# Evaluation of electron-hole recombination properties of titanium(IV) oxide particles of high photocatalytic activity


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Electron-hole recombination in nano-sized titanium(IV) oxide ($TiO_2$) particles of various physical properties, which had been proved to be highly active photocatalysts, was evaluated by quantitative analysis of reduced titanium species ($Ti^{3+}$) that might be formed at crystalline defective sites in $TiO_2$ particles through photoirradiation in the presence of a hole scavenger under deaerated conditions. These highly active photocatalyst samples were synthesized by hydrothermal crystallization in organic media (HyCOM method) and post-calcination. The $Ti^{3+}$ density decreased with the elevation in calcination temperature ($T_c$) and linear correlation was observed between the $Ti^{3+}$ density and rate constant for electron-hole recombination evaluated by femtosecond pump-probe diffuse reflection spectroscopy. Reaction rate ($R_{Ag}$) and the amount of silver ion ($Ag^+$) adsorbed on $TiO_2$ particles ($[Ag^+]_{ads}$) were measured in photocatalytic silver metal deposition along with oxygen formation from an aqueous $Ag^+$ solution under deaerated conditions, and the slope of the $R_{Ag}$-$[Ag^+]_{ads}$ plot was determined. Kinetic investigation of this reaction showed that the reciprocal of the slope approximately related to the ratio of the rates for electron-hole recombination and electron trapping ($k_r/k_e$

ratio). The $k_r/k_e$ ratio decreased as $T_c$ increased, and logarithm of the $k_r/k_e$ ratio was linearly related with the $Ti^{3+}$ density. ~~These quantitative analyses were easily performed and~~ These two parameters were used as a measure for the recombination properties of $TiO_2$ photocatalysts of various physical properties.

## 1. Introduction

The adsorbability, ability of adsorbing chemical substances, of titanium(IV) oxide ($TiO_2$) is one of the significant factors determining the overall photocatalytic activity because the reaction proceeds via surface reactions between adsorbed substrate(s) and electrons ($e^-$) and holes ($h^+$) that are generated by photoabsorption of $TiO_2$ particles. In most of cases, the amount of substrate(s) adsorbed on the surface of $TiO_2$ powders can be measured directly and precisely. Another important factor should be property of $e^-$-$h^+$ recombination, while this had been much difficult to be determined directly. Recent papers have reported that rate of $e^-$-$h^+$ recombination for several kinds of $TiO_2$ powders are directly evaluated using femtosecond pump-probe diffuse reflection spectroscopy (PP-DRS) [1-4]. Relatively high spatial and chronological densities of absorbed photons in the pump-probe measurements induces multiple numbers of $e^-$-$h^+$ in each particle at the same time, i.e., within the lifetime of geminate $e^-$-$h^+$, and thereby second-order kinetics can be adopted for the decay of trapped $e^-$ by recombination with $h^+$. The second-order rate constants thus obtained might not be applied to the estimation of actual rate of photocatalytic reaction operated under continuous photoirradiation of the lower intensity, in which $e^-$-$h^+$ is expected to undergo geminate recombination in first-order kinetics. However, the rate constants must reflect the number (correctly speaking, the density within the depth of photoabsorption) of recombination centers, assuming $e^-$-$h^+$ recombination occurs at those sites, though no structural information could be obtained from the pump-probe measurements.

Crystalline defects are one of the most probable candidates of site for the $e^-$-$h^+$

recombination. A sol method reported so far for the quantitative estimation of crystalline defects in $TiO_2$ involves the evaluation of density of reduced species ($Ti^{3+}$) produced in $TiO_2$ particles under irradiation in the presence of strong $h^+$-trapping agent, i.e., reductants; when an aqueous suspension of $TiO_2$ containing methanol or triethanolamine is photoirradiated under argon (Ar) atmosphere, the suspension turns blue or blue-grey due to formation of so-called $Ti^{3+}$ species. Almost linear relation between the $Ti^{3+}$ density and the second-order rate constant for the $e^-$-$h^+$ recombination obtained by the femtosecond laser spectroscopy suggested that the $Ti^{3+}$ density is a measure of number (or density) of recombination centers in $TiO_2$ samples [4, 5].

