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Titania/Hydroxyapatite Composite Multifunction Photocatalyst Film Coating Using a Hybrid Aerosol Beam Irradiation Coating System

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A titania/hydroxyapatite (TiO_2/HA) composite multifunction photocatalyst was developed for application in air purification and as an antibacterial, antifouling film. This advanced film has the ability to adsorb and decompose organic matter. To obtain the TiO_2/HA composite photocatalyst film, we developed a hybrid aerosol beam (HAB) irradiation coating system by building on the aerosol deposition method (ADM). The HAB system is composed of two aerosol chambers (TiO_2 and HA), an aerosol mixture chamber and a processing chamber. Neither the substrate nor TiO_2/HA particles were heated during deposition. Changes produced in the acetaldehyde level by the TiO_2/HA composite film were also investigated.
Key words: HAB, ADM, Titania, Hydroxyapatite, Photocatalyst

1. INTRODUCTION

Anatase-phase titanium dioxide (TiO_2) is widely used in environmental cleaning because of its photocatalytic properties when irradiated by ultraviolet light (UVL: $\lambda <$ 390 nm), enabling decomposition of organic matter such as bacteria, mold and odors [1,2]. For decomposition to occur, however, the organic matter must contact the surface of the TiO_2. But TiO_2 is not able to adsorb organic matter. Another drawback is that the photocatalytic properties of TiO_2 are not displayed at low UVL intensities or when UVL is absent, such as indoors or at night.

In contrast, hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) actively adsorbs organic matter but is not able to decompose it [3-5], so its surface becomes saturated with organic matter over time. A TiO_2/HA composite film overcomes the respective drawbacks of TiO_2 and HA by both adsorbing and decomposing organic matter, making it highly suitable for environmental cleaning.

For maximum effectiveness, TiO_2 should be anatase rather than rutile phase, which displays lower photocatalytic properties. Plasma spraying, however, is performed at a temperature higher than the phase transition temperature of the submillimeter-size primary powder. With other conventional coating techniques such as sol-gel, physical vapor deposition (PVD) and chemical vapor deposition (CVD), it is extremely difficult to apply a uniformly mixed coating of TiO_2 and HA because of the difference in particle size and density.

This uniformity problem is overcome by the hybrid aerosol beam (HAB) deposition method, which employs a beam formed of sub-micron size particles. The HAB method is based on further development of the aerosol deposition method [6]. This new method enables composite films such as TiO_2/HA to be applied at low temperature with high adhesive strength. This study investigated fabrication of TiO_2/HA composite films using the HAB method, including the influence of the beam's incident angle on adhesion strength, and on the surface and cross-sectional morphology.

2. EXPERIMENTAL PROCEDURE

Figure 1 shows a schematic drawing of the HAB apparatus used to produce the TiO_2/HA film. The experimental conditions are presented in Table I. Gas consumption was 15 L/min. Substrates were as-received commercial soda-lime-silica slide glass measuring 24 x 32 x 0.15 mm. The experimental system was composed two aerosol chambers, one aerosol mixture chamber and one deposition chamber. The TiO_2 and HA powders were commercially purchased. The TiO_2 and HA powders were aerosolized in the respective aerosol chambers by a flow of helium (He) gas and an aerosol vibration system. A hybrid aerosol was formed in the aerosol mixture chamber by mixing the TiO_2 and HA aerosols. The hybrid aerosol was sent to the deposition chamber by the He gas flow. The hybrid aerosol was accelerated and formed into a beam through a fixed nozzle with a slit of 6 x 0.3 mm. The glass substrate was set on a stage 10 mm from the nozzle. The beam's incident angle was varied from 0 to 60 degrees at intervals of 10 degrees by rotation of the θ stage. An area of 6 x 10 mm was scanned for 20 seconds at room temperature.

2.1 Powder characteristics

An electron probe surface roughness analyzer (FE-SEM; ERA-8800FE, Elionix Inc., Japan) was employed to observe the shape of the primary particles, the surface of the as-deposited film, and the cross-sectional morphology of the film obtained by cleaving the glass substrate.

