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A fingerprint of metal-oxide powders: energy-resolved distribution of electron traps†

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Here we propose a method for the identification of metal-oxide powders with the energy-resolved distribution of electron traps and conduction-band bottom position reflecting a surface structure and a bulk structure, respectively, as a fingerprint, based on the degree of coincidence for a given pair of samples, measured using newly developed reversed double-beam photoacoustic spectroscopy.

Who can identify a powder, *e.g.*, in an unlabeled bottle found in a laboratory? How can fluctuation in the quality of powder prepared using a routine procedure be evaluated? In the field of organic chemistry, practical identification is performed by showing a reasonable fit of elemental composition and the NMR pattern with theoretical/authentic ones, but there has been no concept of the identification for powder samples because powders should be evaluated by both bulk and surface properties. Although the former may be characterized *via* their X-ray diffraction (XRD) patterns in general, there are no comprehensive parameters reflecting the latter; the specific surface area (or particle size) has no information on the surface properties. Here we report energy-resolved distribution of electron traps (ERDT), which are located predominantly on the surface, measured for titania and several other metal-oxide powders. We propose that ERDT data coupled with bandgap data can be a fingerprint for the practical identification of metal-oxide powders. The technique for ERDT measurements, reversed double-beam photoacoustic spectroscopy, is expected to be a standard characterization method for metal-oxide powders like NMR or IR for molecules.

It is well known that metal oxides, such as titanium(IV) oxide (titania) and tungsten(VI) oxide, turn grey, blue or black, depending on the kind of metal oxide, when reduced by, for example, heating in a hydrogen atmosphere or photoirradiation in the presence of strong electron donors. For titania, the blue or grey color is attributed to the formation of the trivalent titanium species (Ti^{3+})[1] accompanied by the insertion of a cation such as a proton. In other words, appreciable vacant electronic states, *i.e.*, electron traps (ETs), are present in metal-oxide particles. While the total density of such ETs can be determined by counting the number of electrons captured in those traps, estimation of the energy distribution of those ETs has rarely been performed. To the best of the authors' knowledge, metal-oxide ERDT[2] of samples in their powder forms[3,4] has been estimated for only two titania samples by a photochemical method using methyl viologen as the indicator.[5] The problem is its low energy resolution and narrow energy range; *i.e.*, only shallow ETs can be detected.

Here, newly developed reversed double-beam photoacoustic spectroscopy (RDB-PAS) is reported for the first time as a powerful tool for ERDT measurements. RDB-PAS covers a sufficient energy range of ETs with higher resolution than that of the photochemical method. As a brief explanation of the principle of RDB-PAS (for details, see the ESI†), the procedure involves (i) accumulating electrons in ETs from the lower-energy (more anodic) side to the higher-energy side under irradiation of scanned (from longer wavelengths to shorter wavelengths) continuous light for excitation of valence-band (VB) electrons directly to ETs, (ii) detecting a photoacoustic (PA) signal of the accumulated electrons by modulated LED light (625 nm) [during (i)], (iii) differentiating the resultant spectra from lower energy side to higher energy side, (iv) converting the signal intensity to absolute density of ETs with reference to results obtained using the photochemical method, (v) plotting an ERDT pattern as a function of energy difference from the top of the VB (VBT) and (vi) comparing with the energy of the CB bottom (CBB), in reference to the VBT, which is estimated by

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† Electronic supplementary information (ESI) available: Descriptions of reversed double-beam photoacoustic spectroscopy (RDB-PAS), correlation between total electron-trap density and specific surface area, ERDT/CBB patterns of metal-oxide powders other than titania, ranking of the high degree of coincidence ζ, and the photocatalytic activity test. See DOI: 10.1039/c6cc04999k

