

Anatase-phase titania: preparation by embedding silica and photocatalytic activity for the decomposition of trichloroethylene

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Abstract

Nanophase titania particles were prepared by the sol–gel process using two different precursors; titanium isopropoxide (TTIP) and titanium ethoxide (TEOT). Silica-embedded titania particles were also prepared from TEOT and tetra-ethyl-ortho-silicate (TEOS). In the case of nanophase titania particles prepared from TTIP, the rutile/anatase mixed phase had higher photoactivity than the pure anatase in the decomposition of TCE. However, in the nanophase titania prepared from TEOT, the photoactivity was increased with the heat treatment temperature until rutile phase began to be formed. The surface area was decreased with the heat treatment temperature. The photoactivity of the pure anatase titania prepared from TEOT was higher than that of Degussa P25 and the anatase/rutile mixed titania prepared from TTIP. Therefore, we concluded that, in order to achieve high photocatalytic activity, it was important to prepare titania particles at high temperature, preferably without forming rutile phase but not necessarily. This conclusion was confirmed by the experimental result that the silica-embedded titania particle of pure anatase phase had higher photoactivity than that of Degussa P25 and the pure anatase titania prepared from TEOT. The embedding of small amount of silica into anatase titania matrix enhanced the thermal stability of nanophase titania particle resulting in the suppression of the phase transformation from anatase to rutile phase. This thermal stability enables us to calcine the silica-embedded particles at higher temperature without accompanying the phase transformation and to reduce the bulk defects, which are responsible for the low photocatalytic activity. ©1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

To design a photocatalyst of improved photoactivity, it is necessary to understand the basic mechanism of electron–hole pair generation and its destiny. When the photocatalyst is illuminated by the light higher than its band gap energy, electron–hole pairs are generated. A portion of these photoexcited electron–hole pairs diffuses out to the surface of photocatalyst and participates in the chemical reaction with electron donor and acceptor. The excess electron–hole pairs are consumed through the surface or volume recombination process. To achieve the high photoactivity, it is essential to suppress the recombination process and to increase the lifetime of separated electron–hole pairs, so that fast electron transfer occurs from the surface to the adsorbed intermediates [1,2].

There are several variables that affect the photoactivity; preparation method, particle size, reactive surface area, in-

cident light intensity, crystal structure and pH of solution [3,4]. The crystal structure and crystallinity of titania particles are important factors that determine photoactivity. Many researchers reported that the anatase titania is more reactive than the rutile one [5–7]. Ohtani et al. reported the photoactivity of amorphous titania was negligible due to recombination of photoexcited electron–hole pairs at defects located on the surface and in the bulk of particles and increased linearly with the weight fraction of anatase and further improved by calcination of completely crystallized powder [8]. Nishimoto et al. reported that the photocatalytic activity of titania particles prepared by the hydrolysis of titanium tetraisopropoxide is strongly dependent on the heat treatment temperature [5]. Fotou et al. prepared titania particles using a flame reactor and reported that the anatase phase titania containing small amount of rutile phase had higher photoactivity than that of pure anatase for the decomposition of phenol and salicylic acid [9].

Nanophase titania is prepared frequently by sol–gel process and gas-phase synthesis in a flame reactor [3,7,10]. There always exist structural defects on the surface and

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inside the titania particles [11]. These structural defects are related with the destiny of photoexcited electrons. Surface defects are good for high photoactivity because they are used as an active site on which the electron donor or acceptor is adsorbed. However, the bulk defect lowers the photoactivity because they provide sites for the recombination of the photogenerated electrons. According to electron spin resonance (EPR) spectroscopic study, the photoexcited electrons trap at surface Ti^{3+} sites or Ti^{4+} sites within the bulk and holes trap at lattice oxygen ions [12–14]. Therefore, the bulk defect should be reduced to get high photoactivity. In general, the reduction of bulk defects is achieved by high temperature calcination. Unfortunately, the anatase phase is metastable and transformed to rutile one when the calcination temperature is over about $500^{\circ}C$ [15]. In addition, the surface area is reduced dramatically during the high temperature calcination. Considering the effect of bulk defects or the result of Ohtani et al. [8] and Nishimoto et al. [9], it is expected that titania particles calcined at higher temperature without transforming anatase phase to rutile phase could show a higher photoactivity. Viswanath et al. prepared a titania–silica nanocomposite by a sol–gel method [16]. The composite (titania/silica = 80/20) has pure anatase phase even though the calcination temperature was $900^{\circ}C$. From Viswanath report, the mixing of silica with titania enhances the thermal stability of titania particle resulting in suppressing the phase transform from anatase to rutile.

