Identification and detailed characterization of titania photocatalyst powders with their energy-resolved distribution of electron traps

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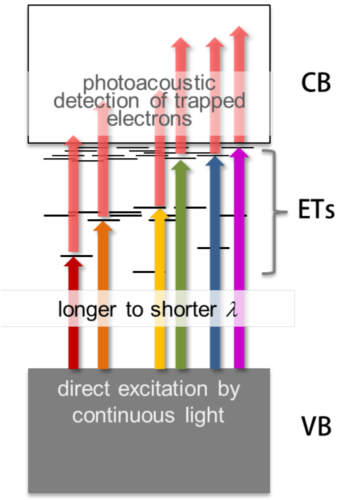
Abstract: Here we report identification of titania powders with their energy-resolved distribution of electron traps (ERDT) measured by reversed double-beam photoacoustic spectroscopy. The ERDT patterns combined with conduction-band bottom (CBB) position data for various titania powders were different depending on the kind of sample. The degree of coincidence (ζ) of ERDT/CBB patterns was evaluated for a given pair of samples as a product of each degree of coincidence for ERDT-pattern matching, total density of electron traps and CBB position. It was shown that the higher the values of ζ was, the higher was the degree of coincidence for photocatalytic activities.

Keywords: Fingerprint, Electron traps, Degree of coincidence.

1. Introduction

Although molecules and metal complexes are practically identified by determining their molecular structure, metal-oxide powders cannot be identified by bulk composition and crystalline structure. Such a difference between molecules and powders is attributable to existence of both surface and bulk of solid materials. What has been conventionally evaluated as structural properties of metal-oxide powders is crystal phase, primary particle diameter, secondary particle diameter and specific surface area (SSA), but those properties reflect only bulk composition or size of bulk/surface. In other words, a lack of sufficient analytical method that enables measurement of a property reflecting surface structure has prevented characterization and thereby identification of metal-oxide powders. In this study, we focus on energy-resolved density of electron traps (ERDT) located mainly on the surface of metal-oxide powders, and evaluate ERDT by newly developed reversed double-beam photoacoustic spectroscopy (RDB-PAS), in which photoabsorption of trapped electrons directly excited from valence band to electron traps by scanned continuous light is measured by photoacoustic spectroscopy (PAS) as shown in **Scheme 1**. The obtained ERDT patterns with conduction bottom position (CBB) were compared with each other to evaluate degree of coincidence for a given pair of samples for identification of titania powder samples and detailed discussion on the similarity of photocatalytic activities.



Scheme 1 Schematic presentation of RDB-PAS. Valence-band (VB) electrons are directly excited to vacant electron traps (ETs) by wavelength-scanned continuous light to be accumulated in ETs from the deeper to shallower sides. The amount of accumulated electrons is deter-mined by in-situ photoacoustic spectroscopy (PAS) by modulated monochromatic light.[4]

2. Experimental

The procedure for measurement of ERDT/CBB patterns was reported previously.[1,2] A brief description follows. A stainless-steel sample holder was filled with a titania powder sample and set in a home-made PAS cell equipped with an electret condenser microphone and a Pyrex window on the upper side. For RDB-PAS measurements, the PAS cell was filled with methanol-saturated argon, and two light beams were introduced simultaneously using a UV quartz combiner light guide. One was a 625-nm light beam from an LED modulated by a digital function generator at 80 Hz, and the other was continuous monochromatic light from a monochromator with a wavelength scanning from 650 nm to 350 nm with 5-nm steps. The raw spectrum obtained was differentiated from the lower-energy side and calibrated with the reported total electron-trap density in units of μmol g^{-1} measured by a photochemical method[3] to obtain an ERDT pattern.

3. Results and discussion

Representative ERDT patterns of titania powders are shown in **Fig. 1**. Conduction-band bottom (CBB) depending on the crystalline phase and total density of electron traps increasing with increase in SSA indicate that CBB and total density of electron traps can reflect bulk composition and bulk size, respectively. On the other hand, ERDT patterns of TIO-1 and TIO-13 with similar seem to be clearly different. This result indicates that ERDT can reflect surface-structural property. By calculating degree of coincidence ζ, multiplied by each degree of coincidence for ERDT pattern matching, total density of electron traps (shown in <> in units of μmol g^{-1}) and CBB position, some given pairs of two samples which are made by the same manufacturing method show higher ζ values than those of other pairs. Thus, it is suggested that an ERDT/CBB pattern can be a fingerprint for metal-oxide powders.[4]

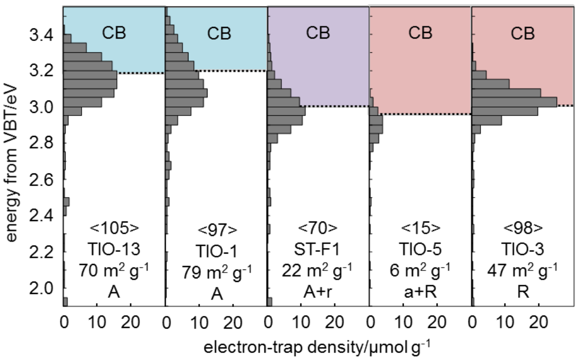


Figure 1 Representative ERDT/CBB patterns of commercially available titania powders. Figures in <> denote total density of ETs in units of μmol g^{-1}. Specific surface area in units of m^2 g^{-1} is shown in the third row. Abbreviations "A" and "R" in the bottom row are anatase and rutile, respectively, and "a" and "r" are anatase and rutile in minor composition, respectively.[1,2]

Three representative photocatalytic reactions, (a) hydrogen (H_2) evolution from deaerated aqueous methanol (H_2 system), (b) carbon-dioxide (CO_2) evolution from aqueous acetic acid under aerobic conditions (CO_2 system) and (c) oxygen (O_2) evolution from aqueous silver fluoride (O_2 system), were carried out, and the ratios of evaluated photocatalytic activities for pairs of titania samples ($0 < \zeta_{pc} < 1$) were compared with ζ as shown in **Fig. 2**. It is clearly seen that the higher the value of ζ at > 0.6 is, the higher becomes ζ_{pc}, i.e., the ERDT/CBB patterns reflect bulk/surface structures which govern photocatalytic activities of titania samples.

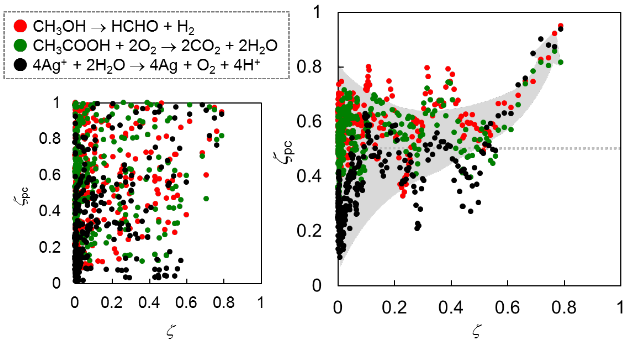


Figure 2 (left) Degrees of coincidence (ratio of rates; see text) for photocatalytic activities (ζ_{pc}), for three representative photocatalytic reactions, hydrogen liberation from deaerated aqueous methanol, carbon-dioxide liberation from aqueous acetic acid under aerobic conditions and oxygen evolution from deaerated aqueous silver fluoride, of pairs of titania samples plotted against corresponding ζ and (right) replotting of those data with non-weighted seven-point moving average.[1]

4. Conclusions

A novel method for measuring ERDT patterns of metal-oxide powders, reversed double-beam photoacoustic spectroscopy has been developed and successfully applied to titania photocatalyst powders for their identification and detailed characterization.

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