Figure 2 shows FE-SEM micrographs of the TiO_2 and HA powders. The TiO_2 powder (Junsei Chemical Co., Ltd., Japan) has a nearly orbicular shape with a diameter of less than 1 μm. The HA powder (Taihei Chemical Industrial Co., Ltd., Japan) has a hexagonal shape with a length of less than 3 μm. Conventional powder X-ray diffraction (XRD; JEOL Ltd., Japan) measurements were made to confirm the crystalline structure of the film. A Joint Committee on Powder Diffraction Standards (JCPDS) card was used for identification of the crystal structure of the powders and film.

2.2 Measurement of photocatalytic properties

The decomposition of organic matter on the film was evaluated by changes in the acetaldehyde level, a conventional method for evaluating the decomposition capacity of TiO_2 film. In this study, this method was applied for continuous evaluation, from adsorption on the film to decomposition. First, the coated substrate was placed in a 1 liter glass container, which was then filled with acetaldehyde adjusted to an initial concentration of 100 ppm. The acetaldehyde concentration was measured at room temperature by gas detection tubes (No.92M, Gastec Corporation, Japan). The acetaldehyde concentration was then measured every 60 minutes for a period of 180 minutes to determine the HA's adsorption capacity. At 180 minutes, the surface of the coated substrate in the glass container was irradiated with UVL from a black light source to investigate the decomposition capacity of the TiO_2 in the composite film. The film was continuously irradiated for 360 minutes, and the acetaldehyde concentration was again measured every 60 minutes.

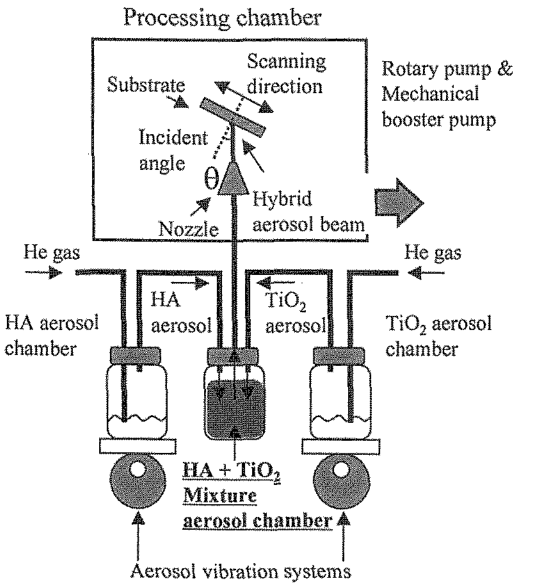

Fig.1 Configuration of Hybrid Aerosol Beam Irradiation Coating System

Table I Experimental conditions

Conditions	Particles	
	HA	TiO_2
Particle size (μm)	< 3	< 1
Gas consumption (L/min)	15	
Vibration frequency (rpm)	800	
Coating time (s)	20	
Beam incident angle (deg.)	0-60	
Substrate	Soda-lime-glass	

3. RESULTS AND DISCUSSION

As-deposited films were cleaned ultrasonically in ethanol for 60 seconds. Films fabricated at an incident angle from 0 to 30 degrees peeled off the substrate after ultrasonic cleaning. Films fabricated at 40 to 60 degrees displayed higher adhesion strength and did not peel off

