The titania/hydroxyapatite (TiO$_2$/HAp) product was prepared by precipitating hydroxyapatite in the presence of TiO(OH)$_2$ gel in the hydrothermal system. The characteristics of the material were determined by using the measurements such as X-ray photoemission spectroscopy (XPS), X-ray diffraction (XRD), diffuse reflectance spectra (DRS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX). The XPS analysis showed that the binding energy values of Ca (2p$_{1/2}$, 2p$_{3/2}$), P (2p$_{1/2}$, 2p$_{3/2}$), and O 1s levels related to hydroxyapatite phase whereas those of Ti (2p$_{3/2}$, 2p$_{1/2}$) levels corresponded with the characterization of titanium(IV) in TiO$_2$. The XRD result revealed that TiO$_2$/HAp sample had hydroxyapatite phase, but anatase or rutile phases were not found out. TEM image of TiO$_2$/HAp products showed that the surface of the plate-shaped HAp particles had a lot of smaller particles which were considered as the compound of Ti. The experimental bandgap of TiO$_2$/HAp material calculated by the DRS measurement was 3.6 eV, while that of HAp pure was 5.3 eV and that of TiO$_2$ pure was around 3.2 eV. The shift of the band gap energy of TiO$_2$ in the range of 3.2–3.6 eV may be related to the shifts of Ti signals of XPS spectrum.

1. Introduction

TiO$_2$ photocatalysis has gained much attention because of its low cost, nontoxicity, high stability, and easy preparation. However, the slow rates of the photocatalytic chemical transformations, compared with other methods, the low quantum yields, the lack of visible-light utilization, and the low adsorption capacity of TiO$_2$ have hindered it from the practical application. To solve these problems, much effort has been made to enhance the photocatalytic efficiency and visible-light utilization of TiO$_2$ by the additional components doping [1], improving its sensitization and metallization [2], or combining TiO$_2$ and absorbable inorganic materials [3]. Recently, the preparation of titania/hydroxyapatite (TiO$_2$/HAp) materials was attracting considerable attention thanks to the photocatalytic property of TiO$_2$ and great adsorption ability of HAp. Among various features of the TiO$_2$/HAp material which have been studied, the band gap evaluation was an important one because it decided the energy separation between the valence and conduction bands, the quantum effect, and the effect of visible-light utilization of that material [4]. The band gap of HAp was reported in [5] to be 3.95 eV by photoluminescence measurement, meanwhile, in some papers, that of HAp was calculated to be around 4.51–5.4 eV [6, 7]. The band gap 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) [8]. However, the band gap of Ti-substituted hydroxyapatite evaluated by both experimental and theoretical methods was 3.65 eV [9]. Generally, the above researches mainly focused on explaining the efficiency and photocatalytic mechanism of TiO$_2$/HAp or Ti-substituted hydroxyapatite materials and have not mentioned the surface chemical bonding, particularly, the binding energy. In this study, the shifts of binding energy (E$_B$) and band gap energy (E$_g$) of TiO$_2$/HAp material prepared by the hydrothermal process were investigated.
2. Experiment

Calcium nitrate tetrahydrate, diammonium hydrogen phosphate, ammonia solution (pure analysis, Merck), and hydrous titania prepared from Ilmenite ore [10] were used as the original materials. The suspension of TiO(OH)$_2$ gel in the aqueous solution of Ca(NO$_3$)$_2$/EDTA was added quickly into the aqueous solution of (NH$_3$)$_2$HPO$_4$/urea and then stirred thoroughly. The mix was contained in the hydrothermal reactor adjusted to 180°C for 3 hours. The precipitate was filtered, washed, dried in vacuum at 65°C for 24 h, and calcined up to 750°C. The percentage of TiO$_2$ in the TiO$_2$/HAp product was below 10 (wt.%).

The crystalline phases of the material were identified by powder X-ray diffraction (XRD) analyses using a ADVANCED A8-Bruker-Model 2006 diffractometer with Cu Ka radiation (λ = 0.15418 nm). The element analysis was carried out by energy dispersive X-ray (EDX) spectroscopy (JSM-6610LA, 30 kV). The morphology, particle size, and size distribution of particles were investigated by JEM 1010 (80 kV) transmission electron microscopy (TEM) and HITACHI S-4800 (5 kV) scanning electron microscopy (SEM). X-ray photoemission spectroscopy measurement (XPS, Physical electronics, Model 04–548, USA) of the TiO$_2$/HAp product was carried out at a pressure of higher than 1 × 10$^{-7}$ Torr. The general scan and the C 1s, P 2p, Ca 2p, O 1s, and Ti 2p core level spectra were recorded with unmonochromatized Mg Kα radiation (photon energy = 1253.6 eV) at pass energy of 58.7 eV and an electron take-off angle (angle between electron emission direction and surface plane) of 45°. The core level spectra were background corrected and the chemically distinct species were resolved using a nonlinear least squares fitting procedure in the Sun Solaris based Vision-2 curve resolver. The core level binding energies ($E_B$) were aligned with the adventitious carbon binding energy of 285 eV. The binding energy should be corrected by using the data of C 1s for the sample. The binding energy of the TiO$_2$/HAp product was compared with those of TiO$_2$ and HAp pure showed in MW175, Handbook of XPS, page 240. The band gap ($E_g$) values of TiO$_2$, HAp, and TiO$_2$/HAp samples were evaluated by using UV-VIS diffuse reflectance spectra method (UV-VIS, JASCO V550).