In previous studies, we have shown that nano-crystalline anatase $TiO_2$ of a large surface area with sufficient crystallinity is obtained by high-temperature hydrolysis of titanium alkoxides with a limited amount of water dissolved in organic solvents and concomitant crystallization (HyCOM) [6,7]. Since HyCOM $TiO_2$ possesses high thermal stability, physical properties of HyCOM $TiO_2$ powders can be controlled in a wide range by changing post-calcination temperature ($T_c$) [7]. The anatase form of HyCOM $TiO_2$ was preserved even after calcination at 1073 K. The HyCOM $TiO_2$ powders were used for photocatalytic silver metal (Ag) deposition together with oxygen ($O_2$) evolution from silver ion ($Ag^+$) solution under deaerated conditions [8]. An almost linear relation was observed between the rate of photocatalytic reaction ($R_{Ag}$) and the amount of $Ag^+$ adsorbed on the $TiO_2$ ($[Ag^+]_{ads}$), which indicates that the rate is proportional to the amount of substrate adsorbed on the particles and thereby the adsorbability is one of decisive factors determining the reaction rate. Another important finding was that the slope of the $R_{Ag}$-$[Ag^+]_{ads}$ plot for HyCOM calcined at 973 K (1.3) was ca. three times larger than that for Degussa P-25 (0.45). Taking that both the adsorbability and the $e^-$-$h^+$ recombination rate may determine the overall rate of photocatalytic reaction into consideration, the difference in the recombination properties between the two samples might reflect the observed difference in the slope.

In the present study, HyCOM $TiO_2$ samples of various physical properties were prepared and their $e^-$-$h^+$ recombination properties were analyzed by comparing their density of $Ti^{3+}$ produced under deaerated conditions in the presence of $h^+$ scavenger and the slope of $[Ag^+]_{ads}$-$R_{Ag}$ plot.

## 2. Experimental

### 2.1. Sample Preparation.

HyCOM $TiO_2$ powders were synthesized by a procedure reported previously [7,8]. The as-prepared powders were calcined in a box furnace at various temperatures under a flow of air (30 $cm^3$ $min^{-1}$); the sample in a combustion boat was heated to the desired temperature at a rate of 10 K $min^{-1}$, kept at that temperature for 1 h, and then cooled to room temperature. The thus-calcined sample is designated HyCOM($T_c$), e.g., HyCOM(973) means a sample calcined at 973 K. Commercial $TiO_2$ samples, Degussa P-25 and Ishihara ST-01, were used as a reference in most of the experiments because these are known to be active photocatalysts.

Characterization of $TiO_2$ powders was performed in the same ways reported in the previous papers [7, 8].

### 2.2 Quantitative analysis of $Ti^{3+}$ density

The amount of reduced species of $TiO_2$, $Ti^{3+}$, was measured quantitatively using methyl viologen ($MV^{2+}$) as a final electron acceptor as follows [5]. A sample $TiO_2$ powder (50 mg) was suspended in an aqueous triethanolamine solution (10%; 5 $cm^3$) and irradiated by a 400-W high-pressure mercury arc (> 300 nm) under Ar for 24 h. A deaerated aqueous solution containing 62.5 μmol of $MV^{2+}$ was added to the photoirradiated reaction mixture. The resulting pale blue suspension containing the reduced form of $MV^{2+}$, methyl viologen cation radical ($MV^{\bullet+}$) was filtered and the supernatant solution was loaded into a quartz cell (light path length 1 mm). These operations were performed in an Ar purged glovebox

(UN-650F, United Instruments) to avoid fading of $Ti^{3+}$ and/or $MV^{\bullet+}$ by $O_2$. From the absorbance of solution at around 600 nm measured by a sensor array photometer (LASA 20, TOA DKK Ltd.) and reported value of the absorption coefficient of 13700 $dm^3$ $mol^{-1}$ $cm^{-1}$ at 606 nm [9], the molar amount of $Ti^{3+}$ was estimated on the assumption that equimolar amount of $Ti^{3+}$ and $MV^{2+}$ react to produce $MV^{\bullet+}$. On the basis of pH-dependence of electron transfer from the photoreduced several (anatase and rutile) $TiO_2$ samples to $MV^{2+}$, it has been concluded that the electronic energy level of so-called $Ti^{3+}$ species is located just below the bottom of conduction band, i.e., the energy level of reduced species in $TiO_2$ seemed are not so different each other. [5] The linear correlation of this $Ti^{3+}$ density and density of defective sites, leading to electron-hole recombination, in $TiO_2$ has been proved in our previous paper[5] and will be discussed in the section of Results and Discussion.

### 2.3 Measurement of $[Ag^+]_{ads}$ and $R_{Ag}$ in silver system

The amount of surface-adsorbed $Ag^+$ under conditions similar to the photocatalytic reaction was measured in the dark by inductively coupled plasma (ICP) emission spectroscopy (Shimadzu ICPS-1000III) taking the difference in $Ag^+$ concentration before and after addition of $TiO_2$ into silver sulfate ($Ag_2SO_4$) solutions of various concentrations.

