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Antibacterial Activity of TiO_2/Ti Composite Photocatalyst Films Treated by Ultrasonic Cleaning

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ABSTRACT

In this work, TiO_2/Ti composite films were fabricated by 2-setp MCT and the following high temperature oxidation. Antibacterial activity of the composite films treated by ultrasonic cleaning to increase the performance reliability was examined. The prepared TiO_2/Ti composite films showed high photocatalytic activity in the degradation of methylene blue solution. It is obvious that TiO_2/Ti composite films have antibacterial activity under UV irradiation.

Keywords: Mechanical Coating Technique; TiO_2/Ti Composite Film; Photocatatlyst; Antibacterial Activity

1. Introduction

In recent years, TiO_2 photocatalysts have showed a high potential in the environmental and energy fields, including self-cleaning Surfaces, air and water purification systems, sterilization, hydrogen evolution and photoelectrochemical conversion, among others [1-3]. To lower the recycling cost and increase the degradation efficiency of pollutants, investigations of TiO_2 photocatalysts are oriented toward the immobilization in the form of films [4,5]. Numerous techniques including physical vapor deposition (PVD), chemical vapor deposition (CVD), and sol-gel method, among others have been used to fabricate TiO_2 photocatalyst films to increase their photocatalytic activity [6-8]. However, some disadvantages limit the applications of these techniques. For example, complicated and large scale equipments are required and their processes can be operated only in vacuum for PVD and CVD. In addition, the production cost is relatively high.

In this condition, we developed ball milling and proposed a novel coating technique called mechanical coating technique (MCT) to fabricate TiO_2 photocatalyst films on alumina (Al_2O_3) balls [9-12]. In MCT, collision, friction and abrasion among Ti powder, alumina balls and the inner wall of the bowl are utilized effectively to form Ti films on alumina balls. After that, TiO_2 films or TiO_2/Ti composite films were fabricated by the following high-temperature oxidation. Although the TiO_2 resultants had rutile crystal type, they showed relatively high photocatalytic activity [11]. Further, we developed 2-step MCT based on the concept of MCT to prepare TiO_2/Ti composite films by coating nano-TiO_2 powder particles on the Ti films without oxidation process [9,12]. The TiO_2/Ti composite films showed high photocatalytic activity in the degradation of methylene blue solution. It is expected that the TiO_2/Ti composite films on alumina balls are applied in the environmental and energy fields.

In this work, TiO_2/Ti composite films on alumna balls were fabricated by 2-step MCT and the following high temperature oxidation. Ultrasonic cleaning was performed for the alumina balls with the TiO_2/Ti composite films to increase the performance reliability. Photocatalytic activity and antibacterial activity of the TiO_2/Ti composite films were evaluated and discussed.

2. Experimental

2.1. Fabrication of TiO_2/Ti Composite Films

First, Ti powder with an average diameter of 30 μm and a purity of 99.1% was used as the coating material. Alumina (Al_2O_3) balls with an average diameter of 1 mm were used as the substrates. Ti powder and Al_2O_3 balls were charged into a bowl made of alumina with a dimension of Φ75 × 70 mm (250 m*l* in volume). Then the mechanical coating was carried out by a planetary ball mill (Pulverisette 6, Fritsch). The rotation speed of the ball mill was set at 300 rpm and the milling time was 10 h. During the fabrication, milling operation was performed 10 min followed by 2 min intermittence to avoid the overheating of the bowl and the contents. The schematic diagram of MCT can be found in our published work [9].

Secondly, TiO_2/Ti composite films were fabricated. The Al_2O_3 balls coated with Ti films and anatase TiO_2 nanopowder of 7 nm in average diameter (ST-01, purity: 99.99 %, Ishihara Sangyo) were used as the substrate and the coating material, respectively. The rotation speed of planetary ball mill was 300 rpm. MCT was carried out for 3 h. Planetary ball mill (Pulverisette 6, Fritsch) was also employed for MCT in the second step.

Further, to enhance the photocatalytic activity and, the alumina balls with TiO_2/Ti composite films were heat-treated at 773 K in air for 10 h. Subsequently, all the samples were cleaned in acetone by ultrasonic (frequency: 28 kHz) for 1.5 h to remove the unstrong adhesions on the surface of the samples to increase the performance reliability.

