

The Synergistic Antibacterial Performance of a Cu/WO₃-Added PTFE Particulate Superhydrophobic Composite Material

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Abstract

The synergistic antibacterial performance against *Escherichia coli* (*E. coli*), *Staphylococcus aureus* and methicillin-resistant *Staphylococcus aureus* (MRSA) of a Cu/WO₃-added PTFE (polytetrafluoroethylene) particulate composite was reported in the previous paper. The origin of the synergistic antibacterial performance investigated by evaluating the photocatalytic decomposition of the Cu/WO₃-added PTFE particulate composite material is reported in the present paper. Addition of Cu/WO₃, visible-light-sensitive photocatalyst, to the PTFE particle dispersed superhydrophobic composite does not deteriorate the superhydrophobic property of the composite. Furthermore the existence of the polytetrafluoroethylene (PTFE) particles dispersed in the composite enhances the antibacterial property caused by the Cu/WO₃. The authors call this "The synergistic effect". In this study, a novel synergistic property of the Cu/WO₃-added PTFE particulate composite was investigated by evaluating the degradation of gaseous acetaldehyde on the composite surface using visible light (10,000 lx) and UV-A (1 mW·cm⁻¹) illumination. The 12 wt% Cu/WO₃-8 wt% binder-80 wt% PTFE composite shows the synergistic visible-light-sensitive photocatalytic property. But 12 wt% Cu/WO₃-44 wt% PTFE-44 wt% binder composite no longer shows the synergistic property of visible-light-sensitive photocatalytic property. The synergetic performance of visible-light-sensitive photocatalytic property appears only when PTFE concentration is larger than the critical point over which superhydrophobic property appears in accordance with the particulate composite model derived by the one of the authors. The hydrophobic surface leads to the low surface free energy derived by the revised Fowkes's theory, which makes it difficult for bacteria to stick to the hydrophobic surface of the composite. Even if bacteria stick to the surface, they are decomposed by the visible-light-sensitive photocatalyst. This is the reason why the synergistic antibacterial

performance against bacteria appears.

Keywords

Cu/WO₃, Photocatalyst, PTFE, Hydrophobicity, Particulate, Composite, Synergistic Antibacterial Performance, *Escherichia coli*, MRSA

1. Introduction

The polytetrafluoroethylene (PTFE) particle dispersed superhydrophobic composite material [1] [2] provides no sterilization performance. This limits its application in the field of disinfection. In order to obtain a superhydrophobic surface exhibiting not only water repellency but also self-cleaning performance, a material that combines TiO₂ nanoparticles with PTFE can be used [1] [3]. TiO₂ photocatalyst has been used to inactivate various bacteria, such as *Escherichia coli* (*E. coli*), methicillin-resistant *Staphylococcus aureus* (MRSA), *Pseudomonas aeruginosa* (*P. aeruginosa*), *Legionella pneumophila* (*L. pneumophila*) [4] [5], and *Clostridium difficile* spores [6]. The inclusion of TiO₂ in a PTFE particulate composite coating is expected to generate antimicrobial and self-cleaning properties, which would expand its scope of application. However, such a composite material could not play a full role indoors under fluorescent and incandescent light exposure, because these types of light emit little UV radiation. Accordingly, the development of powerful visible-light-sensitive photocatalysts, such as lattice-doped TiO₂ [7] [8] and WO₃ [9]-[12] using various dopants, has become a popular area of research.

In recent years, Cu/WO₃ has attracted a great deal of attention because it shows a relatively stronger oxidative power under exposure to visible light (>400 nm). In the recent study [13], a water-repellent composite material with a significant antibacterial effect and self-cleaning performance was developed by the addition of Cu/WO₃ to a PTFE particulate composite material. The antibacterial activities of the composite against gram-negative *E. coli*, gram-positive *Staphylococcus aureus* (*S. aureus*), and MRSA were also evaluated under visible-light irradiation. The remarkable result in the previous paper [13] is that the existence of PTFE has a role of promoting the photocatalytic reaction in the superhydrophobic composite material which was composed of 12 wt% Cu/WO₃ photocatalysis-8 wt% binder-80 wt% PTFE. This is mentioned as “synergistic effect”.