$TiO_2$ powder (50 mg) was suspended in 0.5-25 mmol $dm^{-3}$ $Ag_2SO_4$ aqueous solution (5.0 $cm^3$) in a glass tube, purged with Ar for at least 30 min, and then sealed off with a rubber stopper. The suspension was photoirradiated at 298 K in a way similar to that for the $Ti^{3+}$-density measurement. After the irradiation, amount of evolved $O_2$ was measured by a Shimadzu GC-8A gas chromatograph. Ratio of $Ag/O_2$ was determined to be almost 4, indicating that the reaction ($4Ag^+ + 2OH^- \rightarrow 4Ag + O_2 + 2H^+$) occurred with stoichiometry. The catalyst was recovered by centrifugation, washed repeatedly with distilled water, and dried overnight at 333 K. The photodeposited Ag was dissolved with concentrated $HNO_3$ (1.0 $cm^3$) and measured by ICP emission spectroscopy.

2. 4 Determination of recombination rate constant by PP-DRS

Second-order rate constants for $e^{-}$-$h^{+}$ recombination in HyCOM $TiO_2$ samples were evaluated by PP-DRS using a femtosecond laser system. The details have been reported [4, 5] and briefly described below. An argon-ion-laser pumped Ti:sapphire laser (mode-locked; Spectra-Physics, Tsunami: 3960-L-2S) was used with a regenerative ampliphier (Quantronix, 4812RGA/4823S/C) synchronously pumped by a mode-locked YLF laser (Quantronix, 527DP-H) to generate ca 100 fs pulses. The pulses were split into two almost identical beams to pump two optical parametric generation (OPG) and optical parametric amplification (OPA) systems (Light Conversion, TOPAS). One of the two output beams of 620 nm was used as a probe beam (ca. 1.5 mJ pulse$^{-1}$) and the other was used as pump beam (0.03-0.1 mJ pulse$^{-1}$) after frequency doubling by a BBO crystal. These beams were collinearly focused and overlapped at the sample of dry $TiO_2$ powder and resulting diffuse reflected probe beam was detected by a photodiode and accumulated as absorption (1 - $R/R_0$, where $R$ and $R_0$ represent the intensity at a given delay and that in the absence of a pump pulse, respectively. The procedure of kinetic data analyses is described in the discussion section. Unfortunately, data for a part of HyCOM samples, which had been calcined at relatively higher temperature, could be obtained, since small amount of residual organic species originating from organic solvent and starting materials used in the synthesis produced long-lived colored species during PP-DRS measurements, which obscured the actual reflectance change due to their accumulation in the sample.

## 3. Kinetics model for photocatalytic Ag deposition

Prior to a discussion on the slope in $R_{Ag}$-$[Ag^{+}]_{ads}$ plot, a model used for photocatalytic reactions in aqueous $TiO_2$ suspensions containing $Ag^{+}$ is discussed. The model consists of recombination and trapping of $e^{-}$-$h^{+}$ generated in the $TiO_2$ particles by photoirradiation as shown in eqs. 1-3.

$$TiO_2 + h\nu \rightarrow (e^- \text{-} h^+) \quad (1)$$

$$(e^- \text{-} h^+) \rightarrow TiO_2 \quad (2)$$

$$Ag^+_{ads} + (e^- \text{-} h^+) \rightarrow Ag + h^+ \quad (3)$$

In a system containing no strong electron donors ($h^+$ scavenger), $h^+$ trapping by surface-adsorbed $H_2O$ and/or surface hydroxyls are practically negligible [14,15], and the photocatalytic reactions shown here proceed via $e^-$-trapping by a surface-adsorbed $Ag^+$. Under these conditions, rate of $e^-$-$h^+$ accumulation is assumed to be zero by steady-state approximation as follows:

$$d[e^- \text{-} h^+]/dt = I\phi - k_r[e^- \text{-} h^+] - k_eC_e[e^- \text{-} h^+] = 0 \quad (4)$$

where $I$ is the flux of incident photons, $\phi$ is an efficiency of $e^-$-$h^+$ generation with $TiO_2$ photoabsorption, $C_e$ is the surface concentration of adsorbed $Ag^+$, and $k_e$ and $k_r$ are the rate constants for $e^-$-trapping by surface-adsorbed $Ag^+$ and recombination, respectively. An absorption coefficient of anatase $TiO_2$ in the wavelength range of main ultraviolet emission from a mercury arc seems to be enough large to assume all the photons are absorbed and we assumed that the term $I\phi$ remained constant independent of the kinds of $TiO_2$ samples. The steady-state concentration $[e^-$-$h^+]$ is obtained from eq. 4 as follows:

$$[e^- \text{-} h^+] = I\phi/(k_r + k_eC_e) \quad (5)$$

The rate of Ag metal deposition ($R_{Ag}$) corresponding to the overall rate of this reaction system is derived as

$$R_{Ag} = k_eC_e[e^- \text{-} h^+] = I\phi \cdot k_eC_e/(k_r + k_eC_e) \quad (6)$$

