

Characterization of Various TiO₂ Powders Used for Complete
Decomposition of Organic Wastes by Means of Thermally
excited Holes at High Temperatures

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Disposal of organic wastes is a social problem of high importance. We previously reported on a decomposition system of organic wastes by the use of thermally excited holes in TiO₂ at high temperatures. An appealing feature of our system is that it makes use of a great number of holes formed at, for example, 350°C. In the present investigation, characterization has been carried out on various TiO₂ powders that have nearly the same composition but differ in specific surface and particle size in an attempt to screen and select the most powerful powder. The decomposition ability of TiO₂ has been evaluated using previously investigated polycarbonate (PC)-coated TiO₂ as the model system, with special attention to the interaction between the adsorbate (PC) and the adsorbent (TiO₂). As a result, the specific surface was found to play the most important role, and is closely linked to the adsorption amount of PC on TiO₂, released energy, spin concentration, deep coloration, as well as to the Raman peak-shift. In addition, the crystallinity is also found to be effective in connection with the lifetime of holes.

KEYWORDS: Titanium Dioxide, Thermal Excitation, Oxide Semiconductor, Exhaust

Introduction

Disposal of organic wastes is a social problem of high importance. We previously reported on a complete decomposition system of polycarbonates (PC: used as substrates for optical disks) that utilizes thermally excited holes in TiO₂ at high temperatures (Mizuguchi, 2001; Mizuguchi and Shinbara, 2004; Shinbara *et al.*, 2005). The present system is based upon the powerful oxidation ability of holes which is nearly equivalent to that of hydrogen peroxide. The above investigation was initiated in view of the serious problem of how to dispose of used optical disks. Furthermore, we have extended our system to all kinds of thermoplastic resins and thermosetting polymers (Shinbara *et al.*, 2005), as well as to benzene, toluene, and particulate matter contained in the exhaust of diesel engines (Makino *et al.*, 2007). An appealing feature of our system is that it makes use of a great number of holes formed at, for example, 350°C.

Our decomposition system is similar to a photocatalytic system that makes use of photogenerated holes for the oxidation decomposition of various substances. However, our system differs distinctly in the utilization of thermally excited holes at high temperatures (for example, at about 350°C) in combination with a molten state of PC, as shown in **Figure 1**. A large number of charge carriers are available in TiO₂ at high temperatures as shown by the product of the Fermi-Dirac distribution function and the density of states (Kittel, 1986). The number of carriers at room temperature (RT) and 350°C [$n_{RT} = n_0 \exp(-E_g/2kT_{RT})$ and $n_{623K} = n_0 \exp(-E_g/2kT_{623})$, respectively] gives a ratio of $n_{623K}/n_{RT} \approx 8.8 \times 10^{13}$, where $E_g = 3.2$ eV. This number approximately was confirmed in our previous experiment based on the single crystals of TiO₂ of the rutile phase (Shinbara *et al.*, 2005). The initial process of the PC decomposition is the formation of radicals in PC caused by thermally generated holes, followed by their propagation throughout the material to break up PC into fragments, resulting in their complete combustion with oxygen to yield H₂O and CO₂ (Shinbara *et al.*, 2005).

We have also shown that any semiconductor can basically work as an alternative for TiO₂, provided that they are stable in air at high temperatures. Among these, TiO₂ is found to be still the best material at present. It is then indispensable to screen and select the most powerful TiO₂ powders in order to optimize our decomposition system. For this reason, an attempt has been made in the present investigation to characterize some representative TiO₂ powders with the method described below.

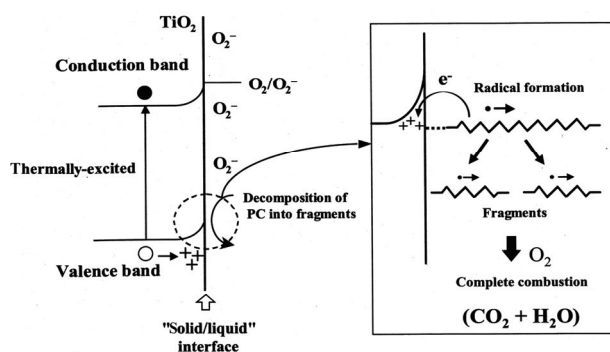
1. Screening Method of TiO₂ Powders

Since the powders with large specific surface are only available in the anatase form, our experiments were carried out with this phase form, while one sample of the rutile form was also used as a reference. The test powders were selected in consideration of the specific surface and the particle size of nearly the same composition. The TiO₂ powders of ST-01, ST-21, and ST-41 of the anatase form (Ishihara Sangyo Kaisha Ltd., (ISK)) were found to meet the requirement. TTO55N of the rutile phase from ISK was also employed as a reference. These attributes are listed in **Table 1**.

