Local structure investigation of WO$_x$ cluster modified on titanium-substituted hydroxyapatite for promoting charge separation under UV illumination

Kana ISHISONE$^{1,\dagger}$, Toshihiro ISOBE$^{1}$, Sachiko MATSUSHITA$^{1}$, Masato WAKUMURA$^{2}$, Takahiro TAKEI$^{3,\ddagger}$ and Akira NAKAJIMA$^{1,\dagger}$

$^1$Department of Materials Science and Engineering, Graduate School of Materials and Chemical Technology, Tokyo Institute of Technology, 2–12–1 O-okayama, Meguro, Tokyo 152–8552, Japan
$^2$Market Exploration Group, Fujitsu Laboratories Ltd., 10–1 Morinosato-Wakamiya, Atsugi, Kanagawa 243–0197, Japan
$^3$Center for Crystal Science and Technology, University of Yamanashi, 7–3 Miyamae, Kofu 400–8511, Japan

The local structure of WO$_x$ clusters modified on Ti-doped hydroxyapatite (Ti-HAp) photocatalyst surface was analyzed using X-ray absorption fine structure (XAFS) measurements. W L$_{1-3}$-edge X-ray absorption near-edge structure (XANES) spectra analyses revealed that WO$_x$ clusters include WO$_4$ and WO$_6$ structures and that WO$_x$ amounts increase concomitantly with increasing WO$_x$ cluster amounts. Results of analyses of W L$_{1-3}$-edge extended X-ray absorption fine structure (EXAFS) spectra confirmed this finding, demonstrating that the average coordination number of W surrounded by O increases from 4 to 5 with increasing WO$_x$ cluster amount. The number of W–O–W bonds increased concomitantly with increasing amounts of modified WO$_x$ clusters, indicating the formation of WO$_x$ cluster aggregates. Assuming that two-dimensional WO$_x$ monolayer domains were formed and that the domain is square, the average WO$_x$ cluster structure was calculated as changing from a monomeric to a trimeric or tetrameric structure with increasing WO$_x$ loading amount. The cluster size obtained from the model is consistent with those found in our earlier experimental study. The cluster structure represented here demonstrated that the modified WO$_x$ clusters included a low coordination structure. Its electronic structure became different from that of doped W or bulk WO$_3$ and a suitable electron transition path from Ti 3d to W 5d was created, showing high photocatalytic activity.

1. Introduction

As reported by Wakamura et al.,$^1$ Ti-doped hydroxyapatite (Ti-HAp), is a promising alternative photocatalyst to TiO$_2$ because of its high affinity for toxic organic substances. In Ti-HAp, a certain amount of Ca ion in hydroxyapatite [Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, HAp] is exchanged with Ti ion. Doping of Ti ions in hydroxyapatite leads to the creation of a Ti hybridized band in the HAp bandgap, which imparts photocatalytic activity under ultraviolet (UV) illumination while retaining high affinity to organic compounds.$^2$–$^5$ The material has already been applied to various industrial environmental purification uses such as air purifiers. However, to retain its structure, the amounts of the Ti ion dopant must be limited,$^2$ which constrains the increase of its photocatalytic activity.

Very recently, we reported the synthesis of WO$_x$ cluster-modified Ti-HAp,$^6$ with modified WO$_x$ clusters adhered onto a Ti-HAp surface through impregnation–calcination cycling using ammonium tungstate [(NH$_4$)$_6$H$_2$W$_{12}$O$_{42}$]·4H$_2$O as the W source. The modification increased the Ti-HAp photocatalytic activity for decomposition of gaseous IPA (2-propanol) under UV illumination. Subsequent experimental and theoretical investigations demonstrated clearly that charge separation was promoted by the WO$_x$ modification. The electronic structure calculated using density functional theory suggests that a W 5d orbital can create the lowest unoccupied W 5d level in a higher energy axis than Ti 3d level. That finding suggests that W-doping does not produce a function of carrier separation for the photoexcited electron in the system. In contrast to doped W, modified WO$_x$ clusters might contain coordinative unsaturated structures with a small coordina-
tion number of W surrounded by O. These WO₃ cluster structures create the W 5d level in the lower location in energy axis. Some of the W 5d level can be created in a suitable location in energy axis for charge transfer from Ti 3d. Therefore, we assumed that WO₃ cluster has a low coordination number structure. Nevertheless, no experimental investigation of the WO₃ cluster local structure on Ti-HAp surface has been conducted to date. Characterization of the WO₃ cluster might provide important insights into designing an efficient charge separation path on the photocatalyst surface.