Assuming that the $e^-$-$h^+$ recombination is much faster than $e^-$-trapping ($k_r >> k_eC_e$), $R_{Ag}$ can be simplified as follows.

$$R_{Ag} = I\phi \cdot k_eC_e/(k_r + k_eC_e) \cong \alpha(k_e/k_r)[Ag^+]_{ads} \quad (7)$$

where $I\phi$ and $C_e$ are replaced by $\alpha$ and $[Ag^+]_{ads}$ (surface concentration of adsorbed $Ag^+$).

## 4. Results and discussion

### 4.1 The $Ti^{3+}$ density of HyCOM $TiO_2$

The effect of calcination temperature on the physical properties and photocatalytic activity of HyCOM $TiO_2$ powders has been reported in the previous papers [8, 10]. The crystallite sizes of HyCOM samples gradually increased with elevating $T_c$ whereas the BET surface area decreased, showing crystal growth and sintering of the anatase crystallites upon calcination (Figure 1). Photocatalytic activity, $R_{Ag}$, increased with the $T_c$ increase, even though $[Ag^+]_{ads}$ decreased along with the decrease in $S_{BET}$ (data not shown), suggesting that another factor enhanced $R_{Ag}$. [line break]

The $Ti^{3+}$ density decreased along with $T_c$. Figure 2 shows the plot of the $Ti^{3+}$ density as function of their $S_{BET}$ of HyCOM $TiO_2$ samples. The decrease in the $Ti^{3+}$ density shows that the amount of the surface defects was reduced upon calcination at higher temperature due to a so-called annealing effect. A noteworthy point is the liner relationship shown in Figure 1(a), i.e., appreciable $Ti^{3+}$ density in samples of relatively small surface area obtained by the higher-temperature calcination, suggested that the present method could measure defects in the bulk, as well as those on the surface. The femtosecond PP-DRS measurement revealed that rate of $e^-$-$h^+$ recombination for HyCOM $TiO_2$ decreased with elevation in $T_c$ [2]. In the PP-DRS measurements, the decay of surface-trapped electrons by the recombination with positive holes could be observed; second-order kinetics could reproduce the decay curves and therefore we could calculate the second-order rate constant, $k_r$, on some assumptions.[2] Figure 3 shows the plot of the $Ti^{3+}$ density and $k_r$ from PP-DRS, suggesting a proportional relation between them. As has been well known, the unit of second-order rate constants contains the inversed concentration of intended chemical species. Since the photoexcitation and recombination occur in the solid materials, we determined $k_r$ in the unit of $cm^3\ ps^{-1}$. The $Ti^{3+}$ density provides an insight into the defective state of $TiO_2$ and $k_r$ [~~gives us structural information in $TiO_2$, i.e., defects and/or anion vacancy, and $k_r$~~] from PP-DRS reflects rate of the $e^-$-$h^+$ recombination. Therefore, the proportionality between them seems reasonable. These results support that calcination improves the crystallinity and reduces crystal defects acting as a recombination centers for $e^-$-$h^+$, resulting in smaller probability of the recombination. Hereafter, the $Ti^{3+}$ density determined by the present method is used as a measure of the recombination property of $TiO_2$ powders. Relationship between $R_{Ag}$ and the $Ti^{3+}$ density of HyCOM samples is shown in Figure 4. $R_{Ag}$ increased with decreasing the $Ti^{3+}$ density, indicating that the recombination property of $TiO_2$ powders is more dominant than the adsorbability for $Ag^+$ over the reaction rate for the present Ag deposition and $O_2$ evolution. The importance of the crystallinity of photocatalyst or high-temperature calcination in photocatalytic $O_2$ evolution systems has been reported by many researchers [11-13].

