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**Selective Oxidation of Benzaldehyde Derivatives on TiO<sub>2</sub> Photocatalysts Modified  
with Fluorocarbon Group**

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Fluorocarbon groups were introduced onto surfaces of SiO<sub>2</sub>-covered TiO<sub>2</sub> particles (SiO<sub>2</sub>-TiO<sub>2</sub>). Oxidation of pentafluorobenzaldehyde on the surface modified TiO<sub>2</sub> powders proceeded much efficiently than that on SiO<sub>2</sub>-covered TiO<sub>2</sub> particles without surface modification. In addition, no enhancement of activity level of surface-modified SiO<sub>2</sub>-TiO<sub>2</sub> for oxidation of benzaldehyde was observed. The enhancement of the

surface-modified SiO<sub>2</sub>-TiO<sub>2</sub> is due to the interaction of F atoms between the substrate and fluorocarbon groups introduced on SiO<sub>2</sub>-TiO<sub>2</sub>.

**KEY WORDS:** photocatalysts; titanium dioxide; surface modification; SiO<sub>2</sub>-TiO<sub>2</sub>; fluorocarbon; interaction of F atom; selective oxidation

## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>)-mediated heterogeneous photocatalysis has attracted much attention recently because of its potential applications to decomposition of pollutants in water and air.[1-3] In many applications, anatase TiO<sub>2</sub> powders consisting of particles with large surface areas are used as photocatalysts. In addition to the importance of the crystal structures of TiO<sub>2</sub> powders for improving photocatalytic activity as described above, the properties of surfaces of TiO<sub>2</sub> particles are also important factors for determining their photocatalytic activity for degradation of organic compounds in aqueous media. Under photoirradiation, the surfaces of TiO<sub>2</sub> particles show a hydrophilic property.[4] This property prevents hydrophobic organic compounds from being adsorbed on the surfaces of TiO<sub>2</sub> photocatalysts in aqueous media. This

condition is a great disadvantage for degradation of organic compounds in aqueous media.

We have reported that the surfaces of TiO<sub>2</sub> particles were modified with hydrocarbon chains through Ti-O-Si bonds. The levels of photocatalytic activity of surface-modified TiO<sub>2</sub> particles is higher than that of TiO<sub>2</sub> particles without surface modification because the surfaces of TiO<sub>2</sub> particles become hydrophobic.[5] By taking these methods, we developed surface-modified TiO<sub>2</sub> powders having fluorocarbon chains and photocatalytic activities for oxidation of aldehydes (pentafluorobenzaldehyde and benzaldehyde) in aqueous media.

## **2. Experimental**

### *2.1. Materials and Instruments*

TiO<sub>2</sub> particles uniformly covered with porous silica (SiO<sub>2</sub>-TiO<sub>2</sub>; average pore size: 50Å; anatase phase, 15% of SiO<sub>2</sub> and 85% of TiO<sub>2</sub>; relative surface area: 170 m<sup>2</sup> g<sup>-1</sup>) were supplied by Taihei Kagaku Sangyo. Tridecafluoro-1, 1, 2, 2-tetrahydrooctyltrichlorosilane, benzaldehyde, and pentafluorobenzaldehyde were obtained from Wako pure chemical Industries Ltd. Other commercial chemicals were of

the highest available grade and were used without further purification. The crystal structures of TiO<sub>2</sub> powders were determined from X-ray diffraction (XRD) patterns measured with an X-ray diffractometer (Philips, X'Pert-MRD) with a Cu target Ka-ray ( $\lambda = 1.5405 \text{ \AA}$ ). The relative surface areas of the powders were determined by using a surface area analyzer (Micromeritics, FlowSorb II 2300). X-ray photoelectron spectra (XPS) of the TiO<sub>2</sub> powders were measured using a Shimadzu ESCA1000 photoelectron spectrometer with an Al Ka source (1486.6 eV). The shift of binding energy due to relative surface charging was corrected using the C 1s level at 284.0 eV as an internal standard. The XPS peaks were assumed to have Gaussian line shapes and were resolved into components by a non-linear least squares procedure after proper subtraction of the baseline. Fourier Transform Infrared Spectroscopy was measured using a Bruker IFS66 with a diffuse reflectance accessory.

