Photocatalytic Reaction of TiO$_2$ Films and Its Application to Lighting Systems

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ABSTRACT
Recently, it has been reported that the organic compounds such as dirt and odors can be decomposed by photocatalytic reaction of titanium oxide (TiO$_2$). In the daily use of lamps and luminaries, the accumulation of dirt often reduces a great amount of light output. We have developed a new type of fluorescent lamp coated with photocatalytic TiO$_2$ film to improve those problems on lighting. At first, we estimated the decomposition of cigarette dirt on the lamps coated with TiO$_2$ films. The loss rate of light output could be decreased to half by decomposition of dirt during operating. Furthermore, we investigated the change in concentration of acetaldehyde in sealed box during lighting. It was found that the lamp could deodorize the air in the box by decomposition. At the same time, UV radiation from the lamp were absorbed by TiO$_2$ films. Thus, it was found that the users could be provided with the comfortable environment by application of the photocatalytic reaction to the lighting systems.

1. Introduction
Recently, the application technique of titanium oxide (TiO$_2$) photocatalyst has gained more and more attention. These studies are on the basis of Honda-Fujishima effect$^{[1]}$: TiO$_2$ surface is activated by photocatalytic reaction when the light with the wavelength less than 380nm is irradiated from lamps or the sun. At this time, the organic materials on TiO$_2$ surface are decomposed to carbon dioxide and water, then decomposed materials finally disappear.

Many researchers have verified that TiO$_2$ photocatalyst is able to decompose the organic compounds such as dirt, bacteria stains and odors$^{[2]}$. Typical organic compounds on lighting systems are the dirt of exhaust-gas from automobile engines on roads, the oil stains in kitchens and the dust with cigarette dirt in living rooms and offices. The accumulation of the dirt on lamps and luminaires reduces light output.

Fig. 1 A spectral transmittance of TiO$_2$ film
If the dirt can be decomposed and the loss of light output decreases, the number of cleaning times will decrease, and it will help to save the maintenance cost. In outdoors, the photocatalytic effect on vehicle exhaust compounds has been examined. We are now producing light sources and luminaires which have this photocatalytic effect.

In the environment around lamps and luminaries, the various odors tend to remain in recent high airtight houses. If the odors can be decomposed by photocatalytic reaction, the users can be provided with the comfortable environment.

At the same time, TiO₂ has the characteristic such as absorbing the hazardous UV radiation as shown in Figure 1. It is known that a small amount of UV rays is radiated from light sources. Therefore, with forming TiO₂ films on the outer surface of them, it becomes possible to reduce the hazardous UV radiation effectively.

Figure 2 schematically shows the effects of photocatalytic reactions on the lamp coated with TiO₂. There are various arguments about the reaction process. Figure 2 gave an example of them.

This paper will introduce our novel application of this photocatalytic reaction to outdoor lighting products, and also describe the effect of our new fluorescent lamps which have TiO₂ films.

**TiO₂ photocatalytic reaction process:**

When TiO₂ photocatalyst is excited by UV irradiation (< 380nm), which has higher energy than the band gap (3.2eV), electron-positive hole pairs are formed on the surface. These pairs and water on the surface repeat complex reaction processes, and forms ·OH and HO₂⁻. Finally, the organic compounds such as dirt and odors are decomposed by these radical ·OH, HO₂⁻ and hole (p⁺). This effect can last semi-permanently because this reaction is the Catalytic Reaction which itself does not change to other materials. Research and development for the application of this reaction to other commercial goods such as decomposition of NOx gas, deodorization, sterilization and dirt proofing, have also attracted a growing interest.

Even though TiO₂ is usually white in condition of powder, TiO₂ thin film becomes transparent for visible light. This is extremely advantageous when we apply it to lighting product. Therefore, the application of photocatalytic reaction to the field of lighting is regarded as suitable technique, and some results about our new product are reported.

2. Application to Outdoor Lighting Product

We give some examples of the application to outdoor lighting products briefly in this section.