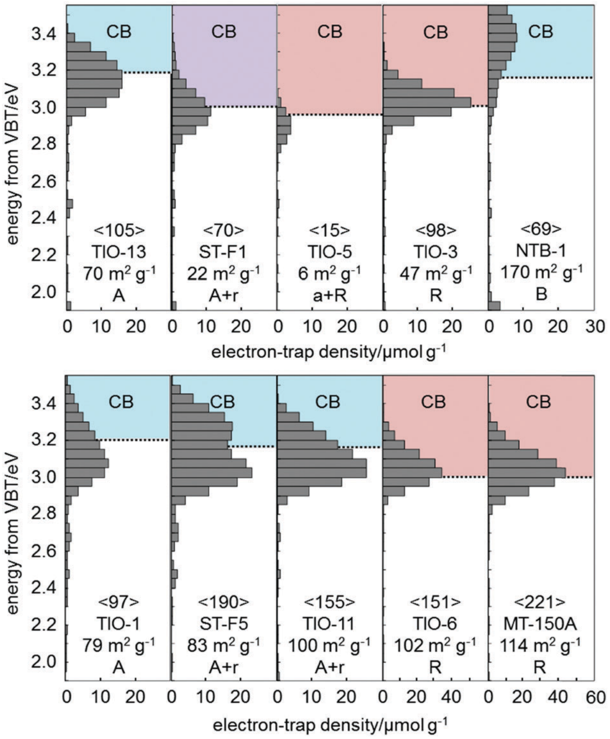

Fig. 1 Representative ERDT patterns with CBB positions for commercially available (Showa Denko Ceramics ST-F1, NTB-1 and ST-F5, Tayca MT-150A) and non-profitably provided (TIO series samples from Catalysis Society of Japan) samples. Figures in ⟨⟩ denote the total density of ETs in the unit of μmol g^{-1}. Specific surface area in the unit of m^2 g^{-1} is shown in the third row. Abbreviations "A", "R" and "B" in the bottom row are anatase, rutile and brookite, respectively, and "a" and "r" are anatase and rutile in minor composition, respectively.

conventional PA spectra (corresponding to photoabsorption spectra).[6] As a result, both ERDT and CBB are plotted as a function of energy difference from the VBT.

ERDTs of several representative titania powders composed of anatase, rutile and brookite crystallites are shown in Fig. 1 (upper). ETs are distributed predominantly at the energy around each CBB, though it is expected that ETs are located within the bandgap, *i.e.*, lower (more anodic) than CBB. There are at least two possible explanations for the unexpected position of ERDTs. One is the shift of ERDT that is shown as a function of the energy gap from the VBT due to possible lower/negligible density of states (DOS) at the VBT. The photoabsorption coefficient for the transition of electrons in the VB to ETs is not entirely zero, but very small. (Practically no absorption is therefore observed in an ordinary photoabsorption spectrum.) Excitation of electrons to ETs may occur preferentially from high-density states in the VB that are appreciably lower than the VBT. ERDT is, thereby, shifted upward by the difference in energy between the high-density states and the VBT. Although the energy resolution in the photochemical method is poor,[5] a slight upward (cathodic) shift of ERDT by RDB-PAS for both anatase and rutile samples was observed as shown in Fig. 2. (Details will be interpreted later.) This is consistent with the above-mentioned possible upward shifts of ERDT with reference to the VBT in Fig. 1. Analysis of VB energy by photoelectron spectroscopy is now in progress. The other explanation is that most ETs are located on the surface of particles (as described below; see Fig. S3, ESI†), and those surface ETs may have a structure different from that of bulk ETs. Therefore the energy of ETs can be located above CBB not limited to be in the bandgap.[7] On the other hand, CBB estimated by ordinary single-beam PAS measurements (shown as dotted lines in Fig. 1) seems to depend on the crystal structure of samples, *i.e.*, their bandgap energy: *ca.* 3.2 eV for pure anatase and brookite and 3.0 eV for rutile. In other words, the CBB data can reflect the bulk structure, but not the surface structure.