3. Results and Discussion

The XRD pattern and EDX spectroscopy of TiO$_2$/HAp sample was shown in Figure 1.

Figure 1(a) revealed that HAp, which is of the hexagonal structure and the molecular formula of Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, had the characteristic peaks at the 2θ angles locations of 25.9, 31.8, 32.3, 39.9, and 49.5° (JCPDS no. 00-009-0432). The characteristic peaks of TiO$_2$ anatase did not appear in the XRD pattern of TiO$_2$/HAp sample, even though TiO(OH)$_2$ gel could be changed to TiO$_2$ anatase after calcining up to 750°C [10]. However, the EDX result showed that there were peaks of Ca, P, and Ti in the sample. That means either the percentage of TiO$_2$ anatase in TiO$_2$/HAp material was so small (below 10 wt.%) or Ti was in a compound which could not be found out by the XRD result.

The SEM and TEM images of the sample were shown in Figure 2.

Figure 2(a) showed that TiO$_2$/HAp material had plate-shaped HAp particles at nanometer in thickness and at micrometer in the two remaining dimensions; meanwhile, Figure 2(b) indicated that the surface of HAp particles had a lot of smaller particles which were considered as the compound of Ti.

The XPS spectra of Ca 2p, O 1s, Ti 2p, and P 2p core levels of TiO$_2$/HAp product were shown in Figure 3.

The figure of XPS result in the product exhibited a narrow scanning spectrum for analysis of chemical bonding. The binding energy of Ca 2p3/2 was 347.3 eV and that of Ca 2p1/2 was 350.7 eV, which were related to hydroxyapatite. In case of the O 1s spectrum, the surface of the product was composed of three kinds of oxygen bonds which were H$_2$O bond from hydrated surface, PO$_4$ bond from hydroxyapatite, and oxide bond from titanium oxide (TiO$_2$). The binding energy of
Figure 2: SEM and TEM images of TiO$_2$/HAp material.

Figure 3: The XPS Ca 2p, O 1s, Ti 2p, and P 2p spectra of TiO$_2$/HAp product.

O 1s attributed to the PO$_4$ bond from hydroxyapatite was 531.4 eV. In case of the P 2p spectrum, the P peak was deconvoluted into two peaks for p$_{1/2}$ and p$_{3/2}$ levels with the binding energy of 133.9 eV, which corresponded with P in hydroxyapatite. The binding energy of Ti 2p$_{3/2}$ in stoichiometric TiO$_2$ has been reported to be in the range of 458.5 to 458.9 eV and that of Ti 2p$_{3/2}$ in Ti$_2$O$_3$ has been reported to be around 456.8 to 456.9 eV [1]. The binding energy of Ti 2p$_{3/2}$ in the product was 458.7 eV, so that of Ti 2p$_{3/2}$ was much closer to that reported value for TiO$_2$ than for Ti$_2$O$_3$.

However, according to the result of Ti 2p spectrum in pure TiO$_2$, the binding energy of Ti 2p$_{3/2}$ in TiO$_2$ was 459.2 eV (shown in Table I) which corresponded with Ti in TiO$_2$ anatase (MW175, Handbook of XPS, page 240). In this case, the shift from 459.2 eV to 458.7 eV may be related to the atoms in different chemical states when TiO(OH)$_2$ gel was converted to TiO$_2$ in the material consisting of
hydroxyapatite. In general, XPS binding energy shift was caused not only by chemical effects but also by matrix effects such as differences in crystal potential, work function, and relaxation energy [12].

The diffuse reflectance spectra of HAp, TiO$_2$/HAp, and anatase TiO$_2$ powders were shown in Figure 4.

The reflection edge wavelengths of TiO$_2$/HAp and TiO$_2$ were in the range of 340–400 nm whereas that of HAp was smaller than 250 nm. In case of both TiO$_2$ and TiO$_2$/HAp, the reflection in the VIS range was imperfect and there seemed to be small absorption in this range. The experimental band gap of TiO$_2$/HAp product calculated by the DRS measurement was 3.6 eV, while that of HAp pure was 5.3 eV and that of TiO$_2$ pure was around 3.2 eV, which were listed in Table 1. The measured $E_g$ of TiO$_2$ of 3.2 eV was the same as a generally known value of 3.2 eV [13]. Additionally, $E_g$ of the pure HAp was 5.3 eV which was in the range of 4.5–5.4 eV reported in the previous studies [7]. However, the experimental $E_g$ of TiO$_2$/HAp product was 3.6 eV which was larger than that of TiO$_2$ anatase, rutile, or brookite [9, 14]. As a result, the analyses indicated that the main phase of the TiO$_2$/HAp product was hydroxyapatite and the secondary phase was amorphous TiO$_2$ or Ti-substituted hydroxyapatite. Moreover, it may have had a correlation between the shift of binding energy and the shift of band gap energy of the material.