In this work, two different titanium precursors, TTIP and TEOT, were used to prepare nanophase titania particles by the sol–gel method and to investigate the effect of the crystal structure and surface area on the decomposition of trichloroethylene (TCE). The crystallinity and the rutile/anatase ratio were controlled by changing the calcination temperature. Silica-embedded titania particle, in which silica or silicon was dispersed into anatase titania particle, was also prepared to increase the thermal stability. The high thermal stability makes it possible to treat the prepared particles at higher temperature, resulting in the increase of crystallinity and the reduction of the bulk defects of nanophase titania particle.

2. Experimental

2.1. Materials

Titanium ethoxide ($Ti(OC_2H_5)_4$, Ti-20% Aldrich), and titanium isopropoxide (TTIP, 97% Aldrich), were used as a precursor of titania. Tetraethylorthosilicate (TEOS, 98% Aldrich) was used as a precursor of silica. The ratio of alkoxide to water, HCl, and alcohol (Et-OH or Pr-OH) was summarized in Table 1.

2.2. Preparation of nanophase titania and silica-embedded titania particles

For the preparation of pure titania particle, each precursor was added into the premixed solution of water, HCl, and the

Table 1

Preparation conditions of titania and silica-embedded titania

Precursor	^a H ₂ O/M ⁺	^a HCl/M ⁺	^b Alcohol/M ⁺
TTIP	193.8	0.3	1.6
TEOT	100	0.2	1
TEOT/TEOS = 49 and 25	156	0.2	1

^a Molar ratio.

^b Propanol for TTIP precursor and ethanol for TEOT precursor.

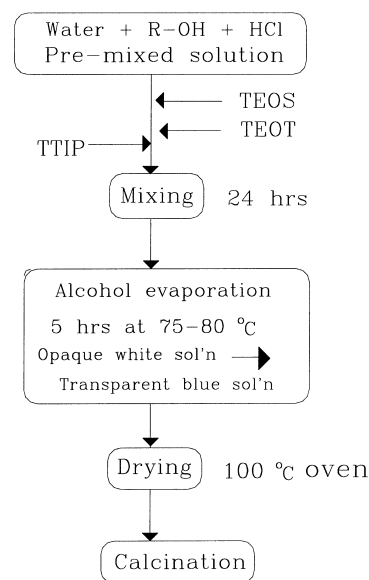


Fig. 1. Schematic diagram for the preparation procedure of nanophase titania and silica-embedded titania by the sol–gel process.

corresponding alcohol at the room temperature. This solution was mixed for 24 h to obtain titania sol and heated at 75 to $80^{\circ}C$ for 5 h to removal the alcohol. The alcohol-removed titania sol was dried in an oven at $100^{\circ}C$ and calcined between 300 to $600^{\circ}C$. The silica-embedded titania particle was prepared by the same procedure for the pure titania particles. The only difference is the addition of TEOS precursor into the premixed solution in the first step to pre-hydrolyze the TEOS to form Si-OH groups. After the hydrolysis, TEOT was slowly added. The obtained silica-embedded titania xerogel was calcined between 400 to $800^{\circ}C$. The mole fraction of silicon was changed from 0.02 to 0.04. The schematic diagram for the preparation process is summarized in Fig. 1.

2.3. Analysis

The major phase of the obtained particles was analyzed by Rigaku D/MAX-III (3 kW) diffractometer using Cu Ka ($\lambda = 0.1506$ nm) radiation. Crystallite size of the prepared particles was determined from the broadening of the anatase main peak at $2\theta = 25.3^{\circ}$ by the Scherrer equation. In this report, the crystallite size of anatase phase was used as a measure of the crystallinity of titania. The percentage of rutile phase was calculated by the following equation [17].

