We had succeeded in the synthesis of a new type of visible light driven photocatalyst called ILUMIO®, which was prepared by an improvement on conventional preparation of ceramic dispersion. The ILUMIO® coating layer decomposes volatile organic compounds (acetaldehyde, formaldehyde and toluene) under fluorescent lamp irradiation. Furthermore, the coating layer exhibits super hydrophilic performance under visible light irradiation. ILUMIO® has dispersing crystalline particles. Thus, the photocatalytic activity is achieved by coating followed by drying without calcination.
doping with sulfur could give TiO₂ visible light reactivity. Research on nitrogen doped and sulfur doped TiO₂ has been carried out worldwide up to the present day, and there have been a large number of reports on the research.

Moreover, the photocatalysts for decomposition of water described in 1 do not exhibit sufficient photocatalytic activity for the decomposition of organic substances, which is due to their low surface areas.

3. Photo-induced Hydrophilicity

It has been reported that a TiO₂ coating layer can be used to not only decompose organic substances under ultraviolet light irradiation, but also has surfaces that exhibit hydrophilic properties. Hashimoto et al. proposed the mechanism of “photo-induced hydrophilicity” described below. This technology is applied to commercial products that perform antifogging and self-cleaning effects under ultraviolet irradiation.

4. Current State and Recent Trends in the Photocatalyst Market

According to a survey targeting members of the Photocatalysis Industry Association of Japan, the market for photocatalyst related products was on the scale of ¥32.8 billion in FY 2007 and expanding every year. The actual scale of the market is estimated to be ¥70 billion in Japan and ¥100 billion worldwide. To have an even greater expansion of the photocatalyst market, it is required to develop higher performance visible light driven photocatalysts.

Recently, WO₃ has been attracting attention as a visible light driven photocatalyst. So far, WO₃ has not decomposed organic substrates completely, and the decomposition reaction was apparently stopped. There have not been many investigations attempting to use WO₃ as a photocatalyst for proactive environmental cleaning.

Abe et al. reported that acetaldehyde and other volatile organic compounds (VOCs) could be decomposed completely over Pt loaded WO₃ photocatalysts. Sayama et al. have reported that WO₃ mixed with Pd or Cu₂O decomposed VOCs under visible light irradiation. Hashimoto et al. have proposed Cu²⁺ or WC loaded WO₃ as a visible light driven photocatalyst.

The New Energy and Industrial Technology Development Organization (NEDO) “Project to Create Photocatalyst Industry for Recycling-oriented Society” made up of universities, the National Institute of Advanced Industrial Science and Technology (AIST) and nine private companies got its start in July 2007 with Professor Hashimoto of Tokyo University as the project leader. The goal of this project is to develop excellent materials that exhibit twice the activity of conventional only ultraviolet light driven photocatalysts and 10 times the activity of conventional visible light driven photocatalysts.

According to a recent press release, the material maker in the NEDO project is producing and carrying out its verification tests on Cu²⁺ loaded WO₃ photocatalysts. Furthermore, they are aiming at developing the market for photocatalysts for indoor applications and their goal is the creation of an approximately ¥2.8 trillion market.

Photocatalytic Mechanism

1. Decomposition of Organic Substances by Photocatalysts

Fig. 1 shows the mechanism of photocatalytic reactions. When semiconductors are irradiated with light that has energy in this band gap or higher, electrons in the valence band are excited to the conduction band, and holes arise in the valence band. These electrons and holes are diffused within the semiconductor as is shown in Fig. 1. Then, (a) hydrogen ion reduction and water oxidation both occur in the water decomposition reaction; and (b) with decomposition of organic substances, active oxygen species are generated with the reduction of oxygen and the oxidation of water. Decomposition of the organic substances and a sterilizing activity are achieved by these active oxygen species. It is known that the holes decompose the
organic substances directly in an atmosphere with a high concentration of organic substances. TiO₂ is the most well-known semiconductor that exhibits the above photocatalytic activity.

