

# 論文の要旨

題目 Preparation of TiO<sub>2</sub>-based thin films with improved photocatalytic activity and super-hydrophobicity by plasma-enhanced chemical vapor deposition  
(プラズマ CVD 法による高い光触媒活性と超疎水性を有する TiO<sub>2</sub> 薄膜の作製)

氏名 Lang Jianghua

The plasma enhanced chemical vapor deposition (PECVD) process is a practical method in film preparation thanks to its simple operation step and relatively low cost. TiO<sub>2</sub> films with photocatalytic activity have been successfully prepared by PECVD methods. In addition, various TiO<sub>2</sub>-based functional materials can also be synthesized by the PECVD methods. By introducing foreign materials, TiO<sub>2</sub>-based composite often exhibits improved and new properties. In this dissertation, efforts have been made to enhance the photocatalytic activity of TiO<sub>2</sub> thin film. In addition, a TiO<sub>2</sub> composite film with super-hydrophobic surface was fabricated by introducing a polymer.

Firstly, a TiO<sub>2</sub>-CNT-Ag (T-C-A) ternary composite film was successfully synthesized using the PECVD by simultaneously feeding a carbon nanotube (CNT)/Ag nanoparticle suspension and titanium tetraisopropoxide (TTIP) vapor. Here, Ag nanoparticles were prepared from AgNO<sub>3</sub> solution in advance. During the film deposition, a suspension containing both CNT and Ag nanoparticles were spray-dried to generate aerosol nanoparticles of those materials. The obtained nanoparticles were fed along with TTIP vapor into a PECVD reactor. The prepared films were evaluated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and ultraviolet (UV)-visible spectroscopy. Moreover, the Ag/Ti content ratio of the films was determined using an inductivity coupled plasma optical emission spectrometer. The performance of the pristine TiO<sub>2</sub> (T) and TiO<sub>2</sub>-composite films for the degradation of Rhodamine 6G was evaluated under the irradiation of simulated solar light. Ternary structures in which CNT and Ag nanoparticles were embedded into TiO<sub>2</sub> matrix were confirmed. Typical thickness of the films was approximately 1 μm. The structures and optical properties of the films were altered by the addition of CNT and Ag nanoparticles. The crystal structure of the films was influenced by the temperature at which the films have been heated (annealed). The addition of CNT and Ag nanoparticles was found to significantly improve the performance of TiO<sub>2</sub>, where the photocatalytic activity of T-C-A was approximately 1.8 times higher than that of T. In addition, a commercial TiO<sub>2</sub> powder (P25) is prepared as a thin film and used as a reference. The T-C-A film with anatase-rutile mixed phase shows a better photocatalytic performance than self-made P25 film.

Next, a simplified PECVD process for the preparation of TiO<sub>2</sub>-Ag nanoparticle composite films was studied. Here, aerosolized droplets of AgNO<sub>3</sub> solution and TTIP vapor were used as the precursors of Ag nanoparticles and TiO<sub>2</sub> film, respectively. Notably, the use of PECVD eliminates the need of preparing Ag nanoparticles in advance, and is thus expected to increase the process efficiency. The deposited films were characterized by UV-visible spectroscopy, XRD, XPS, SEM, TEM and EDS, and the effects of the concentration of the precursors on the photocatalytic activity of the prepared films were investigated by the degradation of methylene blue under UV-light irradiation. The Ag ions in the solution were successfully reduced to metallic nanoparticles that were embedded in the TiO<sub>2</sub> film. The presence of Ag nanoparticles significantly altered the morphology and bandgap of the TiO<sub>2</sub>-Ag composite films. The

increase of  $\text{AgNO}_3$  concentration resulted in a more significant agglomeration of nanoparticles on the surface of the films. The bandgap of the pristine  $\text{TiO}_2$  film was 3.54 eV, while those of the  $\text{TiO}_2$ -Ag composite films decreased from 3.21 to 2.61 eV with increasing  $\text{AgNO}_3$  concentration. And the best photocatalytic activity was achieved for the composite film prepared by supplying 1 wt%- $\text{AgNO}_3$ . Importantly, the photocatalytic activity was 1.75 times that of pristine  $\text{TiO}_2$  film.

Super-hydrophobic hybrid  $\text{TiO}_2$ /polydimethylsiloxane (PDMS) films were fabricated by supplying TTIP and PDMS vapors in a PECVD process. Two different sets of experimental conditions to fabricate the composite films were examined. The prepared composite films were characterized by SEM, TEM-EDS, FTIR, XPS and XRD. The hydrophobicity was characterized by the contact angle of water droplets staying on the film surfaces. The photocatalytic activity was determined by the MB degradation under UV light irradiation. It is worth noting that no curing agent was necessary in this process to immobilize the polymer. Under the first set of experimental conditions, the presence of PDMS changed the morphology of the  $\text{TiO}_2$  matrix and inhibit the crystal growth of  $\text{TiO}_2$  very significantly. The formation of Si-O-Ti bonds indicates an interconnection between inorganic and organic components. The photocatalytic activity of the composite film resulted in the decomposition of approximately 29% of MB after 6 hours irradiation, which is almost the same as the pristine  $\text{TiO}_2$  film. In addition, the contact angle of the composite films before the photocatalytic activity test was approximately  $157^\circ$  that corresponds to a superhydrophobic surface. However, such super-hydrophobicity was lost for many products after the photocatalytic activity tests. Under the second set of conditions, the presence of both  $\text{TiO}_2$  and PDMS in the films was also confirmed. The prepared films showed a photocatalytic activity that resulted in the decomposition of 16% of MB under 6h irradiation. In addition, the super-hydrophobicity of the films, characterized with a contact angle of  $157^\circ$ , was maintained after the activity tests.

Finally, the summary of the content in this dissertation was highlighted. Suggestions for the future research for composite film fabrication by PECVD methods are also proposed