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Abstract of PhD dissertation entitled: A mechanistic study on noble metal-modified titania photocatalysts for inactivation of bacteria and fungi

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Titanium(IV) oxide (titania, TiO_2) is one of the most studied semiconductor photocatalysts, due to its various advantages, such as high photocatalytic activity, stability, abundance, inexpensiveness and non-toxicity (except for the toxicity of nanomaterials). Photocatalysis is considered as one of the best methods for environmental purification since additional chemical compounds, such as strong oxidants (ozone, hydrogen peroxide (H_2O_2) or chlorine), are not introduced into the environment, despite the fact that the energy consumption is also much lower than that of other advanced oxidation technologies (AOTs), e.g., wet air oxidation, supercritical water oxidation, or H_2O_2/UV-C. The removal of chemical and biological pollutants from water environment by titania photocatalysis has been intensively investigated for more than four and three decades, respectively. For water purification, environmentally friendly methods should be considered, e.g., use of solar light, reusable materials, and effective purification in short duration. However, the application of titania to practical use for water purification is limited, due to the requirement of UV irradiation, and thus relatively low activity under solar radiation. Therefore, noble metal-modified photocatalysts have been considered as promising materials, due to the response in visible light, effective charge carriers' separation under UV and intrinsic activity of some noble metals. There are only a few papers systematically showing the decomposition of chemical compounds and wide antimicrobial activity by same photocatalyst. Hence, in this study, various photocatalysts, composed of noble metals (Ag, Au, Cu, Pt and metal oxides) on titania, have been proposed in order to obtain highly active material against both chemical and microbial pollutants and clarify the mechanism of their decomposition.

In Chapter 2, noble metal (Ag or Au)-modified commercial titania has been discussed, and their bactericidal and antifungal activities were investigated by various methods, i.e., disc diffusion, colony growth, spore-counting and suspension. One of the most important tasks in this preliminary study was to propose the most adequate method for reliable evaluation of antimicrobial properties. Ag-modified titania showed excellent bactericidal activity, depending on the properties of noble metals and titania, i.e., the sizes and surface charges. Moreover, it exhibited the complete decomposition of bacterial cells confirmed by SEM

observation and CO_2 evolution. This finding is very important since some bacterial proteins have allergenic properties. On the other hand, antifungal activities were validated by conventional (disc diffusion and colony growth methods) and newly developed method (spore counting method). The inhibition of sporulation must be considered since it is the key step of the fugal proliferation. On the other hand, it is proposed that for simple microorganisms, such as bacteria and yeast, the suspension method is recommended. It was also proposed that, although the disc diffusion method could not evaluate the activity, the stability of photocatalyst was revealed. Gold-modified titania samples could be good candidates for antifungal materials, due to high photocatalytic activity, despite the fact that Ag-modified titania did not show significant inhibition of the spore formation (inhibition of next generation). Therefore, it is expected that bimetallic (Au/Ag) titania photocatalysts should exhibit broad antimicrobial properties (Chapter 3).

The mechanism of bactericidal activity was discussed in Chapter 3. It was shown for the first time that an appropriate amount of bi metal (Au/Ag)-modified titania significantly enhanced the activity for decomposition of organic compounds, inactivation of bacteria and fungi, and furthermore, decomposition of cells. These results indicated the interaction between Ag and Au. Despite the fact that the silver release was considered to be responsible for bactericidal activity, this study showed that the release of silver did not significantly occur, suggesting that the contact between silver and bacteria was essential, as well as the potential stability of samples. Furthermore, the wavelength-dependence of bactericidal activity was clarified by action spectrum analysis. The charge of Ag NPs remarkably changed by the change in irradiation wavelength, resulting in the difference of attractive force between Ag and bacteria. Importantly, it is proposed that positively charged Ag was maintained by visible light irradiation of Au. Moreover, the photocatalytic activity of Au/TiO_2 is enhanced by Ag, due to the inhibition of charge carriers' recombination between Au and titania (e^- transfer: $Au \rightarrow TiO_2 \rightarrow Au$). The surface charge of Ag is correlated to the attraction force toward bacterial cell. This study proposes the new photocatalysts design for antimicrobial property not depending on the silver release.

