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Chapter 7

# Evaluation of the Role of Hydroxyapatite in $TiO_2$/Hydroxyapatite Photocatalytic Materials

Linh Nguyen Thi Truc, Seungbum Hong and Kwangsoo No

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**Abstract**

The $TiO_2$/hydroxyapatite (HAp) composite has attracted much attention as a photocatalyst for pollution treatment in water or air because this composite can improve the properties of pure $TiO_2$ including a low efficiency, narrow light response range, low adsorption capacity for hydrophobic contaminants, and difficult recovery of $TiO_2$ particles after using in Aquarius environment. To obtain the best composite containing the two components including $TiO_2$ and HAp, the role of HAp in $TiO_2$/hydroxyapatite photocatalytic material should be analyzed and evaluated. This chapter will significantly present a review of the role of HAp in the $TiO_2$/hydroxyapatite composite including the adsorption ability of contaminations and the promoted impacts of HAp component.

**Keywords:** hydroxyapatite, $TiO_2$, photocatalytic, absorption, bandgap

## 1. Introduction

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) is one of the most usual forms of calcium phosphate and has the similar chemical composition to the mineral phase of bone tissues. Thus, HAp has attracted the interest of the scientific community in the medicine field, material science, and tissue engineering areas in many years. However, due to the special characteristics of this material, HAp is also studied for various applications including fluorescent lamps, fuel cells, and adsorption of harmful metals, as well as catalysts [1]. $TiO_2$ material was concerned almost 48 years ago. For the first time in 1969, the possibility of solar photoelectrolysis of $TiO_2$ was demonstrated; the powdered $TiO_2$ was studied in the 1980s and $TiO_2$ film photocatalysis

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in the 1990s [2]. $TiO_2$ photocatalysis (in particles or films) has gained much attention because the material has high stability, low cost, and nontoxicity and can be easily fabricated by many processes including precipitation, hydrothermal, sol-gel, plasma, etc. The research on $TiO_2$/hydroxyapatite photocatalytic materials may derive from researches on $TiO_2$/hydroxyapatite composites in medical industry. To achieve biocompatibility, osteoconduction, and osseointegration, the surface of titanium or its alloy, which is used as a permanent implant material, must be modified by developing hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) coating on the surface [3–9]. By inserting $TiO_2$ inner layer between HAp coating and Ti substrate, the adhesion strength of the coating and the substrate increases [10]. The addition of $TiO_2$ inner layer is expected to reduce a thermal expansion mismatch of the layers, to improve the bonding strength between the HAp layer and Ti substrate, to prevent the corrosion of the Ti substrate, as well as to obtain an abundance of surface hydroxyl and superoxide radical groups, sequentially, to achieve a surface free of cracks and a high adhesion of the modified surface to the substrate [7, 11–13]. The reactions of photocatalysis occur on the surface of $TiO_2$; thus, both the surface properties and the mass transfer of the pollutant and degraded products onto the substrate affect to its photocatalytic activity. HAp, which is known as a material having a large surface area and high adsorption ability, may play the role of a transparent or semi-transparent to allow UV and visible radiation to pass through it. In fact, there are numerous materials having larger surface area and higher adsorption ability such as silica gel, zeolite, activated carbon, etc. However, besides these general properties, HAp material was investigated as a support for photocatalysis due to the generation of active superoxide anion radicals ($O_2^{\cdot -}$) under UV irradiation [14]; thus, the $TiO_2$/HAp photocatalysts have gained the interest of many scientists. In this chapter, the role of hydroxyapatite in $TiO_2$/HAp photocatalytic materials will be analyzed and evaluated to supply a clear view of the composites.

## 2. Hydroxyapatite plays the role of adsorption material in the photocatalytic $TiO_2$/HAp composites

Adsorption of biological, organic-chemical molecules on the HAp surface is generally influenced by its physicochemical properties including crystallite size, pore structure, morphology of particles, or coatings [15] which directly depend on the synthesis methods. The synthesis methods of HAp particles include solid-state reaction; sol-gel, plasma, and hydrothermal technique; layer hydrolysis of other calcium phosphate salts; etc. [16–18], while those of HAp coating include sol-gel, chemical vapor deposition, pulsed laser deposition, RF magnetron sputtering, spray pyrolysis, etc. [7, 19, 20]. The choice of a specific method depends on the purpose of research which is synthesis, characteristics, or application of pure HAp or those of $TiO_2$/HAp composites.