## *2.2. Modification of surfaces of SiO<sub>2</sub>-TiO<sub>2</sub> particles*

Modifications of the surfaces of SiO<sub>2</sub>-TiO<sub>2</sub> particles with fluoro-carbon was carried out according to previously reported methods.[5-7] One of typical preparation

procedure of modification of SiO<sub>2</sub>-TiO<sub>2</sub> is as follows. SiO<sub>2</sub>-TiO<sub>2</sub> (6.0 g) was suspended in toluene containing 5.0 mmol of tridecafluoro-1, 1, 2, 2-tetrahydrooctyltrichlorosilane. The solution was stirred for 10 min at room temperature, and methanol was added to the solution to stop the reaction. The precipitate was then dried at 50°C under reduced pressure for 5 h. The resulting powder was labeled SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) (8: number of carbons). Based on weight fractions of carbon and ash components obtained by elemental analysis, the amount of surface fluorocarbon chains was determined by assuming that the remaining ash is composed of a mixture of TiO<sub>2</sub> and SiO<sub>2</sub>. The amount of fluorocarbon groups attached to the photocatalysts was estimated to be 389 μmol g<sup>-1</sup> (coverage; 42.9%), 466 μmol g<sup>-1</sup> (coverage; 51.4%), and 571 μmol g<sup>-1</sup> (coverage; 62.9%) μmol g<sup>-1</sup> (M<sub>a</sub>), respectively. These data were confirmed by XPS analysis. Using M<sub>a</sub>, external surface area and the estimated cross-sectional area of an fluoroalkylsilyl group (0.274 nm<sup>2</sup>), [8] the surface coverage of SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) was calculated.

### *2.3. Physical properties of SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) particles*

The overall hydrophobicity-hydrophilicity of SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) particles was

evaluated by observing their behavior (floatability) when surface-modified powder was added to water-acetonitrile mixtures of various compositions.[7] 10 mg of SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) powder was added to 5 mL of a given concentration of aqueous acetonitrile. After shaking for 5 minutes, the mixture was centrifuged and the precipitate was collected. The percent fraction of floating particles was calculated as the difference between weights of added and precipitated particles.

#### *2.4. Stability of functional groups introduced onto the surface of SiO<sub>2</sub>-TiO<sub>2</sub> particles*

In order to evaluate the photostabilities of surface-modified TiO<sub>2</sub> (SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F)), the photocatalyst was photoirradiated using a 500 W Hg lamp (6.6 mW cm<sup>-2</sup>) for 5.5 h in aqueous solutions. FT-IR analyses and elemental analyses of the powder were performed before and after photoirradiation. The powder before and after photoirradiation was analyzed by means of XPS spectroscopy.

#### *2.5. Photocatalytic degradation of aldehyde compounds on SiO<sub>2</sub>-TiO<sub>2</sub> modified with functional groups*

Activities of  $\text{SiO}_2\text{-TiO}_2\text{-C}_8(\text{F})$  were estimated by photo-degradation of aldehydes in aqueous media as follows.  $\text{SiO}_2\text{-TiO}_2\text{-C}_8(\text{F})$  (50 mg) was added to an aqueous solution of aldehydes (20 mM: pentafluorobenzaldehyde or benzaldehyde) and  $\text{H}_2\text{O}$  (5 ml). Then the mixture was stirred vigorously to make an emulsion, and it was photoirradiated under aerated conditions. Photoirradiation was performed using a super-high-pressure mercury lamp (Wakom BMS-350S, 350 W) from the top of a cylindrical reaction vessel (transparent at  $>300$  nm, 2.5 cm in diameter) at room temperature. The intensity of the incident light was  $6.7 \text{ mW cm}^{-2}$ . The reaction mixture was agitated vigorously with a magnetic stirrer during photoirradiation. Decrease of aldehydes in the aqueous solution was analyzed using a capillary gas chromatograph equipped with an RTx-5 capillary column.

