学　位　論　文　内　容　の　要　旨

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学　位　論　文　題　名

Synthesis of metallic oxide nanoballs via submerged glow-discharge plasma and their photocatalytic effect

(水溶液プラズマ法による金属酸化物ナノボール作製とその光触媒効果)

Titanium oxide (TiO_2) is famous as a photocatalytic material. Other types of nanoparticle-photocatalyst besides TiO_2, such as stainless steel, are also important in many fields such as environmental cleanup or energy production. Stainless steel (grade SUS316L) is commonly used as an industrial material, particularly in the food industry because it is corrosion-resistant. Since photocatalytic nanoparticles have high reactivity compared to bulk materials, nanoparticles of SUS316L have the potential to become a new type of photocatalytic material. Although bulk SUS316L was shown to become catalytically active under acidic conditions, there are no studies being made on the catalytic properties of SUS316L nanoparticles. Plasma processing has shown to be able to synthesize metallic nanoparticles with a relatively low cost than the conventional method of electrolysis and milling. Metallic, spherical nanoparticles of TiO_2, ZnO and SUS316L called “nanoballs” with high photocatalytic activity were synthesized via submerged glow-discharge plasma process. These nanoballs were shown to be photocatalytically active when irradiated with ultraviolet (UV) light, allowing them to decompose methylene blue dye.

Chapter 1 gives a brief introduction regarding the history of photocatalytic materials and plasma processing methods used to synthesize nanomaterials. The potential of the photocatalytic activity of nanoparticles is also given. The background of this research is established. The main purposes of this thesis are highlighted where (a) to synthesize photocatalytic nanoballs via submerged glow-discharge plasma and (b) to characterize them in terms of its physical characteristics and photocatalytic ability.

Chapter 2 shows the experimental setup and procedures of submerged glow-discharge plasma and nanoballs characterization. A platinum wire was used as the anode; this wire was bent into a half-round mesh and fixed onto a glass frame. A titanium/zinc/stainless steel 316L wire was used as the cathode. A glass tube was used as insulation to obtain an exposed length that functioned as the net actual electrode. The electrolyte was a solution of 0.1 mol K_2CO_3. The nanoballs were synthesized via submerged glow-discharge plasma. After glow-discharge, the products were collected via centrifuging and washing with purified water to remove the electrolyte.

FE-SEM images of the nanoballs were taken to observe the morphology of the nanoballs. HRTEM images were taken to evaluate the crystal structure and morphology of the nanoballs. SEM-EDS and TEM-EDS were used to identify the elemental composition of the nanoballs. XRD was used to examine the type of oxides present and their crystal structures. BET test was used to measure the surface area and pore volume of the nanoballs. The photocatalytic ability of the nanoballs was determined by the decomposition of methylene blue (MB). An aqueous solution of MB and nanoballs was exposed

to UV irradiation for 24 hours while enclosed inside a dark chamber. UV/VIS spectrophotometer was used to measure the relative concentration of MB before and after the photocatalysis test. Mass spectroscopy was used to determine the chemical compounds that were present after the photocatalysis test.

Chapter 3 shows the results of the physical characteristics of the nanoballs. SEM and TEM analysis shows that the nanoballs were nanosized (100nm to 1μm) and uniformly spherical. SEM-EDS and TEM-EDS showed that after plasma synthesis, the nanoballs contained much higher amounts of oxygen compared to its starting materials. The oxides were found mainly on the surfaces of the nanoballs. XRD analysis reveals the presence of TiO_2, ZnO, Fe_2O_3 and Cr_2O_3. Additionally, HRTEM analysis for SUS316L nanoballs showed that spinel stainless steel phase is dominant for nanoballs less than 50nm in diameter. BET measurements and size estimation showed that the nanoballs had a very large surface area. This explains their reactivity and photocatalytic activity.

Chapter 4 shows the results of the photocatalytic performance of the nanoballs. The results of photoabsorbance test shows that MB peak intensity was reduced by mixing with these nanoballs when UV irradiation is applied. Characteristic peaks of MB became lower than its initial concentrations after UV irradiation. ZnO nanoballs showed the fastest tendency for MB photodecomposition, followed by TiO_2 and SUS316L nanoballs. Mass spectroscopy showed that for TiO_2 and ZnO nanoballs, MB was decomposed directly into simpler molecules within 24 hours. However, in case of SUS316L nanoballs, MB was decomposed to more simple molecules via oxidation into sulfoxide first. Complete photodecomposition of MB in SUS316L nanoballs then occurred after 72 hours UV irradiation. In all cases, molecules such as phenol, benzenesulfonic acid, Azure A and B were detected after UV irradiation, showing that the photodecomposition of MB had occurred.
The photocatalytic effect of SUS316L nanoballs can be explained by the photosensitivity and semiconductive properties of the oxide layer that formed on the surface of SUS316L nanoballs. Also, the presence of Fe_2O_3 and Cr_2O_3, which had the bandgap energies of 2.2eV and 3.6eV respectively, was confirmed. Both have been shown to have photocatalytic ability under UV light irradiation. The results indicate a new discovery of MB photodecomposition occurring in SUS316L nanoballs, previously regarded as a non-semiconductor material.

Chapter 5 is the conclusion of the above studies. Based on the results, submerged glow-discharge plasma is an effective method to synthesize photocatalytically active nanoballs. It is a cost-effective process that is able to synthesize nanoparticles easily and can be scaled for industrial applications. SUS316L nanoballs have shown potential as a new material for photocatalytic applications, particularly for water treatment.