The effect of dissolved oxygen on the 1,4-dioxane degradation with TiO_2 and Au–TiO_2 photocatalysts

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ABSTRACT

In order to enhance the photocatalytic activity of TiO_2, the recombination of photogenerated electron–hole pairs needs to be suppressed. Noble metals, e.g. Au nanoparticles, have been incorporated with TiO_2 to efficiently separate charge carriers created in/on TiO_2. On the other hand, dissolved oxygen (DO) in an aqueous solution was also known to scavenge the electrons, which avoid the recombination of electrons and holes. In this study, we investigated the combined system of Au nanoparticles incorporated with TiO_2 and DO to gain insight into the relationship between them using a photocatalytic degradation of 1,4-dioxane. The rate constants of 1,4-dioxane photodegradation with respect to TiO_2 catalysts with three different Au loadings, as well as DO levels, indicated the DO dependency is disproportional to the Au loading amount, implying that there is an overlapping function in capturing electrons between Au nanoparticles and DO.

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1. Introduction

TiO_2, a representative photocatalyst, has been successfully applied to the various photocatalytic reactions in a gas phase as well as in an aqueous phase. In contrast to many merits of TiO_2 such as high stability, low cost, and low operating temperature, the poor overlap between its electronic structure, e.g. band gap, and the solar spectrum results in low efficiency in solar energy utilization and therefore limiting its technological applications [1]. To efficiently utilize sunlight to photoexcite TiO_2, the electronic doping of foreign atoms into TiO_2 has been used, which has led to the reduction of the photothreshold energy below the bandgap of TiO_2 [2,3]. Another significant factor for the low efficiency of TiO_2 in a photocatalysis is the high degree of recombination of photogenerated electrons and holes; the electron–hole pairs are recombined in the order of nanoseconds [4]. In order to enhance the photocatalytic activity of TiO_2, therefore, the charge carriers created need to be efficiently separated, which can be achieved by a prompt removal of the electrons by an electron acceptor.

Incorporation of the noble metal nanoparticles has been expected to assist an efficient charge separation of photogenerated electron–hole pairs, leading to promoting the photocatalytic activity of TiO_2. For example, nanosized Pt and Ag particles loaded on

TiO_2 have been applied in the photodegradation of oxalic acid and has shown two times the increase of photocatalytic activity compared with only TiO_2 [5]. Pt/TiO_2 was also tested in photocatalytic degradation of lignin showing a 1–6 times enhancement of the reaction rate [6]. The Au-capped TiO_2 nanoparticles have been shown to improve photocatalytic efficiency more than 40% for thiocyanate oxidation [7]. It was also reported that TiO_2 modified with nanosized Au reveals higher activity for the mineralization of oxalic acid in an aqueous phase than a commercially available TiO_2 (Degussa P25) [8].

Alternatively, dissolved oxygen (DO) in an aqueous solution can play a role as an electron acceptor to avoid the recombination of photogenerated charge carriers. The effect of DO has been demonstrated in many TiO_2 mediated photocatalysis, e.g. the photocatalytic degradation of 2,3-dichlorophenol [9], dichloroacetic acid [4], 2-chlorobiphenyl [10], etc. In addition, since oxygen reacts only slowly with the electrons compared with the reaction between holes and hydroxyl or water species, the rate of electron transfer from TiO_2 to oxygen can be a rate-controlling process in photocatalysis [11].

Now the question arises whether or not the combined system between incorporated noble metal nanoparticles and DO in solution can provide the synergistic effect on photocatalysis of TiO_2 via a more efficient charge separation of photogenerated electron–hole pairs. If the photogenerated electron in/on TiO_2 transferred to metal nanoparticles deposited and efficiently consumed by DO, the photocatalytic activity would be substantially enhanced. Meanwhile,

Table 1
Characteristics of the catalysts used in the photocatalysis.

Catalysts	Surface area (m^2/g)	Carbon impurity (wt%)	Average Au size (nm)	Average particle density ($\times 10^9$/cm^2)
TiO_2	52	0.12	–	–
Au(0.37 wt%)–TiO_2	49	0.14	7.0	7
Au(1.2 wt%)–TiO_2	46	0.06	2.1	430

if the competition in charge separation occurs in between metal nanoparticles and DO, the photocatalytic activity of TiO_2 would not be improved much.

In order to gain insight into this question we investigated the photodegradation behaviors of 1,4-dioxane by both TiO_2 and Au–TiO_2 in an aqueous solution under different DO levels. Among the various noble metal nanoparticles, the Au nanoparticle was particularly chosen due to its typical optical property, a localized surface plasmon resonance. The localized surface plasmon resonance originates from the collective oscillations of the electrons on the surface of the gold nanoparticles and has been proven to promote the interfacial charge transfer between TiO_2 and Au, which ultimately enhances the photocatalytic activity of TiO_2 [7,12].