The adsorption property of HAp in the photocatalytic $TiO_2$/HAp composites has been reported in many researches. Nonami et al. [21] soaked $TiO_2$ powder in a simulated physiological solution containing phosphate ions for periods of about 1 h at 37°C. The apatite film with a thickness of approximately 0.7 μm has formed on the approximately 0.3 μm thick $TiO_2$ layer. The crystals have a plate-like shape, measuring approximately 0.1–0.5 μm in length and

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2–10 nm in thickness. This composite material may adsorb contaminants without exposure to light, and the contaminants are decomposed by $TiO_2$ photocatalyst on exposure to light. As a result, the photocatalytic $TiO_2$/HAp composites can be used to pure the air or play the role of the antimicrobial and antifungal coating with HAp absorber.

Other literatures show that the photocatalytic $TiO_2$/HAp materials not only absorb organic contaminants such as viruses, bacteria, etc. but also decompose these compounds by the photocatalytic process. Hirakura et al. [22] presented that lysozyme (LSZ) and bovine serum albumin (BSA) can be monomolecularly absorbed on HAp by using two types of fibrous crystals elongated in the c-axis. HAp-nanostructured crystals doping $TiO_2$ anatase can selectively remove of the specific proteins by the absorbing and decomposing under UV irradiation. Thus, the photocatalytic activity for the decomposition of proteins could be controlled with the adsorption on the surface of the nanostructured HAp crystals. The adsorption of BSA on $TiO_2$/HAp composite was also presented in the publication of Katayama et al. [23]. The research explained that the adsorption of the acidic protein BSA occurred at $Ca^{2+}$ sites of the HAp component which contained a large number of pores supporting to the physical adsorption.

Ryu et al. [24] fabricated the $TiO_2$-β-TCP nanocomposite photocatalytic thin films by aerosol deposition. The aerosol-deposition films almost fully covered the substrate (glass) and are not porous but extremely rough microstructure. The deposited films maintained good adhesion with the substrate, and the film's pencil hardness was over 9H. The aerosol-deposition $TiO_2$-40 wt% β-TCP composite film has two different phases distinctly: white regions of β-TCP and dark regions of $TiO_2$, 5–50 nm-sized $TiO_2$ nanocrystallites with nanoscaled β-TCP crystallites formed by the collision of the accelerated particles with high kinetic energy during deposition. The films consisting of nano-sized $TiO_2$ photocatalytic crystallites with a dispersion of β-TCP adsorbent crystalline phase show the high photocatalytic activity under both UV and dark conditions due to adsorption effect of β-TCP.

The adsorption role of the HAp layer in Ag-$TiO_2$/HAp/$Al_2O_3$ bioceramic composite membrane was also evaluated in the report of Ma et al. [25]. This composite membrane, which was fabricated by a facile two-step approach, involves sol–gel process and calcination was a microporous membrane structure with average 0.8 m pore size, which comprised of Ag-$TiO_2$/HAp composite layer with a thickness of 10 m overlaid on α-$Al_2O_3$ disk support. HAp component acted as a highly efficient bacterial adsorbent, while Ag-$TiO_2$ provided powerful photocatalytic attack toward *E. coli* strains.

Xie et al. [26] fabricated $TiO_2$/HAp composite with mosaic structure via a facile route without any structure-directing agent. The result proved the increased photocatalytic activity of the composite results from the combination of adsorption capacity of HAp and the high photocatalytic activity of $TiO_2$.