### 4. Conclusions

TiO$_2$/HAp material was successfully synthesized by precipitating hydroxyapatite in the presence of TiO(OH)$_2$ gel in the hydrothermal system. XRD result revealed that TiO$_2$/HAp sample had hydroxyapatite phase, but there was no anatase or rutile phase, even though TiO(OH)$_2$ gel could be changed to TiO$_2$ anatase after calcining up to 750°C. TEM image of TiO$_2$/HAp product showed that the surface of the plate-shaped HAp particles had a lot of smaller particles which were considered as the compound of Ti. The binding energy values of Ca 2p, P 2p, and O 1s levels related to hydroxyapatite phase whereas those of Ti 2p levels corresponded with the characterization of titanium (IV) in TiO$_2$. The shifts of binding energy and band gap energy of TiO$_2$/HAp product compared to those of TiO$_2$ anatase were 0.5 eV and 0.4 eV, respectively. The shifts which may be related to the atoms in different chemical states when TiO(OH)$_2$ gel was converted to TiO$_2$ in the material consisting of hydroxyapatite should be continuously studied in next works.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

### References

[1] M. A. Barakat, H. Schaeffer, G. Hayes, and S. Ismat-Shah, “Photocatalytic degradation of 2-chlorophenol by Co-doped TiO$_2$ nanoparticles,” *Applied Catalysis B: Environmental*, vol. 57, no. 1, pp. 23–30, 2005.

[2] Y. Xie and C. Yuan, “Visible-light responsive cerium ion modified titania sol and nanocrystallites for X-3B dye photodegradation,” *Applied Catalysis B: Environmental*, vol. 46, no. 2, pp. 251–259, 2003.

[3] A. Nakajima, K. Takakuwa, Y. Kameshima et al., “Preparation and properties of titania-apatite hybrid films,” *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 177, no. 1, pp. 94–99, 2006.

[4] A. Fujishima and K. Honda, “Electrochemical photolysis of water at a semiconductor electrode,” *Nature*, vol. 238, no. 3558, pp. 37–38, 1972.

[5] G. Rosenman, D. Aronov, L. Oster et al., “Photoluminescence and surface photovoltage spectroscopy studies of hydroxyapatite nano-Bio-ceramics,” *Journal of Luminescence*, vol. 122-123, no. 1-2, pp. 936–938, 2007.
[6] P. Rulis, L. Ouyang, and W. Y. Ching, “Electronic structure and bonding in calcium apatite crystals: hydroxyapatite, fluorapatite, chlorapatite, and bromapatite,” Physical Review B—Condensed Matter and Materials Physics, vol. 70, no. 15, Article ID 155104, 2004.

[7] K. Matsunaga and A. Kuwabara, “First-principles study of vacancy formation in hydroxyapatite,” Physical Review B, vol. 75, Article ID 014102, pp. 1–9, 2007.

[8] A. Mitsionis, T. Vaimakis, C. Trapalis, N. Todorova, D.Bahnhemann, and R. Dillert, “Hydroxyapatite/titanium dioxide nanocomposites for controlled photocatalytic NO oxidation,” Applied Catalysis B: Environmental, vol. 106, no. 3-4, pp. 398–404, 2011.

[9] M. Tsukada, M. Wakamura, N. Yoshida, and T. Watanabe, “Band gap and photocatalytic properties of Ti-substituted hydroxyapatite: comparison with anatase-TiO₂,” Journal of Molecular Catalysis A: Chemical, vol. 338, no. 1-2, pp. 18–23, 2011.

[10] N. T. T. Linh et al., in Proceedings of the 2nd International Conference on Natural Resources and Materials (ICNRM) and 4th AUN/SEED-Net Regional Conference on Natural Resources and Minerals (RCNRM '11), 2011.

[11] D. Gonbeau, C. Guimon, G. Pfister-Guillouzo, A. Levasseur, G. Meunier, and R. Dormoy, “XPS study of thin films of titanium oxysulfides,” Surface Science, vol. 254, no. 1–3, pp. 81–89, 1991.

[12] K. S. Kim and N. Winograd, “X-ray photoelectron spectroscopic binding energy shifts due to matrix in alloys and small supported metal particles,” Chemical Physics Letters, vol. 30, no. 1, pp. 91–95, 1975.

[13] L. Kavan, M. Grätzel, S. E. Gilbert, C. Klemenz, and H. J. Scheel, “Electrochemical and photoelectrochemical investigation of single-crystal anatase,” Journal of the American Chemical Society, vol. 118, no. 28, pp. 6716–6723, 1996.

[14] A. Di Paola, M. Bellardita, and L. Palmisano, “Brookite, the least known TiO₂ photocatalyst,” Catalysts, vol. 3, no. 1, pp. 36–73, 2013.