4.2 Evaluation of recombination property through kinetic analysis; a $R_{Ag}$-$[Ag^+]_{ads}$ plot

According to eq. 6, $R_{Ag}$ should be proportional to $[Ag^+]_{ads}$. In fact, a linear relation was observed for each $TiO_2$ sample between $R_{Ag}$ and $[Ag^+]_{ads}$ ~~in the multi-point plot~~ as shown in Figure 5 when $[Ag^+]_{ads}$ was intentionally changed using several solutions of different initial $Ag^+$ concentration. The slopes of straight lines correspond to $\alpha \cdot k_e/k_r$ and those for HyCOM(973) and P-25 in this ~~multi-point~~ plot were 1.26 and 0.45, respectively. In order to discuss the recombination property of $TiO_2$, the reciprocal of the slope, i.e., $k_r/(\alpha k_e)$ will be used hereafter as relative $k_r/k_e$ ratio, since this ratio is calculated by normalization of the reaction with $[Ag^+]_{ads}$ to exclude the dependence of the rate on $[Ag^+]_{ads}$. It should be noticed that the $k_r/k_e$ ratio is relative because absolute value of $\alpha$ (= $I\phi$) was not calculated and assumed to be constant not depending on the kind of $TiO_2$ samples.

~~Figure 4(b) shows plots of $R_{Ag}$ and $[Ag^+]_{ads}$ for the experiment using a $Ag_2SO_4$ solution containing 50 mmol dm$^{-3}$ $Ag^+$, extracted from the plot of Figure 4(a).~~ The slopes of the straight lines connecting the plot obtained from the experiment using a $Ag_2SO_4$ solution containing 50 mmol $dm^{-3}$ $Ag^+$ and the origin for HyCOM(973) and P-25 were 1.25 and 0.41, respectively, and are almost identical to those (1.26 and 0.45, respectively) obtained by multi-point plot (Figure 5). Therefore, the $k_r/k_e$ ratios for the rest of samples were calculated, for convenience, using the data of $R_{Ag}$ and $[Ag^+]_{ads}$ when the experiments were performed using a 50 mmol $dm^{-3}$ $Ag^+$ solution.

Figure 6 shows plots of $k_r/k_e$ ratio against $S_{BET}$. The $k_r/k_e$ ratio diminished with decreasing $S_{BET}$ similar to the behavior of the $Ti^{3+}$ density (Figure 2); although the relation between the $k_r/k_e$ ratio and the $Ti^{3+}$ density is ~~seems~~ not ~~strictly to be~~ proportional, it is clear that there is a positive correlation between them (Figure 7). ~~At present, we have no information on the dependence of $k_e$, reactivity of $e^-$ with $Ag^+$, on the structure of $TiO_2$ photocatalysts and if we assume $k_e$ of reactivity large when calcined at higher temperature, i.e., small $S_{BET}$, due to, for example, removal of surface hydroxyls as an insulator layer, the plots of $k_r/k_e$ ratio and $Ti^{3+}$ density become less deviated from a linear line~~. Another factor worth noting is probable over estimation of $k_r/k_e$ ratio for the samples adsorbing relatively large amount of $Ag^+$. To introduce eq. 6, we assumed that $k_r >> k_e C_e$ and a linear relationship between $R_{Ag}$ and $[Ag^+]_{ads}$ when was observed except at very low concentrations. However, a tendency of downward deviation is seen, especially in the plots for P-25, suggesting that the slope has been underestimated for the samples of larger $[Ag^+]_{ads}$, i.e., those of larger $S_{BET}$ obtained by calcination at the lower temperature. These results show that the $k_r/k_e$ ratio can be used as the indicator of recombination property as well as the $Ti^{3+}$ density.

The present evaluation methods were applied for a commercial $TiO_2$, Ishihara ST-01, having large BET surface area (297 $m^2g^{-1}$). Although the $Ti^{3+}$ density was not measured, the extremely large $k_r/k_e$ ratio (97.8) for the present photocatalytic reaction suggests ~~a~~ high recombination efficiency for ST-01 $TiO_2$. Calcination of ST-01 at 973 K decreased the $S_{BET}$ to 39 $m^2g^{-1}$, which was almost identical to that of HyCOM(923) (39 $m^2g^{-1}$). However, the $Ti^{3+}$ density and the $k_r/k_e$ ratio for ST-01(973) (50 μmol $g^{-1}$ and 8.1) were 1.6 and 6.6 times larger than those for HyCOM (973) (32 μmol $g^{-1}$ and 1.23), respectively. The result indicates that density of defective sites in ST-01 is larger than that for HyCOM comparing the samples of similar $S_{BET}$ and that $Ti^{3+}$ density and $k_r/k_e$ ratio strongly depend on the preparation conditions as well as calcination conditions.

## 5. Conclusions

The actual rate of photocatalytic Ag deposition and $O_2$ formation was almost proportional to the surface concentration of substrate ($[Ag^+]_{ads}$) but when the effect of such substrate concentration was excluded, another effect relating to the $e^-$-$h^+$ recombination could be discussed. On the basis of this kinetic analysis, we have determined the $k_r/k_e$ ratio and compared with the $Ti^{3+}$ densities for $TiO_2$ samples of various physical properties. It was found that these parameters were correlated with each other and also with $k_r$ evaluated by femtosecond PP-DRS measurement. Thus, the recombination properties of $TiO_2$ powders can be conveniently evaluated by two novel methods and it is concluded that the photocatalytic activity should be discussed by considering the effects of $e^-$-$h^+$ recombination.


