

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

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H₂O₂ has attracted much attention as a clean oxidant for organic synthesis that emits only water as a byproduct with high atom efficiency¹ while being widely used in industry and households for pulp bleaching, effluent treatment, disinfection, etc. At present, most H₂O₂ is produced by the anthraquinone method *via* multisteps requiring large amounts of energy and organic solvent.² In addition, concentrated H₂O₂ is explosive, and the careful treatment is indispensable for its storage and transport. Direct synthesis of H₂O₂ from H₂ and O₂ using Au and Pd nanoparticle (NP) catalysts has recently been reported.³ Semiconductor photocatalysis mainly studied for the purpose of environmental remediation⁴ is also fascinating with its application as an “ideal green” synthesis.⁵ UV light irradiation to TiO₂ in water yields H₂O₂ from O₂ *in situ* without the usage of H₂ gas. However, the concentration is only on a micromolar order, and so far, the photocatalytic formation of H₂O₂ has been studied from the mechanistic viewpoint.⁶ Such a low yield of H₂O₂ is ascribable to its degradation *via* the reduction of the surface peroxide species resulting from the reaction of H₂O₂ with the surface Ti–OH groups by the excited electrons.⁷ Recently, by using a surface-fluorinated TiO₂ photocatalyst,⁸ the production of H₂O₂ 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 O₂,¹⁰ low-temperature CO oxidation,¹¹ and hydrogenation of C₂H₂,¹² whereas the bulk Au is inactive. Also, in the TiO₂ photocatalysis, the loading of Au NPs is very effective in increasing its activity, for which the photoinduced interfacial electron transfer (IET) from TiO₂ 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 (TiO₂ surface) and the reduction sites (Au surface). On application of the TiO₂ 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 TiO₂-photocatalyzed generation of H₂O₂ from O₂ by the Au NP loading to yield H₂O₂ 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/TiO₂ was synthesized by the deposition–precipitation (DP) method where both heating temperature (*T_c*) and time (*t_c*) were altered.¹⁴ Au/TiO₂-photocatalyzed H₂O₂ synthesis was carried out as follows: Au/TiO₂ (0.2 g) was added to H₂O (200 mL) containing 4% C₂H₅OH as a hole scavenger. After stirring the suspension in the dark for 1 h, UV light (*λ* > 300 nm, *I*_{290–390 nm} = 3.0 mW cm^{–2}) was irradiated

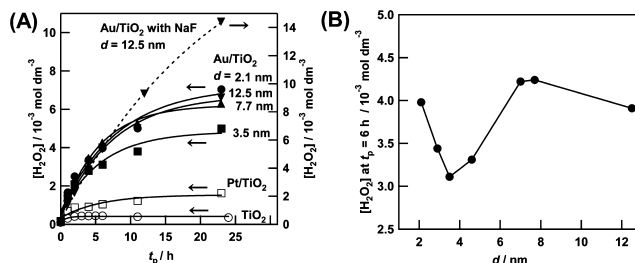


Figure 1. (A) Plots of [H₂O₂] under UV-irradiation in the presence of Au/TiO₂ with various size *d* or TiO₂ or Pt/TiO₂ (*d* = 1.6 nm, *x* = 0.19 mass%) vs *t_p*. (B) Plots of [H₂O₂] at *t_p* = 6 h using Au/TiO₂ vs *d*.

under aerobic conditions. The H₂O₂ concentration ([H₂O₂]) of the filtrate at each irradiation time (*t_p*) was determined by iodometric titration.⁶ Figure 1A shows time courses for the H₂O₂ generation in the presence of various photocatalysts. Noticeably, Au/TiO₂ exhibits a high level of photocatalytic activity much greater than those for TiO₂ and Pt/TiO₂. 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. O₂, C₂H₅OH, 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 TiO₂ surface-fluorinated system, and Au/TiO₂-photocatalyzed reaction with NaF addition (0.1 mol dm^{–3}) afforded a 1 order larger amount of H₂O₂ 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 [H₂O₂] at *t_p* = 6 h as a function of *d*. An inverse volcano-type curve with a minimum at *d* ≈ 3.5 nm is observed, whereas volcano-type profiles have been reported for the thermal catalysis of metal oxide-supported Au NPs.^{11,12}