2.2. Characterization of TiO_2/Ti Composite Films and Evaluation of Photocatalytic Activity

The morphologies and the microstructures of the samples were observed by SEM (JSM-6510, JEOL).

Photocatalytic activity of the samples was evaluated by measuring the degradation rate of methylene blue (MB) solution at room temperature. The samples were spread uniformly on the bottom of a cylinder-shaped cell with Φ20 × 50 mm. To obtain the same initial conditions of evaluating photocatalytic activity for all the samples, pre-adsorption of MB solution was carried out using 3 m*l* MB solution with a concentration of 20 μmol/*l* before evaluating photocatalytic activity. Subsequently, the samples after the pre-absorption were spread uniformly on the bottom of the cell again and 7 m*l* MB solution with a concentration of 10 μmol/*l* was poured into the cell. Then photocatalytic activity was evaluated under UV light irradiation with an intensity of 1 mW/cm^2 for 24 h. These evaluation conditions were referenced to Japanese Industrial Standard (JIS R 1703-2). The absorbance of MB solution was measured by a colorimeter (Sanshin Industrial Co., Ltd) with UV irradiation. The gradient, k ($nmol \cdot l^{-1} \cdot h^{-1}$) of MB solution concentration-irradiation time curve was calculated by the least-squares method with the data from 1~12 h and used as the degradation rate constants. The details of the evaluation can be found in our published work [12].

3. Evaluation of Antibactiral Activity

Antibacterial activity of the alumina balls with TiO_2/Ti composite films was evaluated by using **Escherichia** coli test referred to JIS R 1702 for the flat film sample. The Ti film alumina balls by MCT were used for the control sample. First, the alumina balls (5 g) with TiO_2/Ti composite films were washed by alcohol and air-dried, then spread uniformly on the bottom of a petri dish with Φ50 × 12 mm as shown in **Figure 1**. Subsequently, 0.8 m*l* solution of **Escherichia** coli (NBRC3972) culture with 1.3~5 × 10^5 colony/m*l* was dropped uniformly onto the the alumina balls on the bottom of the petri dish. In order to count the starting colonies of **Escherichia** coli, the control samples of the Ti film alumina balls were immediately washed away by using 9.2 m*l* SCDLP medium as shown in **Figure 2** and the medium was diluted by 10 fold dilution. Besides, the samples of the alumina balls with TiO_2/Ti composite films were placed in the dark and under UN irradiation (by FL15BL-B) with 0.1 mW/cm^2 (by UV-340A) for 8 h respectively as shown in **Figure 3**. Afterwards, the samples were washed away by using 9.2 m*l* SCDLP medium and the medium was diluted by 10 fold dilution as the control samples for counting the colonies of **Escherichia** coli. The all test were carried out at 25.4ºC.

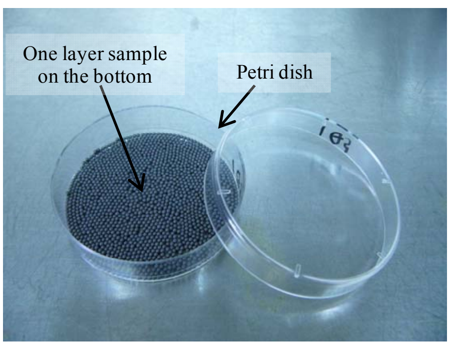

Figure 1. One layer of the alumina balls with TiO_2/Ti composite films spread uniformly on the bottom of petri dish.

4. Reasults and Discussion

4.1. Surface Morphologies and Photocatalytic Activity of the TiO_2/Ti Films

Figure 4 shows the surface morphologies of the TiO_2/Ti films.

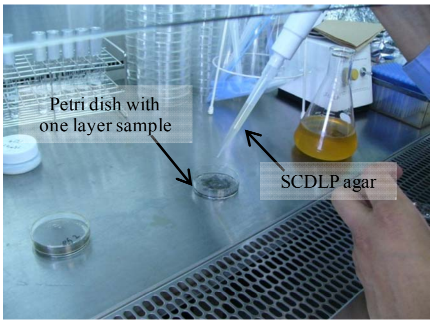

Figure 2. Wash-out of the culture medium in antibacterial activity test.

