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Photocatalytic and Antibacterial Activities over WO_3 on Glass Filters

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WO_3 on a glass filter prepared from peroxotungstic acid (PA) showed not only high photocatalytic activity under solar simulated light but also high antibacterial activity even if light irradiation was not present.

TiO_2 photocatalysts have been utilized practically in air cleaners and self-cleaning glasses under UV light irradiation; however, the activity under visible light over TiO_2-based photocatalysts such as N-doped TiO_2[1,2] is not yet sufficient to use for indoor applications. Recently, it was reported that WO_3 photocatalysts loaded with suitable cocatalysts such as CuO, $CuBi_2O_4$, Cu^{2+}, Pd, WC, and Pt showed higher activities compared to TiO_2-based photocatalysts for the degradation of various organic compounds into CO_2 under visible light.[3–12] WO_3 photocatalytic activities have been evaluated as only powder form so far. However, it is essential for practical use of WO_3 photocatalysts to deposit on substrates or filters. We have investigated the photocatalytic activity of WO_3 on glass filter. It was found that the WO_3 filter showed not only high photocatalytic activity under solar simulated light but also high antibacterial activity even if light irradiation was not present. It is well known that TiO_2 photocatalysts show high antibacterial activity under UV light,[13–15] but they do not in dark conditions. Metal oxide powders such as ZnO, CaO, and MgO, showing antibacterial activity in the dark,[16] are very limited. Here, we describe both the photocatalytic and the antibacterial activities on WO_3 over glass filters in detail.

Two methods (PA and IE) were utilized for the preparation of WO_3 deposited on quartz glass fiber filter (Advantec QR-100). The amount of WO_3 deposition was 40 mg cm^{-2}. The WO_3 powder prepared with PA (peroxotungstic acid) was reported as highly efficient photocatalyst for the degradation of organic compounds under visible light.[11] The porous WO_3 film deposited on conducting glass by IE (ion exchange) was reported as a highly efficient photoelectrode for the water-splitting reaction with high quantum efficiency up to 76%.[17] It is advantageous for both methods that stable coating solution with precursors of WO_3 could be prepared. As for PA method (WO_3-PA), tungsten metal powder was dissolved in aqueous H_2O_2, and the solution temperature was kept at ca. 70 °C for 90 min to age the solution of peroxotungstic acid (2.8 mol L^{-1} tungsten). The colorless solution became orange during this aging treatment. As for IE method (WO_3-IE), tungstic acid solution was prepared by H^+ exchange of aqueous Na_2WO_4 solution. The solution was evaporated and poly(ethylene glycol) (PEG-300) was added (0.75 mol L^{-1} tungsten).[17] The coating solution in each PA and IE method was spread on a glass filter heated on a hot plate, and then it was calcined in air at 450 and 550 °C. These surface areas of WO_3 were similar, 22 (WO_3-PA) and 18 m^2 g^{-1} (WO_3-IE), respectively.

The photocatalytic degradation of organic substances was conducted on WO_3 glass filter (20 × 20 mm) in a glass reactor (22 mL). The CuO co-catalyst (0.1 wt % to WO_3) was loaded by impregnation using aqueous $Cu(NO_3)_2$ solution, and the filter was calcined at 300 °C. The photocatalyst filter was irradiated using a solar-simulator (Seric Co., AM-1.5 and 0.5 sun intensity at around 400–500 nm). The concentration of CO_2 generated in the photocatalytic degradation was measured by a gas chromatograph (FID) equipped with a methanizer. The antibacterial activity tests on WO_3 glass filters (50 × 50 mm) with and without UV light irradiation (0.01 mW cm^{-2}) were conducted at the certification organizations (Japan Synthetic Textile Inspection Institute Foundation and Japan Textile Products Quality and Technology Center) for Japanese Industrial Standards (JIS) R 1702, test method for antibacterial activity of photocatalytic products under photoirradiation and efficacy. The bacteriostatic activity (BA) factor under UV light is calculated as log(viable bacteria count without WO_3/viable bacteria count with WO_3).

The antibacterial activity results of WO_3 photocatalysts prepared by PA method on glass filter with and without UV light irradiation after 8 h are shown in Table 1. The glass filter itself did not show any antibacterial activity. On the other hand, it is noteworthy that all WO_3 on glass filters showed excellent activity for *Staphylococcus aureus* (SA) and *Klebsiella pneumonia* (KP) even if not irradiated. According to JIS L 1902 (Testing for antibacterial activity and efficacy on textile products), the antibacterial activity can be certificated when the BA factor is more than 2 after 8 h. The viable bacteria counts were less than the detection limit in all WO_3 with and without cocatalyst, and the BA factors were around 4. It is suggested that WO_3 itself has an excellent antibacterial activity in the dark. Table 2 shows the comparison between WO_3 filters prepared by PA and IE methods on the antibacterial activity after 4 h. It was found that the activity of WO_3 filters prepared by PA method was much higher than that by IE method. The viable bacteria counts under UV light were always lower than that in the dark. It was difficult for these differences with and without UV light to distinguish the effects by photocatalytic reaction and direct UV reaction.

