学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Studies on inverse opal-structured titania with gold nanoparticles as novel design for photoabsorption-efficiency enhancement in photocatalysis
(光吸収効率増大のための新規デザインとしての金ナノ粒子含有逆オパール構造酸化チタン光触媒に関する研究)

Photocatalysis is an area of chemistry impacting many reactions, such as oxidation reactions (e.g., advanced oxidation processes—AOPs), reduction reactions (e.g., CO_2 reduction), synthesis and hydrogen transfers. Although photocatalysis mechanism might be quite complex for particular reaction, it always consists of two main parts, i.e., "bright part"— photoabsorption, and "dark part"—redox reactions. It should be pointed out that both are highly important for the overall photocatalytic performance, i.e., efficient light harvesting and high quantum efficiency, respectively. However, most of the studies have been focusing only on the dark part to improve the charge-carriers separation and followed photoredox reactions. However, recent studies on photonic crystals (PCs) have suggested possible enhancement of photoabsorption beyond the fundamental photoabsorption-coefficient limitation, due to a slow-photon effect at the edges of the photonic bandgap (PBG) wavelength, i.e., capturing photons of a specific wavelength range in PCs. In this regard, several reports have claimed the amplified photoreaction rates, due to the utilization of PCs, though the possible bright-part enhancement has not been proven yet, due the lack of exclusion of possible dark-part enhancement in the overall reaction rates. Therefore, this study aims to study if the enhancement of only "bright part" might result in the efficient improvements of the overall photocatalytic activity. In this regard, a new photocatalyst with gold nanoparticles (Au NPs) incorporated inside inverse opal titania (IOT) PCs, i.e., one Au NP in each void space, has been developed and investigated.

In Chapter 1, general introduction covering the basic principles of heterogeneous photocatalysis, nanostructures of photocatalytic materials, their applications, plasmonic photocatalysis and utilization of IO PCs for activity enhancement along with the preparation methods, have been presented. Apart from that, short review on the theory of Bragg's law, factors affecting the PBG of PCs in photocatalysis has been presented. In the last part, based on the literature review the purpose of this study has been proposed.

In Chapter 2, materials, equipment and the experimental procedure for preparation and characterization of photocatalysts have been presented. Powdered IOT incorporated with one Au NP per void space (Au-NP@IOT) has been prepared by five-step method, i.e., (1) synthesis of Au NPs, (2) covering of Au NPs with silica shell (Au@SiO_2 NPs), (3) formation of opal structure by self-assembly of Au@SiO_2 NPs (PC), (4) infiltration of opal with titania (Au@SiO_2/TiO_2), and (5) removal of silica to form 3D Au@TiO_2-IO. Apart from that, preparation of reference samples, i.e., IOT with loaded Au NPs on its surface by hydrothermal and photodeposition methods, has been shown. Additionally, the calculation method for PBG peaks and their blue-edges wavelengths for each Au-NP@IOT has been explained.

In Chapter 3, formation, characterization and photonic properties of Au-NP@IOTs samples have been discussed in detail. Two sizes of Au NPs of 30 nm and 44 nm have been prepared with localized surface plasmon resonance (LSPR) at 528 nm and 531 nm, respectively, from which a series of Au-NP@IOT photocatalysts with seven different nanovoids have been obtained. It has been clarified that most importantly, Au NPs remain inside the voids even after the removal of SiO_2, showing the successful design of novel gold-modified titania photocatalysts. The calculated values of PBG peak wavelengths vary in the range of ca. 350–750 nm (considering the nanovoid-size distribution—fluctuation), which covers the wavelengths of photoabsorption by Au NPs and titania in Au-NP@IOT samples.

In Chapter 4, photocatalytic activity of Au-NP@IOT photocatalysts have been examined by performing the oxidative decomposition of acetic acid under monochromatic irradiation with two kinds of LED sources, i.e., at 450 nm and 530 nm. It has been found that in the case of 530-nm LED irradiation, only sample with average nanovoid of 270 nm with estimated PBG-edge wavelength close to the irradiation wavelength exhibits amplified photocatalytic activity, even though similar Au NPs have been incorporated in all Au-NP@IOT samples. Interestingly, low activity of bare IOT (without Au) with same void size as that in Au-NP@IOT sample with the highest activity has been observed. In the case of 450-nm LED irradiation, enhanced photocatalytic activity has been observed only for Au-NP@IOT sample with an estimated PBG-edge wavelength of ca. 450 nm, and this activity is ca. two-fold higher than that by a respective bare IOT. It has been proposed that in this system the photoabsorbing material is titania (not gold), whereas Au NPs might work as the co-catalysts (well-known electron scavenger). Accordingly, it might be concluded that overall activity enhancement in both cases (450-nm and 530-nm LED irradiations) is achieved only by matching wavelengths of photoirradiation, photoabsorption and estimated PBG edge, and thus proving the photoabsorption enhancement by slow-photon effect in Au-NP@IOT.

In chapter 5, morphology, optical properties and photocatalytic activity of reference samples, i.e., gold-loaded on the surface of IOT (similar PBG blue-edge wavelengths range as the most active Au-NP@IOT under 530-nm irradiation), prepared by hydrothermal and photodeposition methods, have been discussed. It has been found that independently on the gold content and Au NPs' properties those samples show much lower activity (almost five-fold) than that by Au-NP@IOT. It has been proposed that the aggregation of gold on the surface of IOT might block the slow-photon effect. Accordingly, the importance of Au NP incorporated inside IOTs for activity enhancement has been confirmed.

Chapter 6 shortly summarizes the study, pointing its novelty, i.e., (i) the novel design of gold incorporated inside the voids of IOT, (ii) the bright-part design strategy for photoabsorption enhancement by allowing wavelengths matching between photoirradiation, photoabsorption and estimated PBG edge, (iii) the evidence on enhanced LSPR effect in the presence of slow photons using monochromatic irradiation, and (iv) the importance of having gold (photoabsorbing material) inside the voids of IOT. Therefore, it is proposed that this study is an important and new strategy on "bright-part design" to improve the performance of any photoabsorping material and PCs.