### **3. Results and discussion**

#### *3.1. Physical properties of $\text{SiO}_2\text{-TiO}_2\text{-C}_8(\text{F})$ .*

The surface coverage of  $\text{SiO}_2\text{-TiO}_2\text{-C}_8(\text{F})$  was changed in range the of 43.9 to 62.9% in order to determine the relationship between coverage and photocatalytic



activity.

Figure 1 shows the floatability of  $\text{SiO}_2\text{-TiO}_2\text{-C}_8(\text{F})$  particles (coverage : 42.9%) as a function of the weight fraction of acetonitrile in water. Almost all surface-modified sample ( $\text{SiO}_2\text{-TiO}_2\text{-C}_8(\text{F})$ ) floated, i.e., without any appreciable precipitation, when the weight fraction of acetonitrile was less than 40%, indicating that the particle surfaces had a hydrophobic property. With increase in the acetonitrile fraction from 45 to 60%, some of the  $\text{SiO}_2\text{-TiO}_2\text{-C}_8(\text{F})$  particles settled, and complete sedimentation of both samples was observed when the acetonitrile fraction became greater than 70%.

### 3.2. Stabilities of $\text{SiO}_2\text{-TiO}_2\text{-C}_8(\text{F})$ .

The stability of the surface modified  $\text{TiO}_2$  particles was estimated by photoirradiation of  $\text{SiO}_2\text{-TiO}_2\text{-C}_8(\text{F})$  particles in aqueous media. After photoirradiation of  $\text{SiO}_2\text{-TiO}_2\text{-C}_8(\text{F})$  particles, no sedimentation of the particles was observed. It was confirmed from elemental analysis of the resulting  $\text{TiO}_2$  photocatalysts that degradation of fluoroalkylsilyl groups hardly proceeds after photoirradiation. The coverage of the photocatalysts before irradiation is 42.9%. This value hardly changed after

photoirradiation. The coverage of SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) particles after irradiation for 3 and 5 h are 42.3 and 41.8 %, respectively. We also observed FT-IR spectra of the photocatalysts before and after photoirradiation in order to elucidate the stability of functional groups introduced onto the surface of the SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) particles. The intensities of IR peaks at around 1320-1370 cm<sup>-1</sup>, which were attributed to vibrations of C-F bonds, hardly change after photoirradiation as shown in Fig. 2. We also observed XPS spectra of SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) particles before and after photoirradiation. Figure 3 shows F1s spectra. The intensity of a peak assigned to F1s did not change before and after photoirradiation as shown in Fig. 3. The coverage of fluorocarbon chain introduced onto SiO<sub>2</sub>-TiO<sub>2</sub> particles were also analyzed before and after photoirradiation. The coverage of fluoroalkylsilyl groups before photoirradiation is 42.9, 51.5, and 62.9 %, respectively. After photoirradiation, the data are 42.2, 51.6, and 62.3%, respectively. These results suggested that the fluoroalkylsilyl groups introduced onto the surfaces of SiO<sub>2</sub>-TiO<sub>2</sub> particles are stable under photocatalytic conditions.

