

Synergistic Antibacterial Performance of a Cu/WO₃-Added PTFE Particulate Superhydrophobic Composite under Visible-Light Exposure

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ABSTRACT

Addition of TiO₂ to a polytetrafluoroethylene (PTFE) particle-dispersed composite contributes to the self-cleaning properties of the water-repellent composite. However, its application is limited to outdoor usage or under ultraviolet (UV) irradiation. In this study, a novel visible-light-sensitive photocatalytic and superhydrophobic material was developed by adding Cu/WO₃ to a PTFE particulate composite material to overcome this deficit. A remarkable property of this novel composite material is the synergistic antibacterial performance against *Escherichia coli* (*E. coli*), *Staphylococcus aureus*, and methicillin-resistant *Staphylococcus aureus* compared with the addition of Cu/WO₃ without PTFE particles material. During 24-h exposure in visible light at 2000 lx, the number of viable cells of the three strains on the surface of the 8 wt% Cu/WO₃-added PTFE particulate composite decreased from $2 - 4 \times 10^5$ colony-formation units (CFUs) to less than 10, the limit of detection. This bactericidal rate is four times higher than that of 8 wt% Cu/WO₃ without PTFE particles material, which is attributed to the air trapped in the rough surface of the novel material providing additional oxygen to the photocatalytic reaction. Even for exposure to visible light at 100 lx, the decrease in CFUs of *E. coli* on the 12 wt% Cu/WO₃-added PTFE particulate composite reached nearly 2.0 logs. The characterization of the Cu/WO₃-added PTFE particulate composite indicated that the composite material containing 80 wt% PTFE maintained a superhydrophobic or water-repellent property with a water contact angle >150°, although the Cu/WO₃ in the composite material remained hydrophilic under visible light. The Cu/WO₃-added PTFE particulate composite displayed photocatalytic reactions to decompose oleic acid adsorbed on its surface and gaseous acetaldehyde under UV-A and visible-light illumination. All results demonstrate that the Cu/WO₃-added PTFE particulate composite material may be used in sterilization, as a water repellent, for self-cleaning, and in the oxidative decomposition of volatile organic compounds (VOC) both indoors and outdoors.

Keywords: Cu/WO₃ Photocatalyst; PTFE-Hydrophobicity; Particulate-Composite; Synergistic Antibacterial Performance; *Escherichia coli*; MRSA

1. Introduction

The conventional superhydrophobic surface associated with polytetrafluoroethylene (PTFE) [1,2] provides no sterilization performance. This limits its application in the field of disinfection. Also, a crucial and unavoidable problem in the commercialization of this superhydrophobic surface is that it is not sufficiently repellent against organic liquids, and this results in a lack of durability. 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 photocatalysis 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 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 current study, a water-repellent composite material with a significant antibacterial effect and self-cleaning performance has been developed by the addition of Cu/WO₃ to a PTFE particulate composite material. The novel composite material is expected to be useful both outdoors and indoors. The surface characteristics of the newly developed composite are examined in this paper. The antibacterial activities of the composite against gram-negative *E. coli*, gram-positive *Staphylococcus aureus* (*S. aureus*), and MRSA are also evaluated under visible-light irradiation with intensities ranging from 100 to 2000 lx, which is equivalent to indoor and outdoor conditions. Furthermore, the photocatalytic decomposition of oleic acid adsorbed on the surface and gaseous acetaldehyde using the Cu/WO₃-added PTFE particulate composite material were examined under UV-A and visible-light illumination.

2. Materials and Methods

2.1. Preparation of Hydrophobic Composite Material

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 at various concentrations (0, 3 wt%, 8 wt%, and 12 wt%) into a mixture composed of PTFE particles, a fluorinated binder, and fluoro-oil. This mixture together with butyl acetate was sprayed over a substrate to form the Cu/WO₃-added PTFE particulate composite material. 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 contact-angle measurements 24 h after the butyl acetate dried.

2.2. Characterization

2.2.1. Surface Characterization

Water contact angles were measured using an automatic contact-angle meter (Kyowa Kaimen Kagaku CA-Z). By using a syringe, a drop of water was deposited on the

sample. The contact angle was measured after the tip of the needle was separated from the drop. The contact angles measured, therefore, represented equilibrium contact angles and not advancing or receding contact angles. The contact angles were measured at five different positions for each sample.