In order to investigate the origin of this “synergistic effect”, the photocatalytic decomposition performance of the Cu/WO₃-added PTFE particulate composite material was evaluated by measuring the degradation of gaseous acetaldehyde concentration on the surface of samples in the following two steps in the present study. The first step was to find the dependency of the photocatalytic reaction on the composition of photocatalyst, binder and PTFE. In the second step, the dependency of the photocatalytic reaction on the binder and PTFE composition was investigated under the fixed photocatalyst concentration condition.

2. Experimental Procedure

2.1. Step 1: Dependency of Photocatalytic Reaction on Photocatalyst, Binder and PTFE Composition

Photocatalytic reaction of the Cu/WO₃-binder-PTFE composite material was investigated. Poly Vinylidene Fluoride (PVDF) was used as binder. Samples were prepared as **Table 1**.

Sample A: 12% wt Cu/WO₃ photocatalysis-88 wt% binder-0 wt% PTFE composite material. This sample was obtained by replacing 80 wt% PTFE with binder in the superhydrophobic composite material mentioned in the previous section.

Table 1. Samples for measurements of photocatalytic degradation of gaseous acetaldehyde (CH₃CHO).

Sample Name	Cu/WO ₃ wt%	Binder wt%	PTFE wt%
A	12	88	0
B	60	40	0
C	12	44	44
D-UV	12	44	44

Sample B: 60 wt% Cu/WO₃ photocatalysis-40 wt% binder-0 wt% PTFE composite material. This was obtained by replacing 48 wt% binder with 48 wt% Cu/WO₃ photocatalysis in Sample A.

Sample C: 12 wt% Cu/WO₃ photocatalysis-44 wt% binder-44 wt% PTFE composite. This was obtained by replacing 44 wt% binder with 44 wt% PTFE in Sample A.

Sample D-UV: 12 wt% Cu/WO₃ photocatalysis-44 wt% binder-44 wt% PTFE composite material. The composition was the same as Sample C but this was for UV illumination.

Cu/WO₃ used in this study is HP-CW091, which was developed as part of the New Energy and Industrial Technology Development Organization (NEDO) Project, “Photocatalytic industry emerging project in pursuit of an environmental society”. The composite material sample was prepared by the addition of Cu/WO₃ into a mixture of PTFE particles and a fluorinated binder. This mixture together with butyl acetate was sprayed over a substrate to form the Cu/WO₃-added PTFE particulate composite materials as follows.

The PTFE particulate composite material formed a layer approximately 5 μm in thickness in a single spray. Particulate composite materials with a thickness of approximately 15 μm were formed by spraying the entire substrate three times. The composite material was ready for measurements of photocatalytic degradation of gaseous acetaldehyde (CH₃CHO). The photocatalytic decomposition performance of the Cu/WO₃-added PTFE particulate composite coatings was evaluated by the degradation of gaseous acetaldehyde in accordance with JIS 1701-2 [14], one of the standard methods for testing air purification performance. The test was implemented in a 500-ml sealed acrylic container by monitoring the concentrations of acetaldehyde and CO₂, a decomposition product, under 10,000 Lx visible light illumination with UV cut filter: N-113 for Sample A, B, C and under UV-A light (1 mW·cm⁻²) illumination for Sample D-UV. The sample was charged into the sealed container, and then 5 ml of standard acetaldehyde gas (1% balanced by N₂; Sumitomo Seika Chemicals Co. Ltd., Osaka, Japan) was injected into the container. By adsorption onto the surface of the Cu/WO₃-added PTFE particulate coating, the acetaldehyde in the container decreased gradually before illumination. The oxidative reaction of the gaseous acetaldehyde occurred by illuminating the A-C sample surface with 20 W tubular-type white fluorescent lamps (Hitachi FL20SSW/18B; Tokyo, Japan) and the D-UV sample with a black-light blue lamp (Toshiba FL10BLB, γ(p) = 310 - 380 nm, Japan) at 1 mW·cm⁻² of light intensity through a quartz window. The illumination was initiated when the adsorption equilibrium of gaseous acetaldehyde onto the sample surface was reached. Meanwhile, gas concentrations were monitored by Gas Chromatography.

2.2. Step 2: Dependency of Photocatalytic Reaction on Binder and PTFE Composition

In the second step experimental procedure, the Cu/WO₃-binder-PTFE composite material samples were prepared under the fixed photocatalyst concentration condition as shown in **Table 2**.

The photocatalytic decomposition performance of the Cu/WO₃-added PTFE particulate composite material was evaluated by the same experimental procedure as Step 1. In Step 2, the samples were illuminated by visible light only.

