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The effects of Au nanoparticles size (5-60 nm) and shape (sphere, rod, cube) over electronic states and photocatalytic activities of TiO_2 studied by far- and deep-ultraviolet spectroscopy

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Absorption spectra of anatase and rutile TiO_2 modified with various size Au nanospheres (5-60 nm) in the 150–300-nm region were measured by using attenuated total reflection spectroscopy. The smaller Au nanospheres induced larger spectral changes, which mean larger electronic state changes and higher charge-separation efficiency enhancements. Actually, TiO_2 with the smaller Au nanospheres showed the higher photocatalytic activities. In contrast, although Au nanorods with various aspect ratios or Au nanocubes were deposited instead of Au nanospheres on TiO_2, their spectra (i.e. electronic states) were not significantly changed. Therefore, it was revealed that while there was little shape dependence, the smaller Au nanoparticles induced the larger electronic states change. This is may be due to the difference of potential gradient generated in the interfacial region between TiO_2 and the metal, and the smaller Au nanoparticles deposition leads to the higher photocatalytic activities.

Introduction

Titanium dioxide (TiO_2) is one of the most attractive materials in a wide range of fields such as photocatalysis and next-generation solar cell materials.[1-6] TiO_2 shows photocatalytic activity under UV light irradiations, as its band gap is about 3.2-3.0 eV.[7] Various kinds of reactions are promoted in the presence of TiO_2 and UV light,[1-3] and TiO_2 is also expected to be applied to a solar cell.[4-6] However, the quantum yields for most photocatalytic reactions and incident photon-to-current conversion efficiency of naked TiO_2 are extremely low ($< 1\%$).[8] Hence, a number of studies on the enhancement of the charge separation efficiency of TiO_2 have been reported.[9-11] For example, doping of various transition metal cations[9] or anions[10] increases the TiO_2 photocatalytic activity. Among others, TiO_2 with metal nanoparticles has extensively been investigated in recent decades by a number of research groups.[12-17] Loading TiO_2 with Pt nanoparticles increases the activity for hydrogen production reaction from water and other photocatalytic reactions.[12,13] Deposition of other metal nanoparticles (Ag, Au, Pd, Ir, and others) also improves the photocatalytic activity of TiO_2.[14]

The photocatalytic activity, which is strongly related to the electronic states of TiO_2, depends not only on metal kinds[14] but also on nanoparticle sizes.[18-22] Therefore, it is important to reveal the effects of modified nanoparticle sizes on electronic states and photocatalytic activities for designing TiO_2-based materials. The effects of the size of Au nanoparticles on the photocatalytic activities of TiO_2 have been reported from several groups.[18-22] Idriss and co-workers measured a catalytic hydrogen production rate from ethanol under UV light irradiation by using TiO_2 with various sizes of Au nanoparticles (3–30 nm).[18] They found that, when they adopted anatase TiO_2, the Au particle size did not affect the normalized reaction rates per Au atom over the 3–12 nm range, and the normalized reaction rate was suppressed at larger Au sizes. In the case of rutile TiO_2 with Au nanoparticles with 20–35 nm diameter, the photocatalytic activity were almost the same independent from the Au nanoparticle size. Tatsuma's group reported that TiO_2 modified with metal nanoparticles such as Au and Ag which absorb visible light due to localized surface plasmon resonance (LSPR) can be applied to visible-light-driven photocatalysis and photovoltaic cells.[23,24] They changed the deposited Au nanoparticle size; 15 nm, 40 nm, and 100 nm; and found that the quantum efficiency increased with increasing particle size while the maximum photocurrent decreased under visible light irradiation.[19] Heretofore, there are few reports about the electronic state changes of TiO_2–Au nanoparticle depending on Au nanoparticle size.[22] Photocatalytic activity is strongly related to its electronic states, and therefore, insight into the electronic states may lead to a mechanism elucidation of the photocatalytic enhancement and developments of high efficiency optical materials such as the solar cells.

Far-UV (FUV, 140–200 nm) and deep-UV (DUV, 200–300 nm) region provides substantial information about the electronic states of materials,[25-28] and therefore, it is of high importance to explore the FUV–DUV region of TiO_2 and metal modified-TiO_2 materials. However, it is difficult to systematically measure its optical properties in the FUV–DUV regions because of their large absorption (the absorbance index α is ~10^6–10^7 cm^{-1} in the 200-300 nm region).[29] We have recently achieved to measure the FUV–DUV (150–300 nm) spectra of TiO_2 and metal-modified TiO_2, and found that the effects of the modified metal (Pt, Pd, and Au)[30] and TiO_2 crystalline forms (anatase and rutile)[31] over their electronic states and photocatalytic activities. To measure the spectra in the FUV and DUV regions, we employed our original spectrometer that is based on attenuated total reflection (ATR),[25] which enables us to obtain the spectra of liquid and solid samples such as water,[26] aqueous solutions,[27] and organic molecules[28] in the 140–300 nm region. In this method, samples are placed on a sapphire internal reflection element (IRE), and the ATR spectra are measured using an evanescent wave as a probe light.