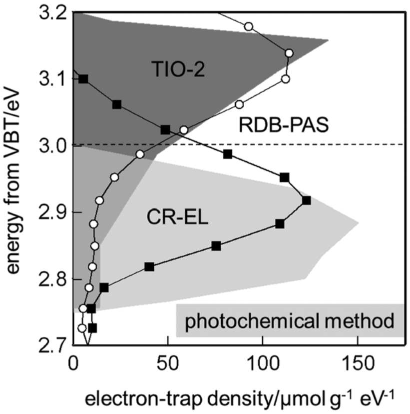

Fig. 2 Comparison of ERDT patterns measured using the photochemical method (grey patterns; ref. 5) and RDB-PAS (plots; this work) for representative anatase (Catalysis Society of Japan Reference titania TIO-2; 18 m^2 g^{-1}) and rutile (Ishihara Sangyo CR-EL; 7 m^2 g^{-1}) samples. The top line at 3.2 eV and the dashed line show the CBB positions of anatase and rutile estimated by the reported bandgaps 3.2 and 3.0 eV (ref. 9), respectively.

Fig. 2 shows a comparison of ERDTs measured using the photochemical method and RDB-PAS for anatase and rutile samples.[8] In the photochemical method, the energy scale of ERDT was measured with reference to the standard electrode potential for methyl viologen/methyl viologen cation radical and plotted as a function of energy difference from the reported VBT positions of anatase and rutile.[9] Fig. 2 also shows that the ERDT patterns (profiles) measured using the two techniques are similar for both anatase and rutile samples.

An almost linear plot of total density of ETs in titania samples used in this study as a function of a specific surface area (SSA) (Fig. S3, ESI†) suggests that titania ETs are predominantly located on the surface (estimated density of bulk ETs: *ca.* 14 μmol g^{-1}, ESI†) and that total electron-trap density reflects the surface area (or particle size) of samples.[10] However, as is shown in Fig. 1 (lower) as examples of titania samples with SSA in the range of 79–114 m^2 g^{-1}, ERDTs of these similar SSA (particle size) samples are clearly different from each other. Also, ERDTs of anatase TIO-13 and TIO-1 with almost the same SSA and total electron-trap density were different. Thus, ERDT may reflect surface electronic properties independently of specific surface area (or bulk size). In this sense, ERDT is possibly a sole, within the authors' knowledge, a comprehensive macroscopic parameter reflecting particle-surface structure among the surface-related parameters reported so far.

In order to compare the ERDT/CBB patterns of titania samples for powder identification, the reproducibility of ERDT/CBB measurements was first examined using an anatase titania sample (Showa Denko Ceramics FP-6), in convenience, by evaluating degrees of coincidence (ζ) in (a) ERDT-pattern shape, (b) total electron-trap density and (c) CBB position; ζ(a) is evaluated for two ERDT spectra f_s (ERDT-pattern profiles as a function of energy from VBT; integrated f is equal to the total density of ETs, D), $f(1)$ and $f(2)$ ($D(1) < D(2)$), as

$$\zeta(\mathrm{a}) = 1 - \int |f(1) - \alpha f(2)| \Big/ \int f(1)$$

with α to minimize

$$\int (f(1) - \alpha f(2))^2,$$

ζ(b) is evaluated as the ratio of D, as $D(1)/D(2)$ ($D(1) \leq D(2)$), and ζ(c) is evaluated as the ratio of CBB, as CBB(1)/CBB(2) for (CBB(1) < CBB(2)). The overall degree of coincidence is calculated, for quantitative comparison of coincidence of ERDT/CBB patterns, as a weighted[11] product of ζ(a), ζ(b) and ζ(c): $\zeta = \zeta(\mathrm{a})^i \times \zeta(\mathrm{b})^j \times \zeta(\mathrm{c})^k$, where i, j and k are weighting coefficients. The value of ζ calculated with $i = 1$, $j = 1/2$ (lightly weighted) and $k = 2$ (heavily weighted) seemed sufficiently high for three independent measurements with powder samples taken from close positions in a bottle to give $\zeta > 0.88$ on average. Although it could be claimed that it is naturally expected to obtain high ζ for the same samples, what we are describing in this communication is defining the term "identical/similar/different" for particulate metal-oxide samples.

Thus, ζ reflecting the bulk structure by ζ(c) and the surface structure/properties by ζ(a) and ζ(b) can provide information on the "identicalness" or the "similarity" without arbitrariness.