The surface free energy of the sample was obtained using the following procedure. The contact angles, θ_{SL} , of α -bromonaphthalene (79°), methylene iodide (77°), and water (152°) were substituted into the Young-Dupre Equation:

$$W_{SL} = \lambda_{LV} (1 + \cos \theta_{SL}) \quad (1)$$

where W_{SL} is the work of adhesion and λ_{LV} is the surface free energy of the liquid as previously reported [13]. Therefore, the value of W_{SL} may be obtained using Equation (1).

The dispersion, polar, and hydrogen-bonding components of W_{SL} lead to the dispersion λ_{SV}^d , polar λ_{SV}^p , and hydrogen λ_{SV}^h bonding components of the surface free energy using the Kitazaki-Hata method [13]. The surface free energy, λ_{SV} , of the sample was obtained via Equation (2).

$$\lambda_{SV} = \lambda_{SV}^d + h\lambda_{SV}^p + \lambda_{SV}^h \quad (2)$$

2.2.2. Antibacterial Test

The bacterial activity of the Cu/WO₃-added PTFE particulate composite against *E. coli* (NBRC 3972), *S. aureus* (NBRC12732), and MRSA (clinically isolated by the Graduate School of Medicine, Yokohama City University) was evaluated, after some adjustments, in accordance with the Japanese Industrial Standard methods (JIS R 1702) [14]. Before testing, all water-repellent composite samples (50 × 50 mm) were pre-sterilized by heat treatment in an oven at 60°C for 1 h. The bacterial strains were cultured twice on nutrient agar plates (Daigo, Eikenkizai, Japan) at 37°C for 16 - 24 h. Each strain was then, respectively, suspended in 1/500 nutrient broth (NB) solution (Daigo, Eikenkizai, Japan) with a pH of 7.0, and diluted to approximately 10⁶ colony-forming units (CFUs)·ml⁻¹ to be utilized for bactericidal tests. An aliquot (100 μL) of the bacterial suspension (approximately 10⁵ CFUs) was inoculated on the sample surface. Because the test surface is hydrophobic, a covering quartz glass (40 × 40 mm) was applied to disperse the suspension drip. These settings were placed into a sealed and humid container, such as a sterilized Petri dish, in which a sterilized moisture-control paper filter was placed. A quartz glass (100 × 100 mm) was placed on the top of Petri dish to maximize transmission of visible light to the surface of the sample. The Petri dishes containing the samples were illuminated

using 20-W tubular, white fluorescent lamps (FL20SSW/18-B; Hitachi, Japan) for 24 h. The influence of the light intensity on the bactericidal activity was examined at 100, 300, 1000, and 2000 lx. Only the 2000 lx intensity included light in the UV region with wavelengths less than 400 nm at an intensity of 0.01 mW·cm⁻². The light intensity incident on the center of the specimen surface was adjusted using a UD-40 radiometer probe head (Topcon Corporation, Japan).

After illumination, the samples were washed with 10 mL soybean-casein digest broth including lecithin and polysorbate 80 (SCDLP) (Daigo, Eikenkizai, Japan). The washout solution was diluted with PBS-saline in a 10-fold dilution series. At each dilution stage, aliquots (1 mL) of the SCDLP solution were mixed with the nutrient agar medium (14 mL) (Becton Dickinson, Franklin Lakes, NJ, USA) at 45°C in a 10 cm Petri dish and allowed to cool to the room temperature. After the medium solidified, the dishes were incubated at 35°C for 24 to 48 h prior to determining the number of CFUs. The Cu/WO₃-free PTFE particulate composite films were used as contrast samples.

Bacterial tests were conducted using three parallel analyses for each sample, and the viable cell count was obtained from the average value of the product of the CFUs multiplied by 10 times the dilution rate, as shown in Equation (3).

$$\text{Viable bacterial cells} = N \times \text{dilution rate} \times 10 \quad (3)$$

where N is the number of cells of viable bacteria (CFUs) on the Cu/WO₃-added PTFE particulate composite films after visible-light illumination for a period of time. The value 10 indicates the solution (SCDLP liquid) volume for sample washing. When no CFUs were observed in undiluted SCDLP liquid, this indicated that the detection limit was no more than 10 CFUs. In such cases, the viable cell count was expressed as “≤10” to indicate the detection limit. The determination of the disinfectant property is given in terms of logarithmic decrease. In order to investigate the key operational parameters which affect the bactericidal activity of the composite materials, the bactericidal tests were carried out using materials containing various percentages of Cu/WO₃, and with different intensities of visible-light irradiation. The antibacterial values, which are suitable for direct comparison, were calculated based on these results and using Equation (4).

