Energy-resolved density of electron traps in metal-oxide particles measured by newly developed reversed double-beam photoacoustic spectroscopy can be used as a fingerprint for identification.
A fingerprint of metal-oxide powders: energy-resolved distribution of electron traps†

Akio Nitta,a Mai Takase,b Mai Takashima,ac Naoya Murakamid and Bunsho Ohtaniac

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 photolrradiation in the presence of strong electron donors. For titania, the blue or grey color is attributed to the formation of the trivalent titanium species ([Ti3+]4) 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 ERDT2 of samples in their powder forms5,4 has been estimated for only two titania samples by a photochemical method using methyl viologen as the indicator.6 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
shifts of ERDT with reference to the VBT in Fig. 1. Analysis of this is consistent with the above-mentioned possible upward observed as shown in Fig. 2. (Details will be interpreted later.)

of ERDT by RDB-PAS for both anatase and rutile samples was 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 m² 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). 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 CB, though it is expected that ETs are located within the bandgap, i.e., lower (more anodic) than CB. 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, 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 shows a comparison of ERDTs measured using the photochemical method and RDB-PAS for anatase and rutile samples. 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. 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. However, as is shown in Fig. 1 (lower) as examples of titania samples with SSA in the range of 79–114 m² 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.

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. 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 CB, though it is expected that ETs are located within the bandgap, i.e., lower (more anodic) than CB. 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, 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. 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.

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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 ($\zeta$) in (a) ERDT-pattern shape, (b) total electron-trap density and (c) CBB position; $\zeta(a)$ is evaluated for two ERDT spectra $f_i$ (ERDT-pattern profiles as a function of energy from VBT; integrated $f$ is equal to the total density of ETs, $D_i$), $f(1)$ and $f(2)$ ($D(1) < D(2)$), as

$$\zeta(a) = 1 - \frac{\|f(1) - zf(2)\|}{\|f(1)\|^2},$$

with $z$ to minimize

$$\left\{ (f(1) - zf(2)) \right\}^2.$$

$\zeta(b)$ is evaluated as the ratio of $D$, as $D(1)/D(2)$ ($D(1) \leq D(2)$), and $\zeta(c)$ 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 product of $\zeta(a)$, $\zeta(b)$ and $\zeta(c)$: $\zeta = \zeta(a)^i \times \zeta(b)^j \times \zeta(c)^k$, where $i$, $j$ and $k$ are weighting coefficients. The value of $\zeta$ 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 $\zeta$ for the same samples, what we are describing in this communication is defining the term “identical/similar/different” for particulate metal-oxide samples.

Thus, $\zeta$ reflecting the bulk structure by $\zeta(c)$ and the surface structure/properties by $\zeta(a)$ and $\zeta(b)$ can provide information on the “identicalness” or the “similarity” without arbitrariness.

Fig. 3 summarizes the values of $\zeta$ among commercially available and non-profitably provided (by Catalysis Society of Japan (CSJ)) titania powders. Although most of the sample pairs show relatively low $\zeta$ ($< 0.5$), there are several stand-outs with high $\zeta$ suggesting the similarities of the bulk/surface properties of samples. The top ranking pairs with higher $\zeta$ are listed in Table S2 (ESI†). For the combination of P25 (Evonik/Nippon Aerosil)/TIO-4 (CSJ) and FP-6/TIO-11 (CSJ), higher $\zeta$ (0.760 and 0.615, respectively) is expected or even matter-of-course because TIO-4 and TIO-11 are known to be P25 (Evonik/Nippon Aerosil)/TIO-4 (CSJ) and FP-6/TIO-11 (CSJ), higher $\zeta$ 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. In other words, the activity of a given photocatalyst is predictable by checking $\zeta$, 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.
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, $\zeta$, can predict the performance, e.g., photocatalytic activity, of titanita samples; a pair of titania powders with high $\zeta$ exhibits almost the same photocatalytic activities, i.e., high $\zeta_{pc}$. This suggests that $\zeta$-controlling properties such as ERDT govern the photocatalytic activity of titanita 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


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. Mushashii, 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 name indicates.

3 A recent paper on electrodes prepared from a few titanita powders reported the ERDT by electrode potential-dependent diffuse reflectance: M. Buchalska, M. Kobielszuz, A. Matuszek, M. Pucia, S. Wojtyla 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 titanita samples: Y. Shirashihi, H. Hirakawa, Y. Togawa, Y. Sugano, S. Ichikawa and T. Hirai, ACS Catal., 2013, 3, 2318–2326.