Table 1 Attributes of various of TiO₂ powders

TiO ₂	Crystalline phase	Particle size [nm]	Purity [wt%]	Specific surface [m ² /g]	
				Before calcination	After calcination
ST-01	anatase	7	93.9	278	96
ST-21	anatase	20	97.9	62	57
ST-41	anatase	200	99.4	10	9.8
TTO55N	rutile	63	98.4	42	39

To test the decomposition ability of the TiO₂ powder, PC-coated TiO₂ (Mizuguchi, 2001) were used to evaluate the degree of PC decomposition by thermally generated holes in TiO₂. Since the adsorption (or adhesion) of PC on the TiO₂ surface is the primary process for the decomposition by holes, the adsorption amount and the released energy (i.e., exothermic energy) due to PC decomposition were studied by thermogravimetric analysis and differential scanning calorimetry, respectively. In parallel, the adhesion force of PC on TiO₂ was evaluated by Raman spectra. Furthermore, the radical concentration in PC-coated TiO₂ was also measured by ESR since the radicals initiate the PC decomposition (Figure 1).

**Fig. 1** Decomposition process of PC at the “TiO₂/PC” interface by means of thermally-generated holes

2. Experiment

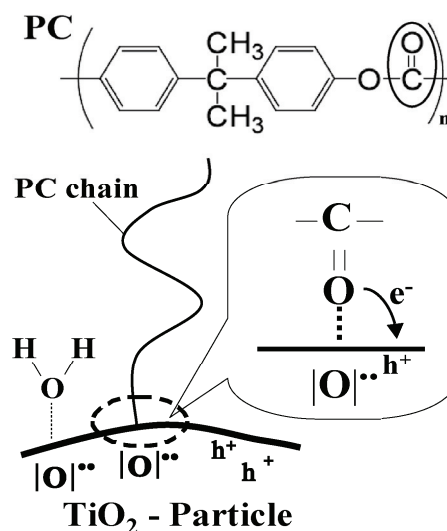
2.1 Materials

ST-01, ST-21, and ST-41 of the anatase phase as well as TTO55N of the rutile phase were obtained from Ishihara Sangyo Kaisha Ltd. (ISK) (Table 1). All powdered samples were calcinated before use in air at 500°C for 1 h unless otherwise stated. The specific surface was reduced on the initial calcination, but no further change was observed for subsequent thermal cycles. Polycarbonate (AD-5503; $M_w = 18000$) was purchased from Teijin Ltd.

2.2 Preparation of PC-coated TiO₂ powders

PC-coated TiO₂ was prepared as follows: 3 mg of polycarbonate was dissolved in 60 mL of toluene at 110°C, followed by addition of 30 mg of TiO₂ powder. The powder

was dispersed in an ultrasonic bath for 3 h and the suspension was then filtered and dried in air for several hours. It is remarkable to note that ST-01, ST-21 and ST-41 turned immediately dark yellow, light yellow and faint yellow upon PC-coating, respectively. The coloration is due to the holes accumulated at the surface of TiO₂ at room temperature (Figure 1) and has been attributed to the formation of a yellowish quinoid which is an oxidation product of stabilizers contained in PC (Mizuguchi, 2001). The deepness of the color is a measure of the number of holes accumulated at the powder surface. Electron capture from PC by holes at the TiO₂ surface is assumed to proceed as shown in **Figure 2**, which shows the adsorbed state of PC and water moisture in air on the TiO₂ surface. The adsorption sites are assumed to be oxygen vacancies in non-stoichiometric Ti_{1+x}O₂ that are positively charged relative to the surrounding (Hauffe and Morrison, 1974; Morrison, 1975). Then, the negatively polarized oxygen atom of the carbonyl group of PC, or of water moisture are electrostatically adsorbed on the oxygen deficient sites of TiO₂.

