

HOKKAIDO UNIVERSITY

Title	Studies on inverse opal-structured titania with gold nanoparticles as novel design for photoabsorption-efficiency enhancement in photocatalysis [an abstract of entire text]
Author(s)	Raja Mogan, Tharishinny
Citation	北海道大学. 博士(環境科学) 甲第14346号
Issue Date	2021-03-25
Doc URL	http://hdl.handle.net/2115/82046
Туре	theses (doctoral - abstract of entire text)
Note	この博士論文全文の閲覧方法については、以下のサイトをご参照ください。
Note(URL)	https://www.lib.hokudai.ac.jp/dissertations/copy-guides/
File Information	Tharishinny_Raja_Mogan_summary.pdf



学位論文内容の要旨

博士 (環境科学) 氏名 Tharishinny Raja Mogan

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., CO2 reduction), synthesis and hydrogen transfers. These different reactions are mainly applied in the area of environmental purification-water/wastewater and air treatment targeting both chemical and microbiological pollutants, self-cleaning materials, as well as energyrelated fields with possible use of solar energy for photocurrent generation, water splitting and fuel production. 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. Based on the literature reviews, reported noble metals-modified photonic crystals could evident in enhanced photocatalytic activity resulting from both bright and dark-part processes, thus, strategy for only the possible bright-part enhancement has not been proved till date due to the lack of exclusion of the possible dark-part enhancement in the overall reaction rates. Accordingly, a novel structured material, titania inverse-opal photonic crystals with a single gold nanoparticle in each void space namely as Au-NP@IOT, has been proposed for the first time. The development of this bright-part design has been evident by idea of checking on the matching of triplicate wavelengths ranges consisting of photoirradiation by using pseudo monochromatic LED irradiation, photoabsorption by TiO₂ and Au and slow photons from the photonic band gap edges.

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@SiO₂ NPs), (3) formation of opal structure by self-assembly of Au@SiO₂ NPs (PC), (4) infiltration of opal with titania (Au@SiO₂/TiO₂), and (5) removal of silica to form 3D Au-NP@IOT. 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 peak positions of all Au-NP@IOT samples by using Bragg's Law and their blue-edges wavelengths for each Au-NP@IOT has been explained. The details on the photocatalytic activity tests of Au-NP@IOT samples under non-stirring (without agitation of the photocatalyst) and stirring conditions at 450 nm and 530 nm irradiation source have been presented.

In Chapter 3, formation, characterization and photonic properties of Au-NP@IOTs samples have been discussed in detail. Three sizes of Au NPs of 20 nm, 30 nm and 44 nm have been prepared via direct citrate

reduction method with localized surface plasmon resonance (LSPR) at 520 nm, 528 nm and 531 nm, respectively. Au NPs with average diameter of 30 nm and 44 nm, respectively, and in spherical and faceted hexagonal shape has been utilized for the further steps. The modification of the Au NPs which resulted in the formation of thin SiO₂ shell with average thickness of 5 nm has been observed to prevent aggregation and the formation of secondary Au particles.

The formation of Au@SiO₂ core-shells with high monodispersity in the shape and diameter (minimum variation of < 5 %) has been achieved by Stuber's method. It has been found that for larger Au NPs (> 44 nm), monodispersed Au@SiO₂ core-shells without coreless SiO₂ are difficult to be formed, but this is crucial for formation of opal. The closely packed opal of face-centered cubic (FCC) structure has been obtained by self-assembly method via centrifugation-accelerated sedimentation of Au@SiO₂ particles. It has been observed that 20-µm thick opal with more than 50 layers of core-shell particles assembled in ordered manner and the presence of Au NPs inside SiO₂ has been confirmed by transmission electron microscopy images. It has been pointed out that disordered template/incomplete opal would lead to disordered formation of inverse opal, which might induce the loss of the photonic effect.

