FULL PAPER

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

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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 - and L_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_6 amounts increase concomitantly with increasing WO_x cluster amounts. Results of analyses of W L_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.

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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 [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, 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 [$(\text{NH}_4)_{10}(\text{H}_2\text{W}_{12}\text{O}_{42}) \cdot 4\text{H}_2\text{O}$] 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 be created in a suitable energy position for electron transition from Ti, but only from modified WO_x clusters, not from doped W species. Computational results indicate that W-doping by exchanging PO_4^{3-} with WO_4^{2-} tetrahedral creates the lowest unoccupied W 5d level in a higher location in 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-

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tion number of W surrounded by O. These WO_x 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 WO_x cluster has a low coordination number structure. Nevertheless, no experimental investigation of the WO_x cluster local structure on Ti-HAp surface has been conducted to date. Characterization of the WO_x 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 WO_x cluster structures modified on various metal oxide surfaces (e.g. TiO_2 ,⁷⁾ ZrO_2 ,⁸⁾ Al_2O_3 ,⁹⁾ Fe_2O_3 ,¹⁰⁾), as examined using XAFS spectra. Those investigations demonstrated that modified WO_x cluster structures differ from those of crystallized WO_3 . 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 WO_x cluster local structure modified on Ti-HAp surface from W L_{1-} and L_{3-} edge X-ray absorption near-edge structure (XANES) spectra and W L_{3-} edge extended X-ray absorption fine structure (EXAFS) spectra. Based on those findings, we discussed the validity of the WO_x -modified Ti-HAp surface model, which was used in earlier reports of the literature.⁶⁾

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, $(\text{Ca}_{8.22}, \text{Ti}_{0.89}, \square_{0.89})(\text{PO}_4)_6(\text{OH})_2$, $\square$: 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 $[(\text{NH}_4)_{10}(\text{H}_2\text{W}_{12}\text{O}_{42}) \cdot 4\text{H}_2\text{O}$; 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 WO_x modification amount. The prepared samples were labeled as W-X, where X represents the number of procedure repetitions.

2.2 W $L_{1,3}$ -Edge X-ray absorption spectroscopy

We analyzed the XAFS spectra of W L_1 and L_3 edges to

ascertain the structure of WO_x cluster on Ti-HAp. The W L_1 -edge spectra were recorded in fluorescence mode at the BL14B2 beamline at SPring-8 (Hyogo, Japan) using a Si (111) monochromator. The W L_3 -edge spectra were measured in transmission mode at the BL5S1 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: WO_3 (Wako Pure Chemical Industries Ltd., Osaka, Japan), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (Kanto Chemical Co. Inc., Tokyo, Japan), WO_2 (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 packages¹¹⁾ (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 k^3 -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 WO_3 ¹²⁾ by calculation using the FEFF 6.0 code¹³⁾ implemented in the Demeter 0.9.26 software package.¹¹⁾

3. Results and discussion

The W species structure can be estimated from the energy gap of the split W L_3 -edge white line and the area of the pre-edge peak of W L_1 -edge XANES spectra.⁷⁾ For this reason, we conducted an analysis of W L_1 , L_3 -edge XANES spectra for WO_x -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 WO_2 , WO_3 , WO_x , WO_4 , and WO_6 . For the sake of clarity, the unit structure of W and O compounds (WO_4 and WO_6) are represented in italics.

3.1 W L_1 -edge XANES spectra

Figure 1 portrays W L_1 -edge XANES spectra of WO_x -modified Ti-HAps. The W L_1 -edge X-ray absorption is attributed to the electron transition from 2s orbitals to vacant levels. The pre-edge peak of W L_1 -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.⁷⁾ The deconvolution results are presented in Fig. S1. The spectra can be fitted within one Lorentz function (pre-edge peak) and one arctangent function.⁷⁾ The obtained pre-edge peak areas of samples are presented

Fig. 1. W L_1 -edge XANES spectra of WO_x -modified Ti-HAps, WO_3 , and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. The pale red area is the region of pre-edge peak.

