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Simple preparation of TiO_2 particles dispersed activated carbons and their photo-sterilization activity

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We report a simple preparation method for TiO_2 particles dispersed activated carbons and their photo-sterilization activity for *E. coli* and *B. subtilis*. The TiO_2 particles dispersed activated carbons were readily prepared by steam activation of pitch containing titanium isopropoxide $Ti(OiPr)_4$ or titanium acetylacetonate $TiO(acac)_3$. The resulting activated carbons have high BET surface area and fine TiO_2 particles are uniformly dispersed. The photo-sterilization activities for *E. coli* and *B. subtilis* were estimated by the sterilization activity for bacteria spores by irradiation of black light to the solutions containing activated carbons. The obtained activated carbons exhibited high photo-sterilization activity for *E. coli* and *B. subtilis* with short irradiation time of 15 min.

1. Introduction

In water purification systems with activated carbons, the growing of bacteria on the surface of activated carbons often spoils the function of activated carbon and the resulting water is polluted by bacteria. In connection with this spoiling of activated carbons, antibacterial activated carbons have recently attracted much attention. Ag deposited activated carbons prepared by impregnation methods are known to be antibacterial activated carbons [1–3]. However, there are some problems for Ag supported activated carbons prepared by impregnation or deposition methods. That is, a few steps are necessary to synthesize Ag-supporting materials by impregnation in Ag solutions and heat-treatment of activated carbons is needed, and Ag ions rapidly elute at the initial stage of usage [1].

Regarding antibacterial activity of metal oxides, Sawai *et al*. [4–6] reported that metal oxide powders such as MgO, CaO, and ZnO showed a growth inhibitory effect for *Staphylococcus aureus* (*S. aureus*) and *Bacillus subtilis* (*B. subtilis*). Based on these results, we prepared activated carbons containing metal oxide particles by activating pitch containing organometallics, and additionally we reported that the activated carbons containing MgO or CoO exhibited antibacterial activity for *B. subtilis* and *S. aureus* although they have no activity for *E. coli* [7].

On the other hand, a strong photo-sterilization effect of titanium dioxide (TiO_2) has been reported [8–12] and the preparation and photo-sterilization activity of activated carbons containing TiO_2 particles has been investigated [13]. For the preparation of TiO_2 supported activated carbons, the deposition of colloidal TiO_2 particles onto activated carbon [13] and vapor deposition of TiO_2 using cluster ion beam [14] were reported. However, these methods need tedious processes and loss of surface area and pores may be caused by deposition of TiO_2.

From these points of view, we explored the preparation of TiO_2 particles dispersed activated carbons by a simple method. We investigated the preparation of activated carbons from pitch containing organotitanium complexes by steam activation. As a result, fine TiO_2 particles dispersed activated carbons were obtained. In addition, we tested the photo-sterilization activity of the resulting activated carbons for *E. coli* and *B. subtilis*. The activated carbons obtained in this manner exhibited strong photo-sterilization activities for these bacteria.

2. Experimental

2.1. Materials

Pitch was coal tar pitch from Osaka Gas Co.(softening point: 72.2°C, C: 93.2%, H : 4.7%, N : 1.1%). Titanium isopropoxide ($Ti(OiPr)_4$, Aldrich) and titanium acetylacetonate ($TiO(acac)_3$), Kanto Chemical Co.) were used without further purification. Polypeptone (Wako Pure Chemical Ind. Ltd.), Extract Yeast Dried (Nacalai Tesque, Inc.), and $MgSO_47H_2O$ (Nacalai Tesque, Inc.) were used for nutrient broth without further purification. *Escheritia coli* (*E. coli*) (HUT8106) and *B. subtilis* (IFO3134) were obtained from Fermentation Technology Department of Hiroshima University.

2.2. Carbons

Various activated carbons were prepared by steam activation of pitch containing organotitanium compounds.

Pitches containing organotitanium compounds were obtained by mixing a THF solution of pitch with THF solutions of organotitanium compunds. A typical preparation method is as follows: 4.22 g of pitch was placed in a 300×10^{-6} m^3 two necked round bottom flask and volatiles were removed under reduced pressure at 120°C. The pitch was dissolved in 90×10^{-6} m^3 of dry THF. $Ti(OiPr)_4$ (1.78 g) dissolved in 90×10^{-6} m^3 of dry THF was added to the pitch solution. After stirring for 2 h, THF was removed by flash distillation. Activated carbons were obtained by activation of pitch containing organotitanium compounds with steam at 900°C.

