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Detection of active oxygen species dynamics in TiO$_2$ sol solutions using single-shot near-field heterodyne transient grating method

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A R T I C L E   I N F O

A B S T R A C T

Active oxygen species generated by photoexcitation of TiO$_2$ sol solutions were directly observed by the single-shot near-field heterodyne transient grating method. Two kinds of dynamics due to chemical species were observed and their lifetimes and diffusion coefficients were determined. From the dependence of the quantity of dissolved oxygen, it was confirmed that one of the species was generated from dissolved oxygen, such as a superoxide anion. Furthermore, this species was found to have a very small diffusion coefficient compared with other molecules with similar molecular weight, thereby suggesting that it was adsorbed onto TiO$_2$ particles.

TiO$_2$ is the most famous photocatalytic material [1–3]. It can decompose and mineralize pollutant and undesirable compounds in air and water. In general, such photocatalytic reactions start with the photoexcitation of electrons and holes by irradiation of ultraviolet light, and the following chemical reaction proceeds [4]:

$$O_2 + e^- \quad \rightarrow \quad O_2^{-\cdot} \tag{a}$$
$$H_2O + h^+ \quad \rightarrow \quad \cdot OH + H^+ \tag{b}$$

The generated superoxide anion and hydroxyl radical are the major reactive species produced during photocatalytic reactions. There are other active oxygen species such as singlet oxygen, hydrogen peroxide, hydroperoxy radical and so on [5–8]. Since active oxygen species have high reactivity, most of organic molecules adsorbed on a TiO$_2$ surface are decomposed into carbon dioxide and water.

Since the efficiency of photocatalytic reactions depends on the quantity and properties of the active oxygen species, several detection techniques have been developed. TiO$_2$ sol solutions and films synthesized by different manufacturers have been analyzed by various methods [9–11]. For the qualitative analysis of the active oxygen species, the electron spin resonance (ESR) technique has been established [12,13]; however, there are few methods for observing their dynamic behavior. Chemiluminescence from luminol solutions is used for observing the dynamic processes of superoxide anions [14–19]. However, there have been no detection techniques that can enable an in situ measurement of the active oxygen species.

The transient grating (TG) technique is a useful technique for detecting photo-induced reaction dynamics [20,21]. Because this technique is capable of monitoring the refractive index change, optically silent dynamics such as molecular volume change can be also monitored [22]. We have recently developed an improved method of the TG technique, the near-field heterodyne transient grating (NF-HD-TG) method [23–25], which features a simple optical setup and highly sensitive detection using a heterodyne technique.

In this Letter, we measured the dynamic behavior of the active oxygen species after irradiation of an ultraviolet pulse using single-shot detection with the NF-HD-TG method. We found that the active oxygen species were successfully observed in an in situ manner and their diffusion coefficients were obtained and discussed.

The principle of the NF-HD-TG method is described in detail previously [23–25]. When a pump beam is incident on a transmission grating, an optical fringe pattern is formed on the opposite side of the diffraction grating. When a liquid sample is placed near the transmission grating, it can be excited by the fringe pattern of the pump light. The refractive index of the liquid changes because of photochemical and photothermal processes with the same pattern as the optical fringe; the pattern of the refractive index change is called a transient grating. When another light beam (probe light) is made incident on the transient grating, it is diffracted by both the transmission grating (reference) and the transient grating (signal). The two diffracted beams are directed in the same direction, and they are mixed and detected. The intensity of the heterodyne component is expressed as follows:

$$I(t) = 2E_{ref}E_{pr}(\Delta n(t)\cos\phi + \Delta k(t)\sin\phi), \tag{1}$$

where E_{ref} and E_{pr} are the electric fields of the reference and probe; ϕ is the phase difference between the signal and the reference; and Δn, Δk are the real and imaginary parts of the refractive index change. The phase difference is adjusted by the optical path difference between the signal and the reference and it can be controlled

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by changing the distance between the transmission grating and the sample. The phase difference is expressed as follows:

$$\phi = (2\pi/\lambda_{\text{probe}})\Delta l = d(1/\cos\theta - 1)(2\pi/\lambda_{\text{probe}}), \qquad (2)$$

where Δl is the optical path difference between the signal and the reference; d is the grating-sample distance; and θ is a diffraction angle. From Eqs. (1) and (2), $\Delta n(t)$ or $\Delta k(t)$ can be selectively detected by setting d to appropriate positions. $\Delta n(t)$ responses were measured throughout the following experiments because transient responses were observed mainly for $\Delta n(t)$, not for $\Delta k(t)$, and theoretical explanations were also given only for $\Delta n(t)$.