In this study, we measured ATR spectra of anatase and rutile TiO_2 modified with spherical Au nanoparticles whose diameters were changed between 5 nm and 60 nm, and revealed their electronic states depending on the Au size. In all cases, spectral intensities changed upon the Au nanoparticle depositions. In the case of anatase TiO_2, the spectral intensities in the longer wavelength region (> ~210 nm) decreased, while that in the shorter wavelength region (< ~210 nm) increased. On the other hand, when rutile TiO_2 was used, spectral intensity over the whole wavelength increased. In both cases, the amount of spectral intensity changes increased with the decreasing of Au nanospheres. The spectral changes mean the electronic state changes; electrons transfer from TiO_2 to Au and enhancement of charge separation efficiency of TiO_2; and thus, the smaller Au nanoparticles induced larger electronic state changes. Subsequently, their photocatalytic activities were estimated based on a photo-induced degradation reaction of methylene blue. As a result, TiO_2 with smaller Au nanoparticles showed larger photocatalytic activity, which means that the larger electronic state changes leads to the higher photocatalytic activities. In addition, Au nanorods and Au nanocubes were deposited on TiO_2 instead of Au nanospheres. There were no significant difference among ATR spectra of TiO_2 with three kinds of Au nanorods which have same diameter (25 nm) and different lengths (34, 47, and 60 nm). Then, an ATR spectrum of TiO_2 with Au nanospheres (diameter ~ 60 nm) and that of TiO_2 with corresponding size nanocubes were almost the same. These results indicate that the amount of electronic state changes of TiO_2 was mainly depends on the Au nanoparticle diameter rather than Au nanoparticle shapes. In this way, we have revealed the effects of Au nanoparticle size and shape in the electronic states of TiO_2, which is strongly related to their photocatalytic activities.

Results and discussion

Au size effect on TiO_2 electronic states

Spherical Au colloids (diameter = 5, 10, 20, and 60 nm, water solution, protected with hexadecyltrimethylammonium bromide (CTAB), absorption spectra are shown in Fig. S1) were purchased from Tanaka Kikinzoku Kogyo. These Au colloids and anatase or rutile TiO_2 powder (5-µm secondary particle diameter) were mixed in an agate mortar until the solvent completely evaporated off to the atmosphere. In this study, the amounts of colloids were regulated so that the numbers of Au nanoparticles were almost the same (~3.8×10^{10} on 1 g TiO_2). Fig. 1a-e show typical SEM images of rutile TiO_2 (5-µm secondary particle diameter, the original particle diameter is several hundred nanometers) and Au nanoparticles on it. High-resolution transmission electron microscopy (HRTEM) images were also measured as shown in Fig. S2. After that, ATR spectra of these TiO_2–Au nanoparticles in the 150-300 nm region were measured. When anatase TiO_2 was adopted (Fig. 1f), upon the deposition of Au nanoparticles, the spectral intensity in the longer wavelength region (> ~210 nm) decreased, while that in the shorter wavelength region increased (< ~210 nm) without any reference to the Au size.

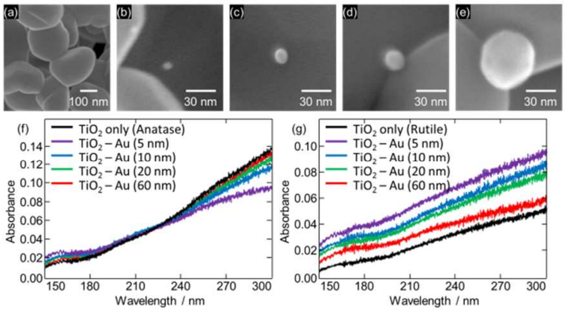

Fig. 1 (a-e) SEM images of (a) TiO_2 only, (b) 5 nm–Au (c) 10 nm–Au, (d) 20–nm Au, and (e) 60 nm–Au nanospheres modified TiO_2. (f-g) ATR spectra of (f) anatase and (g) rutile TiO_2 with or without Au nanospheres (5 nm, 10 nm, 20 nm, 60 nm).