### 3.3. Photocatalytic activities of SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F).

Figure 4 shows the photocatalytic activities of TiO<sub>2</sub> powders for oxidation of aldehydes by irradiation for 1 h at room temperature. When pentafluorobenzaldehyde was used as a substrate, photooxidation proceeded on SiO<sub>2</sub>-TiO<sub>2</sub> photocatalysts with a relatively high yield. Marked acceleration was observed when SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) was used as a photocatalyst. When the coverage was 62.9%, the activity level of SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) was maximum as shown in Fig. 4. The photocatalytic activity level of SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) with 62.9% coverage was about three-times higher than that of SiO<sub>2</sub>-TiO<sub>2</sub> without surface modification. The enhancement of activity of SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) with surface coverage of less than 62.9 % was less because of a weak interaction between the substrate and the surface-modified functional groups introduced onto the surfaces of SiO<sub>2</sub>-TiO<sub>2</sub> particles. The hydrophobic interaction or F atom interaction between pentafluorobenzaldehyde and fluoroalkylsilyl groups on the surfaces of TiO<sub>2</sub> particles is thought to be an important factor for improving their reactivity. These results were supported by the difference in adsorptivities of aldehydes on SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) and SiO<sub>2</sub>-TiO<sub>2</sub> particles. The adsorptivities of pentafluorobenzaldehyde on SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) (Coverage; 62.9%) and SiO<sub>2</sub>-TiO<sub>2</sub> particles were about 3.1 and 1.2 mmol dm<sup>-3</sup>/100 mg, respectively. On the other

hand, no difference was found between the adsorptivities of benzaldehyde on SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) (Coverage; 62.9%) and SiO<sub>2</sub>-TiO<sub>2</sub> particles, the values being 1.2 and 1.1 mmol dm<sup>-3</sup>/100 mg, respectively.

In order to elucidate the efficiency of fluoroalkyl groups for selectivity of the reaction, we also investigated the activities of SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) for degradation of benzaldehyde. Regardless of the coverage, the photocatalytic activity of SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) particles was similar to that of SiO<sub>2</sub>-TiO<sub>2</sub> particles without modification. On the other hand, the enhancement of SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F) for degradation of pentafluorobenzaldehyde increased remarkably with increase in the coverage as shown in Fig. 4. These results indicated that the interaction of F atoms between the substrate and fluorocarbon chain introduced onto SiO<sub>2</sub>-TiO<sub>2</sub> particles is more important than hydrophobic interaction to exhibit selectivity.[9, 10]

#### **4. Summary**

It is notable that oxidation of pentafluorobenzaldehyde proceeded more efficiently on the surface-modified TiO<sub>2</sub> photocatalyst (SiO<sub>2</sub>-TiO<sub>2</sub>-C<sub>8</sub>(F)) than on TiO<sub>2</sub>

particles without surface modification (SiO<sub>2</sub>-TiO<sub>2</sub>). On the other hand, enhancement of photocatalytic activity for oxidation of benzaldehyde was not observed by surface modification of SiO<sub>2</sub>-TiO<sub>2</sub> particles. The difference in photocatalytic activities is mainly due to the interactions of F atoms between fluoroalkylsily groups on SiO<sub>2</sub>-TiO<sub>2</sub> particles and pentafluorobenzaldehyde. Further improvements in TiO<sub>2</sub> photocatalysts surface-modified with various functional groups are currently being investigated.