X-ray absorption fine structure (XAFS) spectroscopy is a conventional characterization method used to evaluate the local structure of clusters. Several reports have described WO₃ cluster structures modified on various metal oxide surfaces (e.g. TiO₂, ZrO₂, Al₂O₃, Fe₂O₃) as examined using XAFS spectra. Those investigations demonstrated that modified WO₃ cluster structures differ from those of crystallized WO₃. Moreover, they change according to the amount of modification. However, cluster structure details vary among the substrates which are used.

Given this background, we investigated WO₃ cluster local structure modified on Ti-HAp surface from W L₁ and L₃-edge X-ray absorption near-edge structure (XANES) spectra and W L₁-edge extended X-ray absorption fine structure (EXAFS) spectra. Based on those findings, we discussed the validity of the WO₃-modified Ti-HAp surface model, which was used in earlier reports of the literature.

2. Experimental

2.1 Sample preparation

All starting chemicals except for the starting Ti-HAp used for this study were reagent-grade. A commercial Ti-HAp powder [Hautform TA, (Ca₈.22, Ti₀.89)(PO₄)₆(OH)₂; □: defect in Ca site, 1 g; Fuji Chemical Ind. Co., Ltd., Osaka, Japan] was used as a source material for modification in every sample preparation. After the Ti-HAp was dispersed into an aqueous solution (200 mL, 1.0 × 10⁻⁴ mol/L) of ammonium tungstate [(NH₄)₁₀[(H₂W₁₂O₄₂)·4H₂O; Wako Pure Chemical Industries Ltd., Osaka, Japan], it was stirred for 5 min at room temperature. After filtration and washing with deionized water, the powder was dried at 80 °C in an oven for 24 h. Then it was fired at 500 °C for 1 h in ambient air. This firing was conducted to remove organic compounds and to convert hydroxides to oxides. This temperature was lower than the heating temperature used for manufacturing Ti-HAp commercially. For that reason, this heating is not expected to induce remarkable differences in the crystalline phase, morphology, or specific surface area of the starting Ti-HAp. This impregnation–calcination cycle was repeated 1–10 times to change the WO₃ modification amount. The prepared samples were labeled as W-X, where X represents the number of procedure repetitions.

2.2 W L₁,3-Edge X-ray absorption spectroscopy

We analyzed the XAFS spectra of W L₁ and L₃ edges to ascertain the structure of WO₃ cluster on Ti-HAp. The W L₁-edge spectra were recorded in fluorescence mode at the BL14B2 beamline at SPring-8 (Hyogo, Japan) using a Si (111) monochromator. The W L₃-edge spectra were measured in transmission mode at the BL55X1 beamline at the Aichi synchrotron radiation center (Aichi, Japan) using a Si (111) monochromator. In addition to the prepared samples, other typical W compounds were measured: WO₃ (Wako Pure Chemical Industries Ltd., Osaka, Japan), Na₂WO₄·2H₂O (Kanto Chemical Co. Inc., Tokyo, Japan), WO₂ (Kojundo Chemical Lab. Co., Ltd., Saitama, Japan), and metal W (Kanto Chemical Co. Inc., Tokyo, Japan). The obtained XAFS data were analyzed in terms of the standard procedures using the Athena and Artemis software packages (Demeter, version 0.9.26). Normalized absorption coefficients were obtained using Athena software. The EXAFS theoretical fittings were found using Artemis software. The EXAFS analysis was conducted as described below. The spectra were extracted using the cubic spline method and were normalized to the edge height. The k²-weighted EXAFS oscillation was Fourier-transformed into r space using the Fourier transformation range of 3.0 and 12.5 Å⁻¹. Curve-fitting analysis was performed for the first shell (W–O shell), with the range of the W–O shell being between 1.0 and 2.6 Å. The W–O phase and amplitude functions were extracted from WO₃ by calculation using the FEFF 6.0 code (Demeter 0.9.26 software package).