**Fig. 2** Schematic representation of the adsorption of water moisture, acetone and PC on the oxygen deficient sites ($|O|\cdot$) of TiO₂: $|O|\cdot \dots O^{\delta-} H_2^{\delta+}$, or $|O|\cdot \dots O^{\delta-} = C^{\delta+}$

2.3 Equipment for measurements

A TGA 8120 and DSC 8230 from RIGAKU Corp. were used for measurements of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in air, respectively. The heating rate was 10°C/min in both measurements. Raman spectra were measured using an NRS-3100 laser Raman spectrophotometer from JASCO Corp. Measurements of electron spin resonance (ESR) were carried out using a JES-FA200 from JEOL Ltd. ESR signals were corrected by Mn markers and the radical concentrations were estimated on the basis of the concentration of α, α' -diphenyl- β -picrylhydrazyl (DPPH) used as the reference. A quadrupole mass spectrometer (model: RG-102 from ULVAC, Inc.) was used for gas analysis.

3. Results and Discussion

3.1 PC adsorption on TiO₂ and released energy due to PC decomposition as measured by TGA/DSC

The amount of PC in PC-coated ST-01, ST-21 and ST-41 was measured by means of TGA. **Figure 3** shows the adsorbed amount of PC as a function of specific surface. The adsorbed amount of PC is linearly proportional to the specific surface. **Figure 4** illustrates the exothermic energy vs specific surface as measured by DSC. The released energy due to PC decomposition increased linearly with the specific surface. This result clearly indicates that the specific surface (i.e., adsorbed PC-quantity) plays an extremely important role in the decomposition ability of TiO₂. However, the temperatures for the exothermic peaks are distinctly different as shown in **Figure 5** for “PC/ST-01 (349°C) and PC/ST-21 (351°C)” and PC/ST-41 (431°C) (The exothermic energy of PC alone is negligibly small in the present temperature range (Mizuguchi, 2001).). This tendency is closely linked to the specific surface of TiO₂ which governs the reaction rate of PC decomposition occurring at the “TiO₂/PC” interface. As shown in Table 1, the specific surfaces of ST-01 and ST-21 are relatively large (96 and 57 m²/g, respectively), while ST-41 has an area of only 9.8 m²/g. This difference exerts a significant influence on the decomposition efficiency of TiO₂. Since ST-41 has a small specific surface, ST-41 is kinetically difficult to decompose all adsorbed PC on TiO₂ at about 350°C in DSC measurements when the temperature increases with a heating rate of 10°C/min. In other words, it requires more time to decompose all adsorbed PC at about 350°C. Therefore, the exothermic peak is displaced toward higher temperatures (ca. 430°C) where the number of thermally generated holes is greatly enhanced.

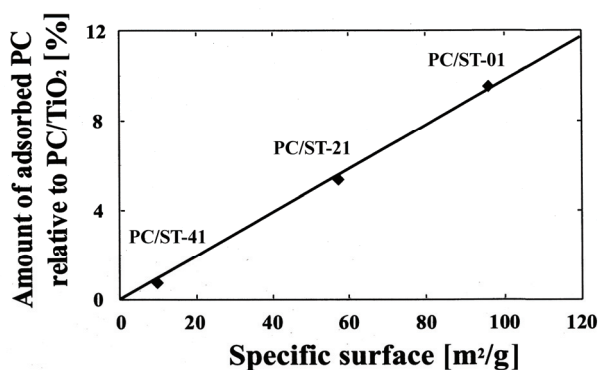


Fig. 3 Linear relation between the amount of adsorbed PC and the specific surface

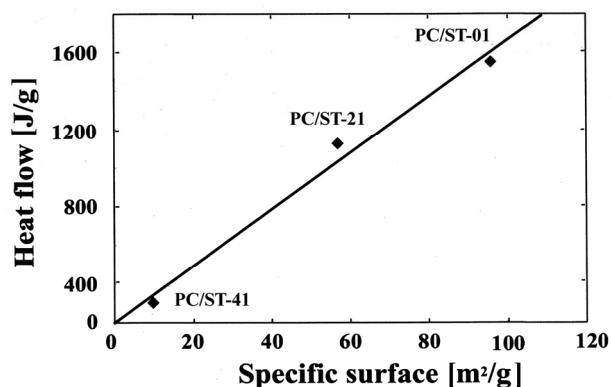


Fig. 4 Linear relation between the amount of exothermic energy and the specific surface

