



Surface changes and radical formation on hydroxyapatite by UV irradiation for inducing photocatalytic activation

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Abstract

Surface changes of stoichiometric hydroxyapatite (HAp) by UV irradiation and radical formation were studied to make clear the factors of the photo-induced catalytic behavior. From the FTIR and XPS studies it was shown that the surface of HAp after heat treatment at 200 °C (HAp 200) became electroconductive by UV irradiation, and the UV irradiation caused the changes of the surface PO₄ group, probably the formation of oxygen vacancy. From the result of the ESR spectrum obtained by subtracting the spectrum of HAp 200 before UV irradiation from that after UV irradiation, the signal at $g = 2.0030$ was assigned to the electron trapped on vacancy. It was concluded that the appearance of the electron trapped on vacancy, in HAp 200 under UV irradiation, must cause the formation of the very active O₂^{•-} species.

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1. Introduction

Hydroxyapatite (HAp) is mainly used in the fields of bioceramics, absorbent for chromatography. Catalytic reactions of organic compounds, such as alcohol [1,2], 1-butene [3], and cyclohexanone oxime [4], and chlorobenzene [5,6] using HAp are also well known. We have reported on oxidative decomposition of gaseous chlorinated organic compounds, such as trichloroethylene and chlorobenzene, over calcium-deficient HAp [7–10].

On the other hand, Monma et al. [11] investigated the radical formation on non-stoichiometric HAp above 473 K, and the radical was assumed to be due to electrons trapped in a strained structure. Recently, Kanai and co-workers [12,13] have reported on the activation of stoichiometric HAp by heat treatment or UV irradiation and on the formation of radical species,

such as O₃⁻ species from UV irradiation. ESR studies of radical species in X-ray or γ -ray-irradiated HAp were also reported by Moens et al. [14,16] and Vanhaelewyn et al. [15], Schramm and Rossi [17,18] and Murata et al. [19]. However, the mechanism for radical formation on HAp under UV irradiation was not clear and there are few reports on the relation between the changes of HAp surface and radical formation. The radical formation on HAp under UV irradiation must be different from that under the higher energy irradiation, such as X-ray or γ -ray. We have reported on thermal behavior of HAp in structural and spectrophotometric characteristics [20] and photocatalytic activity of HAp for methyl mercaptane [21]. It was concluded that the radical species formed by heat treatment or UV irradiation was O₂^{•-} (superoxide anion radical) species in these papers. The photocatalytic activity of HAp after treatment at 200 °C (HAp 200) for methyl mercaptane by UV irradiation was different from that of HAp after treatment at 1150 °C

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(HAp 1150). The radical species formed on HAp 200 by UV irradiation was very active for the decomposition of methyl mercaptane, while HAp 1150 was inactive. The reason of the difference was not clear in our previous work.

In this paper, the author describe on the changes of HAp surface by UV irradiation and the mechanism for the formation of active radical species.

2. Experimental

HAp used was prepared from $\text{Ca}(\text{OH})_2$ and H_3PO_4 as starting materials [21]. The stoichiometric amounts of H_3PO_4 solution was added dropwise to a $\text{Ca}(\text{OH})_2$ slurry. Stoichiometric HAp was prepared by keeping the slurry at pH 7.0 and by aging for 48 h at room temperature. The resulting solid was dried at 100°C for 24 h. Heat treatment for the solid was carried out at 200 and 1150°C for 1 h in air condition in an electric furnace. Ca/P molar ratio of the solid was 1.67 by chemical analysis.

Electron spin resonance (ESR) spectra were recorded on a JEOL JES-FA200 spectrometer at 77 K. The ESR spectrometry conditions at 77 K were as follows: magnetic field: 323.3 mT; power: 4 mW, 9.06 GHz; sweep time: 30 s; modulation: 100 kHz, 0.35 mT; amplitude: 100; time constant: 0.03 s.