5 S. Beda, N. Sugiyama, S.-Y. Murakami, H. Kominnami, 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.


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, 18963–18969.


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 $\zeta(b)$ for the FF-6 samples taken from close positions in a bottle was largest (0.0185 among the SDs of $\zeta(a)$, $\zeta(b)$, and $\zeta(c)$) and thereby the coefficient $j$ for $\zeta(b)$ 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 $\zeta_h$), and thereby the coefficient $k$ for $\zeta(c)$ was heavy-weighted to be 2.


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 crystal-line composition, as one of the possible reasons of fluctuation to lower $\zeta$, is now under investigation.

14 Different kinds of photocatalyst samples may, of course, exhibit different activities to give highly scattered plots at the lower $\zeta$.

15 Reproducibility of photocatalytic activity tests using titanita powder samples taken from close positions in a bottle was ca. 95%, i.e., ca. 3% 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 $i$th point ($ave_i$) is calculated to be an average of seven data from $d_{i-3}$ to $d_{i+3}$, i.e., $ave_i = \frac{d_{i-3} + d_{i-2} + d_{i-1} + d_i + d_{i+1} + d_{i+2} + d_{i+3}}{7}$. 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.
Supplementary Information

A Fingerprint of Metal-oxide Powders: Energy-resolved Distribution of Electron Traps
Akio Nitta, Mai Takase, Mai Takashima, Naoya Murakami and Bunsho Ohtani

Reversed double-beam photoacoustic spectroscopy (RDB-PAS)

The original setups and procedures for conventional photoacoustic spectroscopy (PAS) and double-beam photoacoustic spectroscopy (DB-PAS) have been reported in detail [(ref. 6) N. Murakami, O.-O. Prieto-Mahaney, R. Abe, T. Torimoto and B. Ohtani, J. Phys. Chem. C, 2007, 111, 11927-11935.]. In PAS and DB-PAS, a modulated (chopped) light beam creating a PA signal is wavelength-scanned to obtain a PA spectrum of samples, and continuous monochromatic or polychromatic continuous light, which does not have any effect on the PA signal, is overlapped in DB-PAS to drive photochemical reactions by the continuous light irradiation with in-situ PA spectrum acquisition. In reversed double-beam photoacoustic spectroscopy (RDB-PAS), modulated and continuous light beams in DB-PAS are exchanged; continuous wavelength-scanning light is illuminated to excite VB electrons to electron traps (ETs), and modulated monochromatic light is simultaneously irradiated to a powder sample to detect photoabsorption of electron-filled ETs, i.e., action spectrum for photoinduced trap filling is recorded (Table S1).

The setup for RDB-PAS was as follows (Fig. S1). A home-made aluminum PAS cell with a quartz window and a microphone (Knowles Electronics SP0103NC3-3 electret condenser microphone) was used [(ref. 6) N. Murakami, O.-O. Prieto-Mahaney, R. Abe, T. Torimoto and B. Ohtani, J. Phys. Chem. C, 2007, 111, 11927-11935.]. A powder sample (15–110 mg) was set in a sample holder in the cell, and ambient-temperature argon flow saturated with methanol vapor was made to flow through the cell for at least 30 min and then the cell was sealed off. The purpose of methanol saturation in the measurement is to capture those positive holes irreversibly and thereby to avoid disappearance of once-trapped electrons through the reaction with positive holes. A monochromatic light beam from a xenon lamp (Spectral Products ASB-XE-175 xenon light source) equipped with a grating monochromator (Spectral Products CM110 1/8m grating monochromator) and an LED beam (Luxeon LXHL-ND98 625-nm light-emitting diode) voltage-

Table S1 Comparison of photoacoustic spectroscopy (PAS), double-beam photoacoustic spectroscopy (DB-PAS) and reversed double-beam photoacoustic spectroscopy (RDB-PAS).

