Atomic structure of titania nanosheet with vacancies

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Titania nanosheets are two-dimensional single crystallites of titanium oxide with a thickness of one titanium or two oxygen atoms, and they show attractive material properties, such as photocatalytic reactions. Since a titania (Ti0.87O2) nanosheet is synthesized by the delamination of a parent layered K0.8Ti1.73Li0.27O4 crystal using a soft chemical procedure, substantial Ti vacancies are expected to be included and affect the material properties. The atomic arrangement of a titania nanosheet with vacancies has not been revealed owing to the difficulties of direct observation. Here, we have directly visualized the atomic arrangement and Ti vacancies of a titania nanosheet using advanced lower-voltage transmission electron microscopy (TEM). Analyses of the results of first-principles calculations and TEM image simulations for various Ti vacancy structure models indicate that two particular oxygen atoms around each Ti vacancy are desorbed, suggesting the sites where atomic reduction first occurs.

Results

TEM observation of a titania nanosheet. Figure 1 shows (a) a high-resolution TEM image of a titania nanosheet taken in the [010] direction, along with its (b) Fourier transform (i.e., diffractogram) and (c) crystal structure.
image taken over a relatively wide area is given in Supplementary Fig. S2. As shown in the following TEM image simulation, dark dots correspond to titanium atoms and relatively weak dots correspond to oxygen atoms. Several bright rectangular areas were observed as indicated by arrows, and they are supposed to be atomic vacancies. To clarify the atomic structure of the bright rectangular areas, we summed 28 small portions of TEM images of these areas from the original image shown in Supplementary Fig. S2 (see also Fig. S4). We then obtained an averaged TEM image of the bright areas with a high SN ratio (Fig. 2a).

Structural analyses of Ti vacancies in a titania nanosheet. To investigate the crystal structure of the bright rectangular areas, we compared the experimental TEM image with simulation images obtained using various crystal structure models, in which the atomic arrangements are optimized using first-principles plane-wave basis pseudopotential method. Further details of the first-principles calculations are given in section 3 in Supplementary Information. Figure 3a–c shows three optimized structures and their TEM simulation images, in which the atomic arrangements near the Ti vacancies are different. It is found that the structure optimization is indispensable because it considerably affects each structure and its TEM simulation image. The structures and their TEM simulation images before optimization are given in Supplementary Fig. S8. Figure 3a shows one optimized structure in which a titanium atom is simply removed. In this structure model, some oxygen atoms around the Ti vacancy move slightly outward by about 15 pm from their original positions. The simulation image of this model indicates that the positions of the bright rectangular areas

in the experimental image correspond to the vacancies of titanium atoms. The Ti vacancy in the simulation image in Fig. 3a, however, does not precisely reproduce the experimental result. Quantitative analyses of the image intensities are given in Fig. 3d,e, and the intensity of this model along the a-axis (Fig. 3d) does not agree with the experimental intensity.

Next, we investigate other Ti vacancy structure models with missing adjacent oxygen atoms. As shown in Fig. 2b, the oxygen atoms around a Ti vacancy are coordinated in various ways, i.e., (i) oxygen atoms c1 and c2 coordinated to a single Ti atom, (ii) oxygen atoms a1 and a2 coordinated to two Ti atoms, and (iii) the others coordinated to three Ti atoms. Figure 3b shows the simulation result for the optimized structure model in which the oxygen atoms c1 and c2 are removed (i.e., Ti + O_{c1} + O_{c2} vacancy model). Figure 3c shows the result for the model in which the other two oxygen atoms a1 and a2 are removed (i.e., Ti + O_{a1} + O_{a2} vacancy model). The atomic arrangements in these optimized structures are differently relaxed through the optimization. In the optimized Ti + O_{c1} + O_{c2} vacancy model, oxygen atoms and the outer titanium atoms on both sides of the Ti vacancy moved outward by 15 and 35 pm, respectively (see the arrows in the structure drawing in Fig. 3b). The simulation image of the Ti + O_{c1} + O_{c2} vacancy model well reproduces the experimental
result, as shown in Fig. 3b. By contrast, the Ti + O\textsubscript{a1} + O\textsubscript{a2} vacancy model results in a different configuration of the atoms, for example, the adjacent Ti atoms shift by about 45 pm, and its simulation TEM image has a different appearance, as shown in Fig. 3c.