In this study, three different photocatalysts (TiO_2 only, Au(0.37 wt%)–TiO_2, and Au(1.2 wt%)–TiO_2) were applied in a slurry type of photocatalytic reactions in the aqueous phase with DO levels of 0.4, 8, and 35 mg/L. The comparison of the rate constants of 1,4-dioxane photodegradation with respect to the DO levels for the three different catalysts showed no synergistic effects between incorporated Au nanoparticles and DO in solution implying that there is a competition for the charge separation between them.

2. Experimental

Three photocatalysts were used in this study: TiO_2 (P25), Au(0.37 wt%)–TiO_2 (P25), and Au(1.2 wt%)–TiO_2 (P25). The Au content and the surface area of TiO_2 were determined by an inductively coupled plasma-atomic absorption spectrometer analysis (ICP-AES, PerkinElmer) and a BET (Bel Japan Inc., Belsorp mini II), respectively. TiO_2 (Degussa) and Au(1.2 wt%)–TiO_2 (Mintek) were used as purchased. In order to prepare Au(0.37 wt%)–TiO_2 samples, we have used a leaching procedure in which the gold was selectively removed without perturbing the TiO_2 [13,14]. Specifically, the Au(1.2 wt%)–TiO_2 powder was put into an aqueous solution of NaCN (1%) and stirred for 1 min at room temperature maintaining the pH at 12 with NaOH. After immediate filtering and washing with distilled water, the sample was dried at 120 °C for 10 h followed by annealing in air at 400 °C for 2 h. No change in structure of the TiO_2 was confirmed by an X-ray diffraction (XRD, Shimadzu,

XRD-6000) and a transmission electron microscopy (TEM, FEI Hong Kong Co. Ltd., Tecnai G2), where the ratio of anatase/rutile and the particle size of TiO_2 were consistent before and after the leaching. In contrast, the morphology of Au nanoparticles was remarkably changed. The average size of Au nanoparticles increased from 2.1 to 7.0 nm while the number density decreased about 98%.

1,4-Dioxane (99.9%, Sigma Aldrich) was used as purchased for the photocatalytic reaction, and the initial concentration of the solution (250 mL) was adjusted to 500 mg/L for all reaction experiments. The photocatalytic reaction was carried out in a home-built reactor (10 cm × 5 cm × 10 cm) with a quartz window. During the reactions, TiO_2 or Au–TiO_2 powders were suspended by a magnetic stirrer in distilled water with certain levels of DO. Three different DO level solutions were prepared by purging O_2 (99.99%), air, and Ar (99.999%) for 1 h prior to the photocatalytic reactions. The concentration of DO was measured by a DO meter (HD2109.1, Delta). Notably, the DO level of the air purged water is no different than that of the non-purged water in our preparation conditions.

During the entire reaction an IR filter (distilled water in a quartz box) was installed in front of a light source and cooled by air with a pan, leading to a temperature increase of less than 5 °C. A Xe-lamp (2 kW) was used as a light source, and its irradiation intensity was calibrated to 100 mW/cm^2 with a standard reference solar cell (PVM 153, PV Measurements).

During the reaction, 1 mL of solution was collected by a syringe and filtered through a polymer membrane with a pore size of 0.45 μm to remove the TiO_2 or Au–TiO_2 prior to analysis with a high performance liquid chromatography (HPLC). The calibration curve between the absolute concentration of 1,4-dioxane and the corresponding peak area in an HPLC was used to determine the degree of 1,4-dioxane decomposition. The HPLC was equipped with a UV detector and a C18 column (5 μm), with 3% acetonitrile in the water as the mobile phase.

