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Studies on interparticle charge-transfer excitation: Novel band-structure analysis of semiconducting metal-oxide photocatalysts based on energy-resolved distribution of electron traps

（粒子間電荷移動励起に関する研究－電子トラップ密度のエネルギー分布にもとづく半導体金属酸化物光触媒の新規バンド構造解析）

Metal oxide samples, which are widely used in large quantities as chemical functional materials such as photocatalysts, catalysts, sensors, and oxygen-carriers are categorized as semiconductors or insulators based on its electronic energy structure and the band structure composed of an electron-filled valence band (VB), electron-vacant conduction band (CB) and forbidden band (band gap) separating them from each other, though it seems the real band structure of the metal oxides is still speculative and only conduction band bottom (CBB) and valence band top (VBT) positions have been discussed mainly, presumably because there have been no analytical methods to know the real band structures especially those at the surface.

Semiconductor materials such as titania have been widely used in a variety of applications and products in the energy and environmental fields. The design and development of hetero-structured photocatalysts is a promising strategy to improve photocatalytic activity. Although many researchers have suggested that the reason for the improvement in photocatalytic performance of hetero-structured photocatalyst is that the electron-hole recombination is reduced by the charge transfer between different kinds of particles, there is no direct experimental evidence to prove it. Irie et al. reported that Cu(II)-grafted titania samples are sensitive to visible light to be explained by visible light initiates interfacial charge transfer (IFCT) from the valence band (VB) of the photocatalyst to a co-catalyst deposited on the photocatalyst surface, leading to enhancement of light absorption. When such electron transfer occurs, there must have an electronic interaction. Although there are a lot of researchers published papers claiming electron transfer between neighboring particles (without chemical bond) as a key process controlling the overall performance of various functional materials such as those used for photocatalysts, solar cells and batteries. However, it seems that there is no experimental evidence has been reported to show clearly the spatial and energetic overlap of orbitals (or electronic states) of two particles which is an essential requirement for the interparticle electron transfer. An experimental evidence of electronic interaction is very important for the design and development of hetero-structured photocatalysts and visible-light-sensitive photocatalyst and direct observation of the interaction could provide

significant information for both fundamental and practical studies on wide range of functional materials.

Another problem of characterization of metal oxides samples when they are mixed phase ones is a lack of a measure for how different kind of phases are contacted especially electronically though electronic contact between different kind of particles have been suggested to be decisive factor influencing the performance of materials. Therefore, technique which can quantitatively evaluated the hetero-contact condition between nanoparticles should be developed.

Most metal oxides are categorized as n-type semiconductors which have electron-filled donor levels below CBB due to the oxygen anions of metal oxides samples are easily apt to be detached to leave electrons in an oxygen defect. These electron-filled donor levels will lose electrons and become electron traps (ETs) when donor electrons flow out to adsorbed water or surface hydroxyl groups. It is well known that metal oxides, such as titanium(IV) oxide, turn blue when reduced by photoirradiation in the presence of electron donors in deaerated conditions or calcination under hydrogen atmosphere or in vacuum. The blue color of titania is attributed to that some tetravalent titanium (Ti^{4+}) ions are reduced by electrons excited in the conduction band (CB) to form trivalent titanium (Ti^{3+}) ions. In other words, metal-oxide powders have electron traps (ETs) on the surface. As reported previously, a novel method for identification and characterization of metal-oxide powders with energy-resolved distribution of electron traps (ERDT) measured by reversed double-beam photoacoustic spectroscopy (RDB-PAS) have been developed.

In RDB-PAS measurement, electrons in VB of metal-oxide samples are directly excited to electron traps (ETs) and accumulated in the ETs from the deeper side to the shallower side through wavelength-scanned continuous light. The electron-filled ETs caused the increase of photoabsorption and the increase can be detected by modulated light by PAS. The PA signal was detected by a microphone and plotted against energy of continuous excitation light to obtain RDB-PAS spectrum. The obtained RDB-PAS spectrum which is a plot of total accumulated electron-trap density as a function of photon energy of continuous light was differentiated from the lower energy side to higher energy side to obtain ERDT. Then, the obtained signal value was converted into electron trap density in unit of $\text{g}^{-1} \text{eV}^{-1}$ by the conversion factor determined with the reported total electron trap density measured by photochemical method. The ERDT pattern which differs depending on the kind of sample reflect the surface structure, the total electron trap (ET) density which shows an almost linear relation with specific surface area reflect the particle size, and the CBB position, which is obtained by PAS measurement, reflect the bulk structure of metal-oxide samples. In this study, ERDT analysis using RDB-PAS is expected to be applicable to estimation of band structure of metal-oxide samples and provides quantitative measurement of the interparticle electronic contacts. Chapter 1 describes those backgrounds and purposes of this study.