Fourier transform infrared (FTIR) spectra were measured with a JASCO Hershel FTIR-480 equipped with an infrared microscope Irtron IRT-30.

X-ray photoelectron spectra (XPS) were measured with a JEOL JPS-9000 MX using an X-ray power of 200 W (Mg $\text{K}\alpha$). C1s at 284.5 eV was used as a reference.

ESR, XPS and FTIR spectra of the HAp samples were measured before and immediately after UV irradiation for 1 h in air. The UV lamp used was a Toshiba Lightec GLS-6T (254 nm, 6 W), and the distance between the lamp and the sample was 1 cm.

3. Results and discussion

3.1. FTIR study before and after UV irradiation

FTIR spectra of HAp 200 before and after UV irradiation for 1 h are shown in Fig. 1. The absorbance

Table 1
Absorbance ratio of FTIR spectra in HAp 200 sample

Group	Absorbance ratio	
	Before UV irradiation	After UV irradiation
OH ($3570\text{ cm}^{-1}/960\text{ cm}^{-1}$)	0.82	0.83
PO ₄ ($1030\text{ cm}^{-1}/960\text{ cm}^{-1}$)	31.9	26.8

Irradiation time: 1 h; the peak at 960 cm^{-1} was a reference peak.

ratio of OH (3570 cm^{-1}) and PO₄ (1030 cm^{-1} , ν_3) to the reference peak of 960 cm^{-1} (PO₄, ν_1) was also shown in Table 1. The reason for the choice of the peak of 960 cm^{-1} as a reference peak was that the absorbance of the peak was constant before and after UV irradiation. The shoulder peak at 1090 cm^{-1} corresponds to ν_3 of PO₄. The peak due to PO₄ (ν_3) at 1030 cm^{-1} decreased considerably with UV irradiation, while the band due to apatitic OH group at 3570 cm^{-1} scarcely varied before and after UV irradiation. The facts show that one portion of surface PO₄ group would change by UV irradiation, though apatitic OH in HAp scarcely changed. The electron state of surface PO₄ group on HAp may contribute the catalytic activation as described on phosphorus catalyst by Vadrine [23]. These results are different from the results that active species were labile O⁻ species which are generated from OH splitting by light irradiation as reported by Kanai et al. [13]. It was considered that the O₂^{•-} species would be generated on HAp 200 in connection with the changes of PO₄ group from our FTIR and ESR studies.

3.2. XPS study and surface change by UV irradiation

Surface characterization of HAp by XPS was reported by Lu et al. [24]. However, changes in UV-irradiated HAp were not studied. In order to investigate the surface changes of HAp 200 by UV irradiation, the XPS were measured repeatedly before and after UV irradiation. The results are shown in Table 2 and Figs. 2 and 3.

Each binding energy of Ca(Ca 2p_{3/2}), P (P 2p) and O (O 1s) shifted to lower energy level of 0.05–0.10 eV after UV irradiation and returned nearly to each former level after standing for 1 h in dark place. The facts show that the surface of the HAp sample has a negative