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**Foot note**

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**Figure captions**

Figure 1 BET surface area ($S_{BET}$) (circle) and crystallite size (square) of ~~of~~ HyCOM samples calcined at various temperatures ($T_c$)

Figure 2 The plots of $Ti^{3+}$ density of HyCOM samples calcined at various temperatures as a function of their BET surface area ($S_{BET}$).

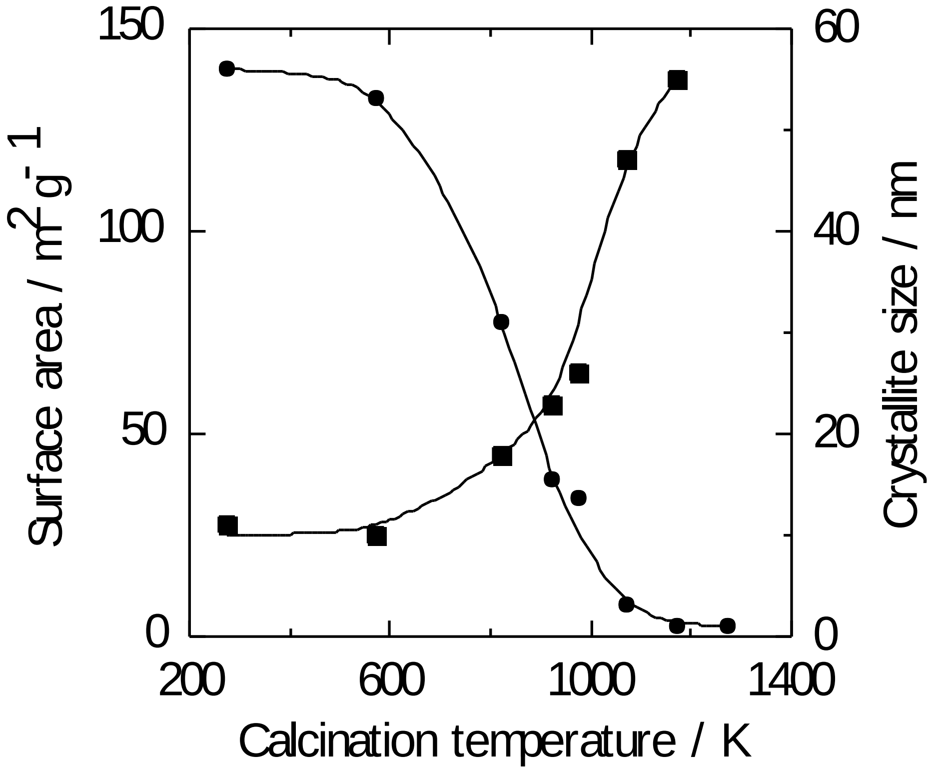
Figure 3 Correlation between $k_r$ from PP-DRS and $Ti^{3+}$ density of HyCOM samples.

Figure 4 Rate of photocatalytic Ag deposition ($R_{Ag}$) as a function of $Ti^{3+}$ density of HyCOM samples.

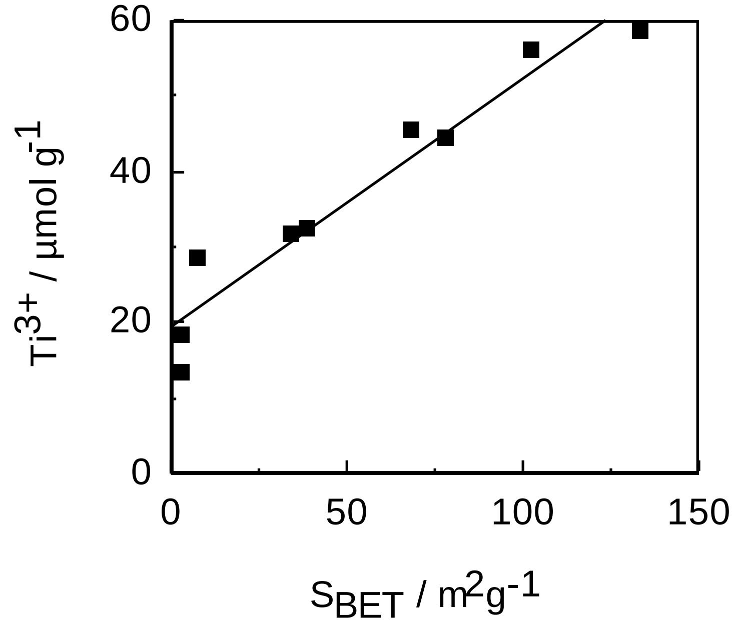
Figure 5 Rate of photocatalytic Ag deposition ($R_{Ag}$) as functions of amount of adsorbed $Ag^+$ ($[Ag^+]_{ads}$) on HyCOM-A(973) (open) and P-25 (closed) ~~in the multi-point plot~~.