2.3. Methods

Specific surface areas and pore size distributions were determined by the BET method, and *t*-plots (for micropore) and BJH [15] (for mesopore) methods, respectively, by applying N_2 adsorption isotherms measured using a Quantachrome Autosorb-6. X-ray diffraction (XRD) analyses were performed using a Rigaku RDA-1B system with Cu K_α radiation. The dispersion behavior of metal oxides in activated carbons was observed by electron probe microanalysis (EPMA) with a JEOL JXA-8900. Images of TiO_2 particles in activated carbons were obtained by transmission electron microscopy using a Topcon EM-002B electron microscope. The metal contents in carbons were measured by particle-induced X-ray emission (PIXE). PIXE analysis was performed using a van de Graaf accelerator of Hiroshima University. The intensity of the characteristic X-ray generated by irradiation of H^+ was measured.

We estimated antibacterial activities of TiO_2 particles dispersed in activated carbons by photo-sterilization activity for spores of *E. coli* and *B. subtilis*. A photo-sterilization activity was determined as follows; A portion of *E. coli* was inoculated in 5×10^{-6} m^3 of sporulation medium (beef extract 10 g, poly-pepton 10 g, NaCl 5 g/1 dm^3 of pure water). The medium was incubated at 37°C for 18 h. The spores were inoculated in sporulation medium. Photo-sterilization of bacteria cells with activated carbons was carried out in a 200×10^{-6} m^3 flask. To the spores in 100×10^{-6} m^3 of sporulation medium, activated carbons were added. The flask was irradiated using a 20 W black light fluorescent lamp at 37°C. The cell viability of bacteria was determined based on the number of colonies developed on nutrient broth agar plates.

3. Results and discussion

3.1. Pore characteristics

Table I shows the carbonization yields and pore characteristics of the activated carbons obtained from pitches containing $Ti(OiPr)_4$ and $TiO(acac)_3$. On sample number in Table I, Ti(P) and Ti(A) express the carbons containing $Ti(OiPr)_4$ and $TiO(acac)_3$ systems, respectively, and the last Arabic numerals indicate activation time. The addition of Ti complexes resulted in the decrease of carbonized yields as compared with Ti complex-free pitch. In both cases using $Ti(OiPr)_4$ and $TiO(acac)_3$, BET specific surface areas and mesopore surface areas increased with increasing activation time. Ti complexes in pitch or Ti compounds formed during steam activation seem to accelerate the carbonization by steam and promote the formation of pores. On the other hand, the high content, 10 wt%, of Ti in pitch decreased BET surface area and mesopore surface area when we used the same activation time. Addition of excess Ti complex is supposed to destroy the initially formed pores throughout activation. The increase of Ti complexes resulted in slightly increased carbonization yields at the same activation time. It seems that most Ti remains in activated carbons even after activation and increases the carbonization yield.

Fig. 1 shows pore radius distribution of Ti10(A)-AC12. The activated carbon contains pores mainly of

TABLE I Pore characteristics of activated carbons

	Organotitanium complex	Ti content in pitch (wt%)	Activation time (min.)	Yield (%)	BET surface area (m^2/g)	Mesopore surface area (m^2/g)
AC	——	——	30	24.7	88	5
Ti2(P)-AC12	$Ti(OiPr)_4$	2	12	30.4	217	54
Ti2(P)-AC18	$Ti(OiPr)_4$	2	18	26.6	270	84
Ti2(P)-AC25	$Ti(OiPr)_4$	2	25	20.7	385	154
Ti5(P)-AC12	$Ti(OiPr)_4$	5	12	35.9	248	47
Ti5(P)-AC18	$Ti(OiPr)_4$	5	18	30.2	336	113
Ti5(P)-AC25	$Ti(OiPr)_4$	5	25	23.2	414	253
Ti10(P)-AC12	$Ti(OiPr)_4$	10	12	40.9	150	46
Ti10(P)-AC18	$Ti(OiPr)_4$	10	18	33.4	230	70
Ti10(P)-AC25	$Ti(OiPr)_4$	10	25	25.5	282	185
Ti2(A)-AC12	$TiO(acac)_3$	2	12	33.0	204	62
Ti2(A)-AC18	$TiO(acac)_3$	2	18	27.0	301	113
Ti2(A)-AC25	$TiO(acac)_3$	2	25	17.9	455	283
Ti5(A)-AC12	$TiO(acac)_3$	5	12	34.2	287	38
Ti5(A)-AC18	$TiO(acac)_3$	5	18	30.3	324	101
Ti5(A)-AC25	$TiO(acac)_3$	5	25	24.2	385	207
Ti10(A)-AC12	$TiO(acac)_3$	10	12	39.3	200	64
Ti10(A)-AC18	$TiO(acac)_3$	10	18	33.8	259	118
Ti10(A)-AC25	$TiO(acac)_3$	10	25	27.0	263	176

Activation temp.: 900°C.