Fig. 2. Pre-edge peak area of the W L_1 -edge XANES of WO_x -modified Ti-HAps, WO_3 , and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. W/Ti ratio in each WO_x -modified Ti-HAP sample was calculated from our earlier XPS results.⁶⁾

in **Fig. 2**. The amount of WO_x cluster in each WO_x -modified Ti-HAP sample was calculated from our earlier X-ray photoelectron spectroscopy (XPS) results,⁶⁾ showing that the amount of modified WO_x cluster increased with repetition of the impregnation–calcination process. The WO_x -modified Ti-HAps have a pre-edge peak area between WO_3 and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, which suggests the average structure of modified WO_x cluster is between the WO_6 and WO_4 structures.

3.2 W L_3 -edge XANES spectra

Figure 3 presents W L_3 -edge XANES spectra of WO_x -modified Ti-HAps. Various tungsten species were also measured for comparison. The W L_3 -edge X-ray absorption white line of transition metals is attributed to electronic transitions from the $2p_{3/2}$ orbital to vacant s and d orbitals of the metal.⁷⁾ Reportedly, the contribution of the

Fig. 3. W L_3 -edge XANES spectra of WO_x -modified Ti-HAps, WO_3 , $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, WO_2 , and metal W. The dashed vertical lines represent the white line edge energy of each sample, which was obtained from the maximum value of the first-order derivatives.

p–d transition in the L_3 -edge absorption white line is 50 times stronger than that of the p–s transition,¹⁴⁾ which means that the L_3 -edge white line mainly reflects the electron transition from the $2p_{3/2}$ to vacant d orbitals. The W L_3 -edge white line therefore mostly derives from electron transition from the $2p_{3/2}$ 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.¹⁵⁾ The white line edge energy, which was obtained from the maximum value of the first-order derivatives (dashed vertical lines in **Fig. 3**), was 10202.2 eV in W metal; it was 10202.9 eV in WO_2 , 10204.4 eV in WO_3 , and 10204.9 eV in $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. 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 WO_x cluster is mostly 6+, which is consistent with XPS results we obtained earlier.⁶⁾ However, closer inspection (**Fig. S2**) reveals that the white line peak shapes in the modified WO_x cluster samples resembled those of WO_3 and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, but they are not exactly the same. The results suggest that the WO_x cluster has a similar structure to those of WO_3 and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, although not exactly the same to either of them. Rather, the sample peaks seem to be the sums of the peaks of WO_3 and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, which means the WO_x cluster has a mixed polyhedral structure of WO_6 and WO_4 . 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 WO_x cluster change from WO_4 to a WO_6 structure with increase of the WO_x loading amount.¹⁰⁾

For further discussion, we specifically examined the W L_3 -edge XANES spectra of WO_3 and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$

Fig. 4. Deconvolution of W L_3 -edge XANES spectra of (a) WO_3 , (b) $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, (c) W-2, (d) W-5, and (e) W-9. Peak 1 and peak 2 are Lorentz functions deriving from the distorted octahedral structure (WO_6), whereas peak 3 and peak 4 are Lorentz functions deriving from the tetrahedral structure (WO_4).

presented in Fig. 3. Results show that WO_3 , which has a distorted octahedral WO_6 structure, exhibits a broad peak with an indistinct top, whereas $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, which has a tetrahedral WO_4 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 $2p_{3/2}$ to 5d level is separable into transitions of two kinds: $2p_{3/2}$ to t_{2g} (t_2) and $2p_{3/2}$ to e_g (e). The splitting energy of these transitions is related to the energy difference between t_{2g} (t_2) and e_g (e) orbitals. Structural distortion of the octahedral symmetry generally engenders a small splitting of the t_{2g} 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 WO_3 . On the other hand, because the energy difference of e and t_2 of tetrahedral structure is smaller than that of an octahedral and distorted octahedral structures,⁷⁾ one narrow peak was observed in $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$.

