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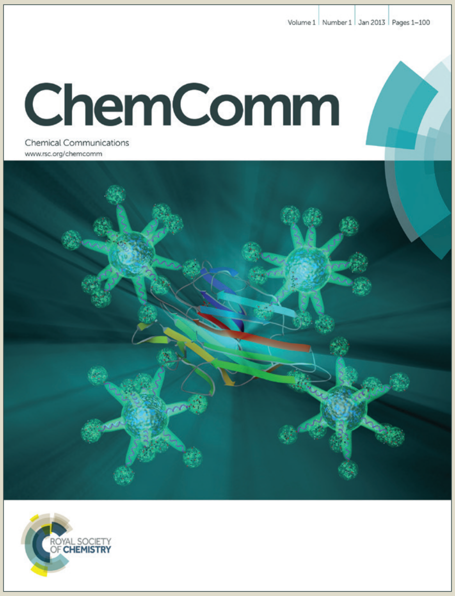

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# Consistent changes of electronic states and photocatalytic activities of metal (Au, Pd, Pt)-modified $TiO_2$ studied by far-ultraviolet spectroscopy

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**Absorption spectra (150–300 nm) of $TiO_2$ and $TiO_2$ modified with metal (Pt, Pd, and Au) nanoparticles were systematically measured using attenuated total reflection–far ultraviolet spectrometer. The deposition of metal nanoparticles altered the spectral shape and intensity, indicating changes in the electronic states and photocatalytic activities of $TiO_2$.**

Titanium dioxide ($TiO_2$) is one of the most attractive materials with applications in a wide range of fields,[1,2] in particular photocatalysis[1] and next-generation solar cell materials.[2] Anatase $TiO_2$ shows photocatalytic activity under ultraviolet (UV) light irradiation (< ~380 nm).[1] A number of investigations regarding the enhancement of the charge-separation efficiency of $TiO_2$ have been reported.[3] $TiO_2$ modified with metal nanoparticles has been extensively investigated in recent decades.[1(a),4-6] Loading $TiO_2$ with metal nanoparticles (Pt, Pd, Au, and others) improves the photocatalytic activity of $TiO_2$,[4,5] and $TiO_2$ modified with metal nanoparticles such as Au and Ag which absorb visible light due to localized surface plasmon resonance can be applied to the visible-light-driven photocatalysis and photovoltaic cells.[6]

Although naked anatase $TiO_2$ shows photocatalytic activity upon irradiation with UV light (< ~ 380 nm), it is difficult to measure its optical properties in the UV region due to its large absorption (the absorbance index $\alpha$ is ~$10^6$–$10^7$ $cm^{-1}$ in the 200–300 nm region).[7] In this paper, we refer to the 140–200 nm region as the far-UV (FUV) region and the 200–400 nm region as the near-UV (NUV) region. The NUV-FUV region provides substantial information about the electronic states of materials,[8] and therefore, it is of high importance to explore the NUV-FUV region of $TiO_2$ and modified-$TiO_2$ materials. However, the measurement ranges in most spectroscopic investigations have been limited to the NUV region (>200 nm),[9] and it is substantially more difficult to systematically estimate the effects of surface modifications on $TiO_2$ electronic states.

We have recently developed a novel FUV spectrometer based on attenuated total reflection (ATR)[8(a)] which enables us to measure the spectra of liquid and solid samples such as water,[8(b)] aqueous solutions,[8(c)] and organic molecules[8(d)] in the 140–300 nm region. During the ATR-FUV measurement, samples are placed on a sapphire internal reflection element (IRE), and ATR spectra measured by using the evanescent wave as a probe light.[8]

In this study, the absorption spectra of $TiO_2$ were successfully measured in the 150–300 nm region by the ATR-FUV method. Subsequently, the ATR-FUV spectra of $TiO_2$ with metal (Pt, Pd and Au) nanoparticles were also obtained, and spectral changes of $TiO_2$ following modification with metals were investigated. As a result, a strong positive correlation was observed between the degree of spectral changes of metal-modified $TiO_2$ and the work function of metals. The spectral changes are due to the charge transfer at the $TiO_2$–metal interface and the enhancement of the charge-separation efficiency. Such a positive relationship is also observed between the degree of spectral changes and photocatalytic activity. Thus, changes in the electronic state of $TiO_2$ in the NUV-FUV region, which is strongly related to the photocatalytic activity, have been systematically studied for the first time using ATR-FUV. By using this ATR-FUV, we can explore the electronic states of $TiO_2$ in the NUV-FUV (150–300 nm) region in order to obtain critical information about the mechanism of enhancement of the charge-separation efficiency and design of semiconductor-based materials.