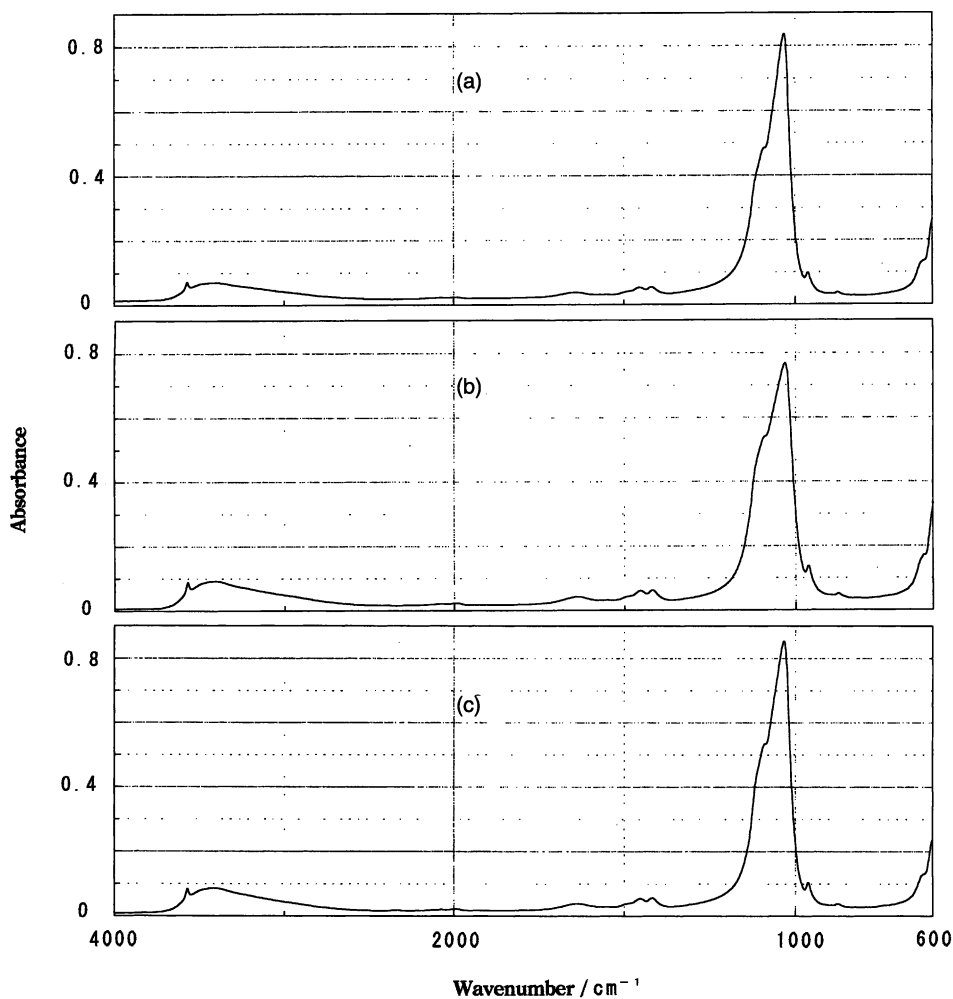


Fig. 1. FTIR spectra of HAp200: (a) before UV irradiation; (b) after UV irradiation; and (c) after standing for 1 h after UV irradiation.

Table 2
XPS data of HAp 200 before and after UV irradiation

Condition	Ca 2p _{3/2}			P 2p			O 1s		
	BE (eV)	HW (eV)	IT (cps)	BE (eV)	HW (eV)	IT (cps)	BE (eV)	HW (eV)	IT (cps)
A	347.11	1.77	25280	133.03	2.03	5535	531.21	1.91	43363
B	347.01	1.67	27102	132.84	1.96	5742	531.13	1.84	46548
C	347.12	1.77	25818	132.91	2.03	5799	531.29	1.93	43117
D	346.98	1.72	26856	132.85	2.02	5823	531.14	1.84	45903
E	347.12	1.81	26270	132.98	2.05	5815	531.21	1.92	45481

A: before irradiation; B: after irradiation for 1 h; C: after standing for 1 h in dark place after irradiation; D: after re-irradiation for 1 h; E: after re-standing for 1 h in dark place after re-irradiation. BE: binding energy; HW: half width; IT: peak intensity.