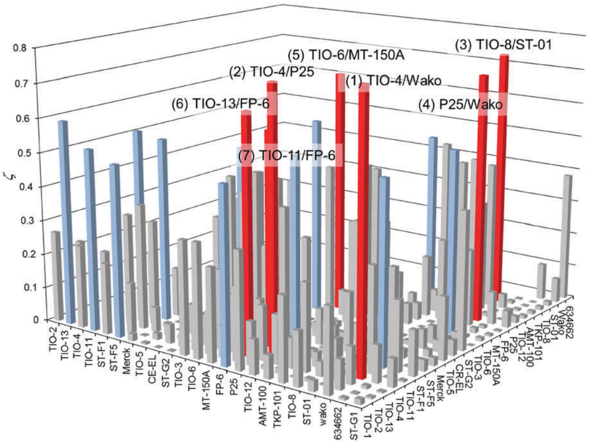

Fig. 3 Summary of the degrees of coincidence (ζ) among commercially available titania powders. Colours of columns denote the ranges of ζ: red: ≥ 0.6, blue-grey ≥ 0.5 and grey < 0.5. Figures in parentheses are ranking up to 7 ($\zeta > 0.6$).

Fig. 3 summarizes the values of ζ among commercially available and non-profitably provided (by Catalysis Society of Japan (CSJ) as reference catalysts) titania powders.[12] Although most of the sample pairs show relatively low ζ (<0.5), there are several stand-outs with high ζ suggesting the similarities of the bulk/surface properties of samples. The top ranking pairs with higher ζ are listed in Table S2 (ESI†). For the combination of P25 (Evonik/Nippon Aerosil)/TIO-4 (CSJ) and FP-6/TIO-11 (CSJ), higher ζ (0.760 and 0.615, respectively) is expected or even matter-of-course because TIO-4 and TIO-11 are known to be P25 and FP-6 provided to CSJ as reference titanias by Nippon Aerosil and Showa Denko Ceramics, respectively. However, it should be noted that the actual ζ values for these two combinations were appreciably lower than those of the above-mentioned reproducibility tests using FP-6 in a bottle (>0.88). This suggests that even if titania powders have been manufactured using the same regulated/fixed procedure with the same code name and even if titania powders in different packages have been produced in the same batch, there is some difference in their bulk/surface properties, *i.e.*, they may be heterogeneous in composition.[13] Of course, this might have been expected, but this is the first report, to the best of the authors' knowledge, showing experimental evidence for such heterogeneity of powder samples. Although the reason for the high ζ for other combinations in Table S2 (ESI†) is unknown at present, they must be similar in surface/bulk properties even if they were manufactured in different batches, processes and/or factories. Thus, the degree of coincidence ζ is definitely a potential index that enables the identification of electron trap-bearing particulate semiconductor materials. Our preliminary experiments revealed that six kinds of metal oxides, *e.g.*, tungsten oxide and tin oxide, exhibited characteristic ERDT/CBB patterns (Fig. S4, ESI†).

Further results using ζ described below also indicate the significance of ERDTs for the performance of titania as a photocatalyst. The degrees of coincidence for photocatalytic activities ($\zeta_{\mathrm{pc}} = A_1/A_2$, $A_1 \leq A_2$), of a given pair of titania samples with activities A_1 and A_2, for three representative photocatalytic reactions (ESI†), hydrogen liberation from deaerated aqueous methanol, carbon-dioxide liberation from aqueous acetic acid under aerobic conditions and oxygen evolution from deaerated aqueous silver fluoride, are plotted against the corresponding ζ in Fig. 4 (left). Although the plots are highly scattered,[14] ζ_{pc} seems to be larger than 0.5 at the higher ζ region >0.7.[15] Replotting of those data with a seven-point moving average[16] (not weighted; Fig. 4 (right)) revealed an almost linear correlation between ζ and ζ_{pc} at $\zeta > 0.6$; the higher ζ is, the higher is ζ_{pc}, and ζ_{pc} is expected to be almost unity at $\zeta \geq 0.8$. This suggests that the similarity in ERDT and CBB induces similar photocatalytic activities in these three independent photocatalytic activity systems, *i.e.*, activity of a titania photocatalyst is predominantly governed by ERDT and CBB or photocatalytic reaction rates are expressed by the functions of ERDT and CBB.[17] In other words, the activity of a given photocatalyst is predictable by checking ζ, and two titania samples of $\zeta > 0.8$ are "photocatalytically" identical. An understanding what kind of ERDT/CBB pattern is observed for photocatalyst samples with high activity is another significant target of research through ERDT/CBB analysis, and study along this line and study on the analysis of absolute positions of ETs, not with reference to VBT, are now underway.