Table 1. The antibacterial activity of WO_3 photocatalysts (PA method) on glass filter after 8 h

Bacteria	Photocatalyst	Viable bacteria count[a]		BA factor
		UV	dark	
SA	filter only	2.9×10^5	8.9×10^5	—
SA	WO_3	<20	<20	>4.1
SA	CuO(0.1 wt %)–WO_3	<20	<20	>4.1
SA	Pd(0.01 wt %)–WO_3	<20	<20	>4.1
KP	filter only	1.9×10^5	2.2×10^5	—
KP	WO_3	<20	<20	>3.9
KP	CuO(0.1 wt %)–WO_3	<20	<20	>3.9
KP	Pd(0.01 wt %)–WO_3	<20	<20	>3.9

[a]Initial viable bacteria count: SA: 2.3×10^4 and KP: 1.9×10^4.

Table 2. The antibacterial activity of WO_3 photocatalysts on glass filter after 4 h

Bacteria	Photocatalyst	Viable bacteria count[a]		BA factor
		UV	dark	
SA	filter only	3.2×10^5	5.7×10^5	−0.2
SA	WO_3-PA	27	40	3.9
SA	WO_3-IE	2100	7000	2.0

[a]Initial viable bacteria count: SA: 2.2×10^4.

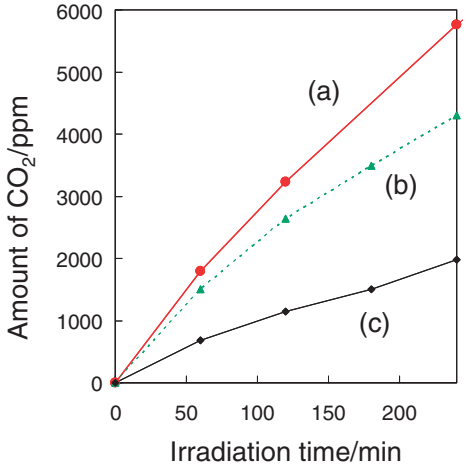

Figure 1. The time course of CO_2 formation during the degradation of hexane (2 mL) over WO_3 on glass filters under solar-simulator (0.5 Sun). (a) WO_3-PA, (b) WO_3-IE, and (c) commercial WO_3 from Wako Chemical Co. on glass plate.

It is fascinating for various commercial products to have the added values of high photocatalytic activity and strong antibacterial activity. The surface of products can be kept clean by both effects. Figure 1 shows the time course of CO_2 formation during the degradation of hexane over WO_3 on glass filters. The activities of WO_3 on glass filters were higher than that of commercial WO_3 powder, and that of WO_3 prepared by PA method was higher than that of WO_3 prepared by IE method. Figure 2 shows the time course of CO_2 formation during the degradation of acetaldehyde over WO_3 on glass filters. The introduced acetaldehyde could be decomposed completely into CO_2 over CuO-loaded WO_3 on glass filters, while it could not over WO_3 without CuO. The activity of CuO–WO_3 filter prepared by PA method was also higher than that by IE method. The CuO–WO_3 filter is practically useful because it also can be expected to show antibacterial activity by Cu^{2+} from CuO as well as by WO_3 with high photocatalytic activity.

The difference of the photocatalytic activities between PA and IE methods can be explained by the light absorption and the crystallinity of WO_3 on the glass filter.[11] The light absorption at 400–470 nm on WO_3-PA was higher than that on WO_3-IE. Moreover, the XRD pattern on WO_3-PA was sharper than that on WO_3-IE. On the other hand, it is difficult to explain the difference of the antibacterial activities between PA and IE methods. The solubility of WO_3 in water is generally negligible. Preliminary antibacterial activity tests of H_2WO_4 (1000 ppm) and Na_2WO_4 (10 ppm) in a solution of *Staphylococcus aureus* for 4 h were conducted; however, the antibacterial activities were not clear. The sizes of these bacteria are from 0.5 µm to a few µm, which are much larger than the primary particle size of WO_3 (30–40 nm),

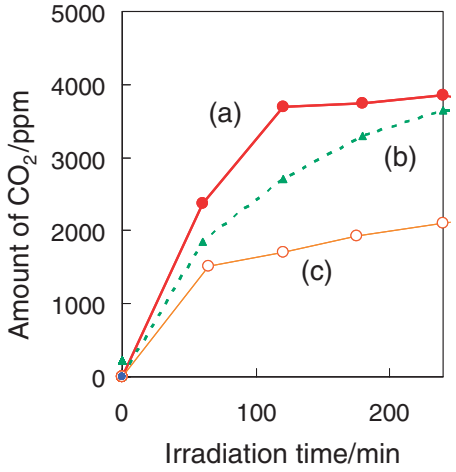

Figure 2. The time course of CO_2 formation during the degradation of acetaldehyde (1800 ppm) over WO_3 on glass filters under solar-simulator (0.5 Sun). (a) CuO-loaded WO_3-PA, (b) CuO-loaded WO_3-IE, and (c) WO_3-PA without CuO.

suggesting that the antibacterial activity is not influenced by surface area of WO_3 directly. Figure S1[18] shows SEM photographs of WO_3 filters prepared by (a) PA and (b) IE methods. The special characteristic of the WO_3 prepared by PA method was a very smooth surface of the secondary particles;[11] therefore, there is a possibility that an intimate adsorption of bacteria on the smooth surface of WO_3-PA might be more suitable for the antibacterial activity compared to the rough surface of WO_3-IE.

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