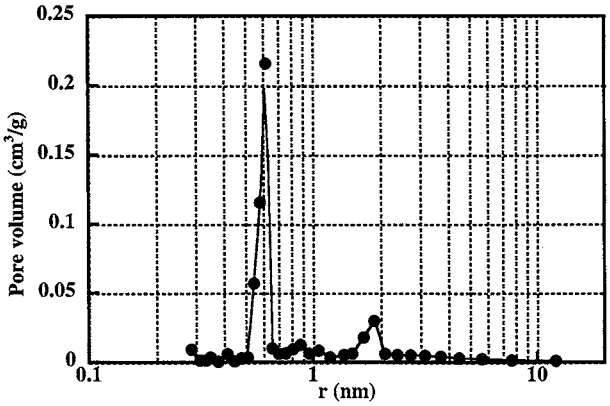

Figure 1 Pore radius distribution of Ti10(A)-AC12.

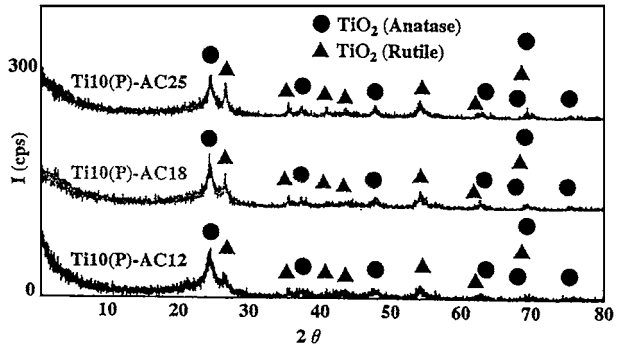

Figure 2 XRD patterns of Ti10(P)-AC.

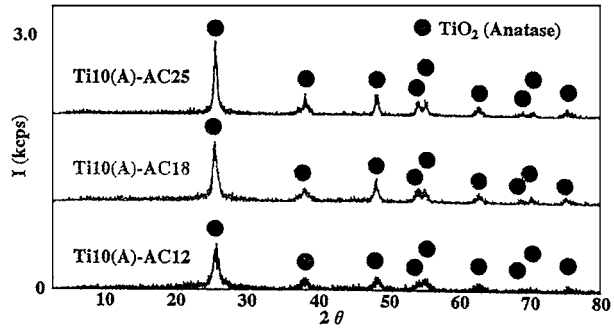

Figure 3 XRD patterns of Ti10(A)-AC.

about 1.2 and 3.6 nm of diameter. Other activated carbons obtained from pitch containing Ti complexes exhibited similar pore size distributions with that of Ti10(A)-AC12.

3.2. TiO_2 particles

In general, steam activation of pitch containing organometallics generates metal or metal oxides in activated carbons. We analyzed the kind of metal species and contents in activated carbons by XRD and PIXE analyses, respectively. Figs 2 and 3 show the XRD patterns of Ti10(P)-AC and Ti10(A)-AC (Ti content in pitch: 10 wt%) activated carbons, respectively. Anatase and rutile (2 : 1–5 : 1) are generated from pitch containing $Ti(OiPr)_4$, while only anatase is formed from pitch containing $TiO(acac)_3$. Ti contents in activated carbons are shown in Table II. Ti contents in activated carbons range from 1.5 to 22 wt%. Ti contents in activated carbons increased with increasing the concentration of Ti complexes and activated time in both cases of $Ti(OiPr)_4$ and $TiO(acac)_3$. The peaks of the XRD patterns shown in Figs 2 and 3 became narrower suggesting that the crystal size of TiO_2 particles slightly increased with increasing activation time. We measured dispersion behavior of TiO_2 particles in activated carbons by EPMA. Fig. 4 shows the EPMA images of Ti on Ti5(A)-AC25. TiO_2 is dispersed uniformly in the activated carbon. Similarly, EPMA images for other activated carbons indicated that TiO_2 was dispersed uniformly in activated carbons obtained in this manner. We measured the dispersion behavior and particle size of TiO_2 in activated carbons by transmission electron microscopy