In Chapter 2, I obtained experimental evidence of interparticle spatial overlapping of orbitals to result in interparticle charge-transfer excitation (ICTE), that is, photoexcitation from the higher DOS (density of states) part of the valence band (h-DOS(VB)) of the higher h-DOS(VB) sample to all ETs

at an anatase-rutile interface proved by energy-resolved distribution of electron traps (ERDT) measured by reversed double-beam photoacoustic spectroscopy (RDB-PAS). Mixture samples of anatase and rutile prepared by different mixing methods were characterized by RDB-PAS and found that their ERDT patterns were completely different. The ERDT pattern of mix-H which prepared by braying in an agate mortar for 10 min has a shift to lower energy side compared to the simple summation of ST-21 and ST-G1 which was completely different from the mix-0 which was just put two original samples half to half on the sample holder. The degree of coincidence of ERDT-pattern shape (ζ_s ; 0–1) was evaluated. It is clear that mix-0 resembled the simulation pattern with maximum energy-shift ($\Delta E_{\max}$) = 0 (ζ_s = 0.8) indicating that excitation of VB electrons in each crystallite particle occurs independently as expected. On the other hand, mix-H showed an obviously different, shifted to lower energy side compare to mix-0. Among simulated ERDT patterns calculated with varied $\Delta E_{\max}$ with 0.01-eV step, SIM(0.19) gave the maximum ζ_s , 0.7, with mix-H. This is the first experimental evidence of interparticle spatial overlapping of orbitals to result in interparticle charge-transfer excitation (ICTE), i.e., photoexcitation from the h-DOS(VB) of the higher h-DOS(VB) sample to all ETs at an anatase-rutile interface. The detailed energy-resolved distribution of electron traps (ERDT) analyses of various anatase-rutile mixtures revealed that all of the photoexcitation occurred from h-DOS in valence band of rutile in thoroughly mixed sample and h-DOS of rutile was located ca. 0.19 eV higher than that of anatase. This is the first experimental results of practical h-DOS energy, which is related to practical photoabsorption of materials. Furthermore, the ICTE analysis suggested a new concept, mixing homogeneity, which can be quantitatively evaluated by comparison of ERDT patterns of mixture sample to simulated patterns with thoroughly adjoined mixture particles and non-contacted particles.

In Chapter 3, different kinds of titania mixtures were examined by ERDT analyses described in Chapter 2 and it was found that the maximum energy-shift ($\Delta E_{\max}$) values for most of the mixtures with rutile and anatase prepared by mix-H (thorough mixing by braying in an agate mortar for 10 min) were 0.18–0.19 eV. The $\Delta E_{\max}$ dependence on anatase content in the mixtures prepared by mix-H was examined and it was found that $\Delta E_{\max}$ values of ST-21 and ST-G1 were constant until the anatase ratio of 0.6 and then decreased with increase in the rutile content, i.e., with lower anatase content, almost all of the anatase ST-21 particles were in sufficient contact with rutile ST-G1 particles, while at a higher anatase content, not all of the ST-21 particles had sufficient contact with ST-G1 particles, resulting in the decrease in observed $\Delta E_{\max}$. In addition, the constant $\Delta E_{\max}$, ca. 0.2 eV, might correspond to the actual energy difference between h-DOS(VB) of anatase and that of rutile. The results suggest that ERDT analysis enables evaluation of the actual apparent difference of h-DOS (VB) energy in mixture samples with different h-DOS(VB)s and these are the first experimental measurements of practical h-DOS, which enable to cause photoabsorption, of materials. This suggests that the h-DOS(VB) of most anatase were lower than that of most rutile by ca. 0.20 eV and that photoexcitation from h-DOS(VB) of rutile samples to ETs of anatase samples might occur in the mixture samples. Meanwhile, the ionization energy of samples was estimated from

photoelectron yield spectroscopy and has been regarded as VBT position and the bandgap can be estimated by PAS spectra. Thus, these results can be used to estimate the relative band structure of metal-oxide samples.