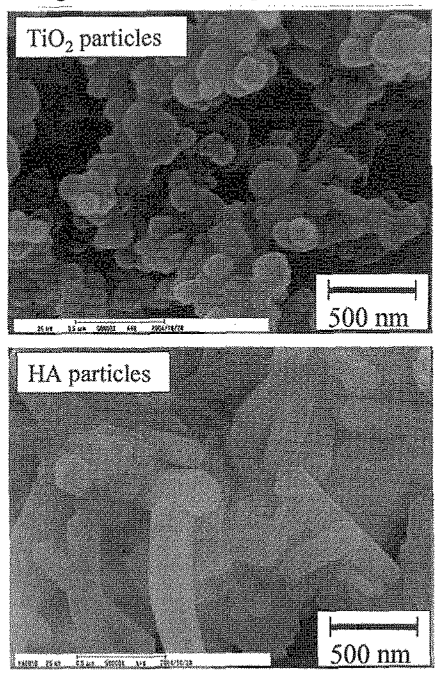

Fig.2 SEM images of the TiO_2 and HA particles as received

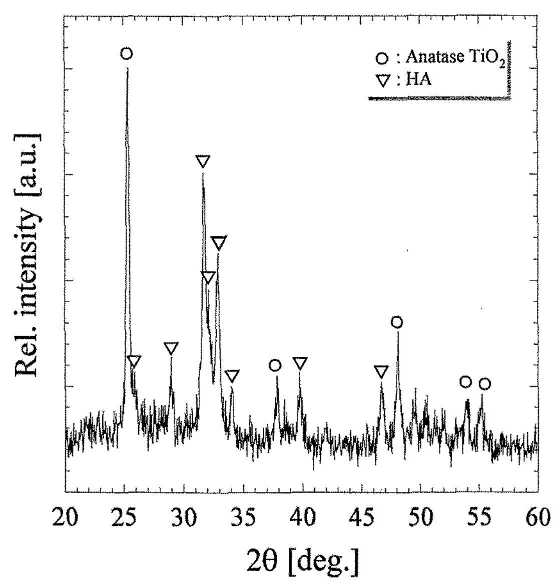

Fig.3 XRD spectra of the TiO_2/HA composite film produced at an irradiation angle of 50 degrees

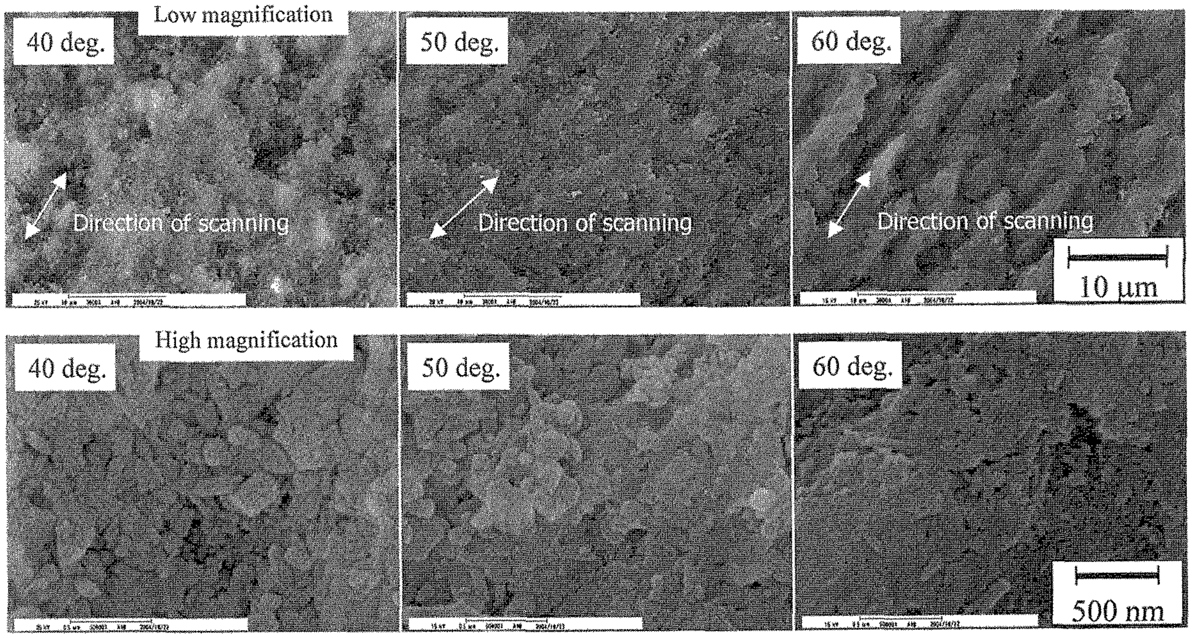

Fig.4 Surface morphology of the TiO_2/HA composite films produced at different incident angles

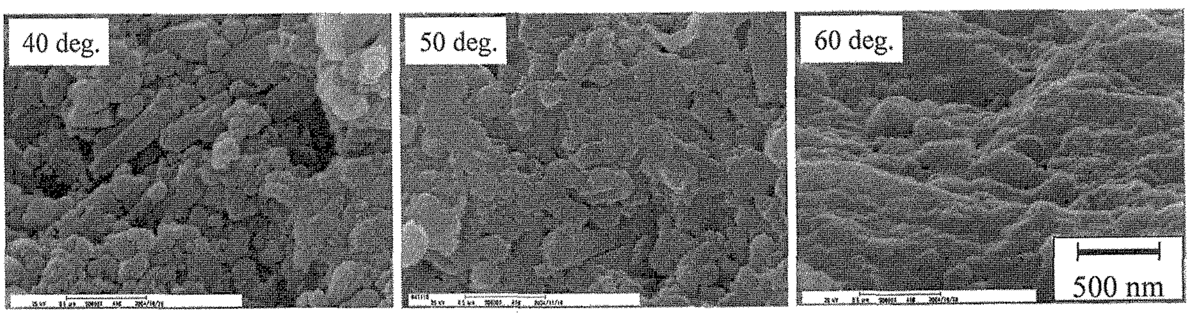

Fig.5 Cross-sectional micrographs of the TiO_2/HA composite films produced at different incident angles

the substrate.