3. Results and discussion

The W species structure can be estimated from the energy gap of the split W L₁-edge white line and the area of the pre-edge peak of W L₁-edge XANES spectra. For this reason, we conducted an analysis of W L₁, L₃-edge XANES spectra for WO₃-modified Ti-HAp and estimated the structures of the W species loaded on the Ti-HAp surface. Afterwards, the chemical formula and its structure of W and O compounds are represented in the form of WO₂, WO₃, WO₄, and WO₆. For the sake of clarity, the unit structure of W and O compounds (WO₄ and WO₆) are represented in italics.

3.1 W L₁-edge XANES spectra

Figure 1 portrays W L₁-edge XANES spectra of WO₃-modified Ti-HAPs. The W L₁-edge X-ray absorption is attributed to the electron transition from 2s orbitals to vacant levels. The pre-edge peak of W L₁-edge XANES spectra (pale red region in Fig. 1) is attributed to the electron transition from 2s to 5d, which is normally an electric-dipole forbidden transition in high symmetry structure. However, in the tetrahedral case or in a low symmetry structure, hybridization of W 5d and W 6p will occur, with intensification of the peak. Correlation between the pre-edge peak area and the local symmetry structure is well known to exist. The deconvolution results are presented in Fig. S1. The spectra can be fitted within one Lorentz function (pre-edge peak) and one arctangent function. The obtained pre-edge peak areas of samples are presented.
in Fig. 2. The amount of WO₃ cluster in each WOₓ-modified Ti-HAp sample was calculated from our earlier XPS results, showing that the amount of modified WOₓ cluster increased with repetition of the impregnation–calcination process. The WOₓ-modified Ti-HAps have a pre-edge peak area between WO₃ and Na₂WO₄·2H₂O, which suggests the average structure of modified WOₓ cluster is between the WO₆ and WO₄ structures.

3.2 W L₃-edge XANES spectra

Figure 3 presents W L₃-edge XANES spectra of WOₓ-modified Ti-HAps. Various tungsten species were also measured for comparison. The W L₃-edge X-ray absorption white line of transition metals is attributed to electronic transitions from the 2p₃/₂ orbital to vacant s and d orbitals of the metal. Reportedly, the contribution of the p–d transition in the L₃-edge absorption white line is 50 times stronger than that of the p–s transition, which means that the L₃-edge white line mainly reflects the electron transition from the 2p₃/₂ to vacant d orbitals. The W L₃-edge white line therefore mostly derives from electron transition from the 2p₃/₂ to a vacant 5d state. The binding energy of the electrons depends on the overall charge of the atom. Therefore, the position of the white line absorption edge is related to the valence of the studied atoms. The white line edge energy, which was obtained from the maximum value of the first-order derivatives, was 10202.2 eV in W metal; it was 10202.9 eV in WO₂, 10204.4 eV in WO₃, and 10204.9 eV in Na₂WO₄·2H₂O. Our sample shows the white line edge at around 10203.9 eV in W-2 and at 10204.2 eV in W-5 and W-9. The result suggests that the W valence number of modified WOₓ cluster is mostly 6+, which is consistent with XPS results we obtained earlier. However, closer inspection (Fig. S2) reveals that the white line peak shapes in the modified WOₓ cluster samples resembled those of WO₃ and Na₂WO₄·2H₂O, but they are not exactly the same. The results suggest that the WOₓ cluster has a similar structure to those of WO₃ and Na₂WO₄·2H₂O, although not exactly the same to either of them. Rather, the sample peaks seem to be the sums of the peaks of WO₃ and Na₂WO₄·2H₂O, which means the WOₓ cluster has a mixed polyhedral structure of WO₆ and WO₄. Furthermore, although the W-2, W-5, and W-9 peaks are almost identical, the peak intensity at lower energy is stronger in W-2 than in W-5 or W-9. This result implies a partial local structure of WOₓ cluster change from WO₄ to a WO₆ structure with increase of the WOₓ loading amount.