3. Results

3.1. Results of Step 1 Experimental Procedure

The existence of PTFE was reported to have a role of promoting the antibacterial performance in the Cu/WO₃-added PTFE particulate super hydrophobic composite materials [13]. The authors investigated this synergistic antibacterial performance through the photocatalytic degradation of gaseous acetaldehyde (CH₃CHO) using the Cu/WO₃-added PTFE particulate composite coating in the 2 steps as described earlier. The reaction time profiles for Step 1 samples are shown in **Figure 1**.

Table 2. Samples for measurements of photocatalytic degradation of gaseous acetaldehyde (CH₃CHO).

Sample Name	Cu/WO ₃ wt%	Binder wt%	PTFE wt%
A	12	8	80
B	12	44	44
C	12	88	0

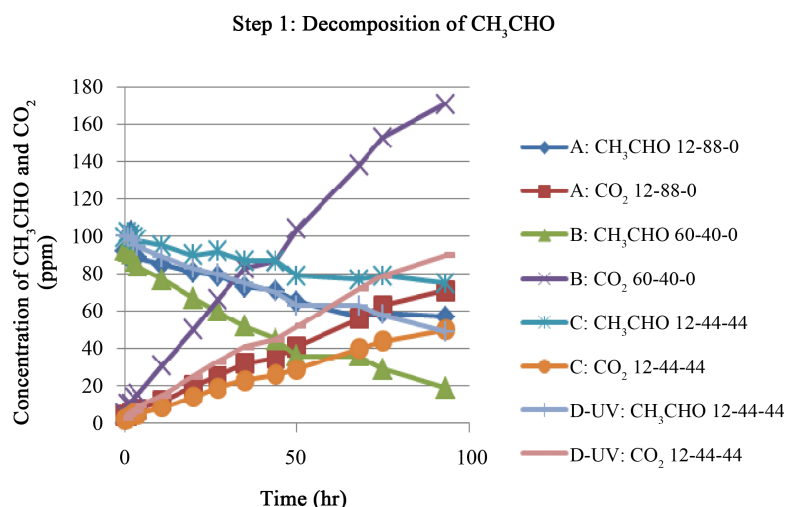


Figure 1. Time profiles of the photocatalytic decomposition of Step 1 samples. The oxidative reaction of the gaseous acetaldehyde occurred by illuminating the A-C sample surface with 20W tubular-type white fluorescent lamps and the D-UV sample with a black-light blue lamp.

The decrease in acetaldehyde concentration on the Cu/WO₃-added PTFE particulate composite samples and the simultaneous formation of CO₂ was observed. We can see from the data that the photocatalytic reactivity of Sample B is 2.4 times larger than that of Sample A. This result is attributed to the larger concentration of the Cu/WO₃ photocatalyst of Sample B as compared with that of Sample A. The photocatalytic reactivity of Sample C is not larger than that of Sample A. This shows that 44 wt% PTFE in Sample C does not accelerate the photocatalytic reactivity. This is considered in Section 4. Discussion.

Sample C and Sample D-UV have the same concentration of Cu/WO₃, binder and PTFE. The larger amount of the decrease of acetaldehyde and the simultaneous formation of CO₂ in Sample D-UV is attributed to the high energy ultraviolet ray illumination for Sample D-UV as compared with the low energy visible light illumination for Sample C.

3.2. Results of Step 2 Experimental Procedure

The reaction time profiles for Step 2 samples are shown in **Figure 2**.

The Cu/WO₃ photocatalyst concentration was fixed as 12 wt% to investigate the dependency of photocatalytic reactivity on the binder and PTFE concentration. We can see from the data that the photocatalytic reactivity of Sample A is 1.8 - 2.6 times larger than that of Sample B and Sample C. The composition of Sample A is the same as the sample that shows the synergistic effect on the photocatalytic reaction reported in the previous report [13]. Although The Cu/WO₃ photocatalyst concentration of Sample A is the same as Sample B or Sample C, only Sample A shows the excellent photocatalytic reactivity. This means the amount of PTFE in the samples relates to the synergistic effect on the photocatalytic reaction. Sample B contains 44 wt% PTFE but photocatalytic reactivity does not exceed that of Sample C which contains no PTFE. This means the amount of PTFE relates to the synergistic effect on the photocatalytic reaction. This is discussed in Section 4. Discussion.