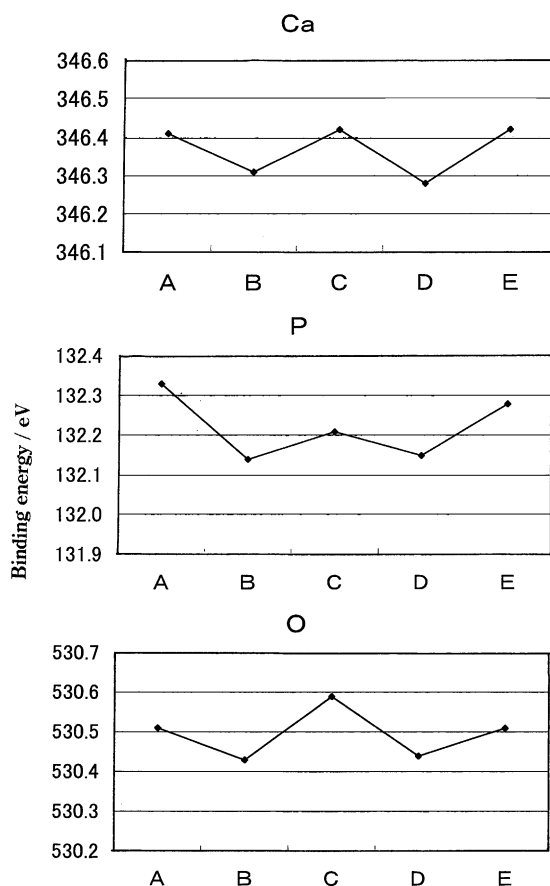


Fig. 2. Changes of binding energy on the XPS measurement of HAp200 before and after UV irradiation: (A) before UV irradiation; (B) after UV irradiation; (C) after standing for 1 h after UV irradiation; (D) after UV re-irradiation; and (E) after standing for 1 h after UV re-irradiation.

electric charge by UV irradiation, that is, the surface of the HAp sample turns slightly electroconductive. This result would prove indirectly the formation of radical species on HAp 200 by UV irradiation as described in the above ESR study. Furthermore, it was shown that these phenomena on HAp 200 were reversible by UV irradiation or not. This supports the generation and degradation of active species on HAp 200 in our ESR studies.

Each half width of Ca, P and O peak narrowed slightly after UV irradiation and returned nearly to the former level after standing for 1 h as shown in Table 2. It was assumed that the unification of electric charge of each element occurred on the surface of the

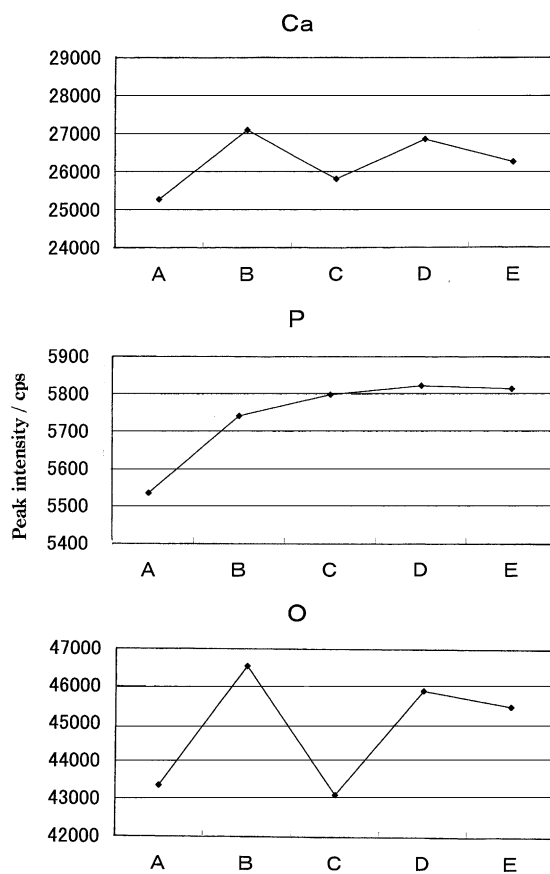


Fig. 3. Changes of peak intensity on the XPS measurement of HAp200 before and after UV irradiation: (A) before UV irradiation; (B) after UV irradiation; (C) after standing for 1 h after UV irradiation; (D) after UV re-irradiation; and (E) after standing for 1 h after UV re-irradiation.