Figure 6 The plots of $k_r/k_e$ ratio of HyCOM samples calcined at various temperatures as a function of their BET surface area ($S_{BET}$).

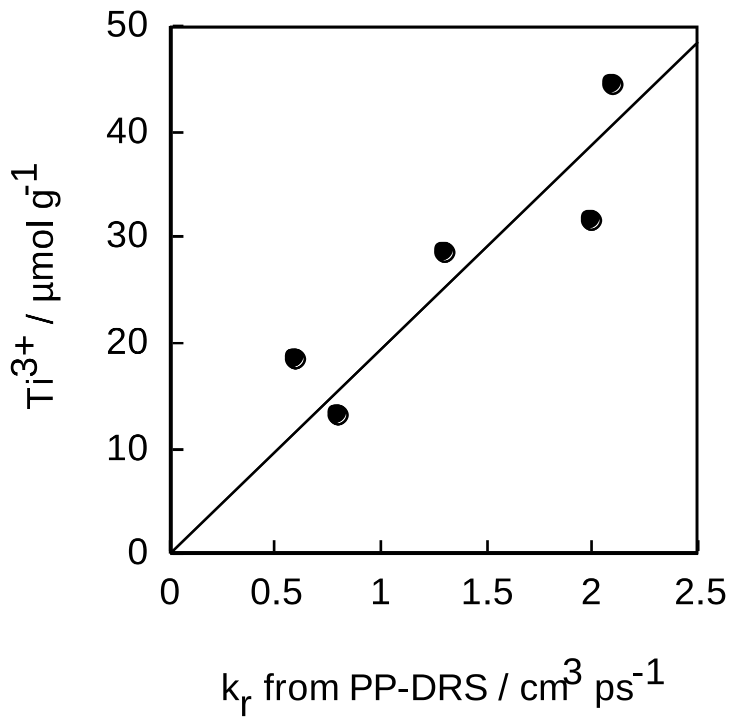
Figure 7 Correlation between $Ti^{3+}$ density and logarithm of $k_r/k_e$ ratio of HyCOM samples calcined at various temperatures.