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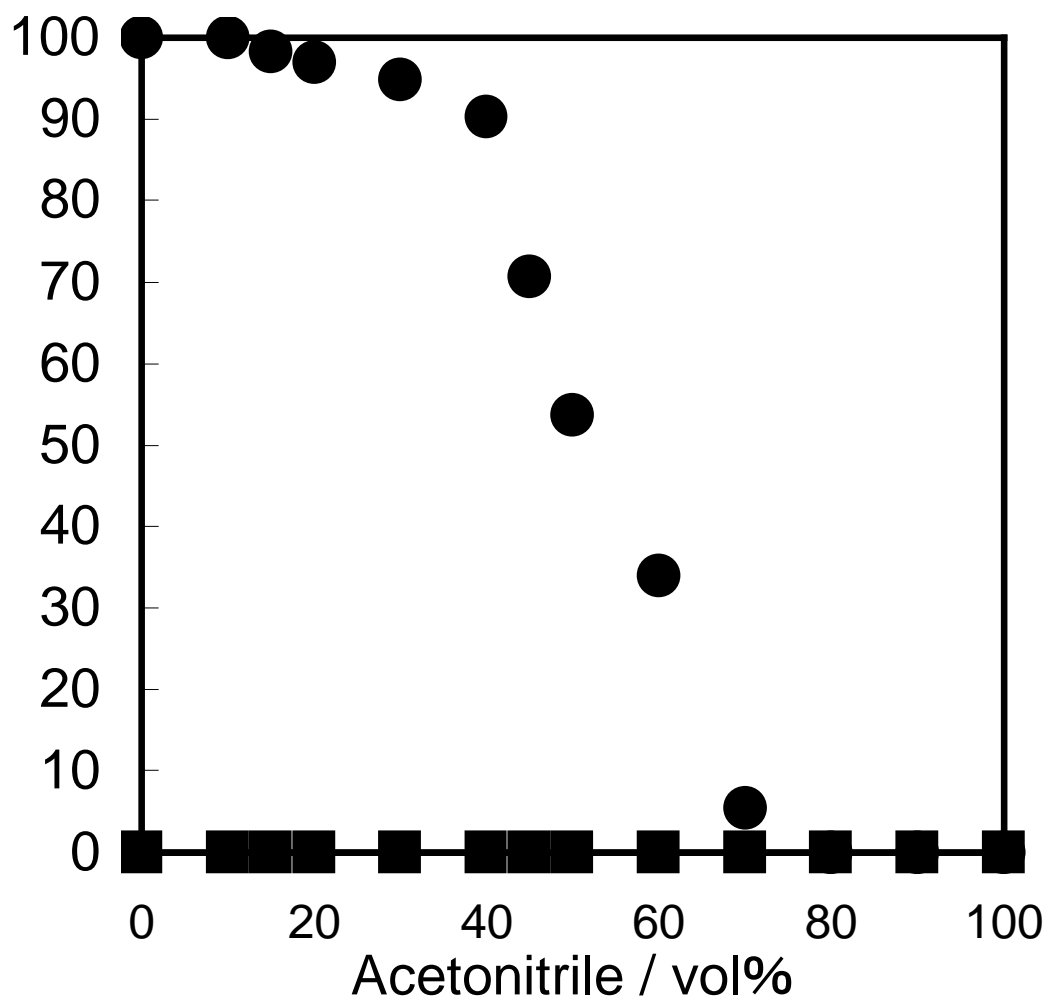
## Figure captions

Figure 1. Dependence of amount of floating particles on the volume fraction of acetonitrile in water. Closed circles,  $\text{SiO}_2\text{-TiO}_2\text{-C}_8(\text{F})$ ; Closed squares,  $\text{SiO}_2\text{-TiO}_2$ .

Figure 2. FT-IR absorption spectra  $\text{SiO}_2\text{-TiO}_2\text{-C}_8(\text{F})$  before and after photoirradiation in water for 5h and  $\text{SiO}_2\text{-TiO}_2$  without surface modification.