For further discussion, we specifically examined the W L₃-edge XANES spectra of WO₃ and Na₂WO₄·2H₂O...
presented in Fig. 3. Results show that WO₃, which has a distorted octahedral WO₆ structure, exhibits a broad peak with an indistinct top, whereas Na₂WO₄·2H₂O, which has a tetrahedral WO₄ structure, has one sharp asymmetrical peak. These white line shape differences are well known to be attributable to splitting of the W 5d states of the ligand field. The electron transition from 2p³/₂ to 5d level is separable into transitions of two kinds: 2p³/₂ to t₂g (t₂) and 2p³/₂ to e_g (e). The splitting energy of these transitions is related to the energy difference between t₂g (t₂) and e_g (e) orbitals. Structural distortion of the octahedral symmetry generally engenders a small splitting of the t₂g and e_g states because the position change of the oxygen ligands on an equatorial plane makes the e_g orbitals stable. Therefore, one broad peak consisting of two peaks was observed in WO₃. On the other hand, because the energy difference of e and t₁ of tetrahedral structure is smaller than that of an octahedral and distorted octahedral structures, one narrow peak was observed in Na₂WO₄·2H₂O.

X-ray absorption of W L₃-edge consists of electron transitions from 2p³/₂ orbitals to vacant 5d orbitals and to the vacuum level. The electron transition to a vacant 5d orbital can be represented by a Lorentz function. The electron transition to the vacuum level can be represented by an arctangent function. Based on these factors, the white line was deconvoluted. Results of the deconvolutions are shown in Fig. 4. In WO₃ and Na₂WO₄·2H₂O, the spectra were fitted within two Lorentz functions (peak 1 and peak 2 for WO₃, peak 3 and peak 4 for Na₂WO₄·2H₂O) and one arctangent function. The peak positions of the Lorentz functions were found based on the values of the two peaks in the second derivative of each sample (Fig. S3). The arctangent function used for all samples was identical. The peak area ratio in WO₃ was peak 1:peak 2 = 61:39, which is consistent with the orbital ratio of t₂g:e_g = 3:2. On the other hand, the peak area ratio in Na₂WO₄·2H₂O was peak 3:peak 4 = 38:62, which is consistent with the orbital ratio of e:t₁ = 2:3. As described earlier, the average local structure of modified WO₃ cluster was considered to be between the WO₆ and WO₄ structures. According to the sample’s second derivative (Fig. S3), some peaks are overlapped, implying they constitute a mixture of several polyhedral structures. For ease of exposition, we consider only WO₆ and WO₄ structures are contained in modified WO₃ clusters. Therefore, the W-2, W-5, and W-9 spectra were fitted within four Lorentz functions and one arctangent function, after fixing their peak positions and the peak area ratios of peak 1:peak 2, peak 3:peak 4 to those values of WO₃ and Na₂WO₄·2H₂O. The results are presented in Figs. 4(c)–4(e). Peak 1 and peak 2 derive from the distorted octahedral structure (WO₆), whereas peak 3 and peak 4 derive from the tetrahedral structure (WO₄). The samples were well fitted in the functions. From deconvolution of the spectra of those peaks, the content ratios between the WO₆ structure and WO₄ structure of the respective samples were calculated: they are shown in Table 1. Although 43% were WO₆ structures in W-2, their proportions decreased with increased amounts of WO₃ clusters. Only a quarter were contained in W-9.

| Table 1. Deconvolution results of W L₃-edge XANES spectra of WO₃-modified Ti-HAps |
|---|---|
| Content Ratio (%) |
| WO₆ | WO₄ |
| W-2 | 57 | 43 |
| W-5 | 72 | 28 |
| W-9 | 76 | 24 |