In TG experiments, the refractive index change mainly occurs because of thermal energy release (thermal grating) and subsequent transiently generated chemical species by the photoreaction (species grating) [26]. In this Letter, the species grating was studied; its signal intensity is proportional to the refractive index change (Δn_p), which is proportional to the concentration of the species. The signal intensity due to the species grating decays by the following two processes: (1) the chemical species disappears due to deactivation or chemical reaction and (2) the spatial modulations of the refractive index become uniform, which is accomplished by the translational diffusion in the direction perpendicular to the grating. In this case, the temporal change of the species concentration can be obtained from the diffusion equation including a decay term in the following:

$$\frac{\partial C}{\partial t} = D_p \frac{\partial^2 C}{\partial x^2} - \frac{C}{\tau_p}, \qquad (3)$$

where C is concentration of species; D_p is the diffusion coefficient of the species; τ_p is the lifetime of the species. Then $I(t)$ is expressed as

$$I(t) \propto \Delta n_p(t) = A \exp\left(-\left(D_p q^2 + \frac{1}{\tau_p}\right)t\right), \qquad (4)$$

where q is the grating wavevector equal to $2\pi/\Lambda$ (Λ: grating spacing); A is a constant. Provided the decay time of Eq. (4) is τ, a $1/\tau$ vs. q^2 plot gives the diffusion coefficient and lifetime of the species as the slope and intercept of the plot, respectively (q is controllable by the grating spacing).

The optical setup was same as the one previously reported except that the pump light was operated in a single-shot mode. The pump light was the third harmonic of a Nd:YAG laser (GAIA, Rayture Systems Inc.) with a wavelength of 355 nm, pulse width of 4 ns, and the pulse energy used was less than 0.5 mJ/pulse, and the probe light was the second harmonic of an CW Nd:YAG laser with a wavelength of 532 nm. The cell has an internal thickness of 1 mm. The grating spacing was 40–60 μm. One of the probe diffraction beams was detected by a fast photodetector. After a single-shot irradiation, the detected response was stored in a digital oscilloscope. After each pump shot, the sample solution was replaced by a flow cell, or the irradiation position was changed to a new location. A sample was a TiO$_2$ sol solution with a pH of 4.3 (Taki Chemical, AM-15) and the average particle size of TiO$_2$ was 20 nm in diameter. When dissolved oxygen in a sol solution was nitrogen-substituted, nitrogen gas was bubbled under stirring condition for more than 30 min in the sol solution. The quantity of dissolved oxygen was measured by a DO meter (Horiba, D-55). Superoxide dismutase (SOD, 10 000 units/mg) was purchased from Wako Chemicals, and a diluted solution (0.3 g/L) was used as a scavenger for superoxide anion. Twenty-five microliter of the solution was added in an optical cell with a volume of 0.5 mL.

Transient responses of the sample solution for different optical fringe spacings are shown in Fig. 1. On the millisecond time range, exponential decays of the thermal grating were observed. It decayed due to thermal diffusion in the perpendicular direction to the grating stripe and the decay times depended on the grating spacing. The decay times agreed with the calculated value of 1/
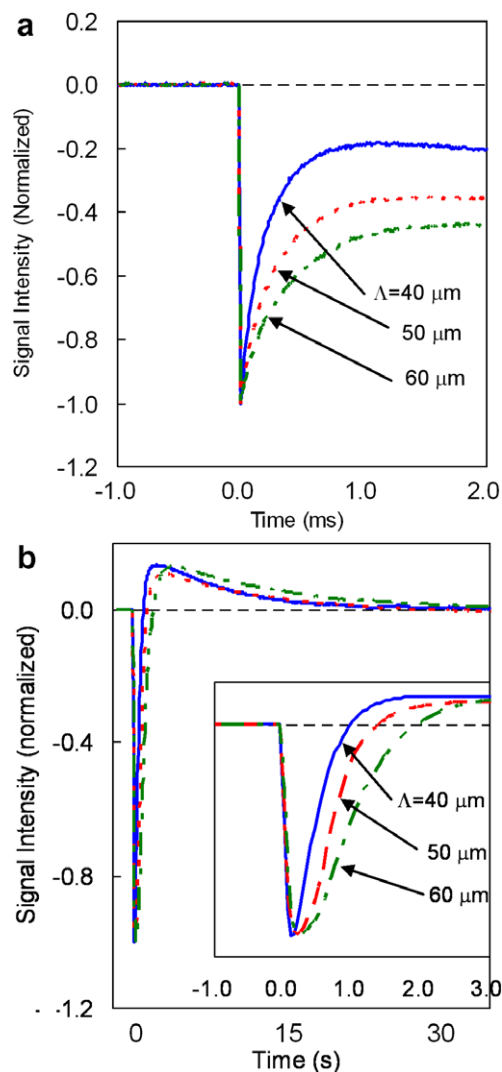

Fig. 1. Transient responses of a TiO$_2$ sol solution for different optical fringe spacings: 40, 50, and 60 μm on the millisecond (a) and second (b) time range. The inset in (b) shows the expansion of the shorter time region. The responses were fitted with a double exponential function.