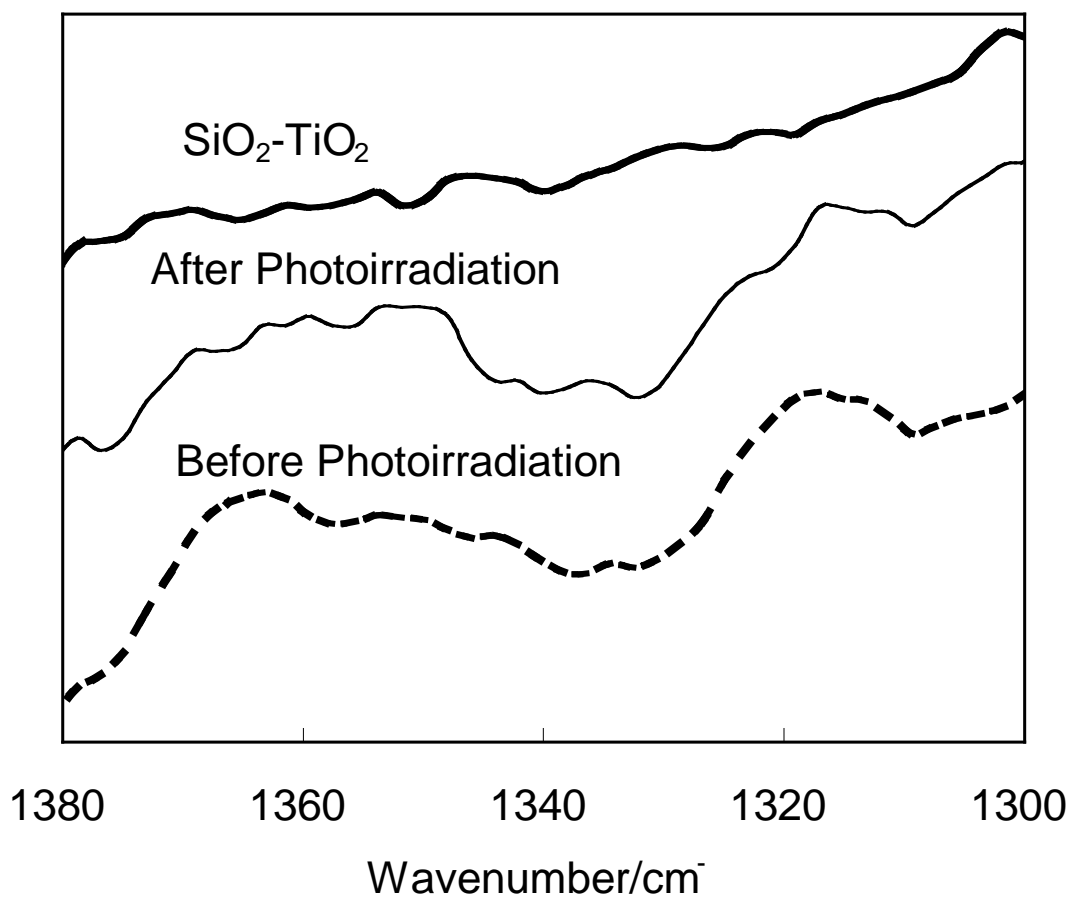
Figure 3. X-ray photoelectron spectra of F1s of  $\text{SiO}_2\text{-TiO}_2\text{-C}_8(\text{F})$  particles before and after photoirradiation.

Figure 4. Photocatalytic activities for oxidation of aldehydes on the surface modified  $\text{TiO}_2$  powders with different coverage.