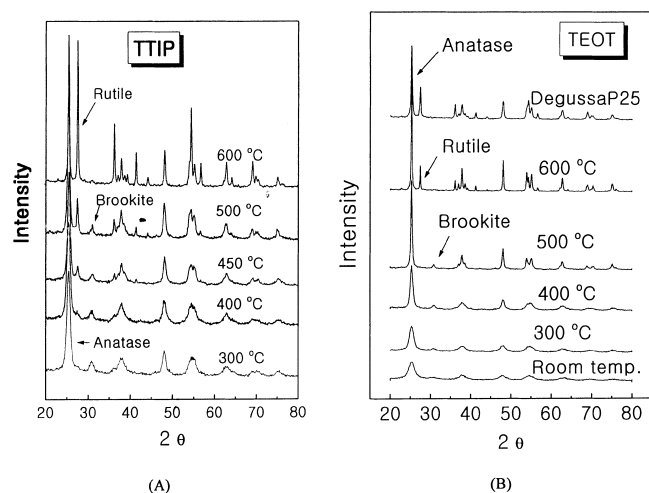


Fig. 2. XRD Patterns of titania particles prepared by the sol-gel process form the precursor TTIP (A) and TEOT (B).

$$\% \text{ Rutile} = \frac{1}{((A/R)0.884 + 1)} \times 100$$

where, A and R are the peak area for the major anatase ($2\theta = 25.3^\circ$) and rutile phase ($2\theta = 27.5^\circ$), respectively.

Surface areas were calculated using nitrogen adsorption method at 77 K and BET analysis. FT-IR spectra of Silica-embedded titania particles were recorded by the Bomem MB-100 spectrometer using the KBr wafer technique.

2.4. Activity test for the decomposition of trichloroethylene (TCE)

The prepared titania or silica-embedded titania particles (1 g) was dispersed in 1.3 l purified water. Semi-circulation batch reactor with annular shape was used. The initial concentration of TCE was 95.7 ppm. The solution, which contained the titania or silica-embedded titania particles, was irradiated by ultraviolet light with the wavelength ranges from 300 to 400 nm. The TCE concentration was monitored by Cl^- electrode (Orion, model 96-17B) as a function of reaction time. This electrode was calibrated with hydrochloric acid (HCl) to account automatically for the relative pH decrease observed during chloride evolution. Degussa P25 titania particle was chosen as a reference to evaluate the photoactivity of prepared particles for the decomposition of TCE.

3. Results and discussion

3.1. Nanophase titania prepared from TTIP and TEOT

3.1.1. Crystal phase and crystallite size

Fig. 2 is XRD patterns of the pure titania particles prepared by the sol-gel process. The major phase of all the

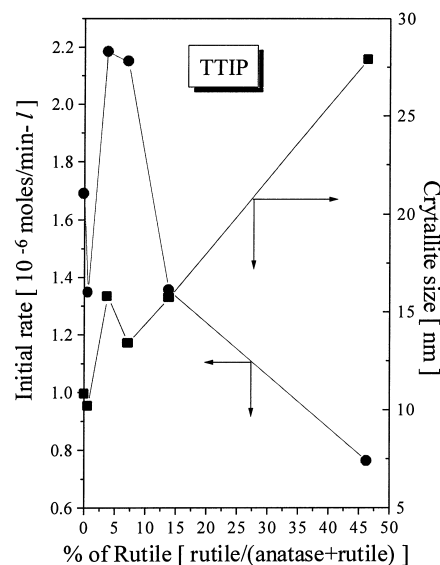


Fig. 3. Initial rates for the decomposition of TCE and the crystallite size as a function of the percentage of rutile phase for nanophase titania particle prepared from TTIP precursor.

prepared particles was anatase. For titania particles prepared from TTIP, rutile peak was observed over 400°C . Brookite phase existed up to 500°C and disappeared at 600°C as shown in Fig. 2(A). For titania particles prepared from TEOT, no rutile peaks were observed up to 500°C . Brookite phase existed as a minor phase and disappeared at 600°C as shown in Fig. 2(B). The heat-induced growth of crystallite of titania particles contributes to the increase of crystallinity because higher ordering in the structure of titania particles makes X-ray peak to be sharper and more narrow. The crystallinity of all the prepared particles was increased with increasing the calcination temperature. The crystallite size and percentage of rutile phase for all the prepared particles were summarized in Table 2. All the prepared particles have nanophase.