Figure 3 shows the relation between the change in transmittance of carbon particle accumulated on the TiO₂ film and irradiation time. When the strong UV energy are irradiated to TiO₂ film, the organic compounds such as exhaust-gas of diesel engine containing carbon particles are decomposed and the transmittance of visible light recovers at the rate of 15 %, as compared to one without TiO₂ film. We have added this function to the front glass of luminaire for the tunnel lighting with HPS as shown in Figure 4, and road-way lighting.
half side of glass globe of the luminaire. The stain on places where TiO₂ was coated was dramatically decomposed by the photocatalytic reaction. Maintenance cost will be reduced largely.

Table 1. The relative light output rate in circumstance with some smokers

<table>
<thead>
<tr>
<th>Operating time [hr]</th>
<th>Relative light output [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>95.3</td>
</tr>
<tr>
<td>2000</td>
<td>94.8</td>
</tr>
<tr>
<td>3000</td>
<td>94.4</td>
</tr>
</tbody>
</table>

* relative light output = luminous flux with dirt / luminous flux without dirt
** Two lamps of 1000hr are picked from different circumstances.

Most of dirt is composed of cigarette dirt and dust. If the cigarette dirt can be decomposed, at least, it must prevent a loss of the light output.

As a preliminary examination, we attached the dirt from cigarette to the fluorescent lamp, on which TiO₂ film (thickness: about 0.3μm) was coated on one half side, and operated the lamp for two days. The cigarette dirt on the TiO₂ film has disappeared as shown in Figure 6.

![Fig. 4](image)
*Fig. 4* The tunnel lighting luminaire added photocatalytic TiO₂ film (Light source : HPS)

![Fig. 5](image)
*Fig. 5* Decomposition effect of dirt on road-way lighting luminaire (a) with TiO₂ film (b) without TiO₂ film

3. Application to the Fluorescent Lamp in Interior

3-1. Prevent of a Loss of the Light Output by Decomposition of Dirt

At first, we checked how much the dirt on the fluorescent lamps reduce light output. Table 1. shows the relative light output rate of four random sample lamps in each room where some smokers reside. Their values are equal to the ratio of the luminous flux of test lamp with dirt to the one without dirt. As shown in Table 1., relative light output values differ in the circumstances where the lamps were set up.

![Fig. 6](image)
*Fig. 6* Oxidative decomposition of cigarette dirt by TiO₂ film coated on fluorescent lamp (a) with TiO₂ film (b) without TiO₂ film

![Fig. 7](image)
*Fig. 7* The plots of the change in the luminous flux of fluorescent lamp against burning time

We also experimented as follows with assuming the real surrounding.

The lamp coated with TiO₂ film was set in the sealed box. Then, the amount of smoke corresponding to the condition that person smokes 20 pieces of cigarette in the room (about 22 m³) for one day was sent into the box. After that, it was allowed to stand for a day. Then, the luminous flux was measured after the lamp was operated. The luminous flux of fluorescent lamp with TiO₂ film and without one were compared against burning time (to 1000 hr) in Figure 7. In this figure, relative light output stands...
for the ratio of the luminous flux of test lamp with dirt to the one without dirt. It was found that the lamp with TiO₂ film can keep a higher light output level by the decomposition of the cigarette dirt than the one without TiO₂ film. Consequently, the loss of light output arising from the dirt was estimated to decrease to half.

3-2. Indoor Environment Purification by Decomposition of Odors.

In the recent housing, the problem that formaldehyde and VOC (volatile organic compounds) are released from new kinds of building materials and furniture have become a subject of discussion. If you are not a smoker, you might disagree to the smell. It must be significant if fluorescent lamp coated with TiO₂ films able to decompose the odors. Dr. Fujishima and Dr. Hashimoto have verified that the quantum efficiency of the TiO₂ photocatalyst is higher at lower concentration under weak UV energy radiating from fluorescent lamp. [2]

We considered about the application of this to the lamp as following.

The acetaldehyde was selected as a test gas for deodorizing; The acetaldehyde is one of the main component in the odors of smoking cigarette, and an odor regulatory substance.

