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Far-ultraviolet spectral changes of titanium dioxide with gold nanoparticles by ultraviolet and visible light

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ABSTRACT

Attenuated total reflectance spectra including the far-ultraviolet (FUV, ≤200 nm) region of titanium dioxide (TiO_2) with and without gold (Au) nanoparticles were measured. A newly developed external light-irradiation system enabled to observe spectral changes of TiO_2 with Au nanoparticles upon light irradiations. Absorption in the FUV region decreased and increased by the irradiation with ultraviolet and visible light, respectively. These spectral changes may reflect photo-induced electron transfer from TiO_2 to Au nanoparticles under ultraviolet light and from Au nanoparticles to TiO_2 under visible light, respectively.

1. Introduction

Titanium dioxide (TiO_2) is a typical inorganic semiconductor material and a photocatalysis [1–5]. As the band gap energy of anatase TiO_2 is about 3.2 eV, anatase TiO_2 shows its photocatalytic activity under ultraviolet (UV, ≤400 nm), deep-UV (DUV, ≤300 nm), and far-UV (FUV, ≤200 nm) light [1]. By an irradiation with the UV, DUV, and FUV light, electrons in the valence band of TiO_2 are excited into the conduction band, and thus, optical properties in these regions are important for understanding the electronic states of TiO_2, which are directly related to its function.

Reflection spectra of TiO_2 single crystals over a wide wavelength range have been measured by using synchrotron orbital radiations [6–9]. For example, Cardona's group and Hosaka's group reported reflection spectra of a rutile TiO_2 single crystal in the energy range from 1 to 12 eV (about 1200–100 nm) [6] and an anatase TiO_2 single crystal in 2–30 eV (about 620–40 nm), respectively [8]. Their optical constants (i.e. refractive index n and extinction efficient k) could be determined based on the obtained reflection spectra and the Kramers-Kronig conversion. However, the radiation measurement needs huge experimental installation and an ultrahigh vacuum environment, and most reported spectra are obtained using single crystals. Since TiO_2 is practically used in the states of powder and polycrystalline film, it is also important to obtain the spectral of TiO_2 powders and polycrystalline films. Sério and coworkers reported the transmission spectra in the 320–115 nm region of polycrystalline TiO_2 thin films using the synchrotron radiation spectrometer, but a reliable region was limited to the DUV region (>200 nm) because of effects of H_2O as they stated in the paper [10]. Although a commercial UV–Vis. spectrometer can measure diffuse reflectance spectra of TiO_2 powder easily, its measurable wavelength is limited to the DUV region (≥200 nm) [11]. This is because oxygen molecules and water vapor in air strongly absorb light in the FUV region. Large absorption of TiO_2 (the absorbance index α is about 10^6–10^7 cm^{-1} for anatase TiO_2) [12] also makes difficult the spectral measurements in the FUV region.

In 2007, Ozaki's group developed a totally novel FUV spectrometer, which adopts an attenuated total reflectance (ATR) system [13–16]. In the ATR-FUV spectrometer, an incident light from a deuterium (D_2) light is irradiated into an internal reflectance element (IRE), and an evanescent wave generated at an interface between the IRE and a sample is used as a prove light. The penetration depth of the evanescent wave is <100 nm in the FUV region, which enables us to measure spectra of various liquid and solid samples such as water [17–19], organic solvents [20–22], and ionic liquids [23]. The obtained spectra in the FUV region provide much information about the electronic states of materials. Recently, using the ATR-FUV spectrometer, spectral measurements of TiO_2 and other inorganic semiconductor powders were achieved [24–28]. We also revealed consistent changes between obtained spectra and photocatalytic activities of TiO_2 modified with metal nanoparticles depending on metal species (Au, Pd, and Pt) [24], size (5–60 nm) [26] and shape (sphere, rod, and cubes) [26]. The larger spectral changes of metal modified TiO_2 compared to the bare TiO_2 indicates the larger electronic states changes, results in the more enhancement of the

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photocatalytic activities [24–26]. It is known that loading metal nanoparticles on TiO_2 improves the photocatalytic activity of TiO_2 [29–35]. More details are described in the previous papers [24–26].

In this study, we introduced an external light-irradiation system into the existing ATR-FUV spectrometer, and measured spectra of TiO_2 and Au modified TiO_2 (Au-TiO_2) before and after UV light (300–350 nm) and visible light (500–800 nm) irradiations. TiO_2 and metal modified TiO_2 show their functions by the light irradiation, and thus, it is important to investigate the electronic state changes upon the light irradiation. In the case of TiO_2 only, no spectral change was observed upon the light irradiations. On the other hand, in the case of Au-TiO_2, spectral intensities around 160 nm decreased by the irradiation with UV light, and increased by the subsequent visible light irradiation. These spectral changes may reflect electron transfers between TiO_2 and Au nanoparticles; from TiO_2 to Au nanoparticles under UV light and from Au nanoparticles to TiO_2 under visible light, respectively.

2. Experimental Setup

Anatase TiO_2 powder (5 μm secondary particle diameter, Wako Pure Chemical Industries, Ltd.) was used as purchased. Au nanoparticle colloid (10 mM in water, 6–9 nm diameter, protected by polyethylenimine) was purchased from Wako Pure Chemical Industries, Ltd. TiO_2 (1 g) and Au colloid (200 mL) were mixed in an agate mortar until the solvent completely evaporated off to the atmosphere. TiO_2 and Au-TiO_2 were placed on a sapphire IRE, and ATR spectra were measured.