Recently, WO₃ has been focused on as a visible light driven photocatalyst. The bandgap of WO₃ are smaller than that of TiO₂. The oxidative energy of the holes generated by photoexcitation for WO₃ is stronger than for TiO₂. On the other hand, the reductive energy of the photo-excited electrons in the former is weaker than that in the latter. In the reduction reaction for oxygen, single electron reduction (generation of O₂⁻) occurs with TiO₂, and with WO₃, two-electron reduction (generation of H₂O₂) occurs. The generation of H₂O₂ has an extremely slow reaction rate. These active oxygen species (O₂⁻ and H₂O₂) play a very important role in decomposing organic substances. It is known that WO₃ does not decompose acetaldehyde completely in the photocatalytic reaction, because WO₃ does not generate a sufficient amount of H₂O₂ for decomposition of acetic acid (intermediate reaction). However, the two-electron reduction reaction is enhanced by loading of Pt or Cu²⁺ on WO₃, which enables acetaldehyde to be decomposed completely.

2. Photo-induced Hydrophilicity

Fig. 2 shows the mechanism of photo-induced hydrophilicity over the TiO₂ surface. As in Fig. 1, when TiO₂ is irradiated with light that has energy greater than the band gap, a photoexcitation occurs in the TiO₂, resulting in a generation of electrons and holes. Almost both species produced active oxygen species. Some of the holes are trapped by bridged oxygen in the Ti-O-Ti bonds, which induces an increase in the Ti-O bond distance. Water vapor is adsorbed dissociatively on the Ti-O-Ti bond, followed by an increase in the amount of Ti-OH, making the surface of the TiO₂ exhibit hydrophilicity. However, since the stability of this Ti-OH is not high, a water molecule desorbs from two neighboring Ti-OH molecules in the dark, and the Ti-O-Ti bond (hydrophobicity) is reproduced.

ILUMIO® High-Performance Photocatalyst

Sumitomo Chemical has already commercialized TP-S201 (powder), TS-S4110 and TS-S4420 (sol) visible light driven photocatalysts, and they are being used for functional shades and curtains.

Higher performance is required for further expansion of the photocatalyst market. Therefore, we made use of ceramic synthesis technology that has been cultivated for many years and developed the high-performance photocatalyst known as ILUMIO®. ILUMIO® is a crystalline photocatalytic particle-dispersed liquid. The average dispersed particle size, the pH and various other properties are listed in Table 1. The appearance of ILUMIO® and an ILUMIO® coated petri dish (amount of coating: 1g/m², petri dish diameter: 66mm (φ)) are shown in Fig. 3. ILUMIO® has a gray color. In general, materials that absorb visible light are seen as

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Characterization of ILUMIO®</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Gray colored aqueous dispersion</td>
</tr>
<tr>
<td>Solid content</td>
<td>5 ~ 10wt%</td>
</tr>
<tr>
<td>Dispersed particle size</td>
<td>100 ~ 150nm</td>
</tr>
<tr>
<td>pH</td>
<td>4 ~ 5</td>
</tr>
</tbody>
</table>

Fig. 2  Mechanism of photo-induced hydrophilic performance over TiO₂ photocatalyst under UV-light irradiation

Fig. 3  Picture of ILUMIO® (a) and ILUMIO® coated petri dish (b)
colored to the human eye, which proves that ILUMIO® absorbs visible light. On the other hand, the coating layer has a high degree of transparency and is not colored. The ILUMIO® coating layer absorbs visible light and exhibits photocatalytic activity without deteriorating the design of the substrate.

**Performance of ILUMIO® High-Performance Photocatalyst in Decomposition of Organic Substances**

1. Evaluation of Photocatalytic Activity by Gas-bag Method

Currently, fluorescent lights are the main type of indoor lighting in Japan. As is shown in Fig. 4, fluorescent lights irradiate a small amount of ultraviolet light, but the ultraviolet light is cut off completely by passing it through an acrylic sheet (N-169, Nitto Jushi Kogyo Co., Ltd.).

The method for evaluating the photocatalytic activity of ILUMIO® is shown in Fig. 5. ILUMIO® was placed and spread in the petri dish at a rate of 1g/m² to form the coating layer. As is shown in Fig. 5, this coating layer has extremely high transparency. Then, this coated petri dish was placed in a gasbag (volume of 1 L). Synthetic air (volume of 0.6 L) with a relative humidity of 50% was sealed inside, and a prescribed amount of acetaldehyde was infused. Subsequently, it was kept in the dark for one hour, irradiated with a white fluorescent lamp (illuminance of 1000 lux) and the acetaldehyde and CO₂ concentrations measured by gas chromatography after a fixed period of irradiation. 1000 lux is almost the same level as the top of a desk in a bright room.

