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In Situ Liquid Phase Synthesis of Hydrogen Peroxide from Molecular Oxygen Using Gold Nanoparticle-Loaded Titanium(IV) Dioxide Photocatalyst

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H_2O_2 has attracted much attention as a clean oxidant for organic synthesis that emits only water as a byproduct with high atom efficiency[1] while being widely used in industry and households for pulp bleaching, effluent treatment, disinfection, etc. At present, most H_2O_2 is produced by the anthraquinone method *via* multisteps requiring large amounts of energy and organic solvent.[2] In addition, concentrated H_2O_2 is explosive, and the careful treatment is indispensable for its storage and transport. Direct synthesis of H_2O_2 from H_2 and O_2 using Au and Pd nanoparticle (NP) catalysts has recently been reported.[3] Semiconductor photocatalysis mainly studied for the purpose of environmental remediation[4] is also fascinating with its application as an "ideal green" synthesis.[5] UV light irradiation to TiO_2 in water yields H_2O_2 from O_2 *in situ* without the usage of H_2 gas. However, the concentration is only on a micromolar order, and so far, the photocatalytic formation of H_2O_2 has been studied from the mechanistic viewpoint.[6] Such a low yield of H_2O_2 is ascribable to its degradation *via* the reduction of the surface peroxide species resulting from the reaction of H_2O_2 with the surface Ti−OH groups by the excited electrons.[7] Recently, by using a surface-fluorinated TiO_2 photocatalyst,[8] the production of H_2O_2 on a millimolar level has been achieved as a result of the suppression of the degradation pathway.[9] On the other hand, Au particles smaller than 10 nm loaded on metal oxides are currently being revealed to exhibit high catalytic activities for many important chemical reactions including the electroreduction of O_2,[10] low-temperature CO oxidation,[11] and hydrogenation of C_2H_2,[12] whereas the bulk Au is inactive. Also, in the TiO_2 photocatalysis, the loading of Au NPs is very effective in increasing its activity, for which the photoinduced interfacial electron transfer (IET) from TiO_2 to Au is essentially responsible. This IET has the following two meanings: one is the enhancement of the charge separation, and the other is the spatial separation of the oxidation sites (TiO_2 surface) and the reduction sites (Au surface). On application of the TiO_2 photocatalysis to synthesis, these are of great importance for achieving high photocatalytic activity and high selectivity.[13]

Herein we report a drastic enhancement of the TiO_2-photocatalyzed generation of H_2O_2 from O_2 by the Au NP loading to yield H_2O_2 on a 10 mM level and a unique activity−Au particle size relation. To vary Au particle size (d) with its loading amount maintained to be constant (x = 0.25 mass%), Au/TiO_2 was synthesized by the deposition−precipitation (DP) method where both heating temperature (T_c) and time (t_c) were altered.[14] Au/TiO_2-photocatalyzed H_2O_2 synthesis was carried out as follows: Au/TiO_2 (0.2 g) was added to H_2O (200 mL) containing 4% C_2H_5OH as a hole scavenger. After stirring the suspension in the dark for 1 h, UV light ($\lambda > 300$ nm, $I_{290-390\ \mathrm{nm}} = 3.0$ mW cm^{-2}) was irradiated under aerobic conditions. The H_2O_2 concentration ([H_2O_2]) of the filtrate at each irradiation time (t_p) was determined by iodometric titration.[6] Figure 1A shows time courses for the H_2O_2 generation in the presence of various photocatalysts. Noticeably, Au/TiO_2 exhibits a high level of photocatalytic activity much greater than those for TiO_2 and Pt/TiO_2. The photonic efficiency (Φ, molecules produced/incident photons) at the light wavelength (λ) = 355 ± 23 nm was calculated to be 13% by assuming a two-electron reduction process. O_2, C_2H_5OH, and UV light irradiation in addition to the photocatalyst were necessary for this reaction to proceed (Figure S1 in Supporting Information (SI)). The Au NP loading was also effective for the TiO_2 surface-fluorinated system, and Au/TiO_2-photocatalyzed reaction with NaF addition (0.1 mol dm^{-3}) afforded a 1 order larger amount of H_2O_2 as compared to the value previously reported (dotted curve in Figure 1A, Figure S2 in SI).[9] Another intriguing point is the d-dependence of the photocatalytic activity. Figure 1B shows the plots of [H_2O_2] at t_p = 6 h as a function of d. An inverse volcano-type curve with a minimum at $d \approx 3.5$ nm is observed, whereas volcano-type profiles have been reported for the thermal catalysis of metal oxide-supported Au NPs.[11,12]