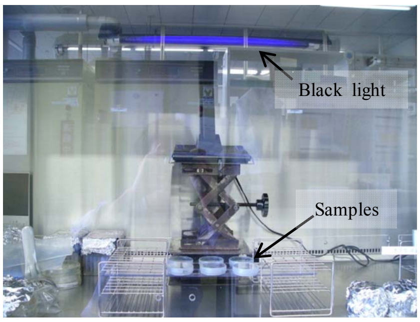

Figure 3. Antibacterial activity test under UV irradiation .

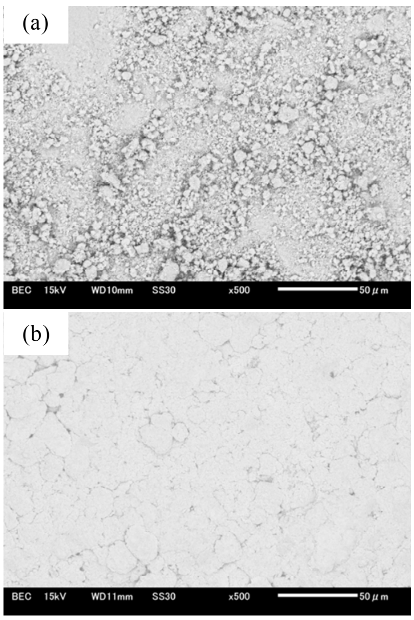

Figure 4. SEM images of surfaces of the films, (a) TiO_2/Ti composite films and (b) TiO_2/Ti composite films after ultrasonic cleaning.

It can be found that the adhered some TiO_2 particles on the surface of the Ti films were removed by ultrasonic cleaning. It must be that the removed TiO_2 particles had relative weak adhesion strength and the performance reliability of the TiO_2/Ti films will be increased by ultrasonic cleaning. **Figure 5** gives the concentration evolution of MB solution as a function of UV irradiation time. After ultrasonic cleaning, although the degradation rate constants k was lower rather than that (k = 574 nmo$l \cdot l^{-1}h^{-1}$) without ultrasonic cleaning, still kept relative large value, 486 nmo$l \cdot l^{-1}h^{-1}$. It hints that there is enough TiO_2, which has strong adhesion on the Ti film base after ultrasonic cleaning.

4.2. Antibactrial Activity of TiO_2/Ti Composite Films

Figure 6 shows photographs of the poured plate cultures samples used the collected bacterial culture liquid. Compared of these photographs, it is obvious that the quantity of the bacillus coli in the case (**Figure 6(d)**) of TiO_2/Ti films is less than that of the Ti films used for the control samples. It shows that TiO_2/Ti films has antibacterial activity. **Table 1** gives antibacterial test conditions and results. The average count of **Escherichia** coli of the control samples had a starting average count, 3.6 × 10^5, however, after 8 h, reached 18.0 × 10^5 and 11.3×10^5 in the dark place and under UV irradiation respectively. On the other hand, the average count of **Escherichia** coli for the TiO_2/Ti films were less than these of the control samples of the Ti films, 9.3 × 10^5 and 1.7 × 10^5 in the dark place and under UV irradiation respectively. The TiO_2/Ti composite films shown obvious antibacterial activity.

Table 2 shows the decision of the antibacterial test validity. In order to all the evaluation conditions, the antibacterial tests in this work passed all the evaluation conditions.

In these years, the antibacterial performance of TiO_2 photocatalysts have been paid close attention. The sterilization performance of **Escherichia** coli for TiO_2 plat films and nano-powder was reported [13,14]. However, the applications of TiO_2 probably are limited by the shapes of plat films and powder. In this work, the TiO_2/Ti composite film balls with the sterilization performance of **Escherichia** coli will lead new applications.