The decrease of the reaction rate with prolonging *t_p* in Figure 1A suggests that the decomposition of H₂O₂ 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 [H₂O₂], respectively, one can obtain the following equation: [H₂O₂] = (*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/TiO₂ and Au/TiO₂ are larger than that for TiO₂, which can be attributed to the increase in the charge separation efficiency due to the IET from TiO₂ to the metal NPs. It has recently been reported that the 2e[–] reduction of O₂ to

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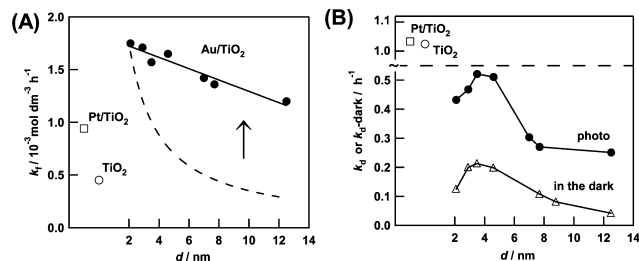
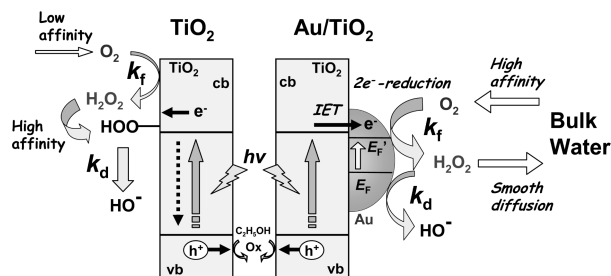


Figure 2. (A) Plots of k_f vs d . (B) Plots of k_d and k_d -dark vs d .

generate H₂O₂ preferentially proceeds on the Au surface, while the 4e[−] reduction to H₂O occurs on the Pt surface.¹⁵ This explains the fact that the k_f for Au/TiO₂ is much greater than that for Pt/TiO₂. Interestingly, all the k_d values of Au/TiO₂ are smaller than half of those of TiO₂ and Pt/TiO₂ (Figure 2B). This is probably because the reduction of O₂ takes place on the Au surface in the Au/TiO₂ system, while the TiO₂ surface peroxides promote the H₂O₂ degradation in the TiO₂ system.⁷ Also, Pt is well-known to have a high catalytic activity for the H₂O₂ decomposition.¹⁶ Evidently, the remarkable accelerating effect of the Au NP loading on the TiO₂-photocatalyzed H₂O₂ 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 TiO₂ and Au NP, respectively, (2) sufficient amounts of O₂ are supplied to the reduction sites on the surface of Au NPs with high affinity to O₂,¹⁷ (3) high solubility of H₂O₂ to H₂O causes its smooth removal from the catalyst surface.

The unique d -dependence in this Au/TiO₂-photocatalyzed H₂O₂ formation is discussed on the presumption that both the formation and decomposition of H₂O₂ mainly occurs at the reduction sites on the Au surface. The Au surface area of Au/TiO₂ 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 TiO₂ at the photostationary state (E_F') rises as the d value increases.¹⁸ Au/TiO₂ with the higher E_F' (i.e., the greater reducing power) would enhance the O₂ 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 H₂O₂ decomposition thermally catalyzed by Au/TiO₂ 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 TiO₂.²⁰ Further, the steep lowering in E_F' at $d < 5$ nm¹⁸ is considered to cause the decrease in k_d at $d < 3.5$ nm. Density functional theory calculations indicated that the Au–TiO₂ interfaces and/or low-coordinated Au atoms become active sites in the Au/TiO₂-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/TiO₂-photocatalyzed H₂O₂

Scheme 1. Au/TiO₂-Photocatalyzed H₂O₂ Formation



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/TiO₂-photocatalyzed H₂O₂ generation from O₂ has a promising prospect for *in situ* H₂O₂ synthesis. Recently, Au/TiO₂ has also been found to exhibit thermal catalytic activity for the chemoselective oxidation of alcohols to aldehydes in the presence of H₂O₂.¹⁹ These results allow us to expect the development of an ideal catalytic organic synthetic process consisting of the Au/TiO₂-photocatalyzed H₂O₂ formation and the subsequent Au/TiO₂-catalyzed oxidation of organic substances using the H₂O₂ as an oxidant.

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Supporting Information Available: Experimental details; time courses for the H₂O₂ 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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