Dq^2 (D: thermal diffusion coefficient of the solvent). After the thermal grating decay, on the second time region, the responses initially showed a negative signal, which increased beyond the baseline and gradually returned to it again. All the responses were fitted with a sum of two exponential decay functions with different signs for pre-exponential factors as follows:

$$I(t) = \sum_{i}^{2} B_i \exp\left(-\frac{t}{\tau_i}\right), \qquad (5)$$

where B_1 and B_2 are pre-exponential factors; τ_1 and τ_2 are the decay times. As explained in theory of the NF-HD-TG method, the lifetime and diffusion coefficient of the photogenerated chemical species was observed a few temporal orders slower than the decay of the thermal grating and can be obtained from the plot of $1/\tau$ vs. q^2. The corresponding plots for the two exponential decay times are shown in Fig. 2. The lifetimes and diffusion coefficients obtained were 1.8 s, 1.0×10^{-10} m^2 s^{-1} and 19.0 s, 3.0×10^{-12} m^2 s^{-1}, respectively.

The lifetime of superoxide anions can be measured by the temporal intensity change of luminol chemiluminescence after photoexcitation of TiO$_2$ because superoxide anion reacts with luminol radicals [14]. It was reported that the lifetime in a alkaline sol solution was several tens of seconds [15,27] which was on the same
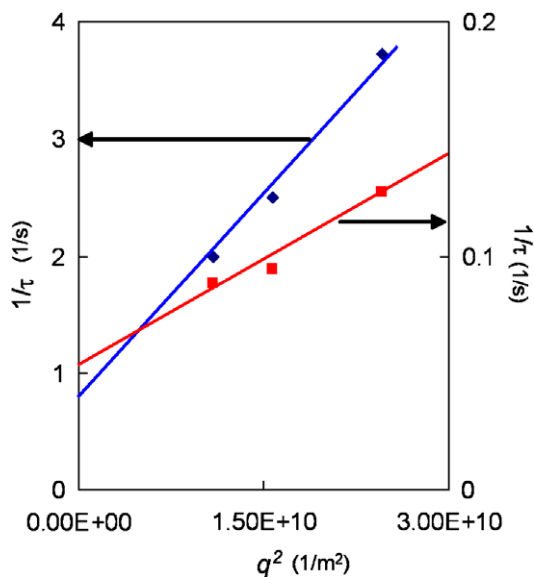
Fig. 2. Relation between the inverse of decay times and the square of q for the two kinds of decay times obtained from the fitting to the transient responses shown in Fig. 1. q is equal to $2\pi/\Lambda$ (Λ: grating spacing).

temporal order as the slower lifetime obtained from our measurement. The lifetime in acid solutions cannot be obtained because luminol chemiluminescence can be measured only in alkaline solutions and it is only an established method to detect the superoxide species. It is suggested that the lifetime in acid solutions is shorter than that in alkaline solutions [28], and it seems that this is why the obtained lifetime is shorter than the reference values.

It is expected that superoxide anions are not generated if the dissolved oxygen in the sol solution is removed. To confirm that the slower dynamics are related to superoxide anion, the dissolved oxygen was substituted by nitrogen in the sol solution. Transient responses of the sample solution before nitrogen substitution, after nitrogen substitution, and after exposure to the air for 30 min after nitrogen substitution are shown in Fig. 3. The concentrations of dissolved oxygen before and after nitrogen substitution and after exposure to the air were 7.75, 1.25, and 5.63 mg/L, respectively.
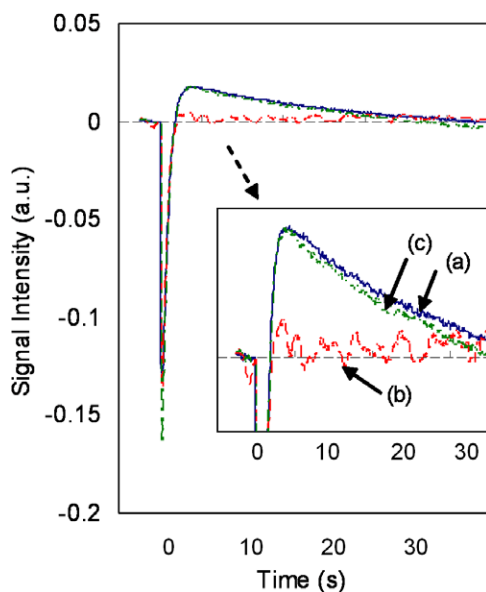

Fig. 3. Transient responses of TiO$_2$ sol solutions (a) before nitrogen substitution, (b) after nitrogen substitution, and (c) after exposure to the air for 30 min after nitrogen substitution.