3.1.2. Effect of heat treatment temperature, BET surface area, and rutile/anatase ratio on the decomposition of TCE

Fig. 3 is the initial rates as a function of rutile/anatase ratio for the decomposition of TCE by nanophase titania particles prepared from TTIP precursor. The change of crystallite size was also plotted in Fig. 3 as a function of rutile/anatase ratio of nanophase particle. The initial rate has a maximum point with the change in the rutile/anatase ratio. Up to ca. 10% of the rutile/anatase ratio, the change of photoactivity was linearly dependent on crystallite size. If the rutile/anatase ratio, however, was over 10%, the photoactivity was dramatically reduced even if the crystallinity was increased. Bickley et al. reported that Degussa P25 consists of three phase such as anatase, rutile, and amorphous [18]. They concluded that the photoactivity of the mixed phase of titania was greater than pure anatase crystalline. Fotou et al. also reported that the anatase titania containing some rutile is most reactive in destroying phenol [9]. In the case of titania particle pre-

Table 2
Crystallite size and percent of rutile phase of nanophase titania and silica-embedded titania particles

Calcination Temperature (°C)	TiO ₂		TiO ₂	
	TEOT	TTIP	TEOT	TTIP
	Crystallite size (nm)	% of rutile	Crystallite size (nm)	% of rutile
300	8.4	0	7.1	0
400	12.1	0	10.2	0.63
450	—	—	13.4	7.21
500	23.1	0	15.7	13.9
600	39.6	13.5	27.9	46.45
	SiO ₂ embedded TiO ₂			
	Ti/Si = 49 (2 at % of Si)		Ti/Si = 25 (3.9 at % of Si)	
400	9.4	0	8.8	0
500	12.0	0	10.4	0
700	22.0	2.6	18.9	0
800	26.4	27.4	21.0	5.2

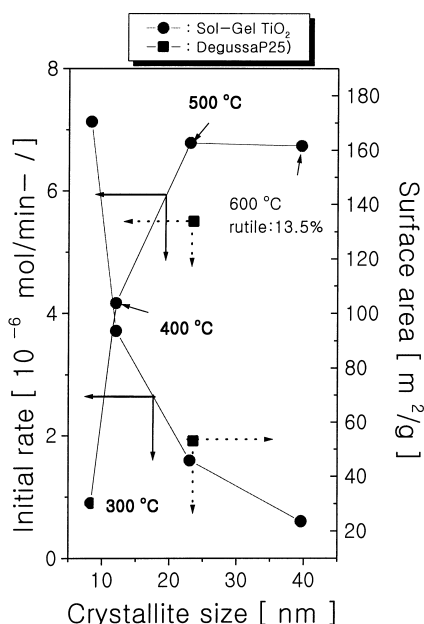


Fig. 4. Initial rates for the decomposition of TCE by titania particles prepared from TEOT precursor and BET surface area as a function of crystallite size.

pared from TTIP, the anatase/rutile mixed titania has higher photoactivity than that of pure anatase titania and this result is consistent with Fotou's or Bickley's results.

Fig. 4 is the initial rates and BET surface area of titania particles prepared from TEOT precursor by the sol-gel method as a function of the crystallite size. The photoactivity of nanophase titania particle was increased with increasing its crystallinity although the surface area is reduced dramatically. The rectangular-shape legend in Fig. 3 is the initial rate and BET surface area of Degussa P25 titania particle. This result indicates that the crystallinity is more important than the surface area of titania particles, of which result is consistent with Nishimoto's and Tanaka's results [5,7].

Nanophase titania particles prepared from TEOT precursor by the sol-gel method and calcined at 500°C for 5 h had higher photoactivity than that of Degussa P25 although its surface area is smaller than that of Degussa P25. Comparing the photoactivity of nanophase titania calcined at 400°C with that of Degussa P25, the initial rate of the sol-gel titania is smaller than that of Degussa P25, although the surface area of the sol-gel titania particle is larger than that of Degussa P25. It should be noted that the pure titania particles prepared from TEOT had higher photoactivity than that of Degussa P25 and nanophase titania prepared from TTIP, which have rutile/anatase mixed phase. The photoactivity of titania prepared with TEOT precursor was saturated with increasing the crystallinity because of the reduction of the surface area and the formation of rutile phase. From this observation, we hypothesized that the increase of crystallinity by treating the sample at high temperature without forming rutile phase was important to get high photoactivity. This hypothesis lead us to the conclusion that if the phase transformation of anatase to rutile was suppressed by modifying titania particles, higher heat treatment could be possible and the photoactivity could be enhanced.