$$R_L = [\log(B_L/A) - \log(C_L/A)] \quad (4)$$

where I_L is the intensity used in the antibacterial tests, R_L is the antibacterial value, A is the number of viable bacteria (CFUs) on the substrate surface collected immediately after inoculation, B_L is the number of viable

bacteria (CFUs) on the substrate surface under visible-light irradiation for a period time, C_L is the number of viable bacteria (CFUs) on the surface of the Cu/WO₃-added PTFE particulate composite coating after visible-light illumination for the same period of time. All viable bacterial cell numbers (A , B_L , and C_L) were obtained by using Equation (3).

2.2.3. Fluorescence Microscopy Observation

Because the viable cells were detected by the colony-formation method which has a limitation set at no more than 10 CFUs, green fluorescent protein (GFP) gene-transformed *E. coli* (pGLO™ Bacterial Transformation Kit, BIO-RAD) was used to investigate the complete sterilization of the Cu/WO₃-added PTFE particulate composite coating. The surfaces of the samples loaded with GFP gene-transformed *E. coli* were viewed by fluorescence microscopy (AsioImagerA1 SP; Carl Zeiss, Tokyo, Japan) and an image analysis system comprising a digital counter (AxioCamMRC SP; Carl Zeiss), before and after visible-light illumination.

2.2.4. Assessment of Self-Cleaning Performance

2.2.4.1. Degradation of Oleic Acid on Cu/WO₃-PTFE Coatings

The oxidative self-cleaning performance of the Cu/WO₃-added PTFE particulate composite coatings was assessed by measurement of the contact angles of the composite coatings contaminated with oleic acid (C₁₈H₃₄O₂) during exposure to UV-A irradiation. This was based on the assumption that Cu/WO₃-added PTFE particulate composite coatings used outdoors are more susceptible to contamination by organic pollutants and sunlight, including strong UV light. This analysis was performed according to the JIS R 1703-1 standard method [15]. Prior to measuring the contact angles, the samples were cleaned for 24 h using 2 mW·cm⁻¹ of UV-A illumination incident on the testing surface to remove organic pollutants. Next, the samples were contaminated by dip coating (60 cm/min) with 0.5 vol% oleic acid diluted in n-heptane. After contamination, the samples were dried at 70°C for 15 min, and then irradiated for 333 h using an unfiltered UV light source (Toshiba FL10BLB; Tokyo, Japan). The Cu/WO₃-free PTFE particulate composite was again used for contrast testing.

2.2.4.2. Degradation of Gaseous Acetaldehyde on Cu/WO₃-added PTFE Particulate Coatings

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 [16], one of the standard me-

thods 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 UV-A light (1 mW·cm⁻¹) illumination. 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 by approximately 40 parts per million by volume before illumination. The oxidative reaction of the gaseous acetaldehyde occurred by illuminating the sample surface with a black-light blue lamp (TOSHIBA FL10BLB, $\lambda(p) = 310 - 380$ 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 using an Innova photo-acoustic field gas monitor (Model 1412; Innova Air Tech Instruments, Denmark). A pure PTFE particulate composite coating without Cu/WO₃ was used as the control.

To imitate actual light conditions, the assessment of photocatalytic degradation of gaseous acetaldehyde was also carried out using UV-A (1 mW·cm⁻¹) plus visible-light (2000 lx) illumination.

3. Results and Discussion

3.1. Surface Characterization

3.1.1. Contact Angles and Surface Free Energy

The results of water contact angles and surface free energy measurements on the surface of different composites are presented in **Table 1**.

All PTFE particulate composite samples exhibited contact angles exceeding 150°, which is consistent with their hydrophobicity despite the presence of the hydrophilic Cu/WO₃ photocatalyst. The contact angles of similar materials usually lie between those of PTFE and