(1) Acetaldehyde and toluene decomposition reactions

Fig. 6 (a) and (b) show the results of photocatalytic decomposition of acetaldehyde over an ILUMIO® coating layer under fluorescent lamp irradiation. A current Sumitomo Chemical product (TS-S4110 visible light...
a Toshiba Lighting and Technology Corp. LED bed lamp). The spectrum of this LED is shown in Fig. 8. The results of the photocatalytic activity are shown in Fig. 9. A commercial ultraviolet driven TiO₂ photocatalyst sol was evaluated as a comparison. The reactive photocatalyst sol) coating layer was evaluated as a comparison photocatalyst. These results indicate that ILUMIO® exhibited a high photocatalytic activity that is five to six times that of TS-S4110 under these evaluation conditions. ILUMIO® exhibited a high photocatalytic activity even under visible light irradiation. The results of a decomposition reaction for toluene are shown in Fig. 7 (a) and (b). ILUMIO® also exhibited a higher photocatalytic activity than TS-S4110, similar to the results of the acetaldehyde decomposition reaction as shown in Fig. 6 (a) and (b).

(2) Acetaldehyde decomposition reaction under white LED irradiation

LEDs (light emitting diodes) are going to become the main light source for indoor space in the future. The LEDs that have been commercialized already are roughly classified into two types: (i) the type that combines three (read, green and blue) colored LEDs; and (ii) the type that combines yellow phosphors with blue LEDs. The LEDs in (i) are used in full-color road display panels and screens, and those in (ii) are used in light sources.

The photocatalytic activity of the ILUMIO® coating layer was evaluated under white LED irradiation (using a Toshiba Lighting and Technology Corp. LED bed lamp). The spectrum of this LED is shown in Fig. 8. The results of the photocatalytic activity are shown in Fig. 9. A commercial ultraviolet driven TiO₂ photocatalyst sol was evaluated as a comparison. The
amount of acetaldehyde decreased with an increasing of the decomposition product CO₂ over ILUMIO®. On the other hand, the commercial ultraviolet light driven photocatalyst hardly decomposed acetaldehyde or produced CO₂. These results indicate that ILUMIO® also performed high photocatalytic activity under white LED irradiation, which means that ILUMIO® is promising to be an excellent photocatalyst for use in indoor spaces in the future.

3. Evaluation of Photocatalytic Activity in Flow Type System

Flat bed flow type reactors have already been made into a JIS standard as an evaluation method for photocatalytic activity. An overview of this method is shown in Fig. 10. ILUMIO® and TS-S4110 were coated on glass substrates (5cm × 10cm) to which 40g/m² was applied. These were placed in the reactor, and 1ppm formaldehyde or acetaldehyde was flowed in at a flow rate of 1 L/min. The reactor was irradiated from above by a fluorescent lamp. An acrylic sheet (N-169, Nitto Jushi Kogyo Co., Ltd.) was used to cut off the ultraviolet light.

The results are shown in Fig. 11. ILUMIO® eliminated the formaldehyde and acetaldehyde with a higher photocatalytic activity than TS-S4110, whether ultraviolet light was irradiated or not.

3. Evaluation of Photocatalytic Activity Using Small Chamber

The small chamber method (JIS A 1901 (Method for Measuring the Dissipation of VOCs, Formaldehyde and Other Carbonyl Compounds in Construction Materials)) is known as a method for testing the amount of VOCs dissipating from construction materials. Since the evaluation of photocatalytic activity using this method is going to be registered with JIS, we evaluated the photocatalytic activity of ILUMIO® using this method.

As shown in Fig. 12, an ILUMIO® coated glass substrate was placed in the chamber, and the chamber was irradiated by a fluorescent lamp (illuminance: 1000 lux) while formaldehyde gas was flowed in at a concentration of 0.08ppm. The formaldehyde concentrations at the inlet and the outlet were measured by liquid chromatography. The formaldehyde flow rate was run at an air change rate of 0.5 times per hour. The air change rate indicates how many times the air in a space is replaced per unit time, and the air change rate for a house is set at 0.5 times per hour and 0.3 times per hour or more for buildings other than houses in the Building Standards Act. The photocatalytic activity was
4. Decomposition of Odors Related to Everyday Living

The deodorizing effect by photocatalysts for actual odors related to everyday living (composite odors) is an extremely important factor in moving toward commercialization. Therefore, we carried out deodorization evaluations on cigarette odors as well as feces and urine using an ILUMIO® coating layer.

