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Article / Book Information

題目(和文)	MoOxで修飾したTiドープヒドロキシアパタイトの作製と光触媒活性
Title(English)	Preparation and photocatalytic activity of MoOx-modified titanium-doped hydroxyapatite
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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In the 1st chapter, fundamental backgrounds of titanium-doped hydroxyapatite (Ti-HAp, $(Ca_{10-2x}, Ti_x, \square_x)(PO_4)_6(OH)_2$, □: defect in Ca site) are mentioned. Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) is a main component of biological hard tissue because it has high affinity against proteins. The Ca ion in HAp structure can be exchanged easily with other cations. Wakamura *et al*. exchanged Ca ions in HAp with Ti ions. A hybridized band of Ti 3d and O 2p orbitals is created between the bandgap of HAp. Then, Ti-HAp exhibits photocatalytic activity under UV illumination while retaining surface chemical properties of HAp.

However, the photocatalytic activity of Ti-HAp is restricted because the maximum substitutable Ti amount is limited at ca. 10 mol% of Ca to retain HAp structure. Therefore, the primary photocatalytic activity of Ti-HAp is inferior to that of TiO_2. The high photocatalytic activity of Ti-HAp against various organic compounds is attributable to its great adsorption capability on their surface. Although several attempts have been conducted to enhance the primary photocatalytic activity of Ti-HAp by surface modification (such as Cu) or cation doping, their outcomes fell short of expectations.

The objective of this study is to improve photocatalytic activity of Ti-HAp. The strategy that we used in this study is surface modification. First, we tried with Fe-modification in 2nd chapter but it did not work well. Then, we changed surface modification technique to MoO_x-modification in 3rd and 4th chapters because MoO_4^{2-} is tetrahedral oxoanion that is similar in many respects to PO_4^{3-}. Although ion exchange between MoO_4^{2-} and PO_4^{3-} in Ti-HAp is expected to be difficult because of their size differences, MoO_4^{2-} might adsorb onto the surface Ca or Ti ion, where it might affect the charge transfer of the material. Then we examined the photocatalytic activity under UV illumination and discusses the role of Mo-modification in photocatalytic activity.

In the 2nd chapter, Fe-modification techniques, which successfully provided visible light photocatalytic activity under visible illumination on TiO_2 via interfacial charge transfer (IFCT), have been applied to Ti-HAp. Their visible light photocatalytic activities were evaluated by decomposition of gaseous IPA. However, Fe-modified Ti-HAp did not exhibit photocatalytic activity under visible illumination. The direct electron transfer from the valence band to Fe cluster via IFCT is insufficient because the bonding nature of the valence band of Ti-HAp is different from TiO_2.

In the 3rd chapter, Ti-HAp powders were modified with a $CaMoO_4$ aqueous solution. Their photocatalytic activity under UV illumination were evaluated by decomposition of gaseous IPA. After Mo-modification, the crystal structure, morphology, light absorption, and specific surface area were almost identical. Small cluster (ca. 1–2 nm) were observed on the surface of MoO_x-modified Ti-HAp. Base on the starting materials, the cluster can be either $CaMoO_4$ or MoO_x. Moreover, the Mo amounts were limited due to the solubility of MoO_x in water. The photocatalytic activity of MoO_x-modified Ti-HAp increased up to about nine times compared to that of bare Ti-HAp. From the density functional theory (DFT) calculation, it indicated that MoO_4^{2-} doping into Ti-HAp structure plays no important role for activity increase. Results of ESR and PL analysis elucidate that the electron transfer from Ti 3d band to MoO_x (Mo^{n+} ($n < 6$)) or Mo metallic cluster via wavefunction hybridization between Ti 3d and Mo 4d orbitals can suppress the recombination of photoinduced electron and hole pairs.

In the 4th chapter, Ti-HAp powder were modified with an ethanol solution of molybdenyl acetylacetonate using chemisorption calcination cycle (CCC) technique, which provides metal oxide cluster on the sample surface. By using CCC technique, we can modify Ti-HAp with MoO_x clusters and can adjust Mo amount on the Ti-HAp surface. Although the crystal structure, morphology, light absorption, and specific surface area were almost identical, the clusters from CCC technique were smaller and had higher distribution compared to that of MoO_x-modified Ti-HAp by using $CaMoO_4$ solution. The photocatalytic activity increased concomitantly with increasing Mo concentration until 0.72 mol% against P; then it decreased considerably. Results of ESR and PL analysis suggest that the electron transfer from Ti-hybridized band to MoO_x clusters leads to charge separation of the photoinduced electron and hole pairs. Results were similar for both MoO_x-modification techniques: the Mo state of MoO_x-modified Ti-HAp by using $CaMoO_4$ solution was also MoO_x. The differences were size and distribution of the clusters.

In the 5th chapter, the overall content from chapter 2, 3, and 4 were summarized. The surface modification with oxide cluster provides remarkable improvement of the photocatalytic activity of Ti-HAp. Based on the DFT calculation, the oxide cluster should have energy level located between Ti-hybridized band and the valence band (hopefully slightly lower than Ti-hybridized band) and have compatible wavefunction hybridization with Ti 3d orbitals. These are important requirements for the effective oxide cluster modification. The content of this research paves the way to development of Ti-HAp with high photocatalytic performance.