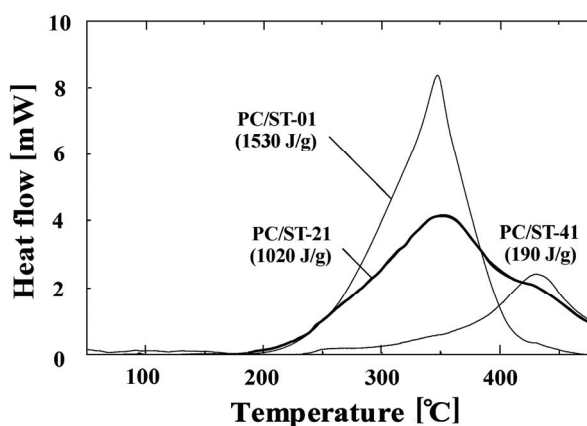


Fig. 5 DSC curves for PC/ST-01, PC/ST-21, and PC/ST-41

3.2 Radical concentration in PC/TiO₂ as studied by ESR

Figure 6 shows the radical concentration in PC/TiO₂ as a function of specific surface for PC/ST-01 (dark yellow), PC/ST-21 (light yellow) and PC/ST-41 (faint yellow). It is evident that the spin concentration increases as the color of PC/TiO₂ becomes deeper. Furthermore, the spin concentration of ST-01, ST-21 and ST-41 prior to the PC-coating was nearly at the same level as that of PC/ST-41. The radical concentration before PC-coating is mainly attributed to O₂⁻ adsorbed on the surface of TiO₂. The above result indicates that a great number of spins are formed in PC/ST-01 and PC/ST-21 upon PC-coating in proportion to the specific surface by means of thermally generated holes. On the other hand, the very low level of spin concentration of PC/ST-41 can again be attributed to the small specific surface.

3.3 PC adsorption on TiO₂ as observed by Raman spectra

As described in Section 2.2, the pure white powders of ST-01, ST-21 and ST-41 are colored upon PC-coating dark yellow, light yellow and faint yellow, respectively. Raman spectra were measured on these samples. **Figure 7(a)** shows a typical Raman spectrum of ST-01 prior to the PC-coating. This is basically in agreement with the reported spectrum of the anatase form (Ohsaka *et al.*, 1978; Krishnamurthy and Haridasan, 1979;

Balanchandran and Eror, 1982). However, we have newly observed that each Raman peak is slightly shifted due to PC-coating toward higher or lower wavenumbers relative to the reference peaks of ST-01, ST-21 and ST-41. **Figure 7(b)** shows one example of the peak-shift around 140 cm^{-1} (E_g mode) for PC/ST-01, PC/ST-21 and PC/ST-41 which are colored dark yellow, light yellow and faint yellow, respectively. The peak-shift suggests that the PC-coating disturbs, to some extent, the lattice vibration of TiO_2 and that the resulting peak-shift can be a measure of the extent of adhesion force of PC on TiO_2 . The peak of PC/ST-01 is displaced toward higher wavenumbers by about 10 cm^{-1} , followed by the peak of PC/ST-21. These peaks contain significant noise and also are characterized by the increased background as compared with that of each reference (ST-01, ST-21 and ST-41). This indicates that the PC-adsorption on TiO_2 makes the surface uneven, resulting in an increase of the scattering background. This suggests that the adhesion strength of PC on TiO_2 is relatively strong in PC/ST-01 and PC/ST-21 as assumed by chemisorption (Figure 2). On the other hand, the band of PC/ST-41 exhibits an extremely small peak-shift of about 0.6 cm^{-1} and the background level is not so much increased. This is presumably due to the small specific surface of ST-41 (Table 1). In other words, the peak-shift arising from PC-adsorption is, for the most part, buried by the bulk fraction of TiO_2 .

The above results indicate that the extent of the peak-shift in Raman spectra for PC/ST-01, PC/ST-21 and PC/ST-41 serves as a good measure of the PC-decomposition ability of TiO_2 , since the PC adsorption is the primary process for the subsequent decomposition by means of thermally generated holes. It is also to be noted that the extent of the peak-shift of PC/ST-01, PC/ST-21 and PC/ST-41 is approximately in accordance with the deepness of the coloration of PC-coated powders (dark yellow, light yellow and faint yellow, respectively), as well as the radical concentration as measured by ESR. However, the extent of the peak shift is not linear as compared with that of the specific surface (Figure 3) and the radical concentration (Figure 6). This is presumably due to the restoring force in lattice vibrations, which limits the displacement of atoms around the equilibrium point.