of the binder with additives, including the hydrophilic Cu/WO₃ photocatalyst. However, the angles measured in this study (151°) were significantly greater than those of pure PTFE (110°) or binder (80°). This is consistent with results previously reported by Yamauchi *et al.* [17] and Miller *et al.* [18]. In that study, a particulate composite model was derived based on the Wenzel equation, which takes into consideration surface roughness [19] and the Cassie equation, which considers heterogeneous surfaces [20]. Yamauchi concluded that the binder wets more easily with water as compared with PTFE in PTFE particulate composite materials. In such a system, the contact angle increases with PTFE concentration, even beyond the contact angle of pure PTFE. When the concentration of the PTFE particles dispersed in an appropriate binder reached 80%, less than 78% of the surface area between the water droplets and composite surface was covered by air due to the surface roughness caused by the PTFE particles. Thus, we consider that the same tendency may be observed in the Cu/WO₃-added PTFE particulate composite materials if a part of the binder is replaced with Cu/WO₃. A similar result was also reported by Nakajima *et al.* [21] in their study in which TiO₂ nanoparticles were added to superhydrophobic thin film. They reported that when the dose of TiO₂ nanoparticles in the film reached a concentration below 20 wt%, the hydrophobicity of the films was not significantly increased even after UV illumination for 800 h at an intensity of 1.7 mW·cm⁻².

The surface free energy of the 8 wt% Cu/WO₃-added PTFE particulate composite material was 5.8 mN·m⁻¹, which was lower than that of the CF₃ groups (6.7 mN·m⁻¹) [22]. The hydrophobicity reflects the low surface energy of the Cu/WO₃-added PTFE particulate composite coating, which is expected to make the adhesion of contaminants difficult.

3.1.2. Scanning Electron Microscope Observation

Scanning electron micrographs of the Cu/WO₃-added PTFE particulate composite coating samples are shown in **Figures 1(a)-(c)**.

Figure 1(a) reveals many small spherical aggregates of PTFE particles, indicating a heterogeneous morphology of the pure PTFE coating. **Figures 1(b)** and **(c)** display the coating composite with 80 wt% PTFE and 3 wt% or 12 wt% Cu/WO₃, respectively. Although some ultrafine particle aggregations are found to be embedded in the composite coating, the surface roughness of the coating was still maintained. Therefore, any analysis of the surface wetting properties must consider the surface heterogeneity and surface roughness resulting from the PTFE particles and the binder. Such an analysis has previously been conducted by Yamauchi *et al.* [17], who attributed

Table 1. Water contact angles and surface free energy of the Cu/WO₃-added PTFE particulate composite film with different doses of Cu/WO₃. The surface free energy of the 8 wt% Cu/WO₃-added PTFE particulate composite material was 5.8 mN/m, and as low as 6.7 mN/m—for the CF₃ group.

Sample Name	Contact Angle (Degree)	Surface Free Energy (mN/m)
PTFE	152	5.0
8 wt% Cu-WO ₃	97	-
3 wt% of Cu-WO ₃ -PTFE	151	-
8 wt% of Cu-WO ₃ -PTFE	151	5.8
12 wt% of Cu-WO ₃ -PTFE	151	-