The slower dynamics disappeared after nitrogen substitution, and it appeared again after exposure to the air.

Furthermore, the transient responses in presence and absence of SOD were compared, and the result is shown in Fig. 4. SOD is well known as a scavenger of superoxide anion radicals [11,19]. The slower dynamics was almost disappeared in the presence of SOD, and this fact also supports that this component corresponds due to superoxide anion. Although it is still difficult to assign this dynamics only due to superoxide anion because superoxide anion is equilibrated with hydroperoxy radical and hydrogen peroxide and also SOD may scavenge all the species, it was concluded that it corresponds to the dynamics of the active oxide species generated from dissolved oxygen such as superoxide anion, hydroperoxy radical and hydrogen peroxide.

Next, we discuss on the diffusion coefficient 3.0×10^{-12} m^2 s^{-1} obtained for the species related to superoxide anion. It was reported that the diffusion coefficient of N$_2$ in methanol [29], and in benzene [30] and CO in heptane [31] generated by photochemical reactions were obtained by measurements using the TG method. The diffusion coefficients obtained were 5.3×10^{-9}, 8×10^{-9}, and 1.2×10^{-8} m^2 s^{-1}, respectively. Comparing the diffusion coefficients for molecules of similar molecular weight with those of superoxide anions, the diffusion coefficient obtained was three orders smaller than those for other molecules. It is reported that superoxide anion adsorbs on a TiO$_2$ surface and stays there in a sol solution [14] or on a film surface [32], the three order smaller diffusion coefficient can be explained by the superoxide anion remaining adsorbed on a TiO$_2$ surface and the diffusion process being dominated by diffusion processes of the TiO$_2$ nanoparticles. To support this assumption, the diffusion coefficient of this TiO$_2$ solution was estimated. At first, the diffusion coefficient of the diluted TiO$_2$ sol solution (300 ppm) was measured by a home-built dynamic light scattering (DLS) equipment to avoid the multi-scattering effect in the DLS method. In addition, the viscosity of the original sol solution was measured. The diffusion coefficient of TiO$_2$ nanoparticles were calculated by dividing the diffusion coefficient obtained by the DLS method (2.1×10^{-11} m^2 s^{-1}) by the relative viscosity of the sol solution (4.7 mPa s). The estimated diffusion coefficient of TiO$_2$ nanoparticles was 4.4×10^{-12} m^2 s^{-1}, which was close to the diffusion coefficient for the slower component.

With regard to the faster decay component, the hydroxyl radical is one of the candidates because it is another major chemical species for ultraviolet light irradiation to TiO$_2$ and furthermore it was reported that its lifetime was assumed to be 1 s for TiO$_2$ powder in air [4], which is close to the lifetime, 1.8 s in the sol solution, obtained in our experiment. However, it has not been established how to measure the dynamics of the hydroxyl radical in solution,
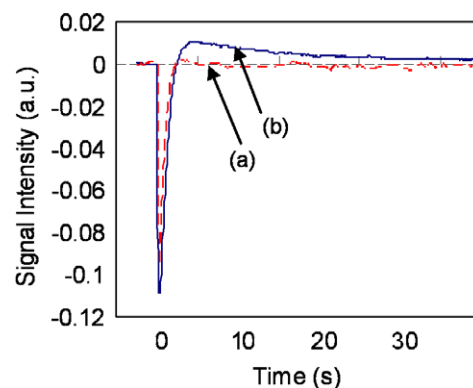

Fig. 4. Transient responses of TiO$_2$ sol solutions in the presence (a) and absence (b) of superoxide dismutase (SOD).

and we are now trying to assign the origin. If the above assignment for the two decay components is correct, there is a question why the pre-exponential factors for them are opposite because both hydroxyl radical and superoxide related species should have absorption in the UV region and then the refractive index due to them have the same signs. Only explanation for this is that the superoxide related species had the opposite sign due to adsorption on TiO_2 nanoparticles, though it is very difficult to predict the refractive index change due to adsorption of a molecule to a nanoparticle.

In summary, we could monitor the dynamics of active oxygen species in TiO_2 sol solutions in an in situ manner for the first time. Different from the conventional methods, active oxygen dynamics can be observed under actual reaction conditions without additional reagents. It is expected that this technique would be utilized for clarifying the mechanism of photocatalytic reactions. Furthermore, there is a possibility that other active oxygen species such as singlet oxygen and hydrogen peroxide could be detected by changing the detection time region. Another merit of this technique is that diffusion coefficients can be obtained and it would shed light on the reaction dynamics of the species or it would help qualitative analysis of the species.

Acknowledgement

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