Besides, the photokilling process of **Escherichia** coli on TiO_2 photocatalyst can be understood as follows [13]. The initial reaction is a partial decomposition of the outer membrane by the reactive species produced by TiO_2 photocatalysis. Correspondingly, the permeability change of the outer membrane enables reactive species to easily reach the cytoplasmic membrane. Thus, the cytoplasmic membrane is attacked by reactive species, leading to the peroxidation of membrane lipid.

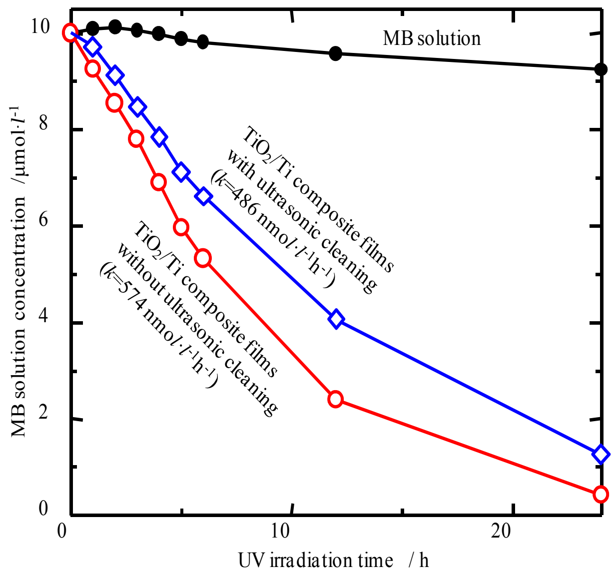

Figure 5. Concentration evolution of MB solution as a function of UV irradiation time for TiO_2/Ti composite films.

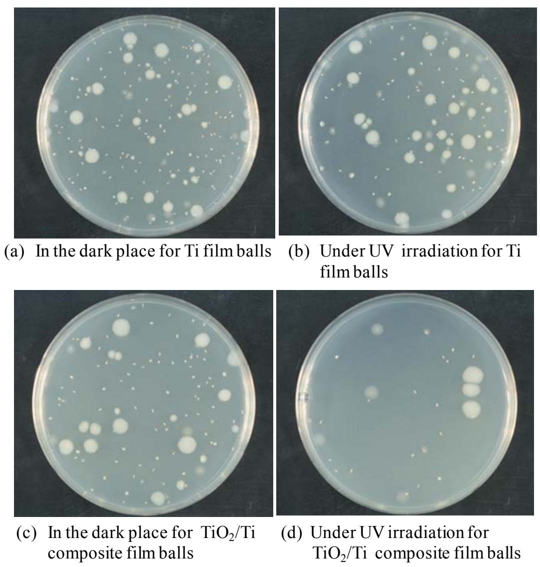

Figure 6. The samples of the standing plate culture used the collected bacterial culture liquid after antibacterial test for 8 h of Ti and Ti/TiO_2 composite films (The white points and circle bodies: bacillus coli).

Table 1. The antibacterial test conditions and results of TiO_2/Ti composite films.

Sample	Irradiation condition	Petri dish number	Total bacteria count (×10^5)	Average bacteria count (×10^5)
Ti films (control sample)	0 h	1	3.6	3.6
		2	3.8	
		3	3.3	
	8 h in the dark place	1	17	18.0
		2	19	
		3	18	
	8 h UV irradiation (0.1 mW/cm^2)	1	11	11.3
		2	12	
		3	11	
TiO_2/Ti composite films	8 h in the dark place	1	9.6	9.3
		2	8.1	
		3	10	
	8 h UV irradiation (0.1 mW/cm^2)	1	1.8	1.7
		2	1.6	
		3	1.8	

5. Conclusions

TiO_2/Ti composite films on alumna balls were fabricated by 2-step MCT and the following high temperature oxidation. Ultrasonic cleaning was performed for the alumina balls with the TiO_2/Ti composite films to increase the performance reliability. Photocatalytic activity and antibacterial activity of the TiO_2/Ti composite films were evaluated respectively. After ultrasonic cleaning, although the degradation rate constants k still kept high photocatalytic activity in the degradation of methylene blue solution. TiO_2/Ti composite films has obvious antibacterial activity.

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