3. Results and discussion

As a case study of photocatalytic degradation, a 1,4-dioxane was targeted. A 1,4-dioxane, widely used as an industrial solvent and as a stabilizer for chlorinated solvent, is known as a toxic hazard
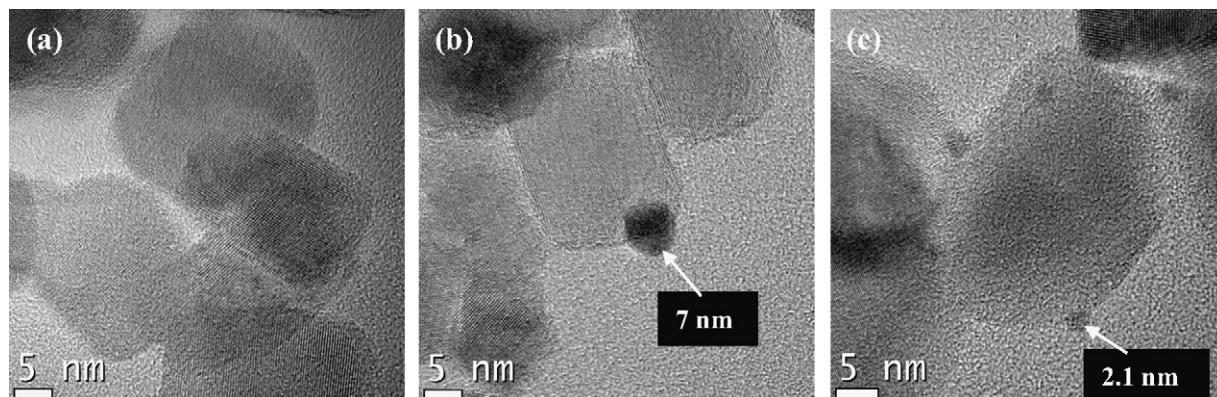

Fig. 1. TEM images of (a) TiO_2, (b) Au(0.37 wt%)–TiO_2 and (c) Au(1.2 wt%)–TiO_2. The sizes of Au nanoparticles presented are the average values obtained from several TEM images.

and is suspected to be a potential carcinogen for humans [15,16]. In environmental aspects, therefore, it is very important to mineralize the 1,4-dioxane in the aqueous phase. Photocatalytic degradation of the 1,4-dioxane using TiO_2 has been suggested as the efficient method for this purpose [15,16].

The physical properties of three TiO_2 based catalysts used in this study are summarized in Table 1. The surface areas measured by a BET were 52, 49, and 46 m^2/g for TiO_2, Au(0.37 wt%)–TiO_2, and Au(1.2 wt%)–TiO_2, respectively. The amount of carbon impurities and the crystalline structure (rutile/anatase ratio) of the catalysts are very similar for all samples. In contrast, the size and number density of gold nanoparticles supported on TiO_2 are significantly different among the catalysts (Fig. 1). Notably, the number density of gold nanoparticles in Au(0.37 wt%)–TiO_2 is only ~1.6% of Au(1.2 wt%)–TiO_2.

In order to investigate the effect of DO on the 1,4-dioxane photodegradation, high (35 mg/L), medium (8 mg/L), and low DO level (0.4 mg/L) solutions were prepared by purging O_2 (99.99%), air, and Ar (99.999%) for 1 h prior to the photocatalytic reactions. Notably, the oxygen levels of each solution were maintained during the entirety of the reaction by continuous purging of a suitable amount of O_2 or Ar gas. The DO levels were checked by a DO meter every hour to confirm there was no change in oxygen concentration. Also, the degradation of the 1,4-dioxane due to gas purging was tested to be negligible in the absence of catalysts and light irradiation.

Fig. 2a–c shows the 1,4-dioxane photodegradation behavior with respect to the irradiation time for the three different catalysts and solutions with different DO levels. As expected, the 1,4-dioxane photodegradation by TiO_2 was substantially enhanced by the increase of the DO levels (Fig. 2a). Notably, the 1,4-dioxane was almost completely degraded in 8 h in high DO conditions. The promoting effect of DO in TiO_2 is not unusual since similar behavior has been observed in many photodegradations of organic molecules by TiO_2 [9,10,17]. As mentioned, this promoting effect of the DO on photodegradation of organic molecules can be explained by the role of DO as an electron scavenger which assists to reduce electron–hole recombination. Similar behavior was also observed in the reaction with the Au(0.37 wt%)–TiO_2 catalyst even though the degree of enhancement of the degradation rate is smaller than that of TiO_2 only (Fig. 2b). On the other hand, significantly different behavior was observed in the reaction with Au(1.2 wt%)–TiO_2 where no apparent promoting effect of DO was observed. The 1,4-dioxane photodegradation behaviors are almost identical irrespective of the DO levels.

To further clarify the relationship between the Au contents and DO levels, the 1,4-dioxane photodegradation with respect to the reaction time were re-plotted (Fig. 3). At the very low DO level (Fig. 3a), TiO_2 showed the least activity compared with the Au nanoparticle contained TiO_2. Also, there is little difference between the Au–TiO_2 samples with different Au contents. At the medium DO level (8 mg/L), however, the Au–TiO_2 catalyst with a high Au content (1.2 wt%) revealed the least activity in an 8 h reaction while the Au(0.37 wt%)–TiO_2 showed higher activity than the others (Fig. 3b). The TiO_2 catalyst without Au showed less initial activity than the Au(0.37 wt%)–TiO_2, but it became comparable over a 6 h reaction time. The enhanced activity of the TiO_2 due to the DO in the solution became more apparent at the higher DO level (35 mg/L). The TiO_2 was superior to Au–TiO_2, and the photodegradation rate of the 1,4-dioxane decreased as the Au content in the TiO_2 increased (Fig. 3c).

