40 kV, 80 mA). Polarization curves were measured in a 0.2 M KCl aqueous solution with a scan speed of 10 mV s⁻¹ using Ag/AgCl and glassy carbon as a reference electrode and a counter electrode, respectively. A 1.0×10^{-5} M solution of 2-NAP (solvent, acetonitrile–water = 1 : 9999 v/v) was irradiated with a 500 W Xe lamp (Wacom HX-500) in the presence of each photocatalyst. Two pieces of SnO_2 film-coated plate glass were used as a cut-off filter ($\lambda_{ex} > 320$ nm, light intensity integrated between 320 and 400 nm = 1.5 mW cm⁻²). The electronic absorption spectra of the reaction solutions were measured using a spectrometer (Hitachi, U-4000) to determine the concentrations of 2-NAP from the absorption peak at 224 nm.

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