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Visible light responsive vanadium-substituted hydroxyapatite photocatalysts

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ABSTRACT

Hydroxyapatite (HAp) has a potential to be an excellent photocatalyst because of its strong adsorption ability for organic substances. However, the HAp has a poor photocatalytic ability without modification. We firstly revealed that after substitution of a part of Ca ions by V ions in HAp lattice (V:HAp), visible light driven photocatalytic activity appeared. The substituted V ions were pentavalent at bivalent Ca sites, causing the introduction of amounts of Ca defects in the HAp lattice to keep electric neutrality. In spite of any amount of the Ca defects, the HAp structure of V:HAp was kept after calcination at 400 °C. Then, the photocatalytic activity was increased with V content. The visible light response of V:HAp would be owing to the generation of an acceptor level due to V ions of which the redox potential was enough negative to reduce O_2 to H_2O_2 via two electron process.

1. Introduction

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) has a strong adsorption ability against organic substances such as proteins, amino acids and virus [1–3]. To develop photocatalytic materials, the adsorption ability is one of the most important factors because adsorption of target substances is first step before photocatalytic decomposition [4]. Therefore HAp has a potential as an excellent photocatalyst in the aspect of the strong adsorption ability. The energy bandgap of HAp was estimated to be 5–6 eV using density-functional theory [5]. Therefore, only under a deep UV light ($\lambda = 254$ nm), its photocatalytic decomposition of organic substances such as methyl mercaptane and dimethyl proceeded [6–8]. To response longer-wavelength light, it was reported that by substitution of a part of Ca^{2+} at a columnar site by Ti^{4+}, its bandgap was decreased to be 3.65 because hybridized band of Ti 3d and O 2p orbitals was formed within the wide bandgap of HAp [9]. Then the titanium-substituted HAp (Ti:HAp, $Ti_xCa_{10-x}(PO_4)_6(OH)_2$) showed a photocatalytic ability under near UV light ($\lambda \sim 350$ nm) [9–12]. However in terms of practical use, visible light driven photocatalytic ability has been required because sun light and interior lamp consist mainly of visible light. Up to now, we examined the grafting effect of Cu^{2+} on the Ti:HAp on development of visible light response [13] because in the case of TiO_2 which is a representative UV responsive photocatalyst, a visible light driven photocatalytic ability appeared after grafting of Cu^{2+}. This visible light response was due to the direct electron excitation from the TiO_2 valence band to the grafted Cu^{2+} [14,15]. However, for the Ti:HAp, visible-light driven photocatalytic ability did not appear even after grafting of Cu^{2+} because electrons at valence band was hardly photoexcited to the grafted Cu^{2+}, probably owing to the covalent character of atoms which constitute of HAp valence band unlike ionic character of that for TiO_2. Therefore, to develop visible light response to HAp based photocatalysts, substitution by elements other than Ti^{4+} is indispensable. Previously, it was reported that by co-substitution of Cr^{3+} and Ti^{4+} at Ca^{2+} sites, the visible light driven photocatalytic activity appeared [16]. However, this visible light response was owing to d–d transition of the doped Cr^{3+}, which was weak adsorption of visible light. To absorb sufficiently visible light, it is required that by forming new energy levels owing to doped elements within the bandgap of HAp, interband excitation from HAp valence band to the new band is induced.

In this work, we firstly revealed that vanadium-substituted HAp (V:HAp, $V_xCa_{10-x}(PO_4)_6(OH)_2$) showed visible light driven photocatalytic activity owing to interband excitation from HAp valence band to the energy band formed by V^{5+}.

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2. Experimental

V:HAp was prepared by a hydrothermal synthesis method. Ca $(NO_3)_2{\cdot}4H_2O$, VCl_3 and H_3PO_4 were dissolved in 75 mL distilled water, and then the pH of the solution was adjusted to 9 by adding NH_4OH solution. In the preparation, total amount of Ca and V was fixed at 0.015 mol and that of H_3PO_4 was fixed at 0.009 mol, and V content defined by molar fraction, V/(Ca + V), was varied to 0, 1, 3, 5, 10 mol%. The resultant solution was aged in a Teflon lined autoclave at 100 °C for 6 h. The precipitate was dried at 70 °C in air, followed by calcination at 400 or 650 °C for 1 h in air. The obtained samples were pale yellow and consisted of agglomerated particles of 100–200 nm-secondly particle size as shown in the Supporting information (Fig. S1).

Crystalline phases of the obtained samples were evaluated using an X-ray diffractometer (Mac Science, M03X-HF22) and optical absorption spectra were measured using a UV–vis spectrophotometer (Shimadzu, UV-3150) equipped with an integration sphere (Shimadzu, ISR-3100). X-ray photo electron spectroscopy (XPS) was employed with a spectrometer (JEOL, JPS-9010TR) using a monochromatic Mg Kα source.

Photocatalytic activities were measured for the acetaldehyde as follows. Photocatalyst powder of 0.1 g was spread on a Petri dish of 4 cm diameter and then the dish was placed in the circulated reactor with mixed gas of $O_2/N_2 = 1{:}4$. The acetaldehyde gas of 50 μL and water of 5 μL were injected into the reactor. The dish placed in the reactor was irradiated by LEDs of λ = 470 nm at the intensity of 20 mW/cm^2, and the amount of generated CO_2 was monitored by a gas analyzer (LI-COR, LI-840) equipped in the circulation reactor system.

The generation of O_2^- was observed by using a luminol chemiluminescence probe method [17]. Photocatalyst of 15 mg was added in 0.01 M NaOH solution of 3.5 mL in a quartz cell (1 cm × 1 cm) and then the suspension was irradiated by a set of LED of λ = 470 nm or λ = 365 nm. After the irradiation, 50 μL of 7 mM luminol solution was immediately added in the suspension. The chemiluminescence intensity was measured using an apparatus with a Peltier-cooled photon-counter head (Hamamatsu Photonics, H7421).

For the measurements of H_2O_2, the photocatalyst suspension was irradiated by the LED and then was kept in dark to eliminate O_2^-. 50 μL of 7 mM luminol solution was added in the suspension and then the suspension was kept in dark for 10 min. 50 μL of hemoglobin (Hb) solution was added in the suspension and then the chemiluminescence intensity was measured. To convert the chemiluminescence intensities to the absolute concentration of O_2^- and H_2O_2, the apparatus factor was calculated from the experiment where all luminol molecules are consumed for the reaction with an excess amount of H_2O_2. From the apparatus factor, the observed chemiluminescence intensity can be converted to H_2O_2 concentration.

3. Results and discussion

Fig. 1 shows XRD patterns of obtained samples with different V contents. Before calcination, all samples in which vanadium contents were 1, 3, 5, and 10% showed a single phase of HAp structure (data not shown). After calcination at 400 °C, the HAp structures were all kept. With V contents, diffraction peaks were broadened, indicating that vanadium ions were substituted in the HAp structure. Lattice parameters *a* and *c* are shown in Fig. 2. Both lattice parameters were irregularly changed, indicating that one-to-one substitution of Ca to V ions did not occur because change of the lattice parameters did not obey the Vegard's law. Then lattice parameter *a* of V:HAps became larger than the bare HAp. After calcination at 650 °C, at V contents of 1 and 3%, each diffraction peak became sharp, indicating the increase of the crystallinity by the calcination at higher temperature. When V contents were 5 and 10%, their HAp structures were decomposed into $Ca_3(PO_4)_2$ and V_2O_5. Therefore, V:HAp was metastable compared to Ti:HAp for which HAp structure was kept after calcination at 650 °C even at Ti content of 10%.

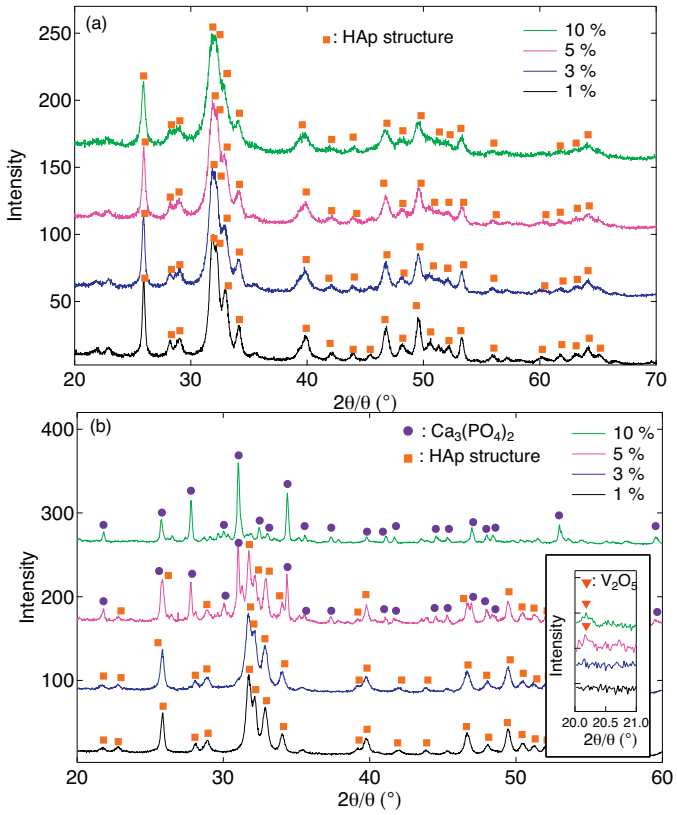

Fig. 1. XRD patterns of V:HAps with different V contents after calcination at (a) 400 °C and (b) 650 °C.

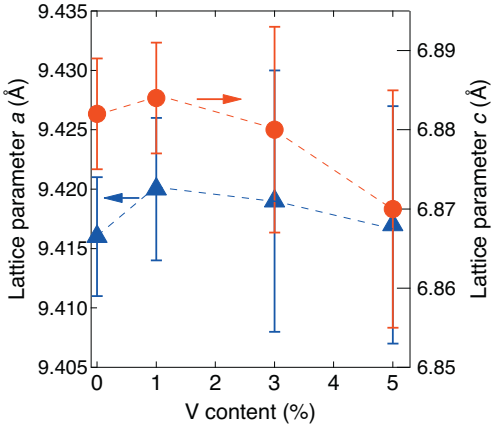

Fig. 2. Lattice parameters *a* and *c* of V:HAps with different V contents after calcination at 400 °C. Error bars show estimated standard deviation obtained by calculation through least-squares method.

Fig. 3 shows $V2p_{3/2}$ XPS spectra of the V:HAps. The $V2p_{3/2}$ spectrum of the sample before calcination was mainly located at 517.2 eV in binding energy with a shoulder at 515.8 eV, which correspond to binding energies for V^{5+} and V^{4+}, respectively [18,19]. On the other hand, when the sample was calcined at 400 and 650 °C, the shoulder of the 517.2 eV peak disappeared. This means