TiO₂ infiltration has been achieved via forced impregnation method under vacuum, which allows the penetration of titania precursor between SiO₂ particles confirmed by the appreciable detection for Ti from quantitative energy dispersive x-ray analysis. In the final step, Au-NP@IOT structure has been formed via base treatment of Au@SiO₂/TiO₂ to remove the SiO₂ template. Inverse opal structures with clear sphere contact points could be observed along with multilayers of periodic structure which has been expected to fulfil the requirement of a good photonic crystal. It has been clarified that most importantly, Au NPs remain inside the voids even after the removal of SiO₂, showing the successful design of novel gold-modified titania photocatalysts. A series of Au-NP@IOT photocatalysts with seven different nanovoids have been obtained by varying the SiO₂ thickness during the formation of Au@SiO₂ core-shell particles to clarify on the slow photons arise at different wavelengths region.

It has been found that that about ca. 5 % of Au NPs has been incorporated to form Au-NP@IOT samples through the flame atomic absorption spectroscopy (FAAS) measurement that has been carried out. The results have further proved that the amount of incorporated Au NP in Au-NP@IOT has been similar, hence the photoabsorbing ability among the samples have been similar. Apart from that, it has been pointed out that that even higher weight percent of Au NPs have been incorporated in newly designed Au-NP@IOT samples, the formation of aggregation and polydispersity were absent. It has been found since Au-NP@IOT samples have been prepared in powdered form, the photonic band gap peak could not be clearly observed in photoabsorption spectra due to the random scattering of incident light as IOT photonic crystals strongly sensitive to angle of light irradiation, thus resulted in a cumulative broad visible light absorption from 400 nm till 700 nm.

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. 0-25 % probability range has been used to estimate the slow photons arising from blue edge of PBG, hence, slow photons range have been varied from 250 nm till 600 nm depending on the nanovoid of samples. It has been found that several Au-NP@IOT samples with photonic band gap blue-edge fitted the photoabsoprtion and photoirradiation wavelengths at 450 nm and 530 nm.

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. Oxidative decomposition of acetic acid has been carried out for samples in two conditions, namely non-stirring and stirring conditions to prevent random light scattering correlating to the angle dependence apart from the periodic structure loss in the latter condition.

It has been found that in the case of 530-nm LED irradiation and non-stirring condition, 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 stirring condition, it has been observed that, all the samples have been practically inactive under green LED emission except for the sample with 270 nm nanovoid which also showed the similar trend of photocatalytic activity enhancement in non-stirring condition. Hence, it

has been further confirmed, that slow photons do exist and arise in that particular sample, as even under stirring the photocatalytic activity enhancement has been observed. Repeatability test on Au-NP@IOT sample with nanovoid of 270 nm has revealed a little lower photocatalytic activity in the second cycle due to the changes in irradiation angle on the powdered sample, however it should be pointed out that the total CO₂ generation has been still much higher in the second cycle than by other Au-NP@IOT samples. It has been clarified that almost two-fold loss of activity has been observed for the sample with 270 nm nanovoid under stirring compared to non-stirring condition, which has been attributed to the loss of the periodic structure as of the specific sample as proven from the electron microscopy images.

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). Importantly, it has been proven that previous reported studies carried out under polychromatic irradiation could not prove the enhancement was solely due to plasmonic effect as it has been proved in this study that TiO₂ could also absorb photons at 450 nm. 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., goldloaded 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. High polydispersity and aggregation of gold deposits covering the surface of TiO₂ skeleton could be observed for the higher gold loading content such as 5 wt%, whereas 0.5 wt% of gold loading sample resulted in more uniform distribution of Au NPs on IOT and further reduction in gold content caused the formation of only few Au NPs of small size (ca. 5-10 nm) on the surface and voids of IOT. 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. It has been found that gold deposited on inverse opal surface as even lower loading amount such as 2 wt% of gold could lead to unlikely phenomenon such as screening effect, aggregation and high polydispersity. Accordingly, the importance of Au NP incorporated inside IOTs for activity enhancement has been confirmed along to prevent the common problems on agglomeration, large Au-NP size distribution and coverage on nanovoid spaces (screening effect) even with higher Au NP loading.

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.