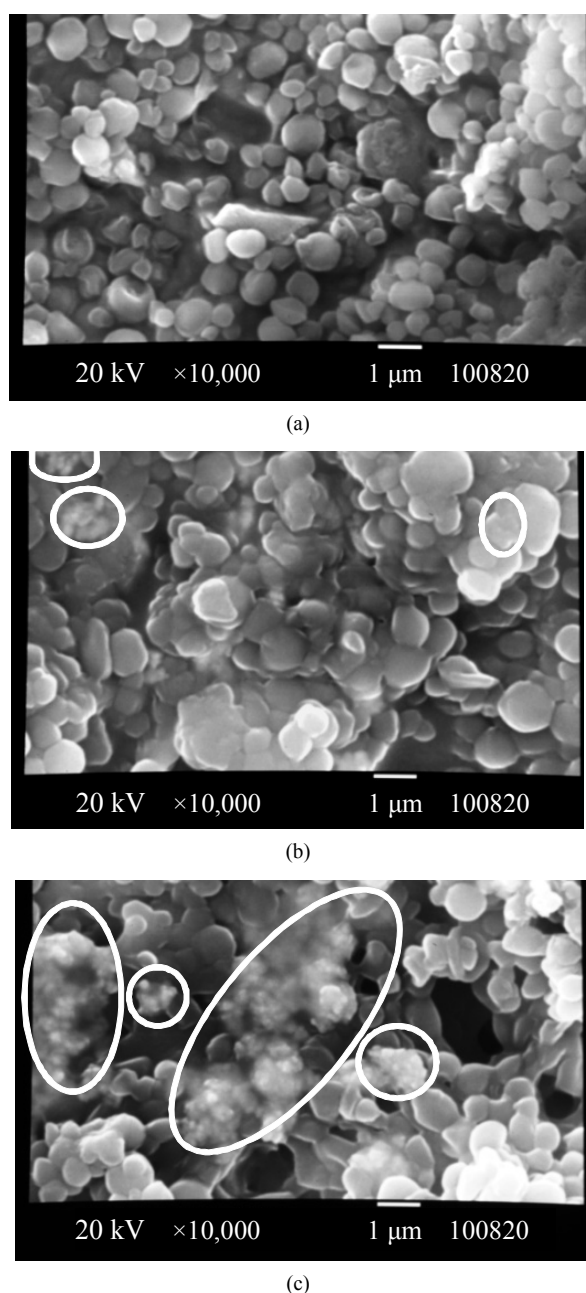


Figure 1. SEM images of the Cu/WO₃-added PTFE particulate composite film and the PTFE particulate composite without Cu/WO₃ film. The magnifications were ×10000. (a) PTFE particulate composite without Cu/WO₃ film; (b) 3 wt% Cu/WO₃-added PTFE particulate composite film; (c) 12 wt% Cu/WO₃-added PTFE particulate composite film. The fine particles circled by white ring are Cu/WO₃.

the extraordinary hydrophobicity to the presence of air between the water droplet and the substrate surface.

3.2. Bactericidal Properties

It is well known that superhydrophobicity, or water

repellency, is not sufficient to repel organic matter. Thus, there is potential for bacteria to adhere to the composite more readily in ambient air. Recently, photocatalytic inactivation has been considered as a possible approach to overcome this shortcoming. The Cu/WO₃-added PTFE particulate composite coating as a novel visible-light-sensitive photocatalyst containing hydrophobic materials is expected to have a role in indoor or outdoor air purification and disinfection. Here we analyzed the bactericidal properties of the Cu/WO₃-added PTFE particulate composite by using the test method described in Section 2.2.2.

Although the *E. coli*, *S. aureus*, and MRSA cells had to be artificially attached to the surface of the Cu/WO₃-added PTFE particulate hydrophobic composite, they could be completely inactivated by the high level of bactericidal activity of the newly developed composite. **Figure 2(a)** shows the decrease in viable *E. coli* cells on the 8 wt% Cu/WO₃-added PTFE particulate composite coatings. It can be seen in the figure that under 2000 lx visible-light illumination, the number of viable bacterial cells decreased from 10⁵ CFUs to a value below the detection limit of the colony-formation method set at 10 CFUs. **Figure 2(b)** shows that the same antibacterial performance was also confirmed on *S. aureus* and MRSA by using the same samples and experimental conditions. The data shows a possible approach to lowering the incidence of nosocomial bacterial infection, since MRSA is the major pathogenic organism and is resistant to many agents [23,24]. **Figure 3** displays the complete disappearance of the GFP gene-transformed *E. coli* cells on the composite coatings after 2000 lx visible-light was illuminated onto the 8 wt% Cu/WO₃-added PTFE particulate composite for 24 h. There is a remarkable finding that the bactericidal activity of the Cu/WO₃-added PTFE particulate composite was significantly enhanced in comparison with Cu/WO₃ without PTFE particles coating (**Figure 2**).

Numerous studies have explained the mechanism of photocatalytic antimicrobial activity as the loss of cell membrane integrity caused by electrons/holes or by reactive oxygen species (ROSs) [25–27]. Therefore, we consider that when the membrane-damaged bacteria were subjected to a continuous photocatalytic reaction, they were finally broken by these ROSs, as shown in the disappearance of the GFP gene-transformed *E. coli* on the composite coatings during exposure to visible-light illumination. We also deem that the greater surface roughness (**Figure 1**) offered by PTFE results in more air pockets that provide additional oxygen for the photocatalytic reaction, which in turn leads to further ROS generation to enhance the bactericidal activity of the Cu/WO₃-added PTFE particulate composite.