Murakami et al. Fig. 1




Murakami et al. Fig. 2

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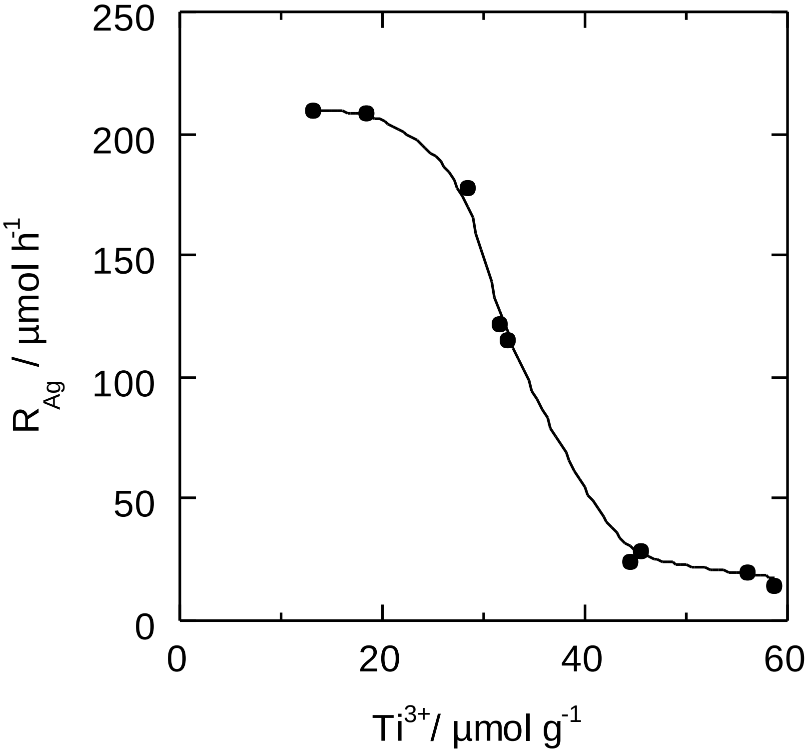
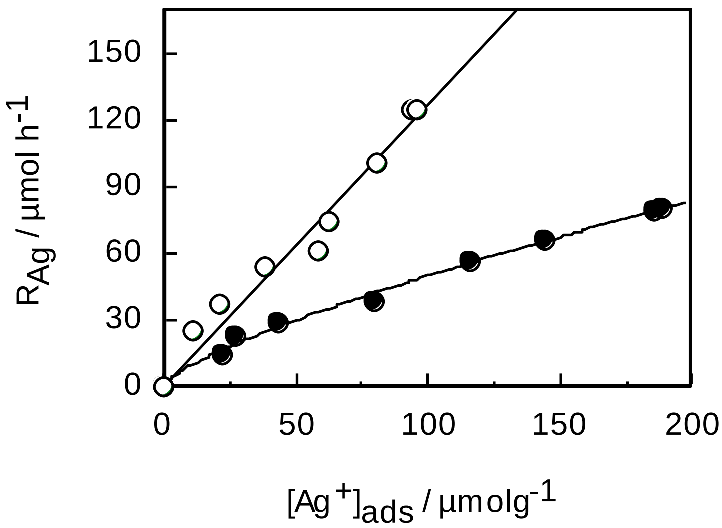
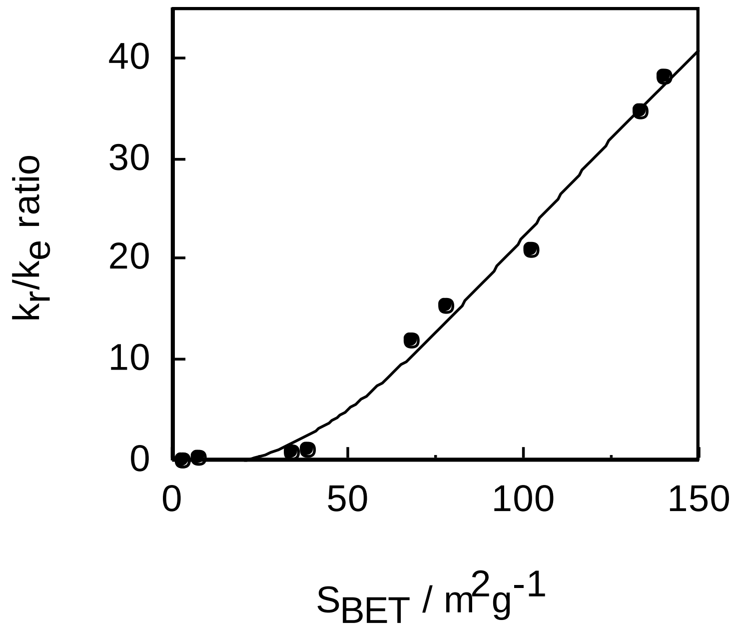


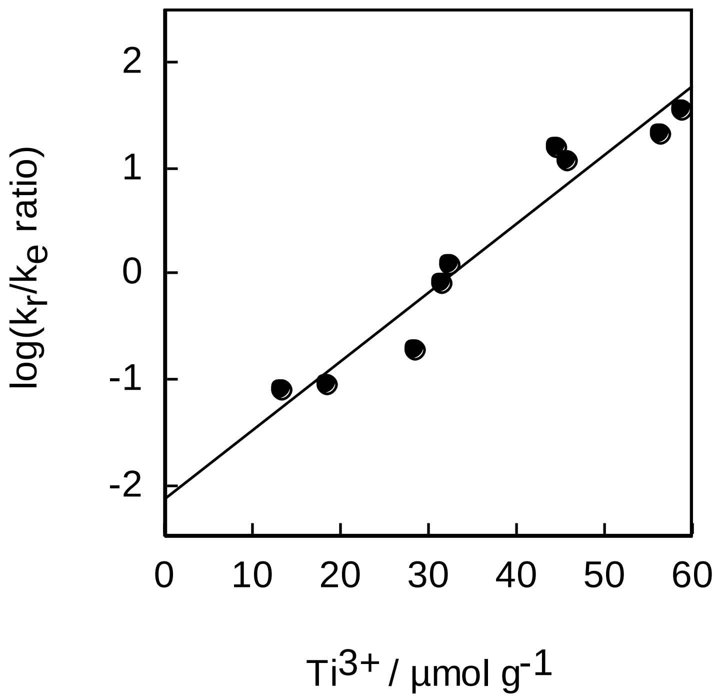

Murakami et al., Fig. 4




Murakami et al Fig. 5




Murakami et al. Fig. 6




Murakami et al., Fig. 7