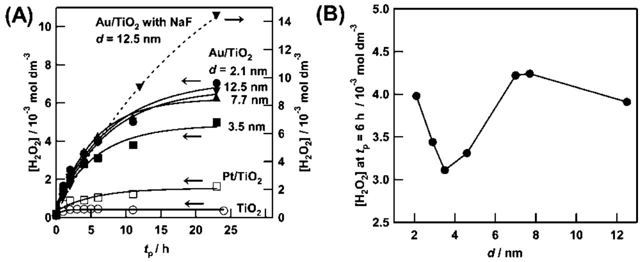

Figure 1. (A) Plots of [H_2O_2] under UV-irradiation in the presence of Au/TiO_2 with various size d or TiO_2 or Pt/TiO_2 (d = 1.6 nm, x = 0.19 mass%) vs t_p. (B) Plots of [H_2O_2] at t_p = 6 h using Au/TiO_2 vs d.

The decrease of the reaction rate with prolonging t_p in Figure 1A suggests that the decomposition of H_2O_2 occurs concurrently with its formation. To evaluate the d-dependencies of the formation and the decomposition, kinetic analysis was carried out. Under the present conditions, by assuming that the formation and decomposition rates follow the zero-order and first-order kinetics toward [H_2O_2], respectively, one can obtain the following equation: $[H_2O_2] = (k_f/k_d)\{1 - \exp(-k_d\,t)\}$, where k_f is the formation rate constant and k_d is the decomposition rate constant. As apparent from the calculated curves in Figure 1A, the experimental data were well fitted with the equation, and Figure 2A shows the plots of k_f as a function of d. The k_f values for Pt/TiO_2 and Au/TiO_2 are larger than that for TiO_2, which can be attributed to the increase in the charge separation efficiency due to the IET from TiO_2 to the metal NPs. It has recently been reported that the 2e$^-$ reduction of O_2 to

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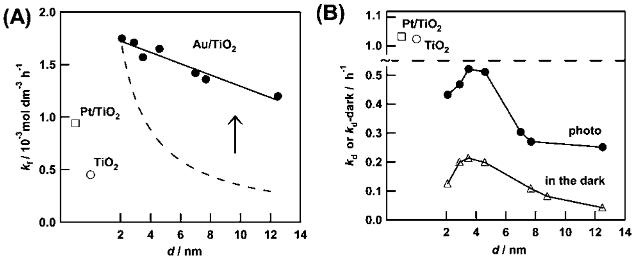
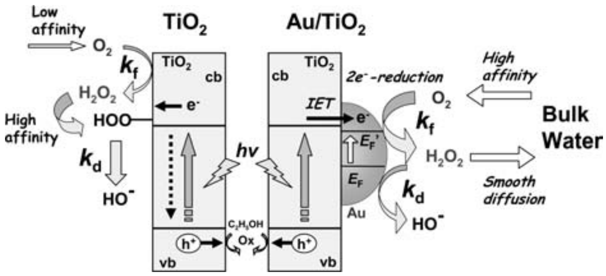


Figure 2. (A) Plots of k_f vs d. (B) Plots of k_d and k_d-dark vs d.