3.2. Silica-embedded titania prepared from TEOT

3.2.1. XRD and FT-IR spectra analysis

For silica-embedded titania particle, no significant rutile phase was observed although the calcination temperature was over 700°C as shown in Fig. 5. The prepared particles had pure anatase phase without brookite phase for all calcination temperatures. No peak for the silica crystal phase was observed at all calcination temperatures. This high temperature treatment is expected to effectively reduce the density of bulk defects in silica-embedded titania particles leading to the higher crystallinity than that of the pure nanophase titania particles, since the bulk defect is much easier to diffuse to the surface at the high calcination temperature.

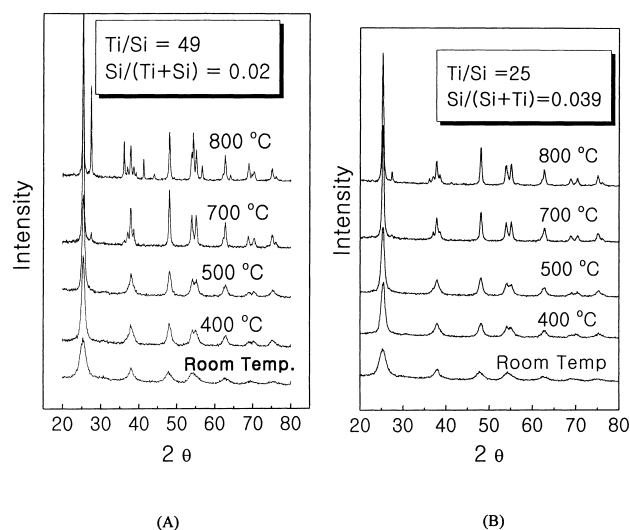


Fig. 5. XRD patterns of silica-embedded titania prepared by the sol-gel process; (A) Ti/Si = 49, (B) Ti/Si = 25.

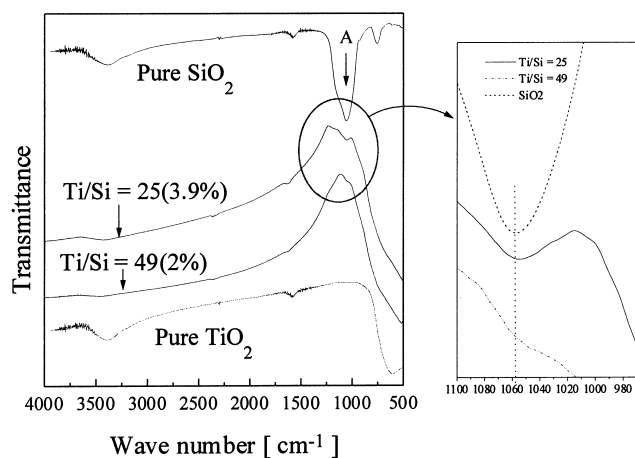


Fig. 6. FT-IR spectra of silica-embedded titania prepared by the sol-gel method.

The crystallite size of silica-embedded titania particles was shown in Table 2. All the prepared particle was nanophase.

Fig. 6 is the FT-IR spectra of silica-embedded titania particles calcined at 800°C. The Si-O-Si asymmetric stretching band (the A position in Fig. 6) was observed, whereas the Si-O-Ti peaks were not observed. From the XRD pattern and the FT-IR spectra, we conclude that amorphous silica phase exists as segregated phase in the matrix of anatase phase titania.

3.2.2. Photoactivity for the decomposition of TCE

The photoactivity of the silica-embedded titania particles was shown in Fig. 7 as a function of crystallite size. For the nanophase particle, in which 2 at.% of silicon was contained, the dependency of photoactivity on the crystallinity was similar to that of pure nanophase titania particles prepared from TEOT precursor. In case of 3.9 at.% silica-embedded titania,