In general, the Langmuir–Hinshelwood (L–H) model has been used to describe the kinetics of many TiO_2 based heterogeneous photocatalytic degradations, e.g. dye degradation, in aqueous phases [18–20]. Similarly, the kinetics of photocatalytic degradation of 1,4-dioxane by TiO_2 has been explained based on the L–H model [21]. To obtain the kinetic parameters for the 1,4-dioxane
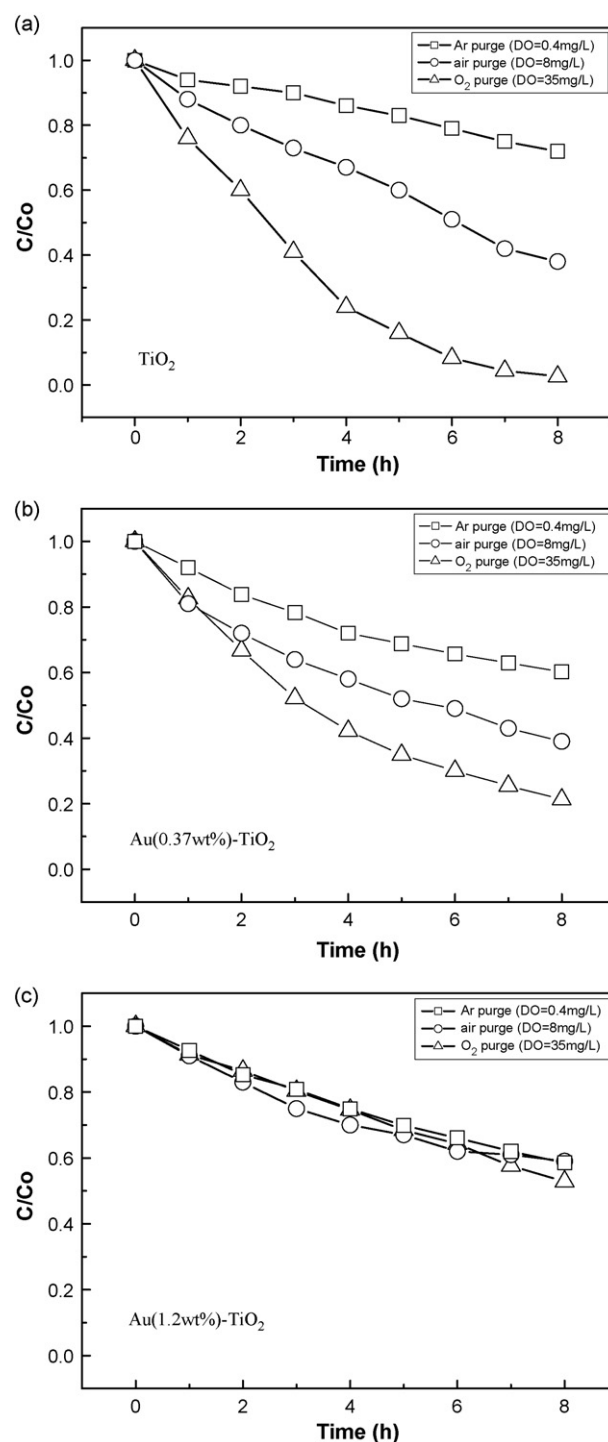

Fig. 2. Photocatalytic degradation of 1,4-dioxane as a function of irradiation time with three different photocatalysts: (a) TiO_2, (b) Au(0.37 wt%)–TiO_2, and (c) Au(1.2 wt%)–TiO_2.

photodegradation in various reaction conditions (catalysts and DO levels), we used Langmuir–Hinshelwood (L–H) kinetics given by the following equations:

$$r = -\frac{dC}{dt} = \frac{k_{LH}K_aC}{1 + K_aC} \tag{1}$$

where r is the rate of 1,4-dioxane degradation, C is the concentration at any time, K_a is the Langmuir adsorption constant, and k_{L-H} is the reaction rate constant based on the L–H model. By integrating the above equation in the limits of $C = C_0$ at $t = 0$ and $C = C$ at $t = t$, the
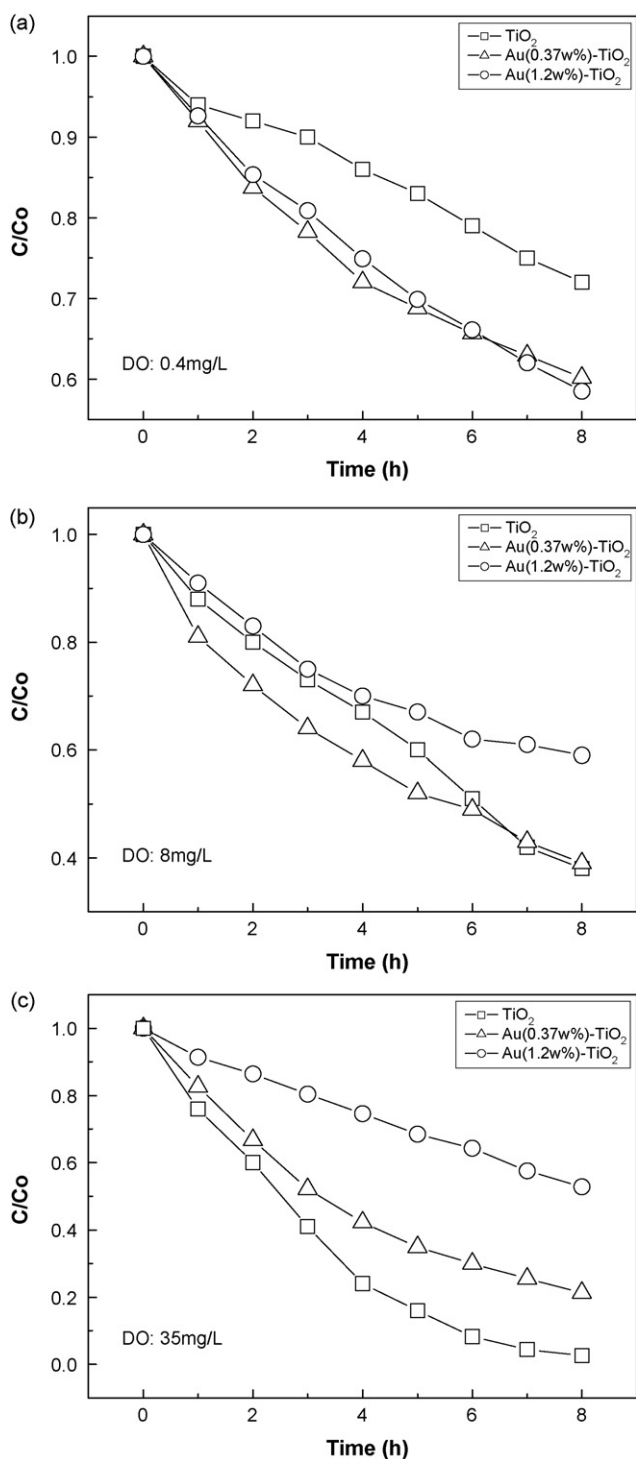
Fig. 3. Photocatalytic degradation of 1,4-dioxane as a function of irradiation time under three different dissolved oxygen levels: (a) 0.4 mg/L, (b) 8 mg/L, and (c) 35 mg/L.

Table 2
Kinetics parameters of 1,4-dioxane photodegradation.

Catalysts	DO (mg/L)	K_a ($\times 10^{-3}$)	k_{app} ($k_{L-H} K_a$)	r^2
TiO$_2$	0.4		0.0019	0.99078
	8	4.3	0.0043	0.98450
	35		0.012	0.99842
Au(0.37 wt%)–TiO$_2$	0.4		0.0028	0.96280
	8	4.3	0.0044	0.96062
	35		0.0067	0.97154
Au(1.2 wt%)–TiO$_2$	0.4		0.0029	0.99129
	8	4.2	0.0029	0.94550
	35		0.0033	0.99818

concentration is substantially low ($K_a C_0 \ll 1$) or high ($K_a C_0 \gg 1$), respectively. In contrast, if the reactant concentration is not sufficiently either low or high ($K_a C_0 \approx 1$), the equation should not be reduced; therefore, an integral form of the L–H model (Eq. (2)) would be used to predict the rate constant in the L–H expression. In order to evaluate the rate constant, k_{app} using Eq. (2), K_a needs to be firstly determined from the adsorption experiment under dark conditions.