Other reports also concerned to the adsorption properties of HAp in the HAp/$TiO_2$ composites, especially in atmospheric environment [27–29]. Komazaki et al. [27] collected NO(x) by an annular diffusion scrubber coated with a mixture of $TiO_2$ and HAp. The research shows that HAp plays the role of adsorption material, while $TiO_2$ produces reactive oxygen species

under ultraviolet light (UV) illumination such as super oxide ($O_2^-$), hydroxyl radical (OH°), and peroxyhydroxyl radical ($HO_2$°), by which nitric oxide is oxidized to nitrogen dioxide and is further oxidized to nitric acid.

Ozeki et al. [28] fabricated $TiO_2$/HAp thin film by sputtering on glass using a radio-frequency magnetron. The film has a higher decomposition rate of formaldehyde gas than either the $TiO_2$ or the HAp film alone. However, in the bacterial survival test, survival of cells on the $TiO_2$/HAp thin film is higher than that on the $TiO_2$ film, which indicates that the $TiO_2$/HAp thin film has a lower bactericidal effect than the pure $TiO_2$ film.

Liu et al. [29] synthesized HAp-modified N-$TiO_2$ by a facile wet-chemical method and evaluated its photocatalytic activity by the decomposition of gaseous acetone under visible-light irradiation. The results demonstrated that 10%-HAp-N-$TiO_2$ sample shows the best photocatalytic activity and the remarkable photocatalytic activity may arise from the synergism between adsorption on HAp and photoactivity by $TiO_2$ which generated oxygen-reactive species diffusing and reacting with the molecules located on the HAp.

Masato Wakamura et al. have many publications on the field [30–32]. The authors evaluated the adsorption behaviors of proteins onto photocatalytic $Ti^{4+}$-doped calcium hydroxyapatite (TiHAp) particles which was synthesized by the coprecipitation method using $Ca(NO_3)_2$, $Ti(SO_4)_2$, $H_3PO_4$, and $NH_4OH$ original materials [31]. The result showed that all the adsorption isotherms of bovine serum albumin (BSA), myoglobin (MGB), and lysozyme (LSZ) from $1 \times 10^{-4}$ mol/dm$^3$ KCl solution were Langmuir type. Generally, the saturated amounts of adsorbed protein value on the TiHAp were much higher than CaHAp.

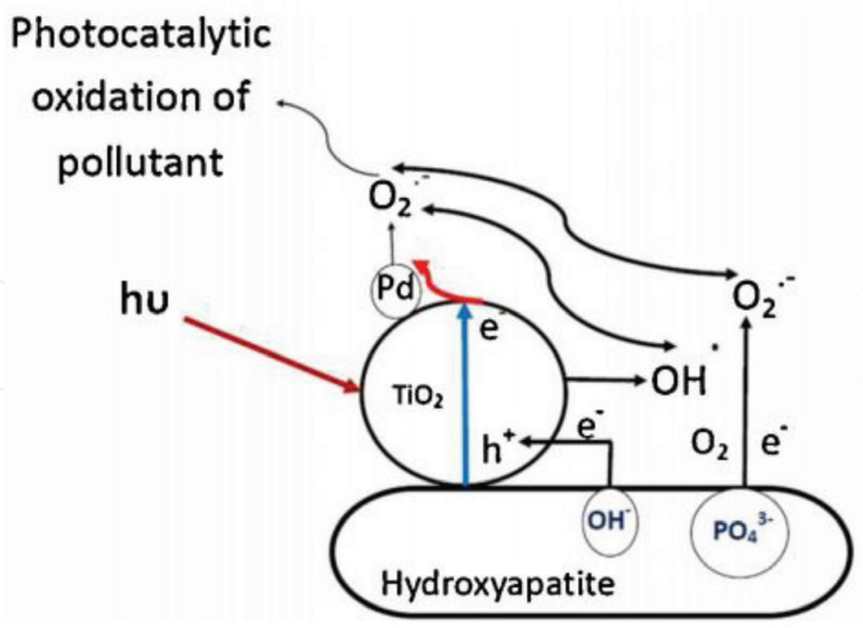
## 3. The promoted impact of hydroxyapatite in the photocatalytic $TiO_2$/HAp composites

Beside the role as an adsorption material in the photocatalytic $TiO_2$/HAp composites, some recent researches have investigated that hydroxyapatite promotes photocatalytic degradation because it can play the role of a support for photocatalysts. The activity of HAp is caused by the generation of active superoxide anion radicals ($O_2^{\cdot -}$) due to a change in the electronic state of the surface $PO_4^{3-}$ group under UV irradiation [14].