As we have previously reported,[30] the decrease in the intensity in the longer wavelength region is due to charge transfer at the TiO_2–metal interface, and the increase in the shorter wavelength region is due to the enhancement of the charge-separation efficiency upon the deposition of metal nanoparticles. The work function of TiO_2 (~4.0 eV for anatase TiO_2) is smaller than that of Au (~4.7 eV).[14] Therefore, when TiO_2 contacts the Au nanoparticles, electrons in TiO_2 inflow to the Au nanoparticles until both the Fermi levels become equal.[1] As a result, the number of electrons in relatively high-energy levels (i.e., electrons that can be excited at a relatively longer wavelength) is decreased, resulting in the suppression of spectral intensity in the longer wavelength region. In this case, Fermi level and band-gap energy of TiO_2 should become lower and smaller by 0.7 eV at a maximum. However, these electronic state changes upon the metal modification are occurred mainly in the interfacial region between metal and TiO_2. Hence, they can't be detected enough by the general UV-

Vis spectroscopy or electrochemical equipment which measured not only the interfacial region but also bulky region. By using our ATR-FUV-DUV spectroscopy, we can obtain the information of the electronic state changes obviously. In contrast, Au nanoparticles on TiO_2 can act as a sink for photo-excited electrons, resulting in the enhancement of the charge-separation efficiency and an increase in the spectral intensity in the shorter wavelength region. This enhancement process may also occur in the longer wavelength region; however, the total change in the spectral intensity is affected by this enhancement as well as by the decrease in the number of electrons upon contact between TiO_2 and Au nanoparticles. Here, it is noted that the degree of spectral changes both in the longer wavelength region and the shorter wavelength region increased with the decreasing of deposited Au nanoparticle size. When the amounts of colloids were regulated so that the weights of Au nanoparticles were almost the same (~1.3×10^{-4} g on 1 g TiO_2), the amount of spectral changes also decreased with the increase of Au nanoparticle size as shown in Fig. S3. In addition, we had examined effects of the protecting agents on the ATR spectra in our previous work.[30] It had been made certain that the protecting agents have no substantial effects on the ATR spectra because the spectra show no substantial changes upon removing or changing the protecting agents.

When rutile TiO_2 was used (Fig. 1g), after the deposition of Au nanoparticles, the spectral intensity increased over the entire wavelength region as in the case of the depositions of Au nanoparticles, which were different from the results of anatase TiO_2. This difference of the spectral changes between anatase and rutile TiO_2 is the same as our previous study which adopted Pt nanoparticles,[31] and it reflects that the charge-separation efficiency of rutile TiO_2 is more enhanced than that of anatase TiO_2 by the deposition of metal nanoparticles. In addition, the differences of the spectral shape between rutile TiO_2 and anatase TiO_2 are due to the differences in the electronic structures of their phase, which is corresponding with previous calculation results.[31] Then, it is important point that the amount of spectral changes also increased with the decrease in the deposited Au nanoparticle size.

Au size effect on photocatalytic activities of TiO_2 modified with Au nanospheres

These results mean that smaller Au nanoparticles induce larger electronic state changes. The electronic state changes should have effects on their photocatalytic activities. Therefore, photocatalytic activity of each sample was estimated by a photo-degradation reaction of methylene blue. A methylene blue aqueous solution (20 μM, 20 mL) including anatase TiO_2 only, TiO_2-Au nanoparticles (5, 10, 20, and 60 nm, 5 mg) was irradiated with UV light (300–400 nm, ~10 μW cm^{-2}) for 15 min. The photocatalytic activity of each sample is estimated by equation (1), where I_0 and I represent the absorption intensities at 665 nm before and after the photo-degradation reaction, respectively.

$$1 - I/I_0 \qquad (1)$$

The photocatalytic activities of TiO_2 only and TiO_2 with 5, 10, 20, and 60 nm Au nanospheres were 0.30 ± 0.030, 0.51 ± 0.031, 0.41 ± 0.024, 0.37 ± 0.043, and 0.33 ± 0.058 (average ± standard deviation, n = 3). As shown in Fig. 2, the photocatalytic activity is enhanced upon the deposition of Au nanospheres, and the photocatalytic activity strongly depends on the Au size; TiO_2 with the smaller Au nanoparticles showed the higher photocatalytic activity. Although Au nanoparticles also have catalytic activities, the amount of Au was quite low and they have little effects on the present activities. Wei and co-workers reported that photocatalytic activity of TiO_2 with ~5-nm Au was larger than that of TiO_2 with ~40-nm Au under the UV light irradiation, and the present results are corresponding with them. From these results of ATR spectra (Fig. 1) and photocatalytic activities (Fig. 2), it is concluded that, with the decrease of the Au size, the electronic state changed more largely and the photocatalytic activities increased. That is to say, the correlative relationship between the electronic state changes and the photocatalytic activities depending on the Au nanoparticle size is revealed.