Fig. 1a shows a schematic diagram of the sample chamber of the ATR-FUV spectrometer used in the present study. The ATR spectroscopic system used a 30 W D_2 lamp as a light source. The light from a monochromator is split into a reference beam and a sample beam by a half mirror. The reference beam and the reflected sample beam pass through a synthetic quartz plate, coated with sodium salicylate, which fluoresces. Finally, the fluorescence of each beam is detected with a photomultiplier. The optics part is purged with dry N_2 gas in order to remove oxygen molecules and water vapor, and the sample part is exposed in air. More details are described in the previous papers [14,15]. In order to irradiate a sample from an external light source, a 1 cm diameter hole covered with a quartz window was made in the front wall of the sample chamber (Fig. 1a), and a mirror was put below the sapphire IRE (Fig. 1b). If an external light is irradiated from above the sample on the IRE, the light is blocked by the sample and cannot reach the measurement area (i.e. an evanescent wave region). The external light sources for the irradiation with UV light (300–350 nm) and visible light (500–800 nm) were a Hg-Xe lamp (Luminar Ace LA-310UV, Hayashi Watch Works) equipped with a wide band-pass filter (UTVAF-34U, Sigma Koki) and a Xe lamp (Luminar Ace LA-251Xe, Hayashi Watch Works) equipped with a wide band-pass filter (SHPF-25C-842, Sigma Koki), respectively.

3. Results and Discussion

Fig. 2 shows typical absorption spectra of TiO_2 in the 150–300 nm region before (black) and after (purple) the UV light irradiation for 30 min. The spectra showed broad bands at about 160, 200, and 260 nm. Sério's group also reported very weak and broad bands at 200 and 260 nm by using polycrystalline TiO_2 thin films [10], and the present spectra correspond with their spectra. Based on the calculated band structures, these two bands at 200 and 260 nm were assigned to the $e_g(\sigma) \rightarrow t_{2g}(\pi^*)$ and $t_{2g}(\pi) \rightarrow t_{2g}(\pi^*)$ transitions, respectively [8,9]. In addition, using the ATR system, the band at 160 nm was successfully observed, and this band was assigned to the $t_{2g}(\pi) \rightarrow e_g(\sigma^*)$ transition [24]. There is no significant change upon the UV light irradiation as shown in Fig. 2.

Subsequently, absorption spectra of Au-TiO_2 before and after the UV light irradiation were measured. As shown in Figs. 3a and b, by the irradiation with UV light, the spectral intensity around 160 nm decreased, while the intensity in the 180–300 nm region was almost the same. This spectral change may be related to an electron transfer from TiO_2 to Au nanoparticles as described below.

It is well known that metal nanoparticles on TiO_2 work as an electron pool [31–34]. If TiO_2 contacts metal with a higher work function than that of TiO_2, electrons in TiO_2 flow towards the metal until both Fermi levels become equal and the Schottky barrier forms [2,4]. When TiO_2 modified with metal nanoparticles is irradiated with the UV light, electrons in the valence band of TiO_2 are excited to the conduction band and transferred into the metal. At the same time, holes are left in the valence band of TiO_2. Because of the Schottky barrier between the metal and TiO_2, recombination of the electrons in the metal and the holes in the TiO_2 is suppressed, results in the enhancement of the charge-separation efficiency.

In the present study, by the irradiation with UV light, the electrons are transferred from TiO_2 to Au nanoparticles, and the charge-separation between TiO_2 and Au continues even after the stop of the UV light because of the Schottky barrier. As a result, the number of electrons in TiO_2 is decreased (Fig. 4a), resulting in the suppression of the absorption as shown in Fig. 3a. Further studies are needed in order to clarify the reason why the spectral intensity only around 160 nm was decreased.

After the irradiation with the UV light, visible light was irradiated to Au-TiO_2, and the absorption spectra were measured. As shown in Fig. 3c and d, by the irradiation with the visible light, the spectral intensity around 160 nm increased up to the original intensity (i.e. before the UV light irradiation). This phenomenon indicates the electron transfer from Au nanoparticle to TiO_2, which is opposite direction to the case of the UV irradiation. Au nanoparticles absorb visible light due to localized surface plasmon resonance (LSPR) [36,37]. When Au nanoparticles on TiO_2 were irradiated with LSPR wavelength light, electrons in resonance Au nanoparticles are transferred to TiO_2 and positive charges are left in the Au nanoparticles. This light-induced charge separation

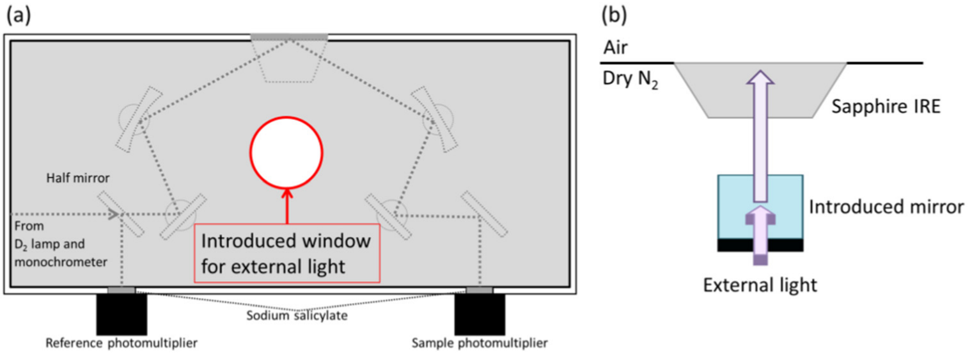

Fig. 1. Schematic diagrams of (a) a sample chamber of an ATR-FUV spectroscopy and (b) a newly introduced external light-irradiation system.

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