We elucidate the intensity profiles of the experimental and simulation TEM images, particularly those for the oxygen sites adjacent to Ti vacancies. Figure 3d,e shows the relative intensity profiles along the a- and c-axes, respectively. TEM image contrast generally depends on atomic potential; therefore, heavy atoms and/or large numbers of atoms exhibit intense dark contrast under the present conditions (a very thin specimen and underfocus imaging). We could estimate the number of oxygen atoms around a Ti vacancy by comparing the contrast of the experimental image with those of simulation images. All the simulation profiles are equally scaled to fit the experimental profiles based on the contrast of Ti atoms. Black dotted lines indicate the experimental intensities. Colored lines indicate intensities in the simulation images: Ti vacancy model (a) shown by blue broken lines, Ti + O\textsubscript{c1} + O\textsubscript{c2} vacancy model (b) shown by pink solid lines, and Ti + O\textsubscript{a1} + O\textsubscript{a2} vacancy model (c) shown by green broken lines.

The results indicate that the Ti + O\textsubscript{c1} + O\textsubscript{c2} vacancy model is more stable than the Ti + O\textsubscript{a1} + O\textsubscript{a2} vacancy model (see also section 3 in Supplementary Information). In the titania nanosheets, oxygen atoms around Ti vacancies are coordinated to fewer Ti atoms than other atoms and are expected to be easily reconstructed and relaxed to ensure structure stability. Missing oxygen atoms coordinated to fewer Ti atoms have also been discussed in the surface terminations and reduction of bulk TiO\textsubscript{2}. In case of the titania nanosheet, single-bonded oxygen atoms around Ti vacancies (O\textsubscript{c1} and O\textsubscript{c2}) are considered to be first desorbed in the reduction process to ensure structure stability.

In our previous study\textsuperscript{19}, we observed a structural phase transformation from Ti\textsubscript{10.87}O\textsubscript{2} nanosheets to Ti\textsubscript{2}O\textsubscript{3} nanosheets owing to topotactic-like reduction by electron irradiation. The transformation could be monitored by observing 100 lattice fringes in TEM images. As shown in Fig. 1, the present result of TEM observation does not show such periodicity; therefore, a substantial structural change did not occur during the present observation. The previous experimental results also indicate that the preparation procedure of the TEM specimen does not affect its crystal structure. It is, however, still considered that the oxygen atoms c1 and c2 tend to be removed by the
very weak electron irradiation. Note that such oxygen desorption is difficult to detect using other methods (e.g., electron diffraction) and that direct TEM observation is indispensable for the structure characterization of the vacancies.

**Distribution of Ti vacancies in a titania nanosheet.** We next observe the distribution of Ti vacancies in the titania nanosheet. Although most of the Ti vacancies are scattered, several types of continuous vacancies can be seen as shown in Fig. 4a–e. The number of these cluster-like Ti vacancies is much smaller than that of single vacancies such as that shown in Fig. 2a, for example, four Ti di-vacancies along the a-axis (Fig. 4a) were found in the original image shown in Supplementary Fig. S2. The distribution of Ti vacancies may arise from that of Li$^{+}$ ions in the parent $K_0.2Ti_{1.73}Li_{0.27}O_4$ layered titanate. In titania nanosheets with the composition of $Ti_{0.87}O_2$, Ti vacancies are considered to be included in an approximate ratio of 13.5%. We can confirm 60 Ti vacancies in Fig. 1a, whose Ti vacancy ratio is calculated to be 7.5% (see also Supplementary Fig. S4). It should be noted that a vacancy ratio of 13.5% is a speculative value based on the mean contents of the parent material and that our present report is the first direct observation of the Ti vacancies in a titania nanosheet.