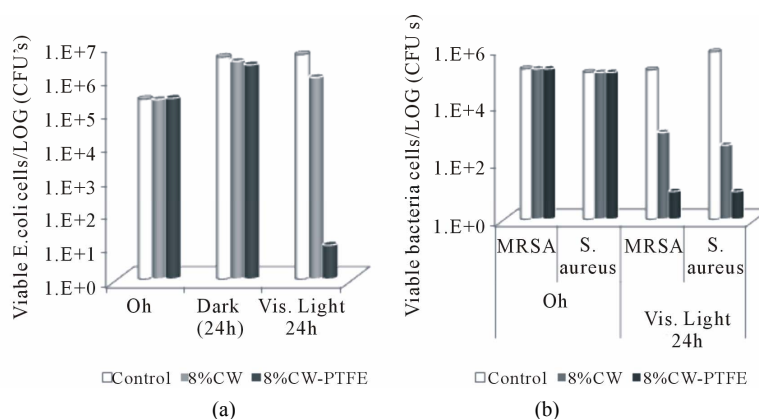


Figure 2. Bactericidal effects of PTFE particulate composite hydrophobic films, without (control) and with the addition of Cu/WO₃ (CW), on (a) *E. coli*; (b) *Staphylococcus aureus* and methicillin-resistant *Staphylococcus aureus* (MRSA), under visible-light illumination at 2000 lx for 24 h. The photo-bactericidal effect was significantly enhanced by combination of Cu/WO₃ and PTFE, compared with the composite coating film having Cu/WO₃ without PTFE.

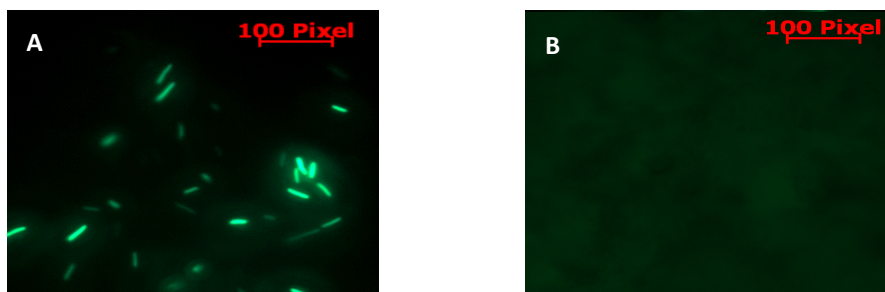


Figure 3. Disappearance of green fluorescent protein (GFP) gene-transformed *E. coli* cells on 8 wt% Cu/WO₃-added PTFE particulate composite coating after 2000 lx of visible-light illumination for 24 h.

Figure 4 shows the key operational parameters which affect the bactericidal activity of the composite materials. By comparison of the bactericidal activity-value calculated using Equation (4), the activity of the newly developed hydrophobic composite material clearly depends on the concentration of Cu/WO₃ and visible-light intensity. No bactericidal activities were observed in the control samples (PTFE without Cu/WO₃). It is reasonable to believe that the Cu/WO₃ nanoparticles are unique materials which contribute to the bactericidal action of the composite material. Furthermore, even with a very low intensity of illumination (100 lx), the antimicrobial value reached 1.7, signifying the decrease in the number of viable *E. coli* cells nearly by two points on a logarithmic scale. Thus, we believe that this novel water-repellent composite material may find application in such places in hospitals and senior citizens' homes.

3.3. Self-cleaning Property

3.3.1. Photocatalytic Degradation of the Cu/WO₃-Added PTFE Particulate Composite Coating on Oleic Acid

It is well known that when a conventional water-repellent

material is contaminated with oil pollutants, its hydrophobicity will be reduced. It is generally considered that this is because of the interaction that occurs between the water molecule dipole moment and the dipole moment of the carboxyl group (COOH) of oleic acid. Therefore, the photocatalytic degradation of the PTFE particulate composite is expected to be ameliorated by adding Cu/WO₃. **Figure 5** shows that the Cu/WO₃-added PTFE particulate composite coating exhibited a self-cleaning performance to oxidatively degrade oleic acid under visible light. From the data, large decreases in the contact angles could be observed in the composite coating with 3% Cu/WO₃ when it was contaminated with oleic acid. After being subjected to 1 mW·cm⁻² of UV irradiation for 333 h, the oleic acid was removed successfully only on the surface of the Cu/WO₃-added PTFE particulate composite coating, after which the contact angle recovered to its initial value.