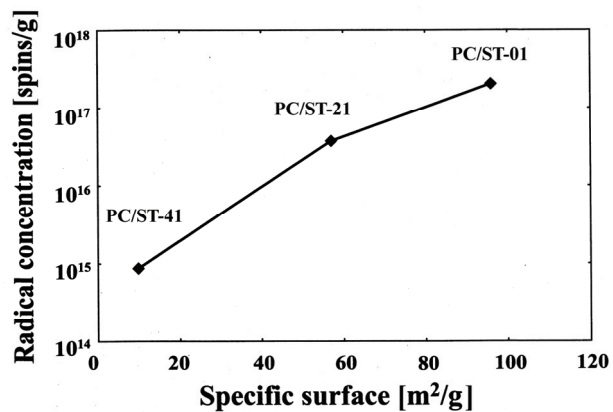
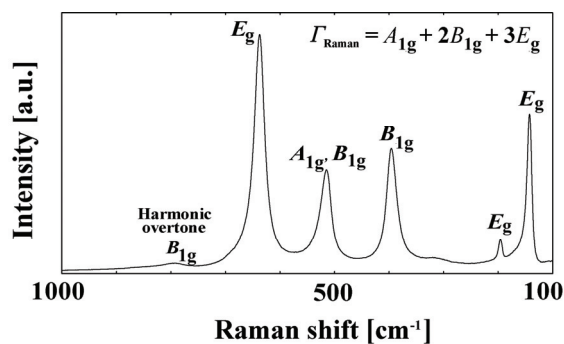


Fig. 6 Radical concentration of PC/ST-01, PC/ST-21, and PC/ST-41 as a function of specific surface

3.4 Calcination effect on the decomposition ability of TiO_2 powders

Upon thermal excitation of TiO_2 , the holes are generated throughout the particle. Therefore, those holes which are formed in the bulk must diffuse to the surface where the oxidation reaction takes place. For this reason, the diffusion length of the hole as determined by the carrier lifetime plays an important role in the decomposition ability of TiO_2 . The diffusion length is closely related to the purity as well as to the crystallinity of TiO_2 . Due to this, the calcination effect on the decomposition ability of TiO_2 has been investigated in both anatase and rutile phases: ST-01 (anatase) and TTO55N (rutile), respectively.

(a)



(b)

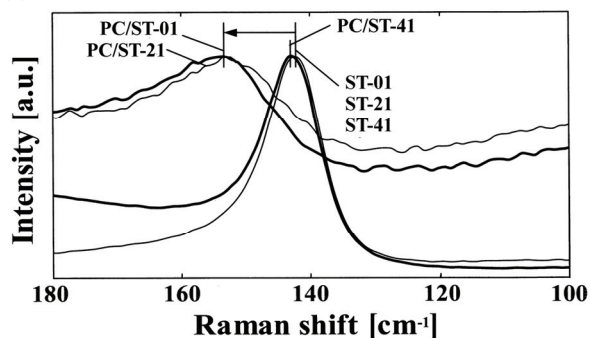


Fig. 7 (a) Raman spectra measured on ST-01, and (b) peak-shifts of the Raman spectra for PC/ST-01, PC/ST-21 and PC/ST-41 where ST-01, ST-21 and ST-41 are used as the reference, respectively

In ST-01, the specific surface reduces due to calcination from 278 to 96 m²/g at 500°C (Table 1). **Figure 8(a)** shows the DSC curves for PC/ST-01 before and after calcination. The total exothermic energy is reduced from 1748 to 1076 J/g. This indicates that the specific surface is reduced to about one-third while the exothermic energy is not so much reduced (nearly at a level of 60% of the initial value). On the other hand, calcination improves the crystallinity as shown in our previous report (Mizuguchi and Shinbara, 2004). This indicates that the reduction in exothermic energy due to the reduced specific surface is well compensated by the enhanced crystallinity. If we turn our attention to the exothermic energy per unit specific surface, this value changes due to calcination from 6.3 to 11.2 J/m², indicating that the decomposition ability of TiO₂ is greatly improved by calcination. This suggests that the reduction in specific surface due to calcination is not always a negative factor for the decomposition system, but can also be a positive factor.