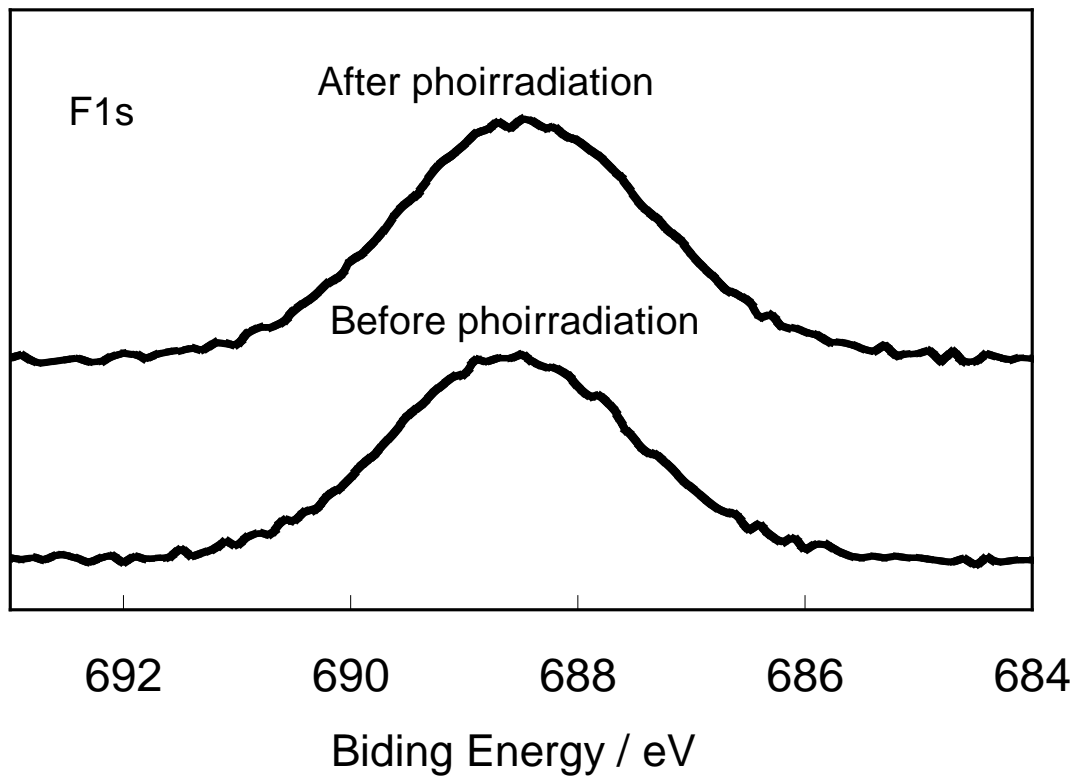


T. Ohno, Figure 1

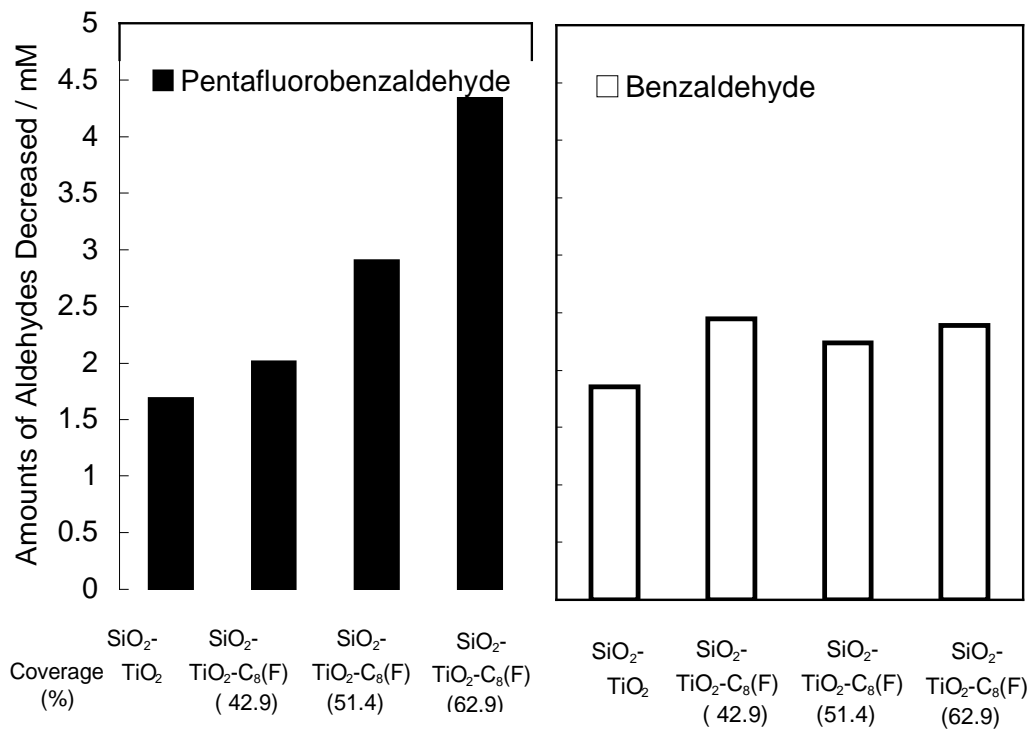




T. Ohno, Figure 2



T. Ohno, Figure 3



T. Ohno, Figure 4