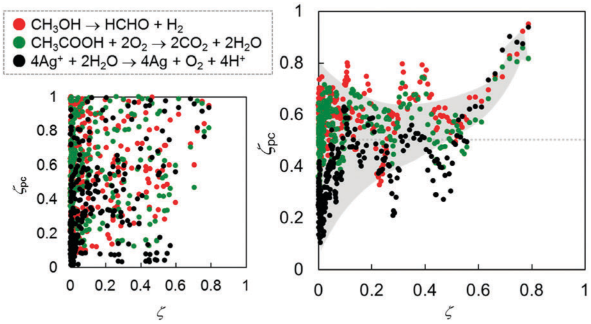

Fig. 4 (left) Degrees of coincidence (ratio of rates; see the text) for photocatalytic activities (ζ_{pc}), for three representative photocatalytic reactions, hydrogen liberation from deaerated aqueous methanol, carbon-dioxide liberation from aqueous acetic acid under aerobic conditions and oxygen evolution from deaerated aqueous silver fluoride, of pairs of titania samples plotted against the corresponding ζ and (right) replotting of those data with non-weighted seven-point moving average.

In conclusion, ERDT analysis solely and exclusively makes it possible to provide data on the degree of coincidence for the identification of particulate metal-oxide samples even for two samples taken from a bottle of a uniquely coded metal-oxide sample. Thus, identicalness or differentness of samples can be quantitatively determined without arbitrariness, due to the fact that ERDT data can be reflected by the surface properties of particles, which are not represented by the specific surface area or the particle size. The measured degree of coincidence, ζ, can predict the performance, *e.g.*, photocatalytic activity, of titania samples; a pair of titania powders with high ζ exhibits almost the same photocatalytic activities, *i.e.*, high ζ_{pc}. This suggests that ζ-controlling properties such as ERDT govern the photocatalytic activity of titania samples. Thus, ERDT analysis provides a novel significant concept, degree of coincidence, for the exact characterization of particulate metal-oxide materials.