On the other hand, no significant reduction in specific surface is recognized in TTO55N of the rutile phase: 42 to 39 m²/g (Table 1). **Figure 8(b)** shows the DSC curves for PC-coated TiO₂ before and after calcination. The exothermic energy is nearly the same before and after calcinations (265 and 233 J/g, respectively). The present result indicates that the rutile phase is quite stable for heat treatment and is appropriate for the stable operation of the decomposition process, although the specific surface is smaller as compared with that of ST-01.

3.5 Determinant factors on the decomposition ability of TiO₂ powders

On the basis of the series of experiments described above, the most influential factor on the decomposition ability of TiO₂ is evidently the specific surface of the powder. The decomposition ability is linearly increased with the specific surface (i.e., amount of PC adsorption). Furthermore, the energy released by PC/TiO₂ also increases with the amount of PC. In addition, the effect of the specific surface is clearly reflected in the spin concentration, the extent of coloration and the Raman peak-shift of PC-coated TiO₂ powders. Another important factor is the crystallinity of TiO₂ powders. Calcination improves the crystallinity and thus largely contributes to the decomposition ability of the powder, although the specific surface decreases due to calcination. This is an inverse relation. The above results allow us to conclude that ST-01 is the most appropriate TiO₂ powder for our decomposition system, although its crystallinity changes upon heat cycling.

It is, however, important to remember that the above conclusion has been drawn in our specific samples that possess nearly the same composition, but differ in specific surface and particle size. Our conclusion is not intended to indicate that the

powders with a large specific surface always exhibit good performance for the decomposition system.

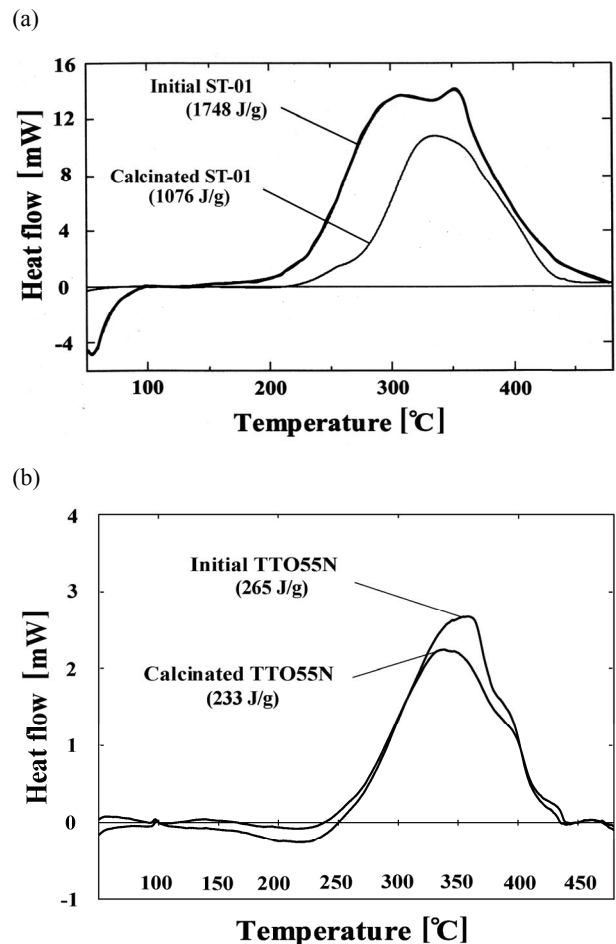


Fig. 8 DSC curves for PC-coated TiO₂ powders with and without calcination of TiO₂: (a) PC/ST-01 and (b) PC/TTO55N

Conclusions

Characterization has been carried out on various TiO₂ powders that possess nearly the same composition, but differ in specific surface and particle size, in an attempt to screen and select the most powerful powder for our decomposition system. The conclusions drawn from the present study can be summarized as follows.

1. The specific surface plays the most important role in the decomposition ability of TiO₂. This is directly linked to the amount of PC on TiO₂, released energy, higher spin concentration, deeper coloration and the Raman peak-shift of PC-coated TiO₂.
2. The crystallinity of TiO₂ powders is also an influential factor. Calcination improves the crystallinity and thus contributes to the increase in decomposition ability of TiO₂ per unit area, although the specific surface decreases due to calcination. This is an inverse relation.
3. ST-01 is the most of the powerful TiO₂ powders for our decomposition system at present, although its crystallinity

decreases upon heat cycling. The rutile phase is found to be stable for thermal cycles. Therefore, the rutile phase is more appropriate for the stable operation of our decomposition system, provided that the specific surface is equivalent to that of the anatase phase.

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