Photocatalytic degradation of oleic acid has been reported in several studies. In 2006, W. Dai, *et al.* reported that the hydroxyl radicals produced by reaction of the photogenerated holes with surface hydroxyl groups is the main oxidant for the photocatalytic degradation of car-

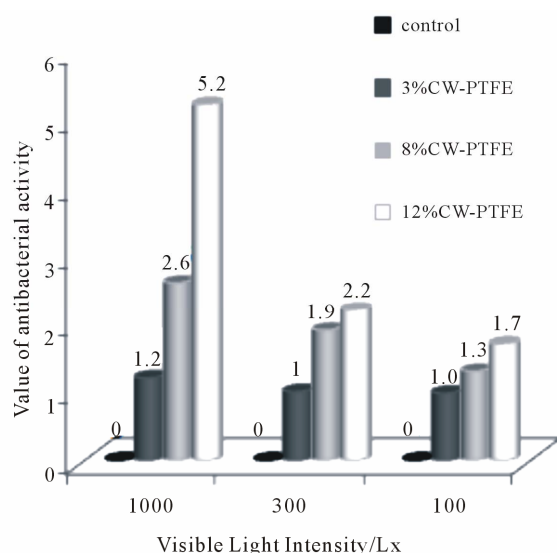


Figure 4. Value of antibacterial activity evaluated on the surface of the Cu/WO₃-added PTFE particulate composite film and the PTFE particulate composite film without Cu/WO₃ (controls), on *E. coli* under visible-light illumination at various intensities for 24 h.

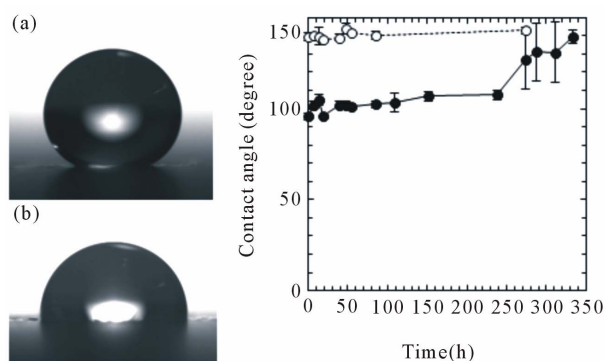


Figure 5. Recovering of the water contact angles of 3 wt% Cu/WO₃-added PTFE particulate composite coating contaminated with 0.5 vol% oleic acid diluted in n-heptane during exposure to 1 mW·cm⁻² of UV-A light for 333 h. ●: Oleic acid (+), ○: Oleic acid (-). (a) Water droplet on 3 wt% Cu-WO₃-added PTFE particulate composite surface without oleic acid contamination and UV-A illumination; (b) Water droplet on 3 wt% Cu/WO₃-added PTFE particulate composite surface after contamination with oleic acid and without UV-A illumination.

boxylic acids at the liquid-solid interface of TiO₂ catalysts [28]. In 2011 J. Rathousky and coworkers proposed that the oxidative degradation of the TiO₂ film was induced by an attack of the hydroxyl radical on the double bond. The eliminated hydroxyl radical could act catalytically and thus cause accelerated degradation of unsaturated compounds including fatty acids, which could be

expected to be proportional to the degree of its degradation, *i.e.*, its transformation into more hydrophilic compounds as well as into gaseous products (CO₂ and H₂O) [29]. These published results and our findings confirm that, although superhydrophobicity is not sufficient to repel organic matter, especially oil, the photocatalytic oxidation could eliminate these organic stains and preserve the superhydrophobic surface after it had been exposed to outdoor conditions for a long period of time.

It is noteworthy that neither the 8 wt% nor the 12 wt% Cu/WO₃-added PTFE particulate composite coatings changed their contact angles even when they were contaminated with oleic acid. This observation was the same in the 3 wt% sample (data not shown). We considered in this case that the relatively high inclusion level of Cu/WO₃ greatly increased the surface energy of the fluorinated binder. This allows the oleic acid to seep through the PTFE particles possessing low surface energy and to adsorb the binder, allowing the superhydrophobicity to still be maintained. These results indicate that the relatively high level inclusion of Cu/WO₃, a novel visible-light-sensitive photocatalyst, into the PTFE particulate composite improved the durability of its hydrophobicity.

3.3.2. Decomposition Performance of the Cu/WO₃-Added PTFE Particulate Composite Coating on Gaseous Acetaldehyde

When a novel composite material is designed for indoor use, an additional property expected is the air deodorizing ability. We investigated this capability through the photocatalytic degradation of gaseous acetaldehyde (CH₃CHO) using the Cu/WO₃-added PTFE particulate composite coating, as described earlier. The reaction time profiles, shown in **Figures 6(a)** and **(b)**, indicate the decrease in acetaldehyde concentration on the Cu/WO₃-added PTFE particulate composite coating under UV-A (a) or UV-A plus visible light (b), while the simultaneous formation of CO₂ is observed. The decomposition rate constant for gaseous acetaldehyde was calculated to be in the range of approximately 0 - 0.3 h. We can see from the data that the degradation rate under UV-A plus visible-light illumination ($k_1 = 0.041$) was four times that under UV-A only ($k_1 = 0.010$). Although the degradation rates shown here were relatively low, the novel composite material applied to a lag area as paint could compensate for this shortcoming. In addition, the increase in CO₂ levels observed in conjunction with a decline in gaseous acetaldehyde indicates the complete oxidation of acetaldehyde. This is very 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 [30,31].