X-ray absorption of W L_3 -edge consists of electron transitions from $2p_{3/2}$ 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.⁷⁾ Based on these factors, the white line was deconvoluted. Results of the deconvolutions are shown in Fig. 4. In WO_3 and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, the spectra were fitted within two Lorentz functions (peak 1 and peak 2 for WO_3 , peak 3 and peak 4 for $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) 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 WO_3 was peak 1:peak 2 = 61:39, which is consistent with the orbital ratio of $t_{2g}:e_g = 3:2$. On the other hand, the peak area ratio in $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was

Table 1. Deconvolution results of W L_3 -edge XANES spectra of WO_x -modified Ti-HAps

	Content Ratio (%)	
	WO_6	WO_4
W-2	57	43
W-5	72	28
W-9	76	24

peak 3:peak 4 = 38:62, which is consistent with the orbital ratio of $e:t_2 = 2:3$. As described earlier, the average local structure of modified WO_x cluster was considered to be between the WO_6 and WO_4 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 WO_6 and WO_4 structures are contained in modified WO_x 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 WO_3 and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. The results are presented in Figs. 4(c)–4(e). Peak 1 and peak 2 derive from the distorted octahedral structure (WO_6), whereas peak 3 and peak 4 derive from the tetrahedral structure (WO_4). The samples were well fitted in the functions. From deconvolution of the spectra of those peaks, the content ratios between the WO_6 structure and WO_4 structure of the respective samples were calculated: they are shown in Table 1. Although 43 % were WO_4 structures in W-2, their proportions decreased with increased amounts of WO_x clusters. Only a quarter were contained in W-9.

3.3 W L_3 -edge EXAFS spectra

For detailed investigation of WO_x cluster local structures, W L_3 -edge EXAFS spectra were analyzed. The W

Fig. 5. (a) W L₃-edge EXAFS Spectra and (b) Fourier Transforms of WO_x-modified Ti-HAps, WO₃, and Na₂WO₄·2H₂O.

L₃-edge EXAFS spectra of the samples and their Fourier transforms are presented in Fig. 5. The peaks in the range of 1–2 Å are attributable to the W–O shell. Because WO₃ has distorted WO₆ 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).¹²⁾ However, Na₂WO₄·2H₂O has an undistorted WO₄ tetrahedron structure and has one intense peak at 1.4 Å. In WO_x-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).^{7),16),17)} Compared to W-2 and W-5, W-9 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 WO_x cluster loading amount. Curve-fitting analysis was conducted for the W–O shell to obtain structural parameters of the WO_x clusters. The coordination number (CN), bond length (*r*), Debye–Waller (σ^2), 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 WO_x cluster in W-2, its EXAFS oscillation S/N ratio is not good especially in high wavenumber region. Debye–Waller factor, σ^2 , is one of the terms in EXAFS equation and reflects the molecular structural and thermal disorder of samples. However, a slightly negative Debye–Waller factor was necessary to minimize the error of fit the result of W-2. Although this value of σ^2 is physically unrealistic, the data were included because they are meaningful for comparison with other samples. All WO_x-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 WO_x cluster. Among the samples, the total coordi-

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

sample	CN ^a	<i>r</i> ^b (Å)	σ^2 ^c (Å ²)	<i>R</i> ^d (%)
Na ₂ WO ₄ ·2H ₂ O	4.0	1.781	0.0014	1.15
WO ₃	4.0	1.770	0.0025	0.73
	2.0	2.180	0.0045	
W-2	2.2	1.770	–0.0020	2.11
	1.9	2.378	0.0187	
W-5	3.6	1.759	0.0022	0.58
	0.8	2.268	0.0027	
W-9	4.3	1.766	0.0039	2.23
	0.7	2.210	0.0006	

^aCN, coordination number; ^b*r*, bond distance; ^c σ^2 , Debye–Waller factor; ^d*R*, R-factor.

nation number is increased from 4 to 5 with increasing WO_x cluster loading amount, which means that the local structure of WO_x cluster is changed from WO₄ to WO₆. This result is consistent with that found through W L₃-edge XANES spectra deconvolution.