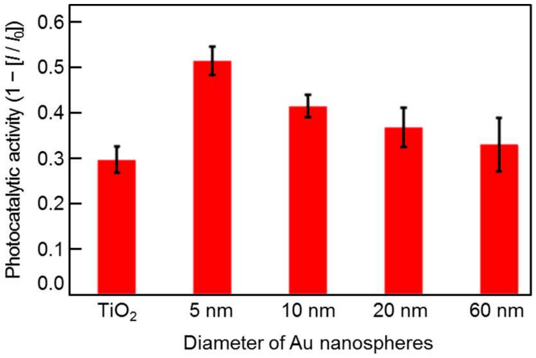

Fig. 2 Photocatalytic activities (1 − [I/I_0]) of (a) anatase TiO_2 with and without Au nanospheres with various sizes.

Au shape effect on TiO_2 electronic states

Subsequently, we used Au nanorod with various aspect ratios and measured ATR spectra of TiO_2–Au nanorods samples. All the Au nanorods have the same diameter (25 nm), and their length are 34, 47, and 60 nm; corresponding aspect ratios are 1.36, 1.88, and 2.40, respectively. The Au nanorods (water solution, protected with CTAB, absorption spectra are shown in Fig. S4) were purchased from Sigma-Aldrich Co. LLC. SEM images of the Au nanorods are shown in Fig. 3a-c. The numbers of Au nanorods were regulated about 3.8×10^{10} on 1 g TiO_2 in the case of the Au nanospheres. As shown in Fig. 3e (anatase TiO_2) and f (rutile TiO_2), there is no significant change in the ATR spectra of TiO_2 modified with three kinds of Au nanorods with different aspect ratios. These results mean that the electronic state of TiO_2 depends mainly on the diameter of modified Au nanoparticles rather than the length (i.e. aspect ratio) of nanorod. In addition to that, we synthesized Au nanocubes (Fig. 3d, ~60 nm length, an absorption spectrum is shown in Fig. S5),[32] and measured an ATR spectrum of anatase TiO_2 with the Au nanocubes (Fig. 3g). There is also no significant difference between the ATR spectrum of TiO_2 with Au nanocubes and that with corresponding size Au nanospheres (60 nm diameter), which means that the electronic state changes are independent from Au nanoparticle shapes. Actually, the photocatalytic activities were also almost the same regardless of the Au shape as shown in Fig. S6. We discussed reasons why the electronic states of TiO_2 with Au nanoparticles strongly depend on the Au size rather than the Au shape.

As ascribed above, upon the contact between TiO_2 and a metal, electrons in TiO_2 are transferred into the metal. At the same time, potential gradient is generated in the interfacial region between TiO_2 and the metal. This potential gradient prohibits re-combination between the electrons in metal and the holes in TiO_2, and leads to the enhancement of charge-separation efficiency. The depth and width of the potential gradient depend on the Fermi levels, sizes, electric conductivity and other factors of TiO_2 and the metal. In the present case, TiO_2 was not changed and only Au nanoparticle size and shape were changed. In addition, even when the Au shape was changed, the width of the Au nanoparticle was not changed. That is to say, the diameter of all of the Au nanorods was 25 nm, though their length was changed. Therefore, from the ATR spectra in Fig. 1 and Fig. 3, it seems that the width of deposited Au nanoparticles largely effects on the electronic states of TiO_2. In the past, Kamat and co-workers have measured Fermi levels of TiO_2–Au nanoparticle samples (average diameters of Au nanoparticle were 3, 5, and 8 nm) under UV light irradiation, and concluded that the Fermi level of 3-nm Au nanoparticle was more negative than 8-nm Au nanoparticle by 40 mV.[22] However, the particle range was strictly limited only from 3 nm to 8 nm, and there is no argument about the effect of shape of Au nanoparticles. The electronic states changes can be detected by using other various methods such as fluorescence analysis, light current measurements, and X-ray photoelectron spectroscopy (XPS).[33-35] In the present study, we have discussed not only the size effect in the wide range of 5~60 nm, but also the shape effect of the Au nanoparticles systematically and easily based on the FUV–DUV spectra. It is also noted here that the contact area between Au and TiO_2 is changed depending on the Au size and shape. However, the spectra and the photocatalytic activities are almost the same, which mean that the difference of the contact area has no significant effect in the present cases.