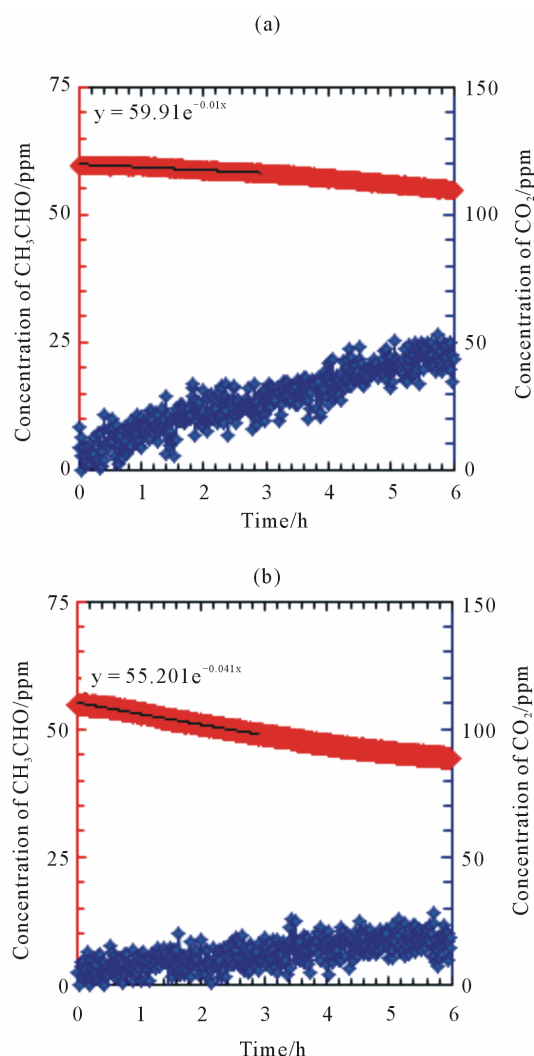


Figure 6. Time profiles of the photocatalytic decomposition of CH₃CHO using 12 wt% Cu/WO₃-added PTFE particulate hydrophobic composite material. (a) Illuminated with 1 mW·cm⁻² of UV-A only; (b) Illuminated with 1 mW·cm⁻² of UV-A plus 2000 lx of visible-light.

4. Conclusion

In this paper, we have developed a novel water-repellent composite material with photocatalytic activity, as shown in antimicrobial and photocatalytic degradation performance. This material is composed of a Cu/WO₃ photocatalyst (a visible-light-sensitive photocatalyst), PTFE particles, a fluorinated binder, and fluoro-oil. The composite material exhibited a water contact angle greater than 150°, and a surface energy as low as 6 mN/m, indicating superhydrophobicity or water repellency. The novel water-repellent material completely inactivated *E. coli*, *S. aureus*, and MRSA from ca. $2 - 4 \times 10^5$ CFUs during 2000 lx of visible-light illumination for 24 h. In particular, the extremely high inactivation of MRSA

showed that the developed superhydrophobic composite material may be resistant to hospital-acquired infections. Even at very low intensity, the visible-light induced photocatalytic inactivation reduced *E. coli* cells by nearly 2 logs. The synergistic effect of the photocatalytic performance and the hydrophobicity of the Cu/O₃-added PTFE particulate composite coating results in the significant enhancement of bactericidal rate compared with Cu/WO₃ without PTFE particles composite coating. This was attributed to the surface roughness provided by the PTFE; more air pockets offered additional oxygen to the photocatalytic reaction leading to greater reactive oxygen species' generation. We also clarified that organic stains adsorbed on the composite surface could be successfully removed utilizing UV-induced photocatalytic oxidation, which resulted in sustainable high hydrophobic states. Furthermore, the novel composite material photocatalytically decomposed gaseous acetaldehyde during UV-A or UV-A irradiation plus visible light, while CO₂ was observed. 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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