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Abstract

論文内容の要旨 (博士)

Title of Thesis 博士学位論文名	Shape Control of Au Nanoparticles Using Oxide Template with Ordered Tubular Mesopores and Their Photocatalytic Properties (規則性細孔を有する酸化物質型を利用した金ナノ粒子の形状制御と光触媒特性)
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(Approx. 800 words)

(要旨 1,200 字程度)

TiO₂ is generally known as a material that is nontoxic, inexpensive and able to decompose many kinds of organic compounds under sunlight. However, one drawback of photocatalysis by TiO₂ is that it can only be excited by ultraviolet (UV) radiation, which occupies only a small portion of solar radiation. Therefore, an extension of its absorption wavelength range to the visible (Vis) is an important issue to improve the photocatalytic performance of TiO₂. Combining plasmonic metal nanoparticles (NPs) such as Au with TiO₂ is an outstanding strategy to improve the photocatalytic efficiency of semiconductor due to the unique optical and electric properties of plasmonic metals. In particular, Au nanorods (NRs) with large aspect ratio can absorb the light in near-infrared (NIR) region by surface plasmon resonance (SPR). The use of NIR light for the photocatalysis is large advantage because the lights in NIR region (over 800 nm) were hardly used for the photocatalysis under sunlight due to low energy of NIR light.

In this thesis, Au NPs and Au NRs were deposited on the photoactive mesoporous SiO₂-TiO₂ template and the photocatalysis using SPR of Au NPs and Au NRs deposited in the template was investigated. The effects of TiO₂-Au interface, surface modification of the template and SPR wavelength of Au NPs and Au NRs on the photocatalysis under Vis and NIR light irradiation were discussed.

In the first study, TiO₂ nanocrystal-containing mesoporous SiO₂ template were fabricated by sol-gel method and Au NPs or Au NRs were deposited in the as-formed tubular mesopores by thermal reduction method. A morphology change of the Au NPs was investigated when the content of TiO₂ in the template was varied. Au NRs with a length of 10 to 400 nm were obtained in the template containing 20 mol% TiO₂ and the length of Au NRs was shortened with increasing in TiO₂ content because thermoexcited conduction electrons are generated from TiO₂ and these generated electrons transfer to the Au ions to accelerate their reduction. Also Au NPs in the template containing 20 mol% TiO₂ were deposited by UV radiation to the sample during heat treatment. UV radiation during Au deposition in the template produced electrons photocatalytically and accelerated the Au deposition rate, leading to the dominant formation of Au NPs. The rate constants per unit area for photobleaching of MB upon UV radiation by SiO₂-TiO₂, Au NPs and Au NRs/SiO₂-TiO₂ containing 20 mol% TiO₂ were evaluated. Bare SiO₂-TiO₂ showed $3.24 \times 10^{-2} \text{ min}^{-1} \text{ m}^{-2}$ of rate constant per unit area, the Au NPs- and Au NRs-deposited SiO₂-TiO₂ possessed rate constants that were two and three times larger than that of the bare template. Vis irradiation of the prepared samples had no significant effect on their photocatalytic properties because the electronic contact between TiO₂ and Au was not

formed by thermal reduction method.

In the second study, Au NPs and Au NRs were deposited in $\text{SiO}_2\text{-TiO}_2$ by photodeposition method with/without surface modification of the template by 3-aminopropyltriethoxysilane (APTES) and Vis light-induced photocatalysis of prepared samples was investigated. Without APTES, spherical Au NPs with a diameter of < 15 nm formed dominantly at the outside of the mesoporous structure and showed the extinction at 542 nm. The surface modification of the template with APTES prior to the deposition of Au resulted in the formation of Au NRs with a diameter of ca. 5 nm and a length of 10–15 nm in the tubular mesopores of the template and this sample showed two extinction peaks at 528 and 700 nm. Au NPs-deposited sample worked well as a photocatalyst to bleach MB under Vis light irradiation. Au NRs-deposited sample showed weak and abnormal photocatalytic activity, showing nonexponential curve in the photobleaching dynamics of MB because APTES being on the surface of the template suppressed the adsorption of MB onto the sample. Heat treatment to remove APTES from the sample led to the amelioration of the photocatalytic activity. The formation of good electronic contact between Au NPs and TiO_2 was found to be essential to the high Vis light-induced photocatalytic performance.

Finally, comparison of the photocatalytic activities of Au NPs/ $\text{SiO}_2\text{-TiO}_2$ with different amounts of Au (0.3, 0.6, 1.2 and 1.8 mol% Au) and Au NRs/ $\text{SiO}_2\text{-TiO}_2$ was carried out under UV, Vis and NIR light irradiation. Au NPs/ $\text{SiO}_2\text{-TiO}_2$ with an amount of 0.6 mol% Au showed the highest photocatalytic activity among the samples with different amount of Au under both UV and Vis light irradiation. The specific surface area of Au/ $\text{SiO}_2\text{-TiO}_2$ decreased with increasing the amount of Au, resulting in the decrease of the photocatalytic activity of 1.2 and 1.8Au/ $\text{SiO}_2\text{-TiO}_2$. Au NRs/ $\text{SiO}_2\text{-TiO}_2$ showed higher photocatalytic activity than Au NPs/ $\text{SiO}_2\text{-TiO}_2$ under both UV and Vis light irradiation. The reasons of the high photocatalytic activity of Au/ $\text{SiO}_2\text{-TiO}_2$ were investigated by measuring the action spectra and were considered to be the high specific surface area ($353.2 \text{ m}^2\text{g}^{-1}$), the formation of Schottky barrier between Au NPs and TiO_2 , the wider light absorption by SPR of Au NRs.