TABLE II Photo-sterilization activities of activated carbons for *E. coli*

	Organotitanium complex	Ti content in activated carbon (wt%)	Number of colony	
			Initial (CFU/10^{-6} m^3)	Irradiation for 24 h (CFU/10^{-6} m^3)
AC	——	——	8.2×10^7	8.2×10^7
Ti2(P)-AC12	$Ti(OiPr)_4$	1.5	8.2×10^7	1.65×10^3
Ti2(P)-AC18	$Ti(OiPr)_4$	1.8	8.2×10^7	1.91×10^3
Ti2(P)-AC25	$Ti(OiPr)_4$	3.3	8.2×10^7	4.10×10^3
Ti5(P)-AC12	$Ti(OiPr)_4$	3.1	8.2×10^7	1.35×10^3
Ti5(P)-AC18	$Ti(OiPr)_4$	4.9	8.2×10^7	1.71×10^3
Ti5(P)-AC25	$Ti(OiPr)_4$	5.1	8.2×10^7	3.10×10^3
Ti10(P)-AC12	$Ti(OiPr)_4$	7.4	8.2×10^7	0.75×10^3
Ti10(P)-AC18	$Ti(OiPr)_4$	8.6	8.2×10^7	0.82×10^3
Ti10(P)-AC25	$Ti(OiPr)_4$	10.2	8.2×10^7	1.84×10^3
Ti2(A)-AC12	$TiO(acac)_3$	3.5	8.2×10^7	1.85×10^3
Ti2(A)-AC18	$TiO(acac)_3$	5.7	8.2×10^7	2.25×10^3
Ti2(A)-AC25	$TiO(acac)_3$	7.2	8.2×10^7	3.75×10^3
Ti5(A)-AC12	$TiO(acac)_3$	10.0	8.2×10^7	1.23×10^3
Ti5(A)-AC18	$TiO(acac)_3$	14.7	8.2×10^7	1.42×10^3
Ti5(A)-AC25	$TiO(acac)_3$	16.2	8.2×10^7	2.50×10^3
Ti10(A)-AC12	$TiO(acac)_3$	19.3	8.2×10^7	0.64×10^3
Ti10(A)-AC18	$TiO(acac)_3$	20.8	8.2×10^7	0.83×10^3
Ti10(A)-AC25	$TiO(acac)_3$	22.0	8.2×10^7	1.56×10^3

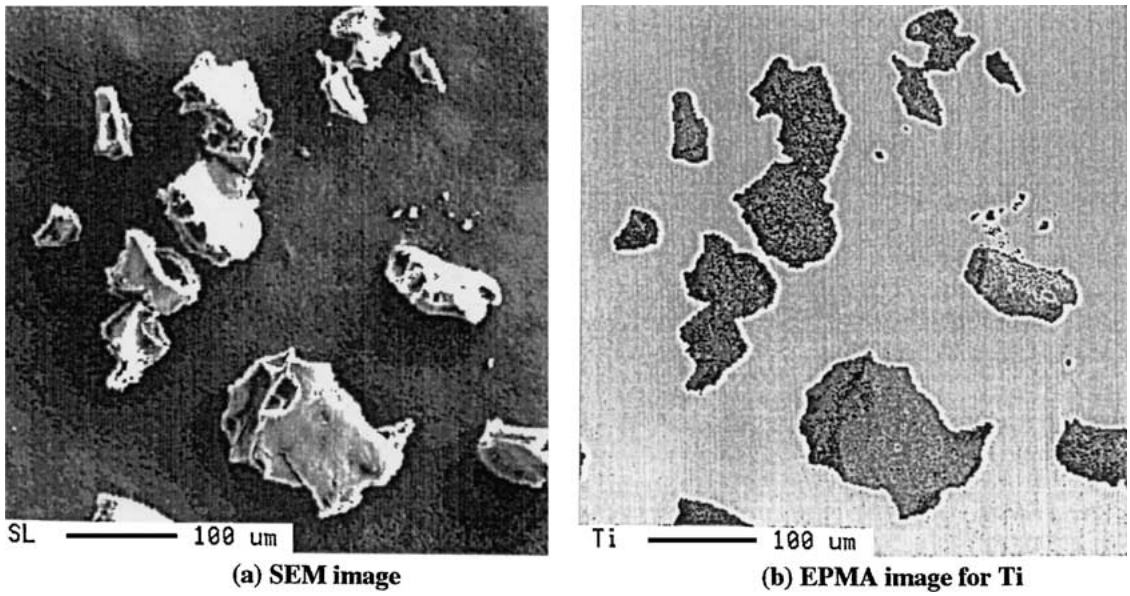

Figure 4 EPMA image of Ti5(A)-AC25.