Fig. 1a shows a typical absorption spectrum in the 150–300 nm region of commercial anatase $TiO_2$ particles (diameter = ~5 μm; ST-41; Ishihara Sangyo Kaisha, Ltd.). There are three spectral bands at ~160, 200, and 260 nm. Because the refraction index of anatase $TiO_2$ (~2.5) is

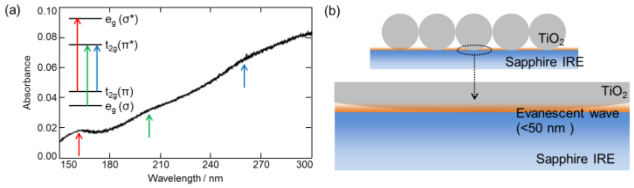

**Fig. 1** (a) Attenuated total reflection–far ultraviolet (ATR-FUV) spectrum of $TiO_2$ and (b) Measurement mechanism of $TiO_2$ using ATR-FUV spectrometer.

higher than that of the sapphire (~1.8), attenuated total reflectance does not occur at their interface. However, the contact area between $TiO_2$ and the sapphire IRE was very small (point contact, ideally) because spherical $TiO_2$ particles were utilized. Therefore, absorption spectra of $TiO_2$ in the evanescent wave range could be measured (Fig. 1b).

Sério and co-workers[10] measured the NUV-FUV absorption spectra of $TiO_2$ using the synchrotron radiation facility; however, reliable data were limited to the NUV region (>200 nm) because of the strong influence of water absorption. In this study, very weak and broad absorption bands at ~200 and 260 nm (Fig. 1a) correspond to the bands observed by the Sério group because the bands observed by them were also very weak and broad. They assigned these two bands at 200 and 260 nm to the $e_g(\sigma) \rightarrow t_{2g}(\pi^*)$ and $t_{2g}(\pi) \rightarrow t_{2g}(\pi^*)$ transitions, respectively, based on a molecular orbital energy level diagram and calculated band structures reported by other groups.[11] Comparing the present absorption spectrum with these calculated results, the defined peak at 160 nm seems to be due to the $t_{2g}(\pi) \rightarrow e_g(\sigma^*)$ transition, as shown in the inset in Fig. 1a. The upper $t_{2g}(\pi^*)$ and $e_g(\sigma^*)$ orbitals are composed primarily of Ti(3d) orbitals, and the lower $t_{2g}(\pi)$ and $e^g(\sigma)$ orbitals are composed largely of O(2p) orbitals.

The spectral shape in the 150–180 nm region is clearly different from that of water, and thus, the absorption spectrum of $TiO_2$ in the 150–300 nm region, including the FUV region, was successfully measured. The electronic state assignments of the three bands have been confirmed with the reported theoretical calculations. Notably, this absorption spectrum can be measured by light from a 30 W deuterium lamp rather than the synchrotron orbital radiation, and using the commercial $TiO_2$ powder instead of a single crystal.

Next, the absorption spectra of $TiO_2$ modified with Pt nanoparticles with a diameter of 1–6 nm were measured. The Pt nanoparticles were deposited by mixing $TiO_2$ particles (1 g) with a commercially available Pt nanoparticle colloid (200 μL, 10 mM in a water/ethanol solution, protected with polyvinylpyrrolidone (PVP), Wako Pure Chemical Industries, Ltd.) in an agate mortar until solvent completely dared off in the atmosphere. Fig. 2a compares the ATR-FUV spectra of $TiO_2$-Pt nanoparticles (purple line) with that of $TiO_2$ only (blue line). The absorption intensity in the longer wavelength region decreases, while the intensity in the shorter wavelength region increases with the Pt nanoparticles deposition. According to the SEM image shown in Fig. 2a (inset), Pt nanoparticles cover the $TiO_2$ surface. We have changed the content of mixed Pt nanoparticle colloid from 100 to 600 μL per 1 g of $TiO_2$ and the absorption spectrum of $TiO_2$ mixed with 200 μL Pt nanoparticle colloid showed the largest increase in the shorter wavelength region (Fig. S1). Then, the sample was heated at 200 °C for 1 h in order to remove the protecting agent;[12] however, the ATR-FUV spectrum remains similar, indicating that PVP has no effect on the spectra (details are shown in Fig. S2).