generate H_2O_2 preferentially proceeds on the Au surface, while the 4e$^-$ reduction to H_2O occurs on the Pt surface.[15] This explains the fact that the k_f for Au/TiO$_2$ is much greater than that for Pt/TiO$_2$. Interestingly, all the k_d values of Au/TiO$_2$ are smaller than half of those of TiO$_2$ and Pt/TiO$_2$ (Figure 2B). This is probably because the reduction of O_2 takes place on the Au surface in the Au/TiO$_2$ system, while the TiO$_2$ surface peroxides promote the H_2O_2 degradation in the TiO$_2$ system.[7] Also, Pt is well-known to have a high catalytic activity for the H_2O_2 decomposition.[16] Evidently, the remarkable accelerating effect of the Au NP loading on the TiO$_2$-photocatalyzed H_2O_2 synthesis is induced by both the enhancement of the formation and the restriction of the decomposition. Further, the high efficiency of this reaction can be explained within the framework of the idea of "reasonable delivery photocatalytic reaction systems":[13] (1) oxidation and reduction sites are separated to TiO$_2$ and Au NP, respectively, (2) sufficient amounts of O_2 are supplied to the reduction sites on the surface of Au NPs with high affinity to O_2,[17] (3) high solubility of H_2O_2 to H_2O causes its smooth removal from the catalyst surface.

Scheme 1. Au/TiO$_2$-Photocatalzyed H_2O_2 Formation



The unique d-dependence in this Au/TiO$_2$-photocatalzyed H_2O_2 formation is discussed on the presumption that both the formation and decomposition of H_2O_2 mainly occurs at the reduction sites on the Au surface. The Au surface area of Au/TiO$_2$ decreases inversely as d when x is constant (dotted line in Figure 2A). We have shown by photoelectrochemical measurements and quantum chemical calculations that the Fermi energy of Au NPs loaded on TiO$_2$ at the photostationary state (E_F') rises as the d value increases.[18] Au/TiO$_2$ with the higher E_F' (i.e., the greater reducing power) would enhance the O_2 reduction to increase k_f, and actually, the k_f normalized with respect to the Au surface area (k_f') significantly increasing with increasing d (Figure S3 in SI). As a result, the $k_f - d$ curve deviates positively from the line proportional to d^{-1} to show a gradual decrease in k_f with increasing d (Figure 2A). On the other hand, plots of k_d vs d show a volcano-type curve with a maximum at $d \approx 3.5$ nm (k_d in Figure 2B). This profile well resembles that for the H_2O_2 decomposition thermally catalyzed by Au/TiO$_2$ in the dark (k_d-dark in Figure 2B).[19] The k_d is larger than k_d-dark at the same d value by a factor of *ca*. 2.5, which is also ascribable to an increase in the reducing power with the photoinduced E_F upward shift of Au NPs loaded on TiO$_2$.[20] Further, the steep lowering in E_F' at $d < 5$ nm[18] is considered to cause the decrease in k_d at $d <$ 3.5 nm. Density functional theory calculations indicated that the Au−TiO$_2$ interfaces and/or low-coordinated Au atoms become active sites in the Au/TiO$_2$-catalyzed CO oxidation.[21] The decrease in k_d at $d > 3.5$ nm can be rooted in the diminution of the number of such catalytic active sites on the Au NP surface. Consequently, the k_d value is determined by the balance between the E_F' value and the number of catalytic active sites on the Au NP surface, and further, the activity−d relation in the Au/TiO$_2$-photocatalzyed H_2O_2 formation (Figure 1B) is rationalized in terms of the d-dependences of k_f and k_d (Scheme 1).

In summary, this study has shown that the liquid-phase Au/TiO$_2$-photocatalzyed H_2O_2 generation from O_2 has a promising prospect for *in situ* H_2O_2 synthesis. Recently, Au/TiO$_2$ has also been found to exhibit thermal catalytic activity for the chemoselective oxidation of alcohols to aldehydes in the presence of H_2O_2.[19] These results allow us to expect the development of an ideal catalytic organic synthetic process consisting of the Au/TiO$_2$-photocatalyzed H_2O_2 formation and the subsequent Au/TiO$_2$-catalyzed oxidation of organic substances using the H_2O_2 as an oxidant.

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Supporting Information Available: Experimental details; time courses for the H_2O_2 generation (Figures S1, 2); d-dependency of k_f' (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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