HAp sample by UV irradiation from this result. The unification of electric charge of each element would be related to the appearance of a conducting surface.

The peak intensity of Ca or O increased with UV irradiation and returned nearly to the former level without irradiation. On the other hand, the peak intensity of P increased gradually in the same experimental conditions. These facts suggest that the bonding of P, that is, one portion of PO_4 group on the surface of HAp 200 might change under UV irradiation. The results of these XPS data correspond to those of the FTIR studies very well. Consequently, it is concluded that the UV irradiation causes the changes of PO_4 group on the surface of HAp 200, probably the changes with

the formation of oxygen vacancy, though the apatitic OH group scarcely changes.

3.3. Radical formation by ESR study

In our previous work [21], it was recognized that the photo-induced catalytic activities of HAp for methyl mercaptane were different at the pre-heating

temperatures. That is, HAp 200 was very active under UV irradiation, though HAp 1150 was inactive. ESR studies were performed to investigate the factors of the difference on activity between HAp200 and HAp 1150. It was shown that the ESR signals assigned as inactive $O_2^{\bullet-}$ species appeared on HAp 1150 in the previous report [20]. ESR spectra of the same HAp sample were measured after standing for over

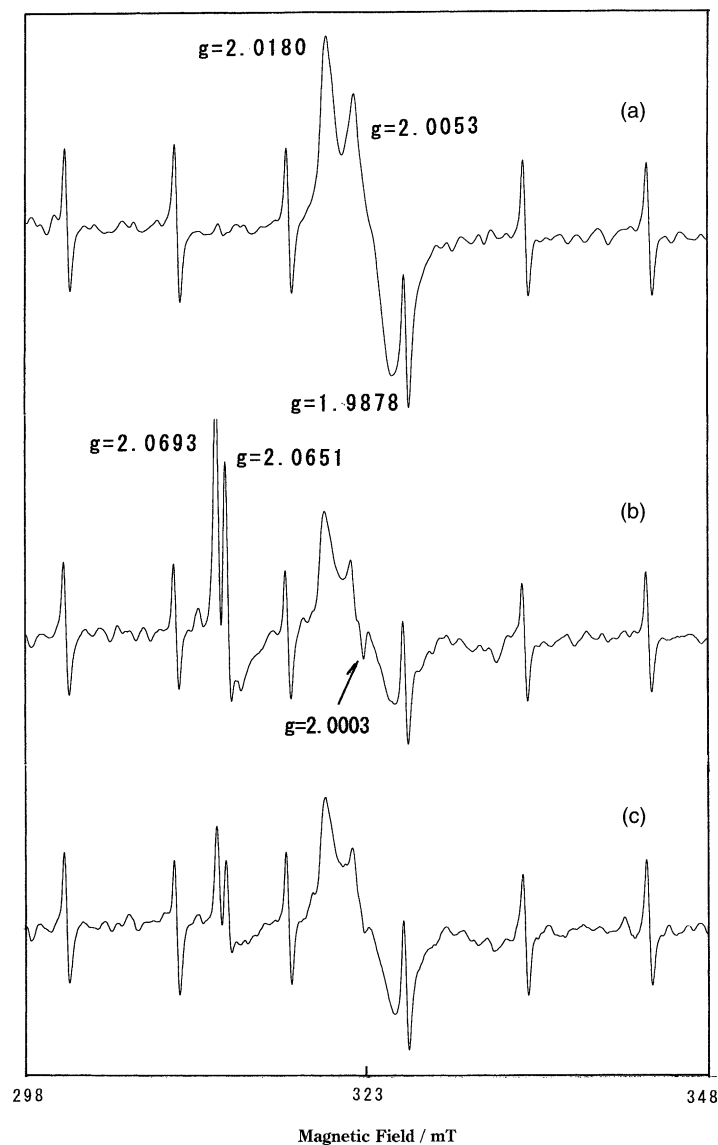


Fig. 4. ESR spectra of HAp1150 at 77 K: (a) before UV irradiation; (b) after UV irradiation; and (c) after standing for 60 min after UV irradiation.

3 months are shown in Fig. 4a. The signals appeared similarly as those measured before standing. The result shows that the radical species are very stable. Three g values ($g_1 = 2.0180$, $g_2 = 2.0053$, $g_3 = 1.9878$) were assigned as stable $\text{O}_2^{\bullet-}$ species as reported by Kanai et al. [13]. The signals of the radical species on HAp 1150 decreased slightly by UV irradiation and maintained almost constant after standing for 1 h in

dark place in air as shown in Fig. 4. The results show that the $\text{O}_2^{\bullet-}$ species were slightly influenced by UV irradiation, but maintained the stable and inactive state. The inactivity of HAp 1150 for methyl mercaptane by UV irradiation, as described in previous paper [21], corresponds to the conclusion. The signals at regular intervals in Fig. 4 are assigned as the signals of small amounts of Mn^{2+} in HAp 1150. The signals

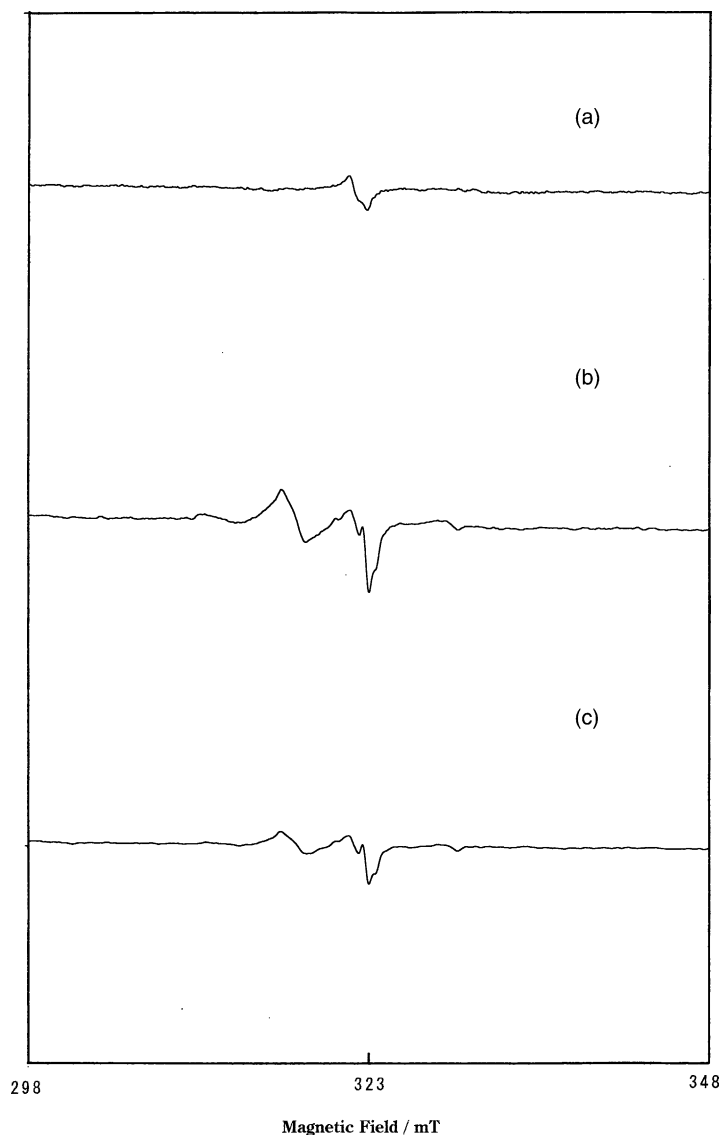


Fig. 5. ESR spectra of HAp200 at 77 K: (a) before UV irradiation; (b) after UV irradiation; and (c) after standing for 60 min after UV irradiation.

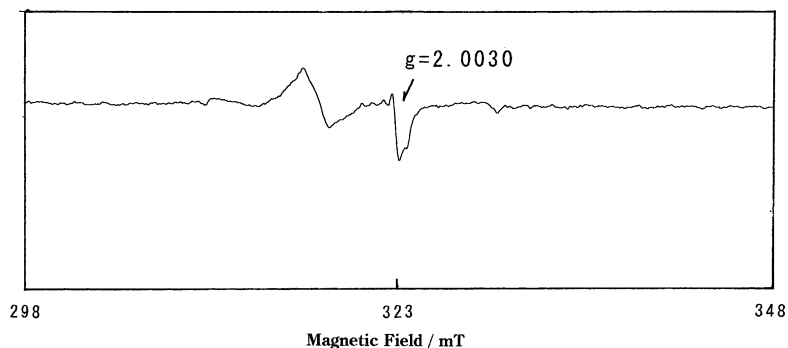


Fig. 6. ESR spectrum subtracted the spectrum of HAp200 before UV irradiation from the spectrum after UV irradiation.

of HAp 1150 scarcely changed before and after UV irradiation. Two sharp peaks at $g = 2.0693$ and 2.0651 appeared after UV irradiation were attributed to be the peaks of O^- radical formed in HAp sample as reported by Moens et al. [16]. The O^- radical on HAp 1150 must be also inactive for the decomposition of organic compounds from the results of our previous study [21].

Fig. 5 shows the ESR spectra of HAp 200 before and after UV irradiation for 1 h. We have already reported that the characteristic signals for the DMPO adduct of $O_2^{\bullet-}$ appeared on HAp 200 by the method with spin trapping reagent after UV irradiation [21]. That is, it was recognized that active $O_2^{\bullet-}$ species produced on HAp 200 by UV irradiation. The signals at $g = 2.0425$, 2.0347 and 2.0305 were unknown in Fig. 5. The spectrum obtained by subtracting the spectrum of HAp 200 before UV irradiation from the spectrum after UV irradiation is shown in Fig. 6. The signal at $g = 2.0030$, probably singlet, was assigned to the electron trapped on vacancy as well as the signal reported on calcium-deficient HAp after heat treatment at 520°C by Monma et al. [11]. The signal decreased after standing for 1 h in dark place. On the other hand, the signal corresponding to the trapped electron did not appear on HAp 1150 after UV irradiation.

Consequently, it was considered that the vacancies were formed on HAp 200 by UV irradiation and the electrons were trapped on the vacancies. Then, the activation of oxygen due to electron trapped by vacancy must occurred on HAp 200, based on the literature [22] and our experimental data. The activation would

be very important for photocatalytic oxidation. It was concluded that organic compounds, such as methyl mercaptane, were decomposed by the active $O_2^{\bullet-}$ species due to the electron trapped on vacancy in HAp 200 under UV irradiation.

3.4. Activation mechanism of photo-induced excited HAp

From the studies as described above and the results of the previous paper [21], it was shown that the surface of the HAp 200 was slightly changed by UV irradiation and the active $O_2^{\bullet-}$ species generated on the material. The changes of surface PO_4 group and the generation of trapped electron suggest the appearance of oxygen vacancy by UV irradiation. The activation of oxygen due to the electron trapped on the vacancy in HAp 200 would occur, followed by the formation of the labile $O_2^{\bullet-}$ species. The radicals must be very active and able to oxidize the organic compounds, such as methyl mercaptane as reported in our previous paper [21]. These phenomena on the HAp 200 would be due to photo-induced electronic excitation and similar to the phenomena on the formation of the electron trapped on oxygen vacancy in the plasma-treated TiO_2 [22].

On the other hand, it was shown that the stable $O_2^{\bullet-}$ species existed on HAp 1150 even without UV irradiation. The species would interact strongly with the surrounding matrix and the trapped electron scarcely generated by UV irradiation. Therefore, HAp 1150 would be inactive for surrounding organic compounds under UV irradiation.

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