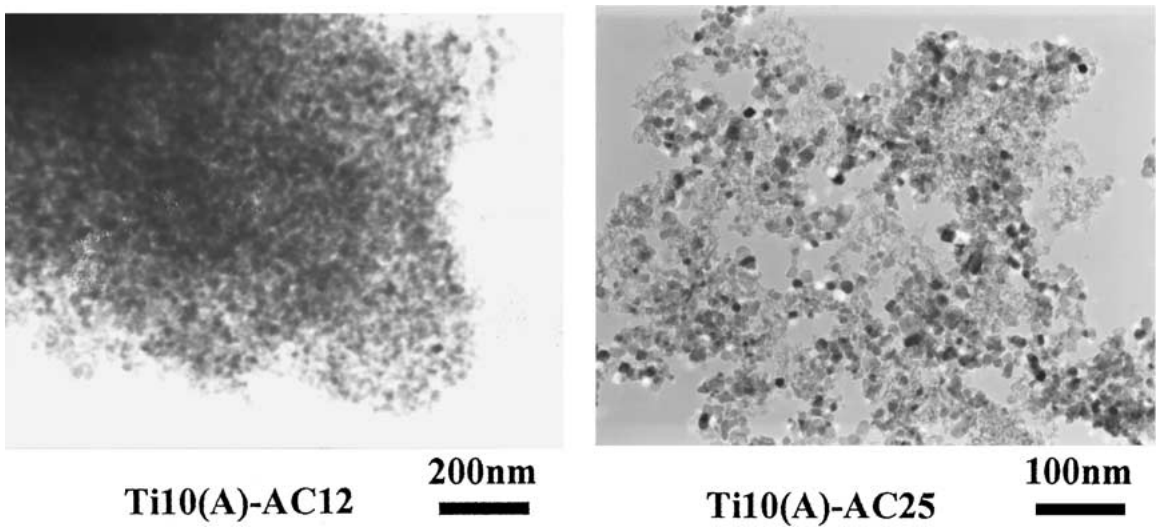

Figure 5 TEM images of Ti10(A)-AC12 and Ti10(A)-AC25.

(TEM). Fig. 5 shows TEM photographs of Ti10(A)-AC12 and Ti10(A)-AC25. With activation of 12 min TiO_2 particles below 10 nm are dispersed in Ti10(A)-AC12 activated carbon. On the other hand, the increase of activation time resulted in an increase in particle size of TiO_2 and the size of TiO_2 increased to 20 nm. The coalescence of TiO_2 particles seems to take place throughout activation.

The sizes of these TiO_2 particles are much larger than those of pores in activated carbons. TiO_2 particles dispersed in carbon matrix are supposed to be partially exposed to the surfaces of pores and the outer surface of activated carbons.

3.3. Photo-sterilization

Fig. 6 shows the (C_t/C_0) values (C: number of colonies) for *E. coli* as against irradiation time using a black light exposed to the dispersions containing Ti10(P)-AC12 and Ti10(A)-AC12, respectively. C_0 and C_t are the number of colonies of *E. coli* cultured on agar before and after irradiation, respectively. With irradiation of short time (15 min), C_t/C_0 falls to below 1/10000. This indicates that more than 99% of spores of *E. coli* was photo-sterilized in both cases of the activated carbons obtained from pitch containing $TiO(acac)_3$ (Ti(A) system) and $Ti(OiPr)_4$(Ti(P) system). Table II shows the influence of the concentration of Ti complexes in pitch and activation time on the number of colonies of cultured *E. coli* at irradiation time of 24 h. The number of colonies of cultured *E. coli* in Ti(A) system is slightly lower than at in Ti(P) system. This seems to be due to higher TiO_2 contents in Ti(A) system than those in Ti(P) system. On the other hand, the increase in activation time lowered the photo-sterilization activity. As noted above, the particle size of TiO_2 increased with increasing activation time. Therefore, the increase in particle size of TiO_2 may decrease the photo-sterilization activity. However, these results strongly indicate that the activated carbons obtained from pitch containing $TiO(acac)_3$ or $Ti(OiPr)_4$ generate strong photo-sterilization activity. On the other

TABLE III Effect of added amount of activated carbons on photo-sterilization activity for *E. coli*