Through Step 1 and Step 2 experimental procedure, the increase in CO₂ levels observed in conjunction with a decline in gaseous acetaldehyde indicates the complete oxidation of acetaldehyde. This is important from the viewpoint of practical applications, because acetaldehyde is known to be one of the principal odor-inducing gases indoors, particularly in cigarette smoke [15] [16].

4. Discussion

PTFE was reported to promote the antibacterial performance in 12 wt% Cu/WO₃ photocatalysis-8 wt% binder-80 wt% PTFE composite material in the previous report [13], although PTFE itself has no photocatalytic activity.

In Step 2 experimental procedure, the photocatalytic degradation measurements of gaseous acetaldehyde

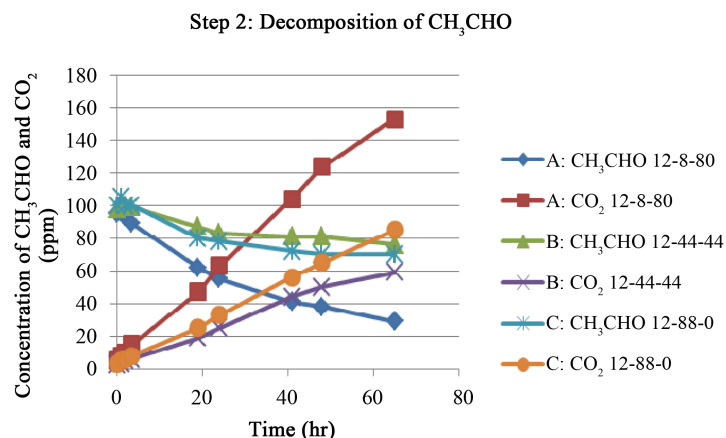


Figure 2. Time profiles of the photocatalytic decomposition of Step 2 samples. The oxidative reaction of the gaseous acetaldehyde occurred by illuminating the A-C sample surface with 20 W tubular-type white fluorescent lamps.

(CH₃CHO) showed that the 12 wt% Cu/WO₃ photocatalysis-8 wt% binder-80 wt% PTFE composite material has larger photocatalytic activity as compared with the 12 wt% Cu/WO₃ photocatalysis-44 wt% binder-44 wt% PTFE composite material and the 12 wt% Cu/WO₃ photocatalysis-80 wt% binder-0 wt% PTFE composite material. The 80 wt% PTFE in the sample has the effect of promoting photocatalytic activity but 44 wt% PTFE in the sample has no promoting effect of photocatalytic activity although Cu/WO₃ photocatalysis concentration was fixed as 12 wt%. In Step 1 experimental procedure, the more the Cu/WO₃ photocatalysis concentration, the more photocatalytic reactivity was observed. Therefore increasing the PTFE concentration has the similar effect of increasing the photocatalysis concentration.

These experimental results are explained by the PTFE particle dispersed particulate composite model [17] [18] as following.

The contact angle of water on the PTFE particle dispersed composite material is shown in Figure 3 [17].

In this composite material, PTFE particles are dispersed in the binder. According to Cassie's model for heterogeneous material [19], the contact angle of water on the PTFE Particulate composite should be between 110 degree of PTFE and 80 degree of binder. Actually the contact angle of water on the PTFE particulate composite increases rapidly for more than 60 vol% (56 wt%) PTFE concentration, which is attributed to the existence of air between water droplet and the surface of the PTFE Particulate composite. The high contact angle 151 degree of water on the 12 wt% Cu/WO₃ photocatalysis-8 wt% binder-80 wt% PTFE composite material is explained by this particulate composite model. This high contact angle corresponds to the low surface free energy of 5.8 mN/m by the revised Fawkes's theory [13] [20]. The low surface free energy makes it difficult for bacteria to stick to the 12 wt% Cu/WO₃ photocatalysis-8 wt% binder-80 wt% PTFE composite material. On the contrary, PTFE concentration of 12 wt% Cu/WO₃ photocatalysis-44 wt% binder-44 wt% PTFE composite material contains less than 60 vol%, which leads to have the low water contact angle from Particulate composite model shown in Figure 3. The low water contact angle surface corresponds to the high surface energy from the revised Fawkes's theory, which makes it easy for bacteria to stick to the surface. In the same manner, the 12 wt% Cu/WO₃-88 wt% binder-0 wt% PTFE composite has no synergistic effect. This is the reason why the 12 wt% Cu/WO₃ photocatalysis-8 wt% binder-80 wt% PTFE composite material shows the synergistic effect of the photocatalytic performance or the antibacterial performance.