In general, the adsorption isotherms of organic molecules with TiO$_2$ follow the Langmuir adsorption model:

$$\theta = \frac{K_a C_e}{1 + K_a C_e} \qquad (3)$$

where θ is the coverage of the organic substrate on the TiO$_2$ surface, C_e is the concentration of the substrate in the solution at equilibrium, and K_a is the Langmuir adsorption equilibrium constant. The coverage (θ) can be expressed as a ratio of the amount of the substrate adsorbed at equilibrium (q_e) to the maximum amount adsorbed (q_{max}):

$$\theta = \frac{q_e}{q_{max}} \qquad (4)$$

From Eqs. (3) and (4), the linear relationship between $1/q_e$ and $1/C_e$ can be derived:

$$\frac{1}{q_e} = \frac{1}{K_a q_{max} C_e} + \frac{1}{q_{max}} \qquad (5)$$

Based on Eq. (5), the isotherm adsorption of the 1,4-dioxane adsorbed on the surface of three different samples is presented in Fig. 4a. Notably, three different amounts of catalysts (5, 7.5, and 10 g/L) were used in the adsorption experiment, and the data presented (Fig. 4a) were the average values. From the linear least square analysis of the plot of $1/q_e$ vs. $1/C_e$, K_a was obtained, and it showed almost identical values ($\sim 4 \times 10^{-3}$ L/mg) for all catalysts used. It is important to note that in our experimental conditions (500 mg/L of 1,4-dioxane initial concentration), $K_a C_0$ was estimated to ~ 2; therefore, the approximation to the first order kinetics may not be appropriate. To gain the rate constant from the L–H model, an integral form (Eq. (2)) would be more feasible.

Fig. 4b–d shows the plots of $\ln(C_0/C) + K_a(C_0 - C)$ vs. t for the various photocatalytic reaction conditions (catalysts and DO levels). From the slope of linear fit the rate constants of k_{app} were evaluated (Table 2). It should be noted that the same values of K_a which were evaluated from the 1,4-dioxane solution prepared at ambient conditions (DO level of 8 mg/L) were used irrespective of the DO levels assuming that there was no competitive adsorption between the oxygen and 1,4-dioxane on the TiO$_2$ (or Au–TiO$_2$) surfaces.

Finally, the rate constants with respect to the DO levels were plotted for the three catalysts (Fig. 5). Since the slope of linear fits indicates the degree of the DO dependency, it is obvious the DO dependency is diminished as the Au contents increase. This result also implies that there is an overlapping function between the DO and Au nanoparticles for the TiO$_2$ mediated photocatalysis. As men-
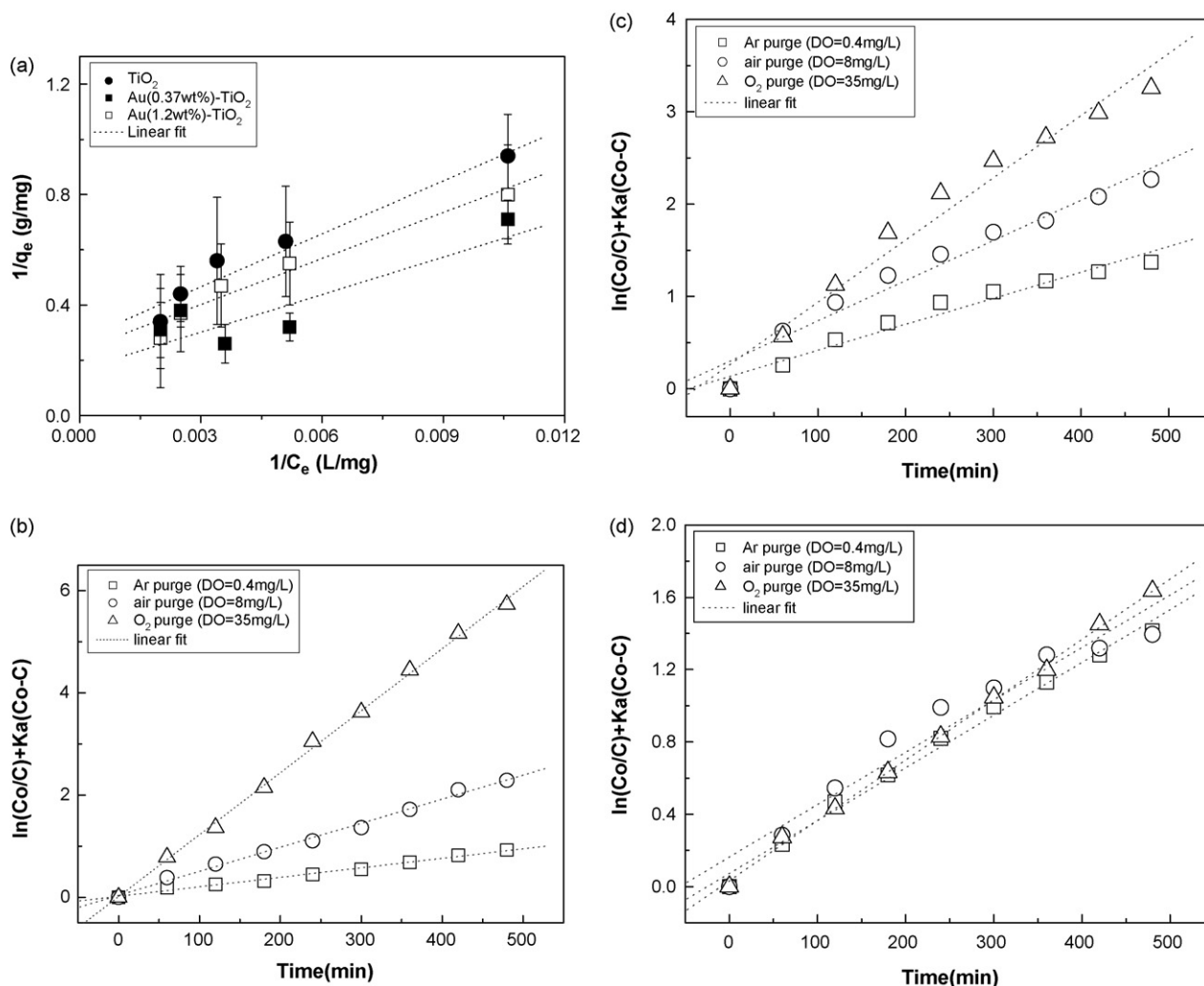
following equation can be derived:

$$\ln\left(\frac{C_0}{C}\right) + K_a(C_0 - C) = k_{app} t \qquad (2)$$

where $k_{app} = K_a k_{L-H}$, and it is the apparent kinetic constant in 1/min. Therefore, the rate constants of k_{app} can be obtained by determining the slope of the linear expression in the plot of $\ln(C_0/C) + K_a(C_0 - C)$ vs. t. It is important to note that the L–H expression in Eq. (2) can be reduced to the first order or zero order kinetics when the reactant

Fig. 4. Adsorption isotherm of 1,4-dioxane on TiO$_2$ and Au–TiO$_2$ obtained from adsorption experiments under dark conditions (a) and the Langmuir–Hinshelwood (L–H) kinetics for 1,4-dioxane photodegradation under the different DO levels by TiO$_2$ (b), Au(0.37 wt%)–TiO$_2$ (c), and Au(1.2 wt%)–TiO$_2$ (d).

tioned earlier, both the DO and Au nanoparticles assist to separate photogenerated electron–hole pairs via electron transfer to the DO and Au nanoparticles, respectively. A major difference (see Fig. 6) between them may be in that the photogenerated electron can be

Fig. 5. The plots of the apparent rate constants vs. DO levels; the slopes indicate the degree of DO dependency.

directly scavenged by DO (k_1) at the surface of TiO$_2$ while it is firstly transferred to gold nanoparticles (k_2) and subsequently removed by the DO (k_3). If the electrons transferred to the Au nanoparticle are not efficiently scavenged by the DO (k_3 is very small), it may recombine (k_{-2}) with the hole most likely at the interface between the Au and TiO$_2$ [22].