Activated carbon	Added amount of activated carbon (mg/100 × 10^{-6} m^3)	Number of colony	
		Initial ($CFU/10^{-6}$ m^3)	Irradiation for 24 h ($CFU/10^{-6}$ m^3)
Ti2(A)-AC12	5	8.2×10^7	0.82×10^3
	10	8.2×10^7	1.00×10^3
	50	8.2×10^7	3.45×10^3
	100	8.2×10^7	3.47×10^3
Ti5(A)-AC12	5	8.2×10^7	0
	10	8.2×10^7	0
	50	8.2×10^7	3.30×10^3
	100	8.2×10^7	3.50×10^3
Ti10(A)-AC12	5	8.2×10^7	0.12×10^3
	10	8.2×10^7	0.12×10^3
	50	8.2×10^7	0.15×10^3
	100	8.2×10^7	0.17×10^3

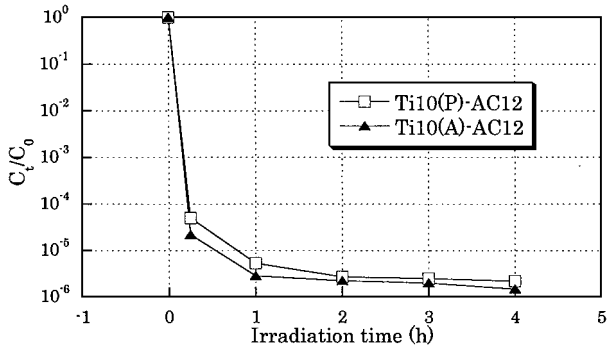

Figure 6 Photo-sterilization activity of Ti10(P)-AC12 and Ti10(A)-AC12 for *E. coli* as a function of irradiation time of black light.

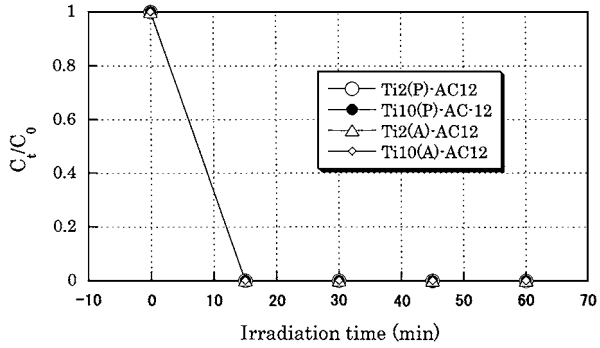

Figure 7 Photo-sterilization activity of activated carbons for *B. subtilis* as a function of irradiation time of black light.

hand, there are some problems for photo-sterilization system using TiO_2 dispersed activated carbon. One of them is transmittance of light into the inner part of the sterilization system, namely, irradiation of light to inner activated carbons in the system. In order to clarify this point, we tested the influence of concentration of activated carbon added to the spores solution of *E. coli*. Table III shows the number of colonies of cultured *E. coli* after photo-sterilization at different concentrations of activated carbon. In the case of Ti5(A)-Ac12, a small amount of addition gave high photo-sterilization activity. However, the number of colonies increased with increase of amount of activated carbons added to spores solutions of *E. coli* solutions. The excess addition of activated carbon hindered irradiation into the inner part of the photo-sterilization system. The addition of a small amount of activated carbon is sufficient for photo-sterilization using activated carbon obtained by the method described in this report.

Fig. 7 shows the C_t/C_0 values for *B. subtilis* as a function of irradiation time of black light. Similarly to *E. coli*, more than 99% of spores of *B. subtilis* was sterilized by 15 min of irradiation of black light. Thus the activated carbons obtained in this work also exhibited strong photo-sterilization for *B. subtilis*.

In general, regarding the photocatalytic sterilization of microbial cells with TiO_2 particles, it is supposed that the cells are killed by hydroxyl radicals (·OH) and hydrogen peroxide (H_2O_2) generated on the surface of photoexcited TiO_2 particles [16–20]. On the other hand, because light cannot penetrate into inner parts of pores of activated carbons, TiO_2 particles on the outer surface of activated carbons are supposed to play an important role in photo-sterilization. TiO_2 dispersed in activated carbons obtained in this work are fine in size and uniformly dispersed. Therefore, we conclude that a strong photo-sterilization activity is attributed to finely dispersed TiO_2 particles on the surface of activated carbons. In addition, from the points that the crystallinity of TiO_2 from $TiO(acac)_3$ is higher than that of TiO_2 from $Ti(OiPr)_4$ as shown in Figs 2 and 3, the high crystallinity of TiO_2 seems to give high photo-sterilization activity.

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