If $TiO_2$ contacts a metal with a higher work function than that of $TiO_2$, electrons in $TiO_2$ inflow in the metal until both Fermi levels become equal.[1(a)] In the present study, the work functions of $TiO_2$, Au, Pd, and Pt are ~4.0, 4.7, 4.9, and 5.7 eV, respectively;[4(b)] thus, the electrons transfer from $TiO_2$ to the metal nanoparticles. As a result, the number of electrons in relatively high-energy levels (i.e. electrons which can be excited by relatively longer wavelengths) is decreased, resulting in the suppression of the absorption intensity in the longer wavelength region. On the other hand, metal nanoparticles on $TiO_2$ can act as a sink for photo-excited electrons,[5(a,c)] which enhances the charge-separation efficiency as previously described. This enhancement of charge separation increases the absorption intensity in the shorter wavelength region. This process may also occur in the longer wavelength region, but the total change of absorption intensity is affected by both this enhancement and the decrease in the number of electrons upon contact between $TiO_2$ and the metal nanoparticles.

We also measured the ATR-FUV spectra of $TiO_2$ modified with Pd and Au nanoparticles (Fig. 2a). In all the cases (Pt, Pd, and Au), the absorption intensity in the longer wavelength region decreases, while that in the shorter wavelength region increases, as shown in the difference spectra (Fig. 2b). The absorption intensity over the entire wavelength region becomes strong or weak within several per cent in intensity for each sample because $TiO_2$ particles are not completely spherical and the content of $TiO_2$ in the evanescent wave is slightly different. However, the spectral shapes of each sample are nearly the same.

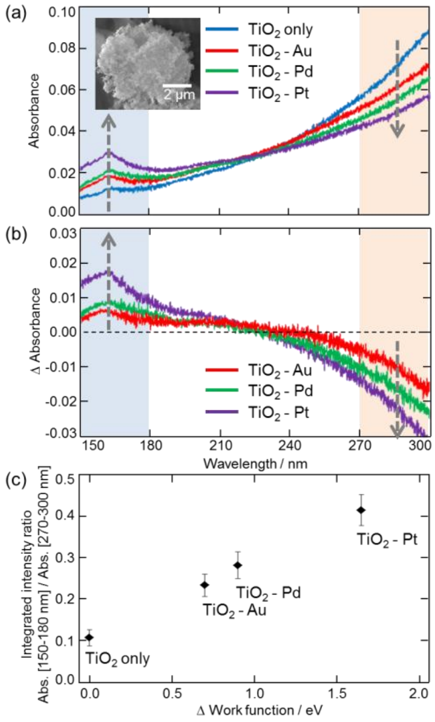

**Fig. 2** (a) ATR-FUV spectra of $TiO_2$ (blue) and Au- (red), Pd- (green), Pt- (purple) modified $TiO_2$. Inset: SEM image of $TiO_2$-Pt nanoparticles. (b) Difference spectra of $TiO_2$ between spectra measured before and after metal modification. (c) Integrated intensity ratio of absorption in 150–180 nm region to that in 270–300 nm region plotted against work function difference between $TiO_2$ and each metal.