5. Conclusions

In the recent study [13], a water-repellent composite material with a significant antibacterial effect and self-cleaning performance was developed by the addition of Cu/WO₃ to a PTFE particulate composite material. The surface characteristics of the newly developed composite were examined in the paper. The antibacterial activities of the composite against gram-negative *E. coli*, gram-positive *Staphylococcus aureus* (*S. aureus*), and

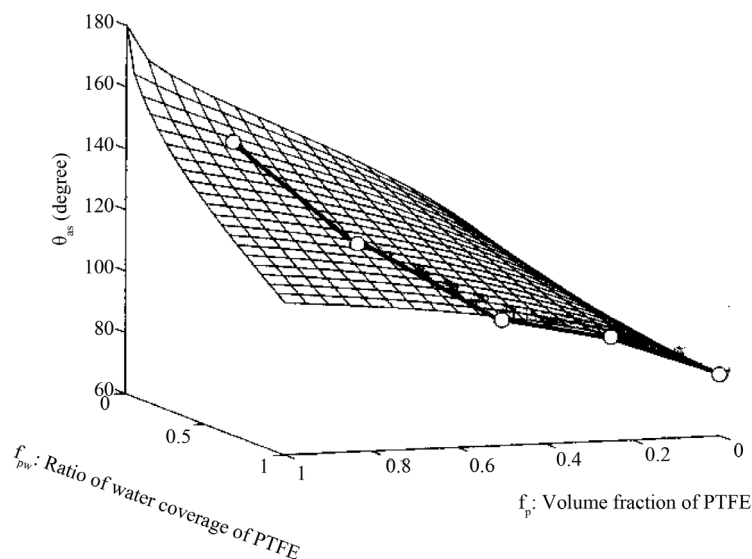


Figure 3. The contact angle θ_{as} of water as a function of PTFE volume fraction f_p and PTFE coverage of water f_{pw} [17].

MRSA were also evaluated under visible-light irradiation [13]. The remarkable result in the previous paper [13] is that the existence of PTFE has a role of promoting the photocatalytic reaction in the super hydrophobic composite which was composed of 12 wt% Cu/WO₃ photocatalysis-8 wt% binder-80 wt% PTFE composite material.

This synergistic antibacterial performance was investigated through the photocatalytic degradation of gaseous acetaldehyde (CH₃CHO) using the Cu/WO₃-added PTFE particulate composite material. The experimental results are summarized as followings.

1) The photocatalytic reactivity of the Cu/WO₃-added PTFE particulate composite material depends on the amount of Cu/WO₃ photocatalysis in the composite from the data of the 60 wt% Cu/WO₃ photocatalysis-40 wt% binder Composite and the 12% Cu/WO₃ photocatalysis-88 wt% binder composite.

2) The more photocatalytic reactivity is induced by Ultra Violet ray illumination than by visible light illumination in the 12 wt% Cu/WO₃ photocatalysis-44 wt% binder-44 wt% PTFE composite.

3) The 12 wt% Cu/WO₃ photocatalysis-8 wt% binder-80 wt% PTFE composite shows larger photocatalytic reactivity than that of the 12 wt% Cu/WO₃ photocatalysis-44 wt% binder-44 wt% PTFE composite and the 12 wt% Cu/WO₃ photocatalysis-88 wt% binder composite, although the Cu/WO₃ concentration is fixed as 12 wt% in these composites. This corresponds to the previously reported synergistic effect [13].

4) The existence of PTFE in the composites does not always guarantees the synergistic effect on the photocatalytic reaction. The 80 wt% PTFE contained composite shows the synergistic effect but the 40 wt% PTFE contained composite shows no synergistic effect.

5) The synergistic effect appears only when PTFE concentration exceeds 60 vol% (56 wt%) in accordance with the Particulate composite model [17] [18]. In this model, the contact angle of water increases up to more than 150 degree, which results in low surface energy. This leads to the synergistic effect.

These results suggest potential applications for the Cu/WO₃-added PTFE particulate hydrophobic composite material both indoors for antibacterial action and air deodorizing, and outdoors for prevention of contamination.

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