Research Article

The Shifts of Band Gap and Binding Energies of Titania/Hydroxyapatite Material

Nguyen Thi Truc Linh,¹ Phan Dinh Tuan,² and Nguyen Van Dzung³

¹ Ho Chi Minh City University of Pedagogy, Vietnam

² Ho Chi Minh City University of Natural Resources and Environment, Vietnam

³ Institute of Applied Materials Science, VAST, Vietnam

Correspondence should be addressed to Nguyen Thi Truc Linh; nttlinh2811@gmail.com

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The titania/hydroxyapatite (TiO_2/HAp) product was prepared by precipitating hydroxyapatite in the presence of $\text{TiO}(\text{OH})_2$ 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 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 experimental band gap 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 $\text{TiO}(\text{OH})_2$ gel in the aqueous solution of $\text{Ca}(\text{NO}_3)_2/\text{EDTA}$ was added quickly into the aqueous solution of $(\text{NH}_4)_2\text{HPO}_4/\text{urea}$ 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 ADVANCE A8-Bruker-Model 2006 diffractometer with Cu K α radiation ($\lambda = 0.15418\text{ nm}$). 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^{-9} 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 K α 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_{Bs}) 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 MWI75, 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 $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, 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 $\text{TiO}(\text{OH})_2$ 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 be not found out by the XRD result.

FIGURE 1: XRD pattern and EDX spectroscopy of TiO_2/HAp sample.

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 2p $_{3/2}$ was 347.3 eV and that of Ca 2p $_{1/2}$ was 350.7, 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_2O bond from hydrated surface, PO_4 bond from hydroxyapatite, and oxide bond from titanium oxide (TiO_2). The binding energy of

(a) SEM

(b) TEM

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 p1/2 and p3/2 levels with the binding energy of 133.9 eV, which corresponded with P in hydroxyapatite. The binding energy of Ti 2p3/2 in stoichiometric TiO_2 has been reported to be in the range of 458.5 to 458.9 eV and that of Ti 2p3/2 in Ti_2O_3 has been reported to be around 456.8 to 456.9 eV [11]. The binding energy of Ti 2p3/2 in the product was 458.7 eV, so that of Ti

2p3/2 was much closer to that reported value for TiO_2 than for Ti_2O_3 .

However, according to the result of Ti 2p spectrum in pure TiO_2 , the binding energy of Ti 2p3/2 in TiO_2 was 459.2 eV (shown in Table 1) which corresponded with Ti in TiO_2 anatase (MWI75, 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 $\text{TiO}(\text{OH})_2$ gel was converted to TiO_2 in the material consisting of

FIGURE 4: The diffuse reflectance spectra of HAp, TiO₂/HAp, and anatase TiO₂ powders.

TABLE 1: The band gap and the binding energy of the samples.

Sample	Band gap (eV)	Binding energy (eV)	
		Ca 2p	Ti 2p
TiO ₂ anatase	3.2	—	459.2
TiO ₂ /HAp	3.6	347.3	458.7
HAp	5.3	347.3	—

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, TiO₂/HAp, and anatase TiO₂ powders were shown in Figure 4.

The reflection edge wavelengths of TiO₂/HAp and TiO₂ were in the range of 340–400 nm whereas that of HAp was smaller than 250 nm. In case of both TiO₂ and TiO₂/HAp, the reflection in the VIS range was imperfect and there seemed to be small absorption in this range. The experimental band gap of TiO₂/HAp product calculated by the DRS measurement was 3.6 eV, while that of HAp pure was 5