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Notes and references

1 For example, a paper showing ETs in colloidal titania particles: R. F. Howe and M. Grätzel, *J. Phys. Chem.*, 1985, **89**, 4495–4499.
2 Deep level transient spectroscopy (DLTS) may be used for such ERDT analysis, though there seems to have been no report on the measurements of particulate photocatalyst samples by DLTS (For an epitaxially grown thin film of anatase titania: T. Miyagi, T. Ogawa, M. Kamei, Y. Wada, T. MitsuhashiI, A. Yamazaki, E. Ohta and T. Sato, *Jpn. J. Appl. Phys.*, 2001, **40**, L404–L406). A problem is that DLTS can be used only for deep ETs as the number indicates.
3 A recent paper on electrodes prepared from a few titania powders reported the ERDT by electrode potential-dependent diffuse reflectance: M. Buchalska, M. Kobielusz, A. Matuszek, M. Pacia, S. Wojtyła and W. Macyk, *ACS Catal.*, 2015, **5**, 7424–7431. To avoid the effect of change in properties during the electrode-preparation process, we attempted to measure in a powder form.
4 Diffuse-reflectance infrared spectroscopic measurements of the total (surface) electron-trap density in a compressed powder were reported for a few titania samples: Y. Shiraishi, H. Hirakawa, Y. Togawa, Y. Sugano, S. Ichikawa and T. Hirai, *ACS Catal.*, 2013, **3**, 2318–2326.
5 S. Ikeda, N. Sugiyama, S.-Y. Murakami, H. Kominami, Y. Kera, H. Noguchi, K. Uosaki, T. Torimoto and B. Ohtani, *Phys. Chem. Chem. Phys.*, 2003, **5**, 778–783. Energy resolution of this method depends on the accuracy of pH control of the suspension to induce transfer of trapped electron to methyl viologen to be *ca.* 60 meV.
6 N. Murakami, O.-O. Prieto-Mahaney, T. Torimoto and B. Ohtani, *Chem. Phys. Lett.*, 2006, **426**, 204–208; N. Murakami, O.-O. Prieto-Mahaney, R. Abe, T. Torimoto and B. Ohtani, *J. Phys. Chem. C*, 2007, **111**, 11927–11935.
7 Within the authors' knowledge, there have been no reports showing ERDTs of particulate samples bearing surface ETs with relatively high energy resolution, and thus the present results could not be compared.
8 Theoretically speaking, the Fermi level of n-type semiconductors is located just below CBB and electronic states below the Fermi level are filled with electrons, *i.e.*, these electron-filled states cannot be ETs. However, a recent paper on a polycrystalline anatase thin film has suggested that its Fermi level is located *ca.* 1.4 eV below the CBB, consistent with our present results; M. Zhu, Y. Mi, G. Zhu, D. Li, Y. Wang and Y. Weng, *J. Phys. Chem. C*, 2013, **117**, 18863–18869.
9 L. Kavan, M. Grätzel, S. E. Gilbert, C. Klemenz and H. J. Scheel, *J. Am. Chem. Soc.*, 1996, **118**, 6716–6723.
10 A similar suggestion has been reported for colloidal titania: U. Kölle, J. Moser and M. Grätzel, *Inorg. Chem.*, 1985, **24**, 2253–2258.
11 The weighting coefficients i, j and k were chosen from 1, 1/2, or 2 for convenience in this study to compensate the difference in experimental error at least partly. In our studies of PAS measurements, it has been revealed that the absolute intensity of the PA signal depends strongly on the conditions of the samples, *e.g.*, a surface flatness or packing density of a packed sample. The total density of ETs (D) may have a relatively large error due to fluctuations of PAS-signal intensity. Actually, the standard deviation (SD) of ζ(b) for the FP-6 samples taken from close positions in a bottle was largest (0.0185 among the SDs of ζ(a), ζ(b), and ζ(c)) and thereby the coefficient j for ζ(b) was light-weighted to be 1/2. On the other hand, measurements of the bandgap by ordinary PAS require only relative intensity of the PA signal (SD = 0.0001, the lowest among ζ_s), and thereby the coefficient k for ζ(c) was heavy-weighted to be 2.
12 Structural and physical properties and photocatalytic activities in representative photocatalytic reaction systems have been reported: B. Ohtani, O.-O. Prieto-Mahaney, F. Amano, N. Murakami and R. Abe, *J. Adv. Oxid. Technol.*, 2010, **13**, 247–261.
13 The heterogeneity in crystal composition, *i.e.*, a property of bulk measured using XRD, of Evonik P25 has been reported: B. Ohtani, O.-O. Prieto-Mahaney, D. Li and R. Abe, *J. Photochem. Photobiol., A*, 2010, **216**, 179–182. Correlation between ERDT patterns and crystalline composition, as one of the possible reasons of fluctuation to lower ζ, is now under investigation.
14 Different kinds of photocatalyst samples may, of course, exhibit different activities to give highly scattered plots at the lower ζ.
15 Reproducibility of photocatalytic activity tests using titania powder samples taken from close positions in a bottle was *ca.* 95%, *i.e.*, *ca.* 5% error, and thereby $\zeta_{pc} > 0.95$ at $\zeta > 0.8$ is expected in Fig. 4.
16 Moving average is a method for smoothing scattered data. For example of seven-point (not weighted) moving average, an average datum of the ith point (ave_i) is calculated to be an average of seven data from d_{i-3} to d_{i+3}, *i.e.*, $ave_i = (d_{i-3} + d_{i-2} + d_{i-1} + d_i + d_{i+1} + d_{i+2} + d_{i+3})/7$.
17 This means that the functions for photocatalytic-reaction kinetics include ERDT and CBB as independent variables, though the formulas of those functions must be different.