In order to discuss the degree of spectral changes, an integrated intensity ratio of absorption in the 150–180 nm region to that in the 270–300 nm region is shown. The integrated intensity ratios of $TiO_2$ only, $TiO_2$-Au, $TiO_2$-Pd, and $TiO_2$-Pt were 0.13 ± 0.018, 0.25 ± 0.025, 0.29 ± 0.030, and 0.42 ± 0.035 nm (average ± standard deviation, n = 15), respectively. Fig. 2c plots these ratios as a function of difference in the work function between $TiO_2$ and each metal (Au, Pd, Pt ~ 0.7, 0.9, 1.7 eV, respectively). Notably, there is a strong positive correlation between the intensity ratio and the work function difference. The strong positive correlation between the intensity ratio and the work function difference (Fig. 2c) indicates that the larger work function difference results in the increased electron inflow from $TiO_2$ to the metal, and thus, a larger enhancement of the charge separation.

Next, photocatalytic activities of $TiO_2$ and $TiO_2$ modified with Au, Pt, and Ad nanoparticles were estimated by a photo-degradation reaction of methylene blue. A methylene blue aqueous solution (10 μM), including $TiO_2$ only, $TiO_2$-Au, $TiO_2$-Pd, or $TiO_2$-Pt was irradiated with UV light (300–350 nm, ~10 μW $cm^{-2}$) for 60 min. Absorption spectra before and after UV light irradiation are shown in Fig. 3a-d. 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.

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

Fig. 3e shows the relationship between the photocatalytic activity and work function difference between $TiO_2$ and each metal. It is markedly noted that there is also a strong positive correlation in Fig. 3e as in the case of the degree of spectral changes (Fig. 2c).

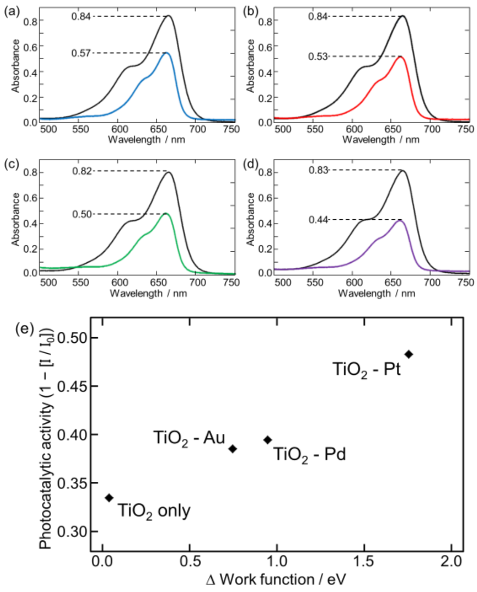

**Fig. 3** (a–d) Absorption spectra of methylene blue aqueous solution before (black) and after (colour) UV light irradiations with (a) $TiO_2$ and (b) Au- (c) Pd- (d) Pt- modified $TiO_2$. Inset values are absorption at 665 nm. (e) Photocatalytic activity (1 – $[I/I_0]$) plotted against work function difference between $TiO_2$ and each metal.

In summary, absorption spectra in the NUV-FUV region (150–300 nm) of $TiO_2$ and $TiO_2$ modified with metal nanoparticles, which contain valuable information about electronic states of the materials, were successfully and easily measured by using an original ATR-FUV spectrometer. These results have demonstrated that ATR-FUV spectroscopy holds considerable promise as a novel method to investigate the electronic states of materials, especially semiconductor materials such as $TiO_2$. The naked $TiO_2$ spectrum corresponded well with the previously reported refraction spectrum and theoretical calculations. The deposition of metal (Pt, Pd, and Au) nanoparticles substantially changed the spectral shape, which indicates changes in the electronic states of $TiO_2$. The decrease in the absorption intensity in the longer wavelength region suggests an electron transfer from $TiO_2$ to metal nanoparticles, while the increase in the shorter wavelength region reveals the enhancement of charge separation. Additionally, these results suggest that the degree of spectral variation strongly depends on the difference in the work function between $TiO_2$ and each metal. The larger spectral changes indicate an increased enhancement of charge separation, which correlates with the improvement of the photocatalytic activity of $TiO_2$. Therefore, the photocatalytic activity of $TiO_2$-based materials is strongly related to the spectral shapes in the FUV region. Consequently, systematic studies regarding the enhancement of the charge-separation efficiency can be executed with this ATR-FUV spectrometer, leading to the development of high-efficiency optical materials such as photocatalysis and solar cells.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Fig. S1-2. See DOI: 10.1039/c000000x/

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