3.4 WO_x cluster local structure modified on a Ti-HAp surface

The W L₁–L₃- XAFS results suggest that WO_x cluster aggregates and the structure change gradually from tetrahedral to octahedral with increase of the WO_x cluster loading amount. From these results, details of the WO_x cluster structure can be discussed. Kitano et al.⁹⁾ reported that the WO_x cluster modified on Al₂O₃ surface has a two-dimensional monolayer structure. For this reason, we assume that WO_x monolayer is modified on the Ti-HAp surface. A transmission electron microscope (TEM) image in our earlier study⁶⁾ shows the WO_x cluster as nearly a circle. Therefore, for ease of exposition, we referred the bulk WO₃ crystal atomistic structure properties from the literature¹²⁾ and assumed that the WO_x cluster has a square-like structure. Because the WO_x cluster is not expected to

Fig. 6. A WO_x cluster model assuming two-dimensional square WO_x monolayer domains were formed and each W has a bond with O atom of Ti-HAp surface. (a) WO_x cluster model of the number of W (n) = 1, 4, 9. The color code is red for O and yellow for W. It is represented using a VESTA program.¹⁸⁾ (b) The relation between n and mean coordination number of W (mean CN) in the assuming model including the mean CN of WO_x-modified Ti-HAps obtained in Table 2. Grey points are calculated mean CN in every n , assuming the cluster structure is close to a square structure, even $n \neq 1^2, 2^2, 3^2, \dots$

be detached from the Ti-HAp surface under room temperature conditions, we inferred that each W in the WO_x cluster has a bond with an O atom of the Ti-HAp surface. It also needs to meet charge compensation. Therefore, overall $4n$ O atoms surround n W atoms in the WO_x cluster. Assuming that the WO_x 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_x clusters as modified in the form of a square structure [Fig. 6(a)]. The structures are represented using the VESTA program.¹⁸⁾ The value of y can be found using the following equation.

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

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_x cluster based on Eq. (2). The grey points presented in the figure include the assumption of mean CN when the $n \neq 1^2, 2^2, 3^2, \dots$ (i.e. WO_x 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 L₃-EXAFS spectra to Fig. 6(b) shows that the WO_x 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.⁶⁾ We should mention that the modified WO_x 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_x cluster structure.

It is meaningful to discuss structural change with increasing WO_x amounts using the model.

From the discussion presented above, the possible WO_x cluster local structure modified on the Ti-HAp surface is presented in Fig. 7. When the modified WO_x amount is low, the WO_x cluster structure consists mostly of a single WO₄ tetrahedron. The WO_x 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_x cluster makes bonds with Ca ion, its bond strength will be weak; the WO_x can detach easily from Ca. For this reason, the WO_x cluster is likely to bind with surficial Ti or P in Ti-HAp. When the amount of WO_x cluster is increased, the WO_x 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 WO₆ octahedron. The structure represented herein supports the computational model we explained in the report of an earlier study,⁶⁾ in which report we assumed that a modified WO_x cluster contains a low-coordination structure. Therefore, these results suggest that, by depositing a WO_x cluster on the Ti-HAp surface, its electronic structure became different from that of doped W or bulk WO₃. 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_x cluster modified on a Ti-HAp surface was analyzed using XAFS measurements. The W L₁- and L₃-XANES spectra showed that WO_x clusters include both WO₄ and WO₆ structures and showed that the WO₆ amount was increased concomitantly with increasing WO_x cluster amounts. Analyses of W L₃-EXAFS spectra demonstrated that the coordination number of W surrounded by O was increased by increasing the modified WO_x cluster loading amount, indicating that the local coordination structure of WO_x cluster changed gradually

Fig. 7. Possible structures of WO_x 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.

from tetrahedral to octahedral structure. The number of W–O–W bonds was increased concomitantly with increase of the WO_x amount, which implied that the WO_x cluster became larger through repeated impregnation–calcination processing. By 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 results presented herein support the computational model described in earlier reports,⁶⁾ in which the study based on the assumption that a modified WO_x cluster includes a low coordination structure. By depositing WO_x clusters on the Ti-HAP surface, its electronic structure became different from doped W or bulk WO_3 . Therefore a suitable electron transition path was created from Ti 3d to W 5d, showing high photocatalytic activity.

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