3.3 W L₃-edge EXAFS spectra
For detailed investigation of WO₃ cluster local structures, W L₃-edge EXAFS spectra were analyzed. The W
L₃-edge EXAFS spectra of the samples and their Fourier transforms are presented in Figure 5. The peaks in the range of 1–2 Å are attributable to the W–O shell. Because WO₃ has distorted WO₃ structures, WO₃ has two peaks in the range (peaks at 1.4 and 1.8 Å). The W–O atomic distance of WO₃ is 1.73–2.19 Å (1.93 Å on average). However, Na₂WO₄·2H₂O has an undistorted WO₃ tetrahedron structure and has one intense peak at 1.4 Å. In WO₃-modified Ti-HAp samples, the spectra consist mainly of a single peak at 1.4 Å, but a slight shoulder at 1.8 Å can be detected in W-2. The peak around 3 Å attributable to W–M (M: Ti, P, W) has a higher peak intensity in this region. This result suggests that the number of W–O–W bonds increases with the increase of the WO₃ cluster loading amount. Curve-fitting analysis was conducted for the W–O shell to obtain structural parameters of the WO₃ clusters. The coordination number (CN), bond length (r), Debye–Waller (σ²), and R factor (R) of each sample are presented in Table 2. For WO₃ and Na₂WO₄·2H₂O, for which the structure is already known, the CN was fixed and then the bond lengths and intrinsic loss factor were calculated. These data were applied to the calculation of W-2, W-5, and W-9. Because of the low amount of WO₃ cluster in W-2, its EXAFS oscillation S/N ratio is not good especially in high wavenumber region. However, a slightly negative Debye–Waller factor was necessary to minimize the error of fitting the result of W-2. Although this value of σ² is physically unrealistic, the data were included because they are meaningful for comparison with other samples. All WO₃-modified Ti-HAp samples can be fitted with two W–O shells, similarly to WO₃. However, the coordination number is smaller than that of WO₃, which suggests that some low coordination number structure is included in the modified WO₃ cluster. Among the samples, the total coordination number is increased from 4 to 5 with increasing WO₃ cluster loading amount, which means that the local structure of WO₃ cluster is changed from WO₃ to WO₄. This result is consistent with that found through W L₃-edge XANES spectra deconvolution.

### Table 2. Structural parameters for the W–O Shells of WO₃-modified Ti-HAps, WO₃, and Na₂WO₄·2H₂O

| Sample          | CN | r (Å) | σ² (Å²) | R (%) |
|-----------------|----|-------|---------|-------|
| Na₂WO₄·2H₂O     | 4.0| 1.781 | 0.0014  | 1.15  |
| WO₃             | 4.0| 1.770 | 0.0025  | 0.73  |
| W-2             | 2.0| 2.180 | 0.0045  |       |
| W-5             | 2.2| 1.770 | -0.0020 | 2.11  |
| W-9             | 1.9| 2.378 | 0.0187  |       |
| W-5             | 3.6| 1.759 | 0.0022  | 0.58  |
| W-9             | 0.8| 2.268 | 0.0027  |       |
| W-9             | 4.3| 1.766 | 0.0039  | 2.23  |
| W-9             | 0.7| 2.210 | 0.0006  |       |

*CN, coordination number; r, bond distance; σ², Debye–Waller factor; R, R-factor.

### 3.4 WO₃ cluster local structure modified on a Ti-HAp surface

The W L₁–L₃ XAFS results suggest that WO₃ cluster aggregates and the structure change gradually from tetrahedral to octahedral with increase of the WO₃ cluster loading amount. From these results, details of the WO₃ cluster structure can be discussed. Kitano et al. reported that the WO₃ cluster modified on Al₂O₃ surface has a two-dimensional monolayer structure. For this reason, we assume that WO₃ monolayer is modified on the Ti-HAp surface. A transmission electron microscope (TEM) image in our earlier study shows the WO₃ cluster as nearly a circle. Therefore, for ease of exposition, we referred the bulk WO₃ crystal atomistic structure properties from the literature and assumed that the WO₃ cluster has a square-like structure. Because the WO₃ cluster is not expected to
be detached from the Ti-HAp surface under room temperature conditions, we inferred that each W in the WO$\x3csub x\x3e$ cluster has a bond with an O atom of the Ti-HAp surface. It also needs to meet charge compensation. Therefore, overall 4$n$ O atoms surround $n$ W atoms in the WO$\x3csub x\x3e$ cluster. Assuming that the WO$\x3csub x\x3e$ cluster has $y$ W-O-W bonds, the average coordination number (mean $CN$) around W can be expressed as $(4n + y)/n$.

