HOKKAIDO UNIVERSITY

Title	A mechanistic study on noble metal-modified titania photocatalysts for inactivation of bacteria and fungi [an abstract of dissertation and a summary of dissertation review]
Author(s)	遠藤, 摩耶
Degree Grantor	北海道大学
Degree Name	博士(環境科学)
Dissertation Number	乙第7071号
Issue Date	2019-03-25
Doc URL	https://hdl.handle.net/2115/74575
Rights(URL)	https://creativecommons.org/licenses/by-nc-sa/4.0/
Type	doctoral thesis
File Information	Maya_ENDO_review.pdf, 審査の要旨

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

学 位 論 文 審 査 の 要 旨

博士（環境科学）　　氏 名 遠 藤 摩 耶

審査委員　主査　准教授　KOWALSKA EWA KATARZYNA
副査　教 授　大 谷 文 章
副査　教 授　沖 野 龍 文
副査　教 授　神 谷 裕 一

学 位 論 文 題 名

A mechanistic study on noble metal-modified titania photocatalysts for inactivation of bacteria and fungi
（貴金属担持酸化チタン光触媒による細菌及びカビの不活性化メカニズムに関する研究）

Environmental pollution and the lack of clean water are main issues facing human development. Therefore, environmentally friendly methods (using solar light, reusable materials, and effective purification in short duration), e.g., advanced oxidation processes (AOPs) with efficient generation of highly reactive hydroxyl radicals (˙OH), have been proposed. Among AOPs, titania photocatalysis has been widely studied for removal of both chemical and microbiological pollutants. Although titania has already been used for water purification, there are still some limitations, which should be overcome for broader applications, e.g., the requirement of UV irradiation and low activity under solar light. Recently, visible-light responsive titania, e.g., plasmonic photocatalysts (titania modified with nanoparticles (NPs) of noble metals (NMs)), has been intensively studied. However, there are only few reports on inactivation of microorganisms on plasmonic photocatalysts, and the mechanism is not fully understood. Therefore, this study aimed to develop highly active titania photocatalysts against various pollutants, and to clarify the bactericidal mechanism on noble metal-modified titania photocatalyst.

One of the most important tasks of preliminary study was to propose the most adequate method for reliable evaluation of antimicrobial properties, and thus various methods were examined. It has been found that although disc diffusion and colony growth methods are very popular for antimicrobial tests, they are not recommended for present study, i.e., stable photocatalyst should not diffuse from the support, and the effect of colony growth is difficult for reliable evaluation when coloured media are used (plasmonic photocatalysts). Therefore, suspension and spore-counting (newly developed) methods have been proposed for evaluation of bactericidal and antifungal activities, respectively. It was found that Ag-modified titania showed excellent bactericidal activity, depending on the properties of noble metals and titania, i.e., the sizes and surface charges. Moreover, Ag-modified titania could decompose the bacterial cells completely, which is very important for water purification, considering that some bacterial proteins have allergenic properties. On the other hand, Au-modified titania samples exhibited effective

antifungal activity, especially to limit the sporulation. Therefore, it was proposed that bi-metallic plasmonic photocatalysts could possess broad antimicrobial effect, and this was studied in this thesis in detail.

It was clarified that the appropriate amount of NMs (Au/Ag) significantly enhanced the activity for decomposition of organic compounds, inactivation of bacteria and fungi, and furthermore, decomposition of bacterial cells. The mechanism was investigated by quenching tests, action spectrum and XPS analysis. It was found that the bactericidal activity was attributed not only to positively charged Ag, but also to reactive oxygen species. In addition, the negligible release of silver was not responsible for bactericidal effect, indicating the direct reaction between bacteria and deposited silver on titania. Interestingly, it was found that the charge on Ag NPs changed, depending on the irradiation wavelength, and thus resulting in the different activities. This study was a first report showing the dependence of irradiation wavelength (action spectrum) on the bactericidal activity. Similar action spectra of Au/TiO_2 and $Ag/Au/TiO_2$ and enhanced bactericidal activity for bimetallic sample suggested that the back electron transfer ($Au \rightarrow TiO_2 \rightarrow Au$) was hindered. Moreover, it was proposed that high activity and stability of bimetallic photocatalyst were achieved by keeping positively charged silver, i.e., by possible electron transfer ($Ag \rightarrow Au \rightarrow TiO_2$).

Moreover, NM-modified titania photocatalysts composed of NM (Au, Ag, Cu, Pt) NPs and faceted anatase titania particles (the most active titania photocatalysts) were investigated, especially their property-governed activity for decomposition of chemical and antimicrobial pollutants. Two kinds of faceted anatase titanias were studied, i.e., octahedral anatase particles (OAPs) with eight, equivalent {101} facets, and decahedral anatase particles (DAPs) with two additional {001} facets. It was found that even low content of noble metal (2 wt%) resulted in significant enhancement of UV-activity and appearance of vis-response for decomposition of organic compounds. It was proposed that high bactericidal activity of Ag- and Cu-modified faceted titania was mainly attributed to the +1-oxidation state of metals. Interestingly, the modification of DAPs with Au and Pt suppressed the activity under UV irradiation, indicating that bacterial cells were directly inactivated on DAP surface.

Since NPs of less NM, such as Ag and Cu, are usually covered with oxide layer, the antimicrobial activity of metal oxides (Ag_2O and Cu_2O)-modified titania was also studied. It was found that these heterojunctions possessed high bactericidal and fungicidal properties, probably due to a release of metal. Moreover, the activity of Ag_2O- and Cu_2O-modified titania was enhanced under light irradiation. It was clearly shown that Ag_2O/TiO_2 heterojunction inhibited the generation of spore. Therefore, it was concluded that antimicrobial activity depended not only on intrinsic activity of positively charged metal, but also heterojunction between metal oxide and titania.

The examination committee recognized that this thesis presents important findings, such as (i) evaluation of appropriate method for antimicrobial activity testing, (ii) development of plasmonic photocatalysts with broad activity for decomposition of both organic compounds and microorganisms, (iii) mechanism elucidation of bacteria inactivation for bi-metallic photocatalysts. The committee concluded that the applicant is eligible for the degree of Doctor of Philosophy (Environmental Science).