<table>
<thead>
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<th>mode</th>
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<th>continuous light</th>
<th>spectrum</th>
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<tr>
<td>PAS</td>
<td>wavelength scanning</td>
<td>–</td>
<td>photoabsorption</td>
</tr>
<tr>
<td>DB-PAS</td>
<td>wavelength scanning</td>
<td>no scanning</td>
<td>in-situ photoabsorption</td>
</tr>
<tr>
<td>RDB-PAS</td>
<td>no scanning</td>
<td>wavelength scanning</td>
<td>trap-filling action</td>
</tr>
</tbody>
</table>

Figure S1 Schematic representation of the setup for RDB-PAS.
modulated (80 Hz) by a function generator (NF Corporation DF1906 digital function generator) were mixed by a UV quartz combiner light guide (Moritex MWS5-1000S-UV3) and irradiated from the upper side of the sample cell. The PA signal was acquired in lock-in mode (NF Corporation LI5630 digital lock-in amplifier) and averaged at each wavelength of continuous light during scanning from 650 nm to 350 nm with a 5-nm step. In the conventional PAS analysis, PA signal intensity is calibrated with a blank using graphite as a black body to compensate for wavelength-dependent light intensity, but no such calibration is made in RDB-PAS since the signal intensity, corresponding to the total accumulated trapped-electron density, is independent of continuous-light intensity and modulated-light intensity is constant throughout an acquisition. The thus-obtained RDB-PAS spectrum, a plot of total accumulated electron-trap density as a function of photon energy ($E$/eV = 1240/(wavelength/nm)) of continuous light (Fig. S2(a)), was differentiated from the smaller-energy side to obtain ERDT as a function of energy as reference to the VBT (valence-band top) (Fig. S2(b)). The absolute density of ETs was calibrated by comparison with total density of ETs observed by the photochemical method ([ref. 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.) for samples of TIO-2 and CR-EL shown in Fig. 2.

In this study, it is assumed that photoabsorption coefficient of electron-filled ETs is constant not depending on their energy (position) without any supporting results. However, similarity in shape of ERDT patterns obtained using RDB-PAS and the photochemical method in Fig. 2 for two kinds of titania samples suggests the reasonableness of the assumption, since results the photochemical method does not depends on the photoabsorption coefficient of electron-filled ETs.

Conventional PA spectra using a single chopped light beam were recorded in the setup of RDB-PAS; the wavelength-scanned light from a xenon lamp/monochromator was attenuated and chopped (80 Hz), and the PA signal was detected and averaged. The spectra were calibrated with the spectrum taken for graphite to compensate for wavelength-dependent light intensity. The bandgap of a sample was simply determined by extrapolating the linear part of a rise in the shorter wavelength region (Fig. S2(c)); a Tauc plot, which is frequently used for determination of the bandgap, was not used due to the ambiguity of decision of direct/indirect transitions (D. E. Scaife, Solar Energy, 1980, 25, 41-54.; B. Ohtani, Phys. Chem. Chem. Phys., 2014, 16, 1788-1797.).

Figure S2 Examples of data acquisition and processing for a representative sample (Catalysis Society of Japan TIO-1). (top) RDB-PAspectrum, (middle) ERDT pattern in the unit of $\mu$mol g$^{-1}$ as a function of wavelength of the continuous light by differentiation of RDB-PA spectrum and (bottom) conventional PA spectrum for determination of the band-gap energy. The ERDT pattern (middle) is replotted as a function of energy from VBT as shown in Fig. 1.
Correlation between total electron-trap density and specific surface area

Figure S3 shows the correlation. An almost linear relation that did not depend on the kind of crystallites, anatase, rutile and their mixture was observed. The y-intersect, ca. 14 \( \mu \text{mol g}^{-1} \) (= \( 2.1 \times 10^{-18} \text{ cm}^3 \) assuming a density of 4 g cm\(^{-3}\)), one or two orders of magnitude higher than the electron-trap density reported for thin films of anatase ([ref. 2] T. Miyagi, T. Ogawa, M. Kamei, Y. Wada, T, Mitsuhashi, A. Yamazaki, E, Ohta and T. Sato, Jpn. J. Appl. Phys. 2001, 40, L404–L406.], might correspond to ETs in bulk. The slope of the linear plot, ca. \( 1.6 \times 10^6 \) mol m\(^{-2}\) = 1.0 nm\(^{-2}\), might reflect the surface density of ETs.

ERDT/CBB patterns of metal-oxide powders other than titania

Since metal oxides are, in general, n-type semiconductors having bandgaps and donor levels below the CBB, it is no surprise that metal oxides other than titania may exhibit ERDT/CBB patterns, as shown in Fig. S4. As expected, the CBBs were different, reflecting different electronic structures of their bulk. The ERDT patterns were also different depending on the kind of metal oxide, but ERDT patterns of the same metal-oxide samples may also be different as has been seen for titania samples.