Figure 3 shows the XRD pattern of a TiO_2/HA film fabricated at an incident angle of 50 degrees. The crystal structure observed was anatase TiO_2 and hydroxyapatite. Neither amorphous phase nor rutile phase TiO_2 were observed, and neither calcium oxide nor tricalcium phosphate phases were observed.

Figure 4 shows the composite film's surface morphology. A double-headed arrow indicates the scanning direction. Scale-like structures in the scanning direction became visible on the film surface as the incident angle increased to 60 degrees. The TiO_2 and HA particle shapes can be clearly observed in the high magnification micrograph of the surface fabricated at an incident angle of 40 degrees. At higher incident angles the particle shapes are less distinct and the film becomes finer, with the size of the particles composing the film reduced from the primary particle size. This indicates that the primary particles were fractured when they struck the substrate.

Figure 5 shows the cross-sectional morphologies of films formed at an incident angle of 40, 50 and 60 degrees. Films at an incident angle of 40 degrees were porous and both particle shapes could be clearly distinguished. However, films formed at 60 degrees

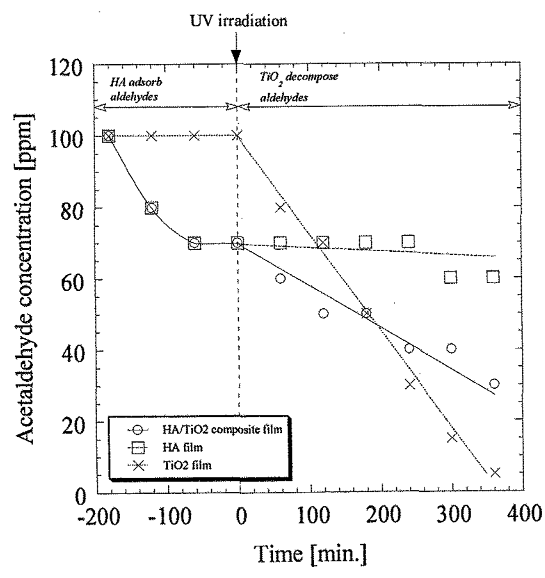

Fig.6 A comparison of the acetaldehyde adsorption and decomposition properties of TiO_2, HA and TiO_2/HA films

were non-porous and the shapes of individual particles were not clearly discernable. With an increasing incident angle, the film became denser.

Figure 6 illustrates the acetaldehyde decomposition characteristics of TiO_2, HA, and TiO_2/HA composite films. Without UVL irradiation, the decomposition rates of the TiO_2/HA and HA films is the same, with the acetaldehyde concentration decreasing from 100 to 70 ppm in 180 minutes. For the TiO_2 film, the acetaldehyde concentration did not change without UVL irradiation. This result reveals that the TiO_2/HA film's adsorption capacity is the same as for an HA film. Although the acetaldehyde concentration decreased from 70 to approximately 0 ppm after UVL irradiation of the TiO_2 film for 360 minutes, the concentration only decreased from 70 to 30 ppm for the TiO_2/HA film, probably due to the reduced TiO_2 surface area in the composite film.

4. CONCLUSION

(1) A TiO_2/HA film was successfully formed using a hybrid aerosol beam irradiation coating system.
(2) Films fabricated at an incident angle of 40 to 60 degrees displayed satisfactory adhesion strength and did not peel off the substrate.
(3) The XRD pattern of the composite film formed at an incident angle of 50 degrees indicated that anatase phase TiO_2 and the HA structure were retained during the HAB process.
(4) A porous film was produced at an incident angle of 40 degrees, with both particle shapes clearly observable.
(5) The TiO_2/HA composite film displayed the same adsorbtion capacity as an HA single film, but less decomposition capacity than a pure TiO_2 film, probably due to the reduced TiO_2 surface area in the composite film.

5. References

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