An ILUMIO® coated glass plate (50cm²) was placed in a 5L gasbag, and a tobacco odor or feces and urine odors were put into it. The odor concentration was measured using a FF-2A identification device (Shimadzu Corp.) after fluorescent lamp (1000 lux) irradiation for 16 hours. The time for the fluorescent lamp irradiation was set at 16 hours from the time for everyday living (24 hours – 8 hours sleeping time). The initial concentrations of the tobacco odor and the feces and urine odor were set with reference to the odor concentration in the smoking room at Sumitomo Chemical for the former and the odor concentration when diapers were changed in a sick room for the latter (no ventilation fan, odor concentration: 74). For comparison, evaluations were done using a glass plate without coating photocatalyst.

Judging from the results of smell identification expressed by the converted air change rate as well as by the decomposition rate. The converted air change rate can be calculated by the following equation.

\[
\text{Converted air change rate} = \frac{(C_{\text{in}} - C_{\text{out}}) \times 0.02 \times 0.5 \times (h^{-1})}{C_{\text{out}} \times \text{sample surface area}(m^2)}
\]

A visible light driven photocatalyst coating agent (TC-S4115) that exhibits a high photocatalytic activity in formaldehyde decomposition reactions was used for comparison. ILUMIO® exhibited a high photocatalytic activity at 83% compared with the elimination rate of 51% for TC-S4115 as shown in Fig. 13 (a). Additionally, the converted air change rate of these results is shown in Fig. 13 (b). It was approximately 2.4 times per hour while for TC-S4115 the air change rate was approximately 0.6 times per hour. This means that if ILUMIO® is coated in a room at an air volume ratio of 1 (surface area of walls coated with ILUMIO®/room volume = 1 (m²/m³)), air cleaning equal to completely replacing the air in the room is possible with a 2.4 times per hour margin.

4. Decomposition of Odors Related to Everyday Living

The deodorizing effect by photocatalysts for actual odors related to everyday living (composite odors) is an extremely important factor in moving toward commercialization. Therefore, we carried out deodorization evaluations on cigarette odors as well as feces and urine using an ILUMIO® coating layer.

An ILUMIO® coated glass plate (50cm²) was placed in a 5L gasbag, and a tobacco odor or feces and urine odors were put into it. The odor concentration was measured using a FF-2A identification device (Shimadzu Corp.) after fluorescent lamp (1000 lux) irradiation for 16 hours. The time for the fluorescent lamp irradiation was set at 16 hours from the time for everyday living (24 hours – 8 hours sleeping time). The initial concentrations of the tobacco odor and the feces and urine odor were set with reference to the odor concentration in the smoking room at Sumitomo Chemical for the former and the odor concentration when diapers were changed in a sick room for the latter (no ventilation fan, odor concentration: 74). For comparison, evaluations were done using a glass plate without coating photocatalyst.

Judging from the results of smell identification
Ultraviolet light was irradiated to the laminated layer to allow photo-excitation of the WO3 as well as the TiO2. The holes generated in the WO3 diffused to the TiO2 and the number of holes in the TiO2 were increased, making for a larger amount of surface hydroxyl groups. However, when a silica layer was inserted between the TiO2 layer and the WO3 one, the diffusion of the holes from the WO3 to the TiO2 was blocked, resulting in an inhibition of the photo-induced super hydrophilicity.

An ILUMIO coating layer on glass substrate (amount of coating: 0.5g/m2) was fabricated by spin coating, and its photo-induced super hydrophilicity was examined. The results are shown in Fig. 15 (a) through (d). The following four conditions were employed: (a) no initialization (irradiation with ultraviolet light before hydrophilicity evaluation) and storage in the dark; (b) no initialization and visible light irradiation; (c) initialization and storage in the dark; and (d) initialization and visible light irradiation.

As shown in Fig. 15 (a) and (c), the water contact angle over the ILUMIO coating layer maintained a low value of 5° or less over a long period in the dark, regardless of whether initialization was carried out. Typically, it is known that a substrate having a water contact angle of 7° or less exhibits antifogging properties (no clouding), and that of 10° or less has a self-cleaning effect. It is probably that ILUMIO coated materials exhibit antifogging properties even in the dark because the ILUMIO coating layer maintains a water contact angle of 5° or less in the dark. On the other hand, although a commercial ultraviolet light driven TiO2 photocatalyst coating layer exhibited a water contact angle of 4° in the dark, the ILUMIO coating layer exhibited a water contact angle of 5° or less in the dark.