**Discussion**

Consequently, we have successfully observed the atomic structure of Ti vacancies in a titania nanosheet using advanced TEM and by first-principles calculations. Lower-voltage TEM with a spherical aberration corrector, a monochromator, and a low-dose technique allows the direct observation of the atomic arrangement around Ti vacancies. In addition, the results of our experiment and analyses by first-principles calculations and TEM image simulations suggest that two particular oxygen atoms around Ti vacancies tend to be removed. This result may be a key to revealing the mechanism and atomic process in the reduction of various titanias materials or the fatigue mechanism of titania photocatalysts on their surface.

**Methods**

**Preparation of the TEM specimen.** A titania ($Ti_{0.87}O_2$) nanosheet was derived by delamination of a $K_aTi_{1.7}LaO_2$ layered titanate through a soft chemical procedure.$^{13,14}$ In this procedure, K$^+$ and Li$^{+}$ ions in the layered titanate were extracted, and negatively charged $Ti_{0.87}O_2$ layers were formed as colloidal sheets surrounded by tetrabutylammonium ions ([C$_4$H$_{25}$N]+). The colloidal suspension of the nanosheets was mounted onto a holey carbon film on a TEM grid. The TEM grid was illuminated with ultraviolet (UV) light in air to photocatalytically decompose the tetrabutylammonium ions surrounding the nanosheets. This self-cleaning treatment by UV light illumination is a standard procedure used in the application of photocatalysts.$^{15,16}$ Further details of the self-cleaning treatment are described in section 1 in Supplementary Information.

**TEM experiments.** To achieve high-resolution and high-sensitivity observation, we used a transmission electron microscope (FEl, Titan-Cubed) equipped with a spherical aberration corrector and a monochromator. The acceleration voltage of the microscope was set to 80 kV to decrease knock-on damage. We also applied a low dose rate of $2.5 \times 10^6$ electrons/nm$^2$ and a beam blanking system to reduce the total dose. To improve the contrast and resolution of the TEM images, the energy spread of the incident probe was reduced to 0.1 eV in full width at half maximum using the monochromator. TEM images were recorded by a charge-coupled device (CCD) camera. The defocus of the objective lens was set at an underfocus of about 4 nm. Ten TEM images were acquired each with an exposure time of 2 s, the specimen drift between the TEM images was then corrected, and finally we obtained an image with a high signal-to-noise (SN) ratio by summation of the ten images. Further details of the TEM observation are given in section 2 in Supplementary Information.

**TEM image simulation.** The TEM image simulation was performed using a multislice simulation program (HREM Research Inc., xHREM). We examined the TEM imaging parameters and selected a third-order spherical aberration coefficient $C_s = 0$ nm, a defocus spread $\Delta = 2$ nm, and a defocus $z = 4$ nm of underfocus at an acceleration voltage of 80 kV (see also section 2 in Supplementary Information). The effect of the transmission cross coefficient was included in the simulation. Since the experimental TEM image contrast is produced due to various factors such as modulation transfer function of the CCD camera, the simulated TEM contrast in Fig. 3d,e is reduced to 67% to fit the experimental results.

**Figure 4 | Various types of cluster-like Ti vacancies in the titania nanosheet.** (a) Ti di-vacancy along the a-axis (four images were summed). (b) Ti di-vacancy along the c-axis (four images were summed). (c) Ti tri-vacancy along the a-axis (two images were summed). (d) Ti tri-vacancy along the c-axis (one image). (e) $2 \times 2$ Ti vacancy (three images were summed).

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Author contributions
TEM measurements were done by K.K. and M.O. T.S. and Y.E. contributed to the synthesis of the materials and discussion of the results. T.M. contributed to first-principles calculations. M.O. and K.K. analyzed the data and wrote the paper with contributions from all authors.

Additional information
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