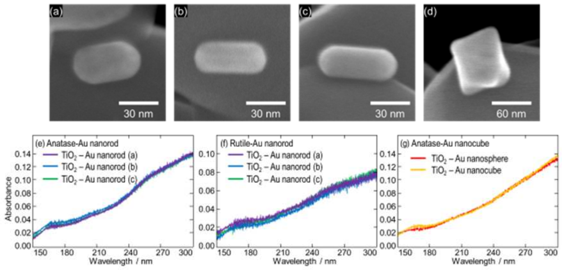

Fig. 3 (a-d) SEM images of (a-c) Au nanorods and (d) Au nanocubes. ATR spectra of (a) anatase and (b) rutile TiO_2 modified with Au nanorods of various aspect ratios and (c) anatase TiO_2 with Au nanocubes (~60 nm). Sizes of Au nanorods are 25 nm × (a) 34 nm, (b) 47 nm, and (c) 60 nm, respectively.

Experimental

Anatase and rutile TiO_2 were purchased from Wako Pure Chemical Industries, Ltd. TiO_2 particles were used as purchased. Au nanoparticle colloids (diameter = 5, 10, 2, and 60 nm, water solution, protected with hexadecyltrimethylammonium bromide (CTAB)) were purchased from Tanaka Kikinzoku Kogyo. During the ATR–FUV–DUV measurement, the samples were placed on a sapphire internal reflection element (IRE), and the ATR spectra were measured using an evanescent wave as a probe light.

TiO_2 (1 g) and metal colloids (200 μL) were mixed in an agate mortar until the solvent completely evaporated off to the atmosphere. TiO_2 particles with and without Au metal nanoparticles were placed on the sapphire IRE, and the FUV–DUV spectra were measured using an ATR spectrometer. In the FUV region, both H_2O and O_2 present in the atmosphere yield very intense absorptions, and thus the spectrometer must be purged with N_2 gas. The ATR system employed in this study used a 30-W deuterium lamp as a light source. SEM images were observed by model S-5000 (Hitachi Ltd., Tokyo, Japan), operated at 20 kV.

Methylene blue was purchased from Wako Pure Chemical Industries, Ltd. A Hg–Xe lamp (Luminar Ace LA-300UV, Hayashi Watch Works) equipped with a UV-pass filter (Wavelength = 300–350 nm, UTVAF-50S-34U, CVI Laser, LLC) was used as the UV light source. An aqueous solution of methylene blue (20 μM, 20 mL) was mixed with TiO_2 only and TiO_2–Au powder (5 mg) using a magnetic stirrer, followed by UV irradiation (~10 μW cm^{-2}) for 30 min. After the irradiation, TiO_2 was separated from the solution by centrifugation (15,000 rpm, 1 min). The absorption spectra of the methylene blue aqueous solutions were measured both before and after UV irradiation.

Conclusions

In summary, the effects of Au size and shape on TiO_2 over their electronic states and photocatalytic activities were revealed by measuring ATR spectra in the FUV-DUV region (150–300 nm) and photo-induced degradation reaction of the methylene blue. The smaller Au nanosphere caused the larger ATR spectral changes for both anatase and rutile TiO_2. The spectral changes in the FUV–DUV region correspond to the electronic state changes of TiO_2, which have the effects on their photocatalytic activities. TiO_2 with the smaller Au nanospheres also showed the higher photocatalytic activities. In other words, the larger electronic state changes leaded to the higher charge-separation efficiencies. On the other hand, the ATR spectra of TiO_2 with Au nanorods with various aspect ratios were almost the same, and there is no significant difference between the spectrum of TiO_2 with Au nanocubes (~60 nm) and that with corresponding size Au nanospheres. Therefore, it is obvious that the Au shape had little effect on the electronic state changes of TiO_2.

In this way, it is concluded that the electronic states of TiO_2 depend largely on the modified Au size rather than Au shape. These results also show the usefulness of our original ATR spectroscopy for the investigation the electronic states of TiO_2-based materials. Consequently, the electronic states of TiO_2 depending on the deposited metal size and shape, which is strongly related to their photocatalytic activities, were systematically studied by this ATR spectrometer, leading to the development of high-efficiency photo-functional materials such as photocatalysis and solar cells.

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Notes and references

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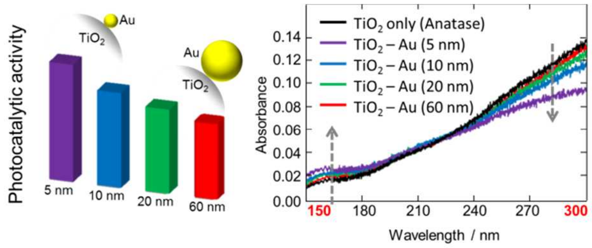

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