In order for oxygen to capture the electron, molecular oxygen needs to adsorb on the TiO$_2$ or Au surface. Oxygen is believed to adsorb exclusively on Ti^{3+} sites on TiO$_2$ [19] while it hardly adsorbs on the Au surface due to its inert nature [23]. Therefore, it is reasonable that the rate of electron consumption by DO is much higher on the TiO$_2$ than on the Au ($k_1 \gg k_3$). For the TiO$_2$ without Au nanoparticles, k_1 is the only way to consume the photogenerated electron; therefore, the DO dependency would be high, which is consistent with our experimental results (Fig. 5c). On the other hand, for the TiO$_2$ with high coverage Au nanoparticles, the electron transfer to Au nanoparticles may be predominant, leading to the insignificant DO dependency (Fig. 5a). However, since k_3 is not sufficiently high k_{-2} also increases, which resulted in overall low photocatalytic efficiency (Fig. 2c). The Au(0.37 wt%)–TiO$_2$ catalyst may be in the middle where the electron is consumed by DO at the TiO$_2$ surface as well as transferred to the Au nanoparticles. Since the density of the gold nanoparticles of this catalyst is only about 1.6% of Au(1.2 wt%)–TiO$_2$, the former effect could be larger, resulting in some degree of DO dependency (Fig. 5b).
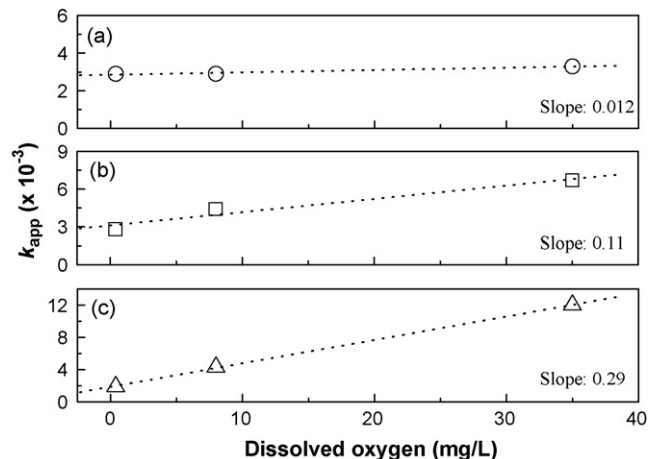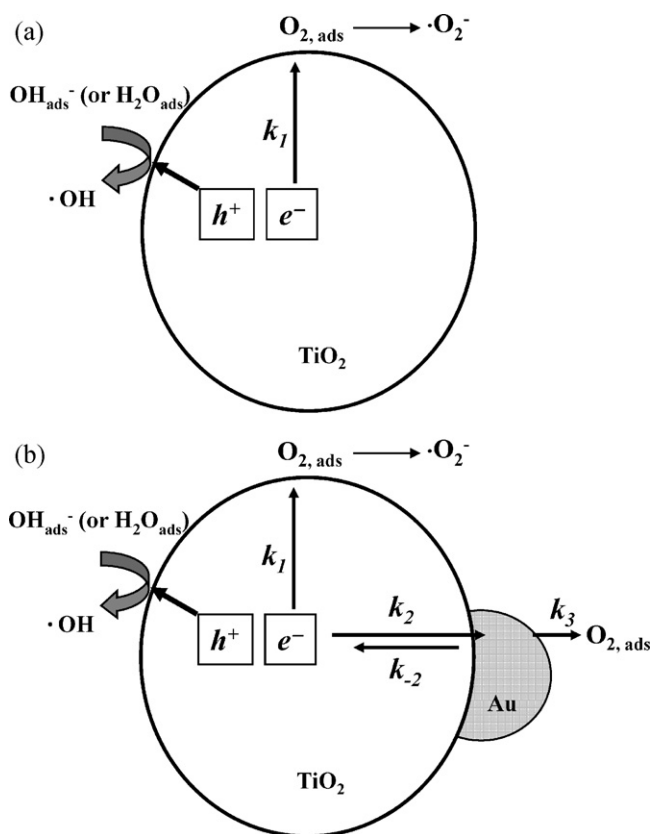
Fig. 6. Schematics for a qualitative explanation of the photogenerated electron transfer mechanisms in TiO_2 (a) and $Au–TiO_2$ (b). k indicates the electron transfer rate.

Many studies have shown that Au nanoparticles incorporated with TiO_2 are more efficient in photocatalysis than TiO_2 only, but it is not always the case [24,25]. The promoting effect of Au nanoparticles in the photocatalysis by TiO_2 was generally observed only in the low loading of Au (higher loadings of Au have a negative effect). The inhibition of adsorption of organic molecules or hydroxyl species on TiO_2 surface due to Au nanoparticles (screening effect) has been suggested as the reason for the negative effect of the high Au loadings [24,25]. In our case, however, the photocatalysts had very similar surface area of TiO_2; therefore, the adsorption of 1,4-dioxane would not be different, which was already confirmed by the identical values of Langmuir adsorption equilibrium constants (Table 2). The adsorption of hydroxyl and/or water species on TiO_2 is also possibly prevented by Au nanoparticles as suggested by Orlov et al. [25], but it seems to be effective only for the ambient DO condition (DO = ~8 mg/L) because the effect of Au loadings was not apparently observed in the high DO condition. We observed a similar Au loading effect; Au(0.37 wt%)–TiO_2 is initially more active than Au(1.2 wt%)–TiO_2 in the ambient reaction condition (DO = ~8 mg/L). Our results further elucidated that the Au loading effect on photocatalytic activity of TiO_2 is closely correlated with DO levels in aqueous solutions.

4. Conclusion

In brief, the photocatalytic degradation of the 1,4-dioxane in an aqueous phase was carried out by three different photocatalysts: (TiO_2 only, Au(0.37 wt%)–TiO_2, and Au(1.2 wt%)–TiO_2) with the DO levels of 0.4, 8, and 35 mg/L. Using the L–H kinetic model, the apparent rate constants of the 1,4-dioxane photodegradation were evaluated for all different conditions (catalysts and DO lev-

els). The relation of DO levels and rate constants indicated that there is a strong correlation between Au loadings and DO levels: low DO effect on high Au loading TiO_2 and high DO effect on TiO_2 only. The competitive charge transfer mechanism between DO and Au nanoparticles was tentatively suggested to explain our experimental results.

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