Anatase and rutile particles isolated from a typical commercial titania, Evonik P25, by a chemical dissolution method were characterized by RDB-PAS to estimate their band structure; the h-DOS(VB) of isolated-rutile (RUT) was same as those of most of commercial rutile samples. However, the isolated-anatase (ANA) showed an h-DOS(VB) position that was ca. 0.12 eV higher than most of commercial anatase titania samples presumably because the surface of anatase particles in P25 may be covered by a thin rutile layer to result in the ERDT pattern of ANA shifted to the low-energy side compared to the other anatase samples. Considering the above results that the isolated-anatase (ANA) and isolated-rutile (RUT) can be seen as the anatase and rutile composition of HomoP25, the surface of anatase composition of HomoP25 may tightly attached with some fine rutile layer.

$\Delta E_{\max}$ values of different kinds of metal-oxide mixtures were also examined and estimated their relative band structure through energy-resolved distribution of electron traps analysis. Thus, RDB-PAS analysis of ERDT patterns of mixtures of different titania samples is a novel method to clarify the relative band position of semiconducting metal oxides such as titania.

In chapter 4, the ERDT pattern of mix-L could be reproduced by second simulation which was a simple summation of 65% SIM(0) and 35% SIM(0.19) with ζ_s of 0.80. Thus, the interesting ERDT pattern of mix-L might be due to the presence of two kinds of ST-21 (anatase) particles, with and without electronic contact (orbital overlapping) with ST-G1 (rutile) particles, in 35% and 65% composition. In other words, ERDT analysis provides quantitative measurement of "hetero-contact degree" (how much proportion of one kind of particles (anatase in this study) are electronically contacted with the other kind of particles), which is a new concept and has not been measured so far, because such quantitative measurement requires macroscopic analysis collecting the information on particle contact; XRD is one of the representative macroscopic powder analyses, but no information on anatase-rutile particle contact, and SEM and TEM might give information on anatase-rutile particle contact, but they are microscopic and no average cannot be obtained. The mix-L can be reproduced by second simulation with 35% hetero-contact degree. On the other hand, mix-H also can be reproduced by second simulation with 80% hetero-contact degree and shown a 0.81 ζ_s , which is higher than the 0.70 ζ_s in chapter 2. This suggest the hetero-contact degree of mix-H is 80% and for the samples hetero-contact degree lower than 100%, second simulation results are more suitable and shows higher reproducibility. The gas phase photocatalytic reaction performance of mixtures of anatase and rutile with different mixing homogeneity shown that the lowest activity of mix-H which as a sample with the highest hetero-contact degree for carbon-dioxide liberation may suggest that good contact of ST-21 and ST-G1 reduces the reaction efficiency. The possible reason might be in the sample of homogeneously mixing with thoroughly adjoined mixture particles, a considerable part of ST-21 particles is evenly dispersed in the pores of ST-G1 and cannot absorb photons (particle size

of ST-21 is smaller than ST-G1). Since ST-21 shown much higher activity than ST-G1, these ST-21 particles, which cannot absorb photons, caused the photocatalytic activity of the mixture to decrease. This suggests that the particle mixing-homogeneity degree may affects the photocatalytic activities.

In conclusion, I obtained experimental evidence of interparticle spatial overlapping of orbitals to result in interparticle charge-transfer excitation (ICTE) at an anatase-rutile interface through ERDT measured by RDB-PAS. The detailed ERDT analyses of various anatase-rutile mixtures revealed that all of the photoexcitation occurred from h-DOS in valence band of rutile in thoroughly mixed sample and h-DOS of rutile was located ca. 0.2 eV higher than that of anatase. ERDT analysis using RDB-PAS is expected to be a novel method to clarify the relative band position of semiconducting metal oxides such as titania. In addition, the ERDT analysis suggested a novel concept, mixing degree which means "hetero-contact degree" in this study, could be quantitatively evaluated.