In Chapter 4, it was discussed that noble metal modified faceted titania (OAP and DAP) samples showed the enhanced activity for the decomposition of chemical compounds and inactivation of bacteria. In the case of decomposition of chemical compounds, facet type-dependent activity under UV-vis and visible induced reactions was proposed, i.e., under UV-vis, DAP showed higher activity than OAP, possibly due to the efficient charge separation, and under vis OAP possessed higher activity than DAP, probably due to the preferential deposition of metal nanoparticles on {101} facets of DAP. The bactericidal activity of Ag and Cu-modified faceted titania samples were very high, even by few orders in magnitude higher than that in the dark conditions. It was proposed that positively charged Ag, the contents of Cu_2O in Cu_xO clusters and CuO-TiO_2 heterojunction were responsible for bactericidal activity. Interestingly, according to the results of Au-, Pt-modified and bare DAP under UV irradiation, the enhanced photocatalytic activity by the modification with metals did not affect the bactericidal activity, but rather, shielding the surface of DAP by metals suppressed the activity, suggesting that the direct redox reactions on the bacteria and titania interface was responsible for the activity. Moreover, enhanced activity of Ag-modified titania by visible light irradiation, indirectly supports the mechanism of plasmonic activation of titania by transfer of charge carriers, i.e., electron transfer from Ag NPs to titania (instead of energy transfer), resulting in formation of more positively charged Ag, and thus an increase in overall bactericidal activity. The morphology of bacteria during reaction with Ag/DAP was significantly changed under vis, UV irradiation and in the dark, suggesting the direct attack of Ag on the cell walls and membranes inducing cell death.

Additionally, as suggested in Chapter 4, it was found that metal oxide (Ag_2O or Cu_2O)-modified titania samples possessed high bacterial and fungicidal properties (Chapter 5). In the case of Ag_2O/TiO_2, although antibacterial and anti-yeast activity was mainly caused by the presence of Ag_2O, independently on applied conditions (UV, vis and dark), antifungal activity for filamentous fungi was mainly caused by Ag_2O/TiO_2 composites. It was found that vis irradiation could significantly improve antibacterial and anti-yeast activities, due to the electrostatic attraction between the negative surface of microorganisms and the positively charged Ag_2O (after electron transfer to titania). As for Cu_2O/TiO_2, it was found that the heterojunction of Cu_2O/TiO_2 remarkably promoted the anti-yeast activity under irradiation and even in the dark. Therefore, the activity was not only attributed to the sole activity of Cu_2O but also to the direct contact between microorganisms and Cu_2O/TiO_2. Under visible light irradiation, the formation of electron-deficient Ag_2O (Cu_2O) could significantly improve antimicrobial activity, probably due to photo-excited electron transfer from Ag_2O (Cu_2O) to TiO_2 under vis irradiation facilitated adsorption of positively charged Ag_2O (Cu_2O) on bacteria. On the other hand, it was also proposed that the release of metal oxide (confirmed by the measurement of resultant amount of Ag_2O on Ag_2O/TiO_2) was significant, and thus it might participate in the antimicrobial activity substantially. However, it is expected that the release of metals decreases the activity of the repetitive use. In this regard, the consideration of deposition method of metal (oxide) is important for not only the activity but also the stability. Therefore, under visible light irradiation, the formation of electron-deficient Ag_2O (Cu_2O) could significantly improve antimicrobial activity, probably due to photo-excited electron transfer from Ag_2O (Cu_2O) to TiO_2 under vis irradiation facilitated adsorption of positively charged Ag_2O (Cu_2O) on bacteria.

Consequently, titania modification with noble metals (Au, Ag and Cu) resulted in excellent activity for the environmental purification, suggesting that the electron transfer played a key role for antimicrobial activity. Mechanistic study showed the visible light-induced activity of noble metal-modified titania, i.e., the maintenance of highly active state of metal by irradiation was crucial for the high antimicrobial activity. These results can be an important strategy for designing further high active materials for water purification.