学　位　論　文　内　容　の　要　旨

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学　位　論　文　題　名

A mechanistic study on noble metal-modified titania photocatalysts for inactivation of bacteria and fungi

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Environmental pollution and the lack of clean water are main issues facing human development. For water purification, environmentally friendly methods should be applied, e.g., using solar light, reusable materials, and effective purification in short duration. The conventional chlorination method is inexpensive, easy to use and can completely inactivate most microorganisms. However, it influences negatively the aquatic organisms, due to the ability to bind to nitrogen and organic compounds, resulting in generation of highly toxic by-products. Therefore, other methods, mainly Advanced Oxidation Processes (AOPs) with efficient generation of highly reactive hydroxyl radicals ($^{\bullet}OH$), have been investigated. Among AOPs, titania photocatalysis has been widely studied for removal of both chemical and microbiological pollutants. Although titania has already been commercially 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, due to the charge carriers' recombination and its wide band-gap. Recently, visible-light responsive titania, e.g., plasmonic photocatalysts (titania modified with nanoparticles (NPs) of noble metals), 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 aims to develop highly active titania photocatalysts against various pollutants, and to clarify the bactericidal mechanism on noble metal-modified titania photocatalyst.

In Chapter 1, general introduction on titania photocatalysis, exemplary applications of titania for environmental purification, and the aim of this study has been presented.

In Chapter 2, preparation, characterisation and photocatalytic activities of noble metal (silver (Ag), gold (Au)) NPs-modified commercial titania photocatalysts have been discussed. One of the most important tasks in this 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 (e.g., by 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 finding 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 investigated in this thesis (Chapter 3).

In Chapter 3, the mechanism of bactericidal activity was proposed. It was clarified that the appropriate amount of metals (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 (e.g., $^{\bullet}OH$). In addition, the negligible release of silver was not responsible for bactericidal effect, indicating the direct surface 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 back electron transfer ($Au \rightarrow TiO_2 \rightarrow Au$, i.e., the main reason of low activity of plasmonic photocatalysts) was hindered. Moreover, it was proposed that high activity and stability of bimetallic photocatalyst were achieved by keeping positively charged silver, because of vis irradiation of gold, i.e., possible electron transfer ($Ag \rightarrow Au \rightarrow TiO_2$).

In Chapter 4, noble metal-modified titania photocatalysts composed of noble metal (Au, Ag, Cu, Pt) NPs and faceted anatase titania particles (the most active titania photocatalysts) were discussed, 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.

In Chapter 5, the antimicrobial activity of metal oxides (Ag_2O and Cu_2O)-modified titania was discussed. It was found that these heterojunctions (Ag_2O/TiO_2 and Cu_2O/TiO_2) 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. According to the sporulation test, 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.

Chapter 6 shortly summarized the study, i.e., for the first time it has been found that (i) bi-metallic photocatalysts are prospective for environmental purification due to the synergy of metals, (ii) the electron transfer between metal and titania, and photocatalysts and bacteria, plays a key-role for microbial inactivation, (iii) the direct contact between photocatalyst and bacteria (interface), due to the attractive force is crucial for antimicrobial activity. Therefore, it is proposed that this study is important for designing highly active nanomaterials for water purification.