We now consider WO$\x3csub x\x3e$ clusters as modified in the form of a square structure [Fig. 6(a)]. The structures are represented using the VESTA program.\textsuperscript{18} The value of $y$ can be found using the following equation.

$$y = 2\sqrt{n}(\sqrt{n} - 1) (n = 1^2, 2^2, 3^2, \ldots) \quad (1)$$

Therefore, the mean $CN$ can be expressed as shown below.

$$\text{mean } CN = 6 - \frac{2}{\sqrt{n}} \quad (2)$$

Figure 6(b) shows the relation between the mean $CN$ and the number of W in WO$\x3csub x\x3e$ cluster based on Eq. (2). The grey points presented in the figure include the assumption of mean $CN$ when the $n \neq 1^2, 2^2, 3^2, \ldots$ (i.e. WO$\x3csub x\x3e$ cluster is not in the form of square structure), but we considered the cluster structure as nearly a square structure as well. Although some of the assumed mean $CN$ deviate from the equation, the points are generally well fitted in the Eq. (2). Application of each sample’s $CN$ obtained from W L$3$-EXAFS spectra to Fig. 6(b) shows that the WO$\x3csub x\x3e$ cluster was almost in the form of monomeric in W-2, and that it was increased to trimeric or tetrameric in W-9. The length of one side of the tetrameric cluster is about 1.0 nm, which is close to the cluster size (0.5–1 nm), as shown in TEM images obtained in our earlier study.\textsuperscript{6} We should mention that the modified WO$\x3csub x\x3e$ clusters are expected to be a mixture of various structures. Therefore, the model based on its mean $CN$ is not a complete model. However, this model reflects the mean $CN$ to the average WO$\x3csub x\x3e$ cluster structure.

It is meaningful to discuss structural change with increasing WO$\x3csub x\x3e$ amounts using the model.

From the discussion presented above, the possible WO$\x3csub x\x3e$ cluster local structure modified on the Ti-HAp surface is presented in Fig. 7. When the modified WO$\x3csub x\x3e$ amount is low, the WO$\x3csub x\x3e$ cluster structure consists mostly of a single WO$\x3csub x\x3e$ tetrahedron. The WO$\x3csub x\x3e$ cluster has several bonds with the Ti-HAp surface, which inhibit its detachment from the surface. Because Ca ion in Ti-HAp has a large ionic radius and a low oxidation number, even if O in the WO$\x3csub x\x3e$ cluster makes bonds with Ca ion, its bond strength will be weak; the WO$\x3csub x\x3e$ can detach easily from Ca. For this reason, the WO$\x3csub x\x3e$ cluster is likely to bind with surficial Ti or P in Ti-HAp. When the amount of WO$\x3csub x\x3e$ cluster is increased, the WO$\x3csub x\x3e$ cluster aggregates and increases to a trimeric or tetrameric structure, leading to an increase in the number of O surrounding W. Eventually, the structure approximates a WO$\x3csub x\x3e$ octahedron. The structure represented herein supports the computational model we explained in the report of an earlier study,\textsuperscript{6} in which report we assumed that a modified WO$\x3csub x\x3e$ cluster contains a low-coordination structure. Therefore, these results suggest that, by depositing a WO$\x3csub x\x3e$ cluster on the Ti-HAp surface, its electronic structure became different from that of doped W or bulk WO$\x3csub x\x3e$. A suitable photo-excited electron transition path from Ti 3d to W 5d was created, showing high photocatalytic activity.