Photo-induced Hydrophilicity of ILUMIO High-Performance Photocatalyst

Besides the oxidative decomposition of organic substances, photocatalysts also have a photo-induced super hydrophilicity. Photo-induced hydrophilic technology has been applied to various glass products such as door mirrors for automobiles, tents, and so on. The photo-induced hydrophilicity provides a water thin film on the photocatalyst coating layer with self cleaning properties as well as antifogging ones. The water thin film weakens the adhesion between dirt and the photocatalyst coating layer, allowing the dirt to be washed away easily by rainwater.

Irradiation with ultraviolet light of 5μW/cm2 is necessary to exhibit super hydrophilic properties (water contact angle of 5° or less) over a TiO2 photocatalyst coating layer. Ultraviolet light was irradiated to the laminated layer to allow photo-excitation of the WO3 as well as the TiO2. The holes generated in the WO3 diffused to the TiO2 and the number of holes in the TiO2 were increased, making for a larger amount of surface hydroxyl groups. However, when a silica layer was inserted between the TiO2 layer and the WO3 one, the diffusion of the holes from the WO3 to the TiO2 was blocked, resulting in an inhibition of the photo-induced super hydrophilicity.

An ILUMIO coating layer on glass substrate (amount of coating: 0.5g/m2) was fabricated by spin coating, and its photo-induced super hydrophilicity was examined. The results are shown in Fig. 15 (a) through (d). The following four conditions were employed: (a) no initialization (irradiation with ultraviolet light before hydrophilicity evaluation) and storage in the dark; (b) no initialization and visible light irradiation; (c) initialization and storage in the dark; and (d) initialization and visible light irradiation.

As shown in Fig. 15 (a) and (c), the water contact angle over the ILUMIO coating layer maintained a low value of 5° or less over a long period in the dark, regardless of whether initialization was carried out. Typically, it is known that a substrate having a water contact angle of 7° or less exhibits antifogging properties (no clouding), and that of 10° or less has a self-cleaning effect. It is probably that ILUMIO coated materials exhibit antifogging properties even in the dark because the ILUMIO coating layer maintains a water contact angle of 5° or less in the dark. On the other hand, although a commercial ultraviolet light driven TiO2 photocatalyst coating layer exhibited a water contact angle of 4° in the dark, the ILUMIO coating layer exhibited a water contact angle of 5° or less in the dark.
contact angle with a low value when initialization was conducted prior to the evaluation, the water contact angle became larger and the hydrophilicity deteriorated with the passage of time. This result indicates that the OH groups on the TiO₂ surface increase to give hydrophilicity under the ultraviolet light irradiation during initialization. Then, the dark condition did not allow an increase in the newly created OH groups and desorption of water from the neighboring Ti-OH groups, followed by a generation of the Ti-O-Ti oxygen bridging bond.

As shown in Fig. 15 (b) and (d), the ILUMIO® coating layer exhibited a water contact angle of 0° to 2° under visible light irradiation, and that state was maintained for a long time. Here, a florescent lamp was used as the light source and an acrylic sheet (N-169, Nitto Jushi Kogyo Co., Ltd.) was employed as an ultraviolet light cut-off material. The ILUMIO® coating layer maintained a water contact angle of 0° to 2° under visible light as well as 1000 lux irradiation. To the best of our knowledge, a characteristic hydrophilic photocatalyst coating layer has not been reported.

Conclusion

Sumitomo Chemical has developed the ILUMIO® high-performance visible light driven photocatalyst. ILUMIO® exhibits high photocatalytic activity for decomposition of formaldehyde, acetaldehyde and toluene under irradiation from LEDs as well as from fluorescent lamps. Additionally, ILUMIO® exhibited high photocatalytic activity in the deodorization of odors associated with everyday living, such as cigarette odors and the odors of feces and urine. Furthermore, the ILUMIO® coating layer exhibit a high hydrophilicity, and the water contact angle is 5° or less even in the dark and is 0° to 2° under visible light irradiation.

At present, we are starting to provide ILUMIO® for applications indoors, and are putting great effort toward commercializing it and improving its photocatalytic performance.

References