Figure S3 Correlation between total density of ETs and specific surface area of representative titania samples. Open circles and squares denote anatase and rutile samples, respectively, and closed circles and squares denote anatase-rich and rutile-rich samples, respectively.

\[ y = 1.59x + 13.66 \]

Figure S4 Representative ERDT patterns with CBB position for commercially available tungsten(VI) oxide (Kojundo Chemical Laboratory), cerium(IV) oxide (Kojundo Chemical Laboratory), strontium titanate (Sigma-Aldrich), tin(IV) oxide (Wako Pure Chemical Industries), zinc oxide (Wako Pure Chemical Industries) and potassium tantalate (Kojundo Chemical Laboratory). Figures in <> show total electron-trap density in the unit of \( \mu \text{mol g}^{-1} \).
Applicability of the degree of coincidence of ERDT/CBB patterns for identification of samples of metal oxides other than titania is now being examined and the results will be reported in the future.

**Ranking of high degree of coincidence** \(\zeta\)

The top seven ranked high-\(\zeta\) (> 0.6) pairs of commercially available or non-profitably provided titania samples are shown in Table S2.

**Table S2** Top seven ranked high-\(\zeta\) (> 0.6) pairs of commercially available or non-profitably provided titania samples

<table>
<thead>
<tr>
<th>rank</th>
<th>pair</th>
<th>(\zeta)</th>
<th>(\zeta) (a): ERDT pattern shape</th>
<th>(\zeta) (b): total density of ETs</th>
<th>(\zeta) (c): CBB</th>
<th>(\zeta_{pc})^a</th>
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<tbody>
<tr>
<td>1</td>
<td>TIO-4(^b)</td>
<td>Wako(^c)</td>
<td>0.788</td>
<td>0.863</td>
<td>0.941</td>
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<td>5</td>
<td>TIO-6(^b)</td>
<td>MT-150A</td>
<td>0.705</td>
<td>0.856</td>
<td>0.828</td>
<td>0.995</td>
</tr>
<tr>
<td>6</td>
<td>TIO-13(^b)</td>
<td>FP-6</td>
<td>0.684</td>
<td>0.847</td>
<td>0.827</td>
<td>0.976</td>
</tr>
<tr>
<td>7</td>
<td>TIO-11(^b)</td>
<td>FP-6</td>
<td>0.615</td>
<td>0.620</td>
<td>0.998</td>
<td>0.994</td>
</tr>
</tbody>
</table>

\(^a\)Average of \(\zeta_{pc}\) for the three photocatalytic reactions.  \(^b\)Reference titania provided by Catalysis Society of Japan.  \(^c\)Code 207-11121 (208-18231), Wako Pure Chemical Industries Ltd.

**Photocatalytic activity test**

Three representative photocatalytic reactions, (a) hydrogen liberation from deaerated aqueous methanol, (b) carbon-dioxide liberation from aqueous acetic acid under aerobic conditions and (c) oxygen evolution from aqueous silver fluoride, were used.  A brief explanation of the experimental procedures is as follows [(ref. 12) B. Ohtani, O.-O. Prieto-Mahaney, F. Amano, N. Murakami and R. Abe, *J. Adv. Oxidat. Tech.* 2010, **13**, 247–261.].  A standard amount of the powder photocatalyst (50 mg) was suspended in an aqueous solution (5.0 mL) in a borosilicate glass tube (transparent for wavelength > 290 nm, 18 mm in inner diameter and 180 mm in length) containing methanol (50 vol%) and chloroplatinic acid (H\(_2\)PtCl\(_6\)·6H\(_2\)O; corresponding to 2-wt% platinum (Pt) loading), acetic acid (5.0vol%), and silver fluoride (50 mmol L\(^{-1}\)) in reactions (a), (b), and (c), respectively.  Air was purged off from the systems by passing argon through the suspensions for at least 15 min, and the sample tubes were tightly sealed using a double-capped rubber septum and a sheet of Parafilm to prevent leakage of gas and/or contamination.  The samples were irradiated by a 400-W high-pressure mercury arc (Eiko-sha) at 298 K under vigorous magnetic stirring (1000 rpm).  Reactions (a), (b) and (c) were monitored by analyzing liberation of hydrogen (H\(_2\)), carbon dioxide (CO\(_2\)) and oxygen (O\(_2\)), respectively, by gas chromatography (Shimadzu GC-8A gas chromatograph equipped with a TCD and columns of molecular sieve 5A for H\(_2\) and O\(_2\) and Porapak Q for CO\(_2\)).  Activities (As) were calculated as the rate of product formation.