4. Conclusion

The local structure of a WO$\x3csub x\x3e$ cluster modified on a Ti-HAp surface was analyzed using XAFS measurements. The W L$3$- and L$3$-XANES spectra showed that WO$\x3csub x\x3e$ clusters include both WO$\x3csub x\x3e$ and WO$\x3csub x\x3e$ structures and showed that the WO$\x3csub x\x3e$ amount was increased concomitantly with increasing WO$\x3csub x\x3e$ cluster amounts. Analyses of W L$3$-EXAFS spectra demonstrated that the coordination number of W surrounded by O was increased by increasing the modified WO$\x3csub x\x3e$ cluster loading amount, indicating that the local coordination structure of WO$\x3csub x\x3e$ cluster changed gradually.
from tetrahedral to octahedral structure. The number of W–O–W bonds was increased concomitantly with increase of the WOₓ amount, which implied that the WOₓ cluster became larger through repeated impregnation–calcination processing. By assuming that two-dimensional WOₓ monolayer domains were formed and that the domain is square, the average WOₓ cluster structure was calculated as changing from a monomeric to a trimeric or tetrameric structure with increasing WOₓ loading amount. The results presented herein support the computational model described in earlier reports, in which the study based on the assumption that a modified WOₓ cluster includes a low coordination structure. By depositing WOₓ clusters on the Ti-HAp surface, its electronic structure became different from doped W or bulk WO₃. Therefore a suitable electron transition path was created from Ti 3d to W 5d, showing high photocatalytic activity.

Acknowledgments Experiments at SPring-8 were conducted with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposals 2019B1833). Experiments at Aichi synchrotron radiation center were performed with the approval No. 201904011.

References
1) M. Wakamura, K. Hashimoto and T. Watanabe, Langmuir, 19, 3428–3431 (2003).
2) M. Tsukada, M. Wakamura, N. Yoshida and T. Watanabe, J. Mol. Catal. A-Chem., 338, 18–23 (2011).
3) K. Kandori, M. Oketani, Y. Sakita and M. Wakamura, J. Mol. Catal. A-Chem., 380, 54–60 (2012).
4) K. Kandori, M. Oketani and M. Wakamura, Colloid. Surf. B, 101, 68–73 (2013).
5) K. Kandori, T. Kuroda and M. Wakamura, Colloid. Surf. B, 87, 472–479 (2011).
6) K. Ishisone, N. Jiraborvompongs, T. Isobe, S. Matsushita, M. Wakamura, M. Oshikiri and A. Nakajima, Appl. Catal. B-Environ., 264, 118516 (2020).
7) S. Yamazoe, Y. Hitomi, T. Shishido and T. Tanaka, J. Phys. Chem. C, 112, 6869–6879 (2008).
8) T. Yamamoto, A. Orita and T. Tanaka, X-Ray Spectrom., 37, 226–231 (2008).
9) T. Kitano, T. Hayashi, T. Uesaka, T. Shishido, K. Teramura and T. Tanaka, ChemCatChem, 6, 2011–2020 (2014).
10) F. Liu, W. Shan, Z. Lian, J. Liu and H. He, Appl. Catal. B-Environ., 230, 165–176 (2018).
11) B. Ravel and M. Newville, J. Synchrotron Radiat., 12, 537–541 (2005).
12) P. M. Woodward, A. W. Sleight and T. Vogt, J. Phys. Chem. Solids, 56, 1305–1315 (1995).
13) S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers and M. J. Eller, Phys. Rev. B, 52, 2995–3009 (1995).
14) B.-K. Teo and P. A. Lee, J. Am. Chem. Soc., 101, 2815–2832 (1979).
15) J. P. L. Kenny, H. Veeramani and D. S. Alessi, Analytical Geomicrobiology: A Handbook of Instrumental Techniques, Cambridge University Press, Cambridge (2019) p. 242.
16) F. Hilbrig, H. E. Gobel, H. Knozinger, H. Schmelz and B. Lengeler, J. Phys. Chem., 95, 6973–6978 (1991).
17) S. Hosokawa, S. Kamishima, K. Kubo, H. Kanai, K. Wada and M. Inoue, J. Jan. Petro. Inst., 54, 361–365 (2011).
18) K. Momma and F. Izumi, J. Appl. Crystallogr., 44, 1272–1276 (2011).

Fig. 7. Possible structures of WOₓ cluster modified on Ti-HAp surface. The color code is red for O, yellow for W, green for Ti, pink for P, and blue for Ca.