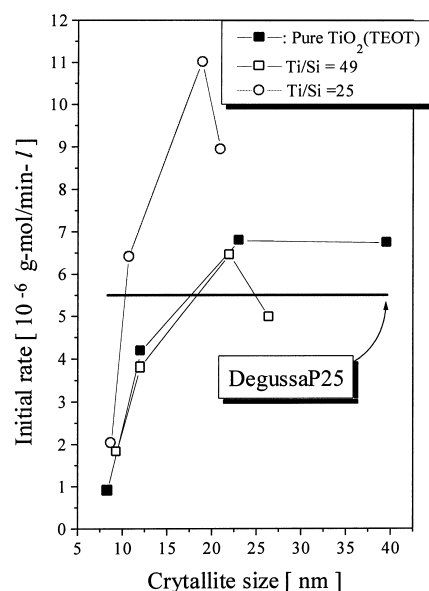


Fig. 7. Initial rates for the decomposition of TCE by SiO₂-embedded TiO₂ particle prepared by sol-gel process.

the photoactivity was increased dramatically. Formation of the segregated amorphous silica phase in the anatase phase titania suppressed the phase transformation of nanophase titania particle from anatase to rutile one as shown in Fig. 5 as well as suppressing the growth of anatase crystallite. The reduction of the bulk defect and the increase of crystallinity of anatase phase at the calcination temperature over 700°C leads to the high rate of electron diffusion to the surface by suppressing the electron-hole recombination. Therefore, the embedding of amorphous silica phase in nanophase titania enhanced the photoactivity for the decomposition of TCE. One should notice the relationship between the crystallite size and its corresponding photoactivity. In the Fig. 7, it seems that greater crystallite size of titania and silica-embedded titania leads higher photoactivity for the decomposition of TCE. However, the increase of photocatalytic activity is not due to the increase in the crystallite size of pure titania or silica-titania particles, because the greater crystallite size does not absolutely mean higher crystallinity. The higher photoactivity of silica-embedding titania is due to higher heat treatment without the formation of rutile phase resulting in the production of anatase phase of high crystallinity and effectively reducing the bulk defects which serve as the recombination centers [8]. This result gives us a guideline to increase the photoactivity of nanophase titania. If one uses some additive like silica in this work to suppress the phase transformation of titania particles from anatase to rutile and enable to calcine the titania particles at much higher temperature, the photoactivity is supposed to be enhanced.

The photoactivity of silica-embedded titania particles had a maximum point with increasing the calcination temperature because of the formation of rutile phase. This result is

another evidence that the formation of rutile phase with the fully crystallized anatase titania particles is not effective for the photoactivity. Therefore, it is critical for high photoactivity to increase the heat treatment temperature leading high crystallinity of anatase titania without forming rutile phase.

4. Conclusions

Nanophase titania particles were prepared by the sol–gel process using two different precursors, titanium isopropoxide (TTIP) and titanium ethoxide (TEOT). Silica-embedded titania was also prepared from tetra-ethyl-ortho-silicate (TEOS) as silicon source and TEOT as titanium source. In case of nanophase titania particles prepared from TTIP, the rutile/anatase mixed phase titania had higher photoactivity than pure anatase one in the decomposition of TCE. This result is consistent with that of Fotou et al. [9] and Bickley et al. [18]. However, in the nanophase titania prepared from TEOT, the photoactivity was increased with the heat treatment temperature until rutile phase began to be formed, although the surface area was decreased with temperature. The photoactivity of pure anatase titania particles prepared from TEOT by the sol–gel method was higher than that of anatase/rutile mixed titania prepared from TTIP and Degussa P25. From this result, it was concluded that the heat treatment at high temperature without forming rutile phase is a key to the high photocatalytic activity due to the increase of crystallinity and the reduction of bulk defects.

From the result of XRD and FT-IR spectra, the prepared silica-embedded titania particle had the structure that amorphous silica was embedded into anatase titania matrix. The embedding of small amount of silica into anatase titania matrix enhanced the thermal stability of nanophase titania particle resulting in the suppression of the phase transformation from anatase to rutile phase. This thermal stability enables us to calcine the silica-embedded particles at higher temperature without accompanying the phase transformation and to reduce the bulk defects, which are responsible for the low photocatalytic activity. Therefore, the silica-embedded titania particle of pure anatase phase had higher photoactivity than that of pure titania prepared from TEOT by the sol–gel method and Degussa P25.

The results in this work give us a guideline to prepare the photocatalyst with high photoactivity. If one uses some additive like silica in this work to suppress the phase transformation of titania particles from anatase to rutile and enable to calcine the titania particles at much higher temperature, the photoactivity is supposed to be enhanced.

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