First experimental setup is illustrated in Figure 8. We set the lamp coated with TiO₂ film at the center of test vessel, and sent acetaldehyde gas (conc. 500ppm in the air balance) into the closed system, and measured the concentration at regular time intervals using Gas chromatography. We also measured in the no lighting condition, to know the characteristic of absorption on TiO₂ film. Figure 9 shows that the concentration is also decreased by absorption under the no lighting condition. However, as soon as the lamp lights on, a sharp fall was observed. It was confirmed that the lamp with TiO₂ film has the strong deodorizing effect.

Secondary, we assumed in real space, and set up the lamps and the source of odors in the larger sealed box as shown in Figure 10. Figure 11. shows the decreasing rate of acetaldehyde. It was observed that the concentration decreased by absorption to the wall of system under the background condition. However, the test gas decreased much more when the lamp with TiO₂ film was lighting on. The concentration decreased about 20 percent in three hours. In spite of no churning in the box, the lamp with TiO₂ film has been proved to be effective also for
deodorization by the diffusion of concentration and the convection of air. Figure 12 shows the decreasing rate of ammonia in the same box. Ammonia gas was absorbed to the wall of system much more than acetaldehyde. Barely, the test gas decreased much more when the lamp with TiO$_2$ film was lighting on. In the case of ammonia, there was only a slight effect. If the inside air is churned, it will be more effective.

4. Acceleration of Photocatalytic Reaction

If it is assumed that the quantum efficiency is 100%, the concentration which can be decomposed by photocatalytic reaction is proportional to the quantum numbers; the quantum efficiency is equal to the number of electron occurring / the number of incident electron. In the real environment, if it is assumed that the concentration of compounds absorbed to TiO$_2$ film is "Q", and the one decomposed by TiO$_2$ film is "D", they can be written as follows

under the circumstance where much dirt and odors exist:

\[ D \ll Q \]  \hspace{0.5cm} (1) \\

under the circumstance where a little dirt and odor exist:

\[ D \gg Q \]  \hspace{0.5cm} (2) \\

When \( Q-D \leq 0 \), the surface on TiO$_2$ film is kept clean. However, when \( Q-D > 0 \), the surface becomes dirty and stinking, and the catalyst can not decompose the compounds completely. As the result, the effects is invisible. Especially, titanium oxide falls into such condition easily, because it is more absorptive than usual glass such as describing in chapter 4. However, if the quantum numbers increases, "D" will also increase, and the condition should approach from (1) to (2). We added a phosphor which radiate UV rays at the range where TiO$_2$ film can absorb and react sensitively, to increase the quantum numbers. We prepared the two types of lamps which were added the phosphor with peak emission in 392nm, and in 368nm. The same test as shown in Figure 9. was carried out, and we measured the decreasing rate of acetaldehyde on their lamps coated with TiO$_2$ film. As shown in Figure 14., the one which had peak in 368nm worked most efficiently.

It was proved that adding those phosphor is effective for acceleration of photocatalytic reaction.
5. Application to the Interior Luminaire

The total light comes from the amount of both lamps and luminaires. We have validated the same effect on the interior luminaire coated with TiO₂ film. However, if the lamp with TiO₂ films is set in the luminaire, UV radiation for the reaction are not supplied to it. In this case, dirt and odors on the luminaire can not be decomposed. Thus, it should be considered how the photocatalytic reaction is used in practical lighting situation.

6. Conclusion

In this paper, we have shown that the fluorescent lamp with photocatalytic TiO₂ film has the following advantages at the same time.

1. The prevention of the loss of light output.
   The luminous flux of the lamp can be maintained at high level by decomposing cigarette dirt during lighting. Therefore, the loss of light output arising from the dirt is estimated to decrease to half.

2. The deodorizing in the environment.
   It was established that acetaldehyde gas can be decomposed by the photocatalytic reaction when the lamps were set and lighted in our experimental sealed box. Therefore, the lamp was estimated to be useful for the environment purification.

3. The absorption of UV radiation.
   UV radiated from the lamp disappeared from the spectral distributions.
   It was found that UV radiation can be used efficiently for photocatalytic reaction, and the users can be provided a comfortable environment by applying of the photocatalytic reaction to the lamp.
   This technique will bring the new types of lighting systems in the future.

7. Acknowledgement

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8. References

(4) M. Kiyono, *Titanium oxide*, 175 (1976)