Hu et al. [33] proved the promotion role of HAp to $TiO_2$ in photocatalytic degradation by using experimental observations and kinetic modeling. The derived kinetic parameters including reaction rate constant, Langmuir adsorption constant, apparent activation energy, etc. confirm that the activity of $TiO_2$/HAp composite is more effective than that of $TiO_2$. A negative effect of HAp on the photo absorption ability of the $TiO_2$/HAp composite is characterized by UV-vis reflectance spectra. The existence of superior chemisorption between HAp and the organic molecules leads to a better performance of $TiO_2$/HAp for photocatalytic degradation.

Mohamed et al. [34] determined photocatalytic activities of Pd-$TiO_2$-hydroxyapatite nanoparticles, which are synthesized by a template-ultrasonic-assisted method, by photocatalytic removal of cyanide under visible-light irradiation (**Scheme 1**). **Scheme 1** shows that the

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**Scheme 1.** Photocatalytic mechanism of cyanide degradation by Pd-$TiO_2$-HAp [34].

vacancies formed on the surface of the excited $PO_4^{3-}$ group in visible illumination will lead to the formation of $O_2^{\cdot-}$ and will attack the surrounding organic molecules adsorbed on HAp.

The research [34] investigated that the amount of hydroxyl radials formed in the Pd-$TiO_2$-hydroxyapatite nanoparticle was higher than those of Pd-$TiO_2$ and $TiO_2$ nanoparticles. The absorption of radiation in the visible-light region, the small recombination rate of the electron-hole pair, as well as the high surface area of HAp material are the promoted impacts of hydroxyapatite in the photocatalytic $TiO_2$/HAp composites.

The recombination rate of the electron-hole pair is also concerned in another publication [35]. Zhang et al. [35] demonstrated the increased photocatalytic performance of $TiO_2$ nanoparticles which was supported on electrically polarized HAp films. The separation of photogenerated electrons and holes in $TiO_2$ nanoparticles is promoted by the internal polarization of the HAp support, and consequently, the recombination of charge carriers is mitigated. It can be concluded that the materials with large internal polarization can be used in strategies for enhancing quantum efficiency of photocatalysts.

The surface area of HAp material was concerned in the research of Kobayashi et al. [36]. The $TiO_2$/HAp photocatalytic coating was deposited by gas tunnel-type plasma spraying using powders with nano-sized grains. The photocatalytic reaction occurs on powder surface; as the grain size becomes smaller, the specific surface area becomes larger, and the degradation efficiency of organic pollutants also increases.

The promoted impact of hydroxyapatite in the photocatalytic $TiO_2$/HAp composites was presented in the report of Liu et al. [37]. The photocatalytic activities of Ag-$TiO_2$-HAp powders synthesized by a facile wet-chemical strategy were evaluated by photocatalytic oxidation decomposition of acetone in air under visible-light illumination. The high photocatalytic activity

of the Ag-$TiO_2$-HAP hybrids could be attributed to its strong absorption in the visible-light region, low recombination rate of the electron-hole pair, and large BET-specific surface area.

Aramendia et al. [38] studied on the $TiO_2$/natural phosphate material synthesized by sol-gel process and tested the photocatalytic activity in the photo-oxidation process of propan-2-ol. The results show that the presence of natural phosphate makes a retardation of $TiO_2$ crystallization and creates a certain interaction with titanium.

Nishikawa et al. [39] indicated that the difference in photocatalytic activity of the materials containing HAp and without HAp may be originated from the properties of the electronic state that forms the valence band of HAp-containing $PO_4$ group.

Li et al. [40] synthesized Ti-substituted hydroxyapatite (TiHAp) by the coprecipitation method. The adsorption and photocatalytic degradation of bisphenol A (BPA, an environmental endocrine disrupting chemical) over TiHAp and P25 $TiO_2$ photocatalysts were studied using liquid chromatography-mass spectrometry. The results indicated that the adsorption of BPA on TiHAp and $TiO_2$ obeyed the Langmuir adsorption equation, and the adsorption capacity and photocatalytic degradation activity of BPA of TiHAp material were much higher than those of $TiO_2$. To explain for the results, the authors presented that the zeta potentials of TiHAp, and $TiO_2$ did not show significant difference when the pH was about seven, suggesting that the surface charge was not the reason for the different adsorption capacities of the particles. In addition, the specific surface area and average pore diameter of TiHAp and $TiO_2$ were comparable, so these would not lead to the different adsorption capacities either. In fact, TiHAp material is produced from a substitution of some Ca sites in HAp by Ti, which resulted in multiple Ti-OH groups on the TiHAp surface. Large amounts of phosphates and hydroxyls in the crystal lattice of TiHAp can adsorb the hydroxyls of BPA by hydrogen bonding.

The bandgap of $TiO_2$/HAp materials were mentioned in some publications because it decides the energy separation between valence and conduction bands, the quantum effect, as well as the effect of visible-light utilization, etc. The bandgap of HAp was reported in [41] to be 3.95 eV by photoluminescence measurement; meanwhile, in other reports, the bandgap of HAp was calculated to be around 4.51–5.4 eV [42, 43]. The bandgap of $TiO_2$/HAp composites calculated by UV-vis diffuse reflectance spectra was between 3.06 and 3.08 eV while that of pure $TiO_2$ was broader (3.12 eV) [44]. However, the bandgap of Ti-substituted hydroxyapatite evaluated by both experimental and theoretical methods was 3.65 eV [45]. Masato Wakamura et al. determined the effect of Ti substitution in HAp synthesized by the coprecipitation method on the bandgap which was compared with that of a typical anatase-$TiO_2$ photocatalytic powder. The experimentally obtained optical bandgap energies of TiHAp, HAp, and $TiO_2$ powder measured by diffuse reflectance spectroscopy were 3.65, >6, and 3.27 eV, respectively. The authors explained the increase of bandgap in TiHAp due to hybridizing of Ti 3d orbital with O 2p orbital and forming an internal state in the HAp bandgap, consequently, causing the absorption-edge lowering of TiHAp. Researching on the acetaldehyde gas decomposition of TiHAp by UV with VIS irradiation, the authors investigated the increase of activity comparing with when UV irradiation alone was used. Linh et al. [46] also indicated the shift of bandgap of $TiO_2$/HAp material synthesized by the hydrothermal process containing $TiO(OH)_2$ and HAp gels. The binding energy values of Ca 2p, P 2p, and O1s levels are related to hydroxyapatite phase, whereas those of Ti 2p

levels corresponded with the characterization of titanium (IV) in $TiO_2$. The experimental bandgap of $TiO_2$/HAp material calculated by the DRS measurement was 3.6 eV, while those of pure HAp and $TiO_2$ were 5.3 and 3.2 eV, respectively. The shifts may relate oxidation states of titanium in the annealing process of $TiO(OH)_2$/HAp gel. The increase of bandgap may affect the absorption ability of radiation in the visible-light region; consequently, in some cases, it is a demoted impact which reduces the photocatalytic activity of $TiO_2$/HAp composites.

## 4. Conclusion

In the photocatalytic $TiO_2$/HAp composites, HAp plays the role of an adsorption of contaminations which is generally influenced by the physicochemical properties of HAp material. On the other hand, the promoted impacts of hydroxyapatite in the composites are experimentally collected in the specific cases including the absorption of radiation in the visible-light region, the small recombination rate of the electron-hole pair, and the high surface area of HAp component. However, the role of HAp in $TiO_2$/hydroxyapatite photocatalytic materials has been continuously researched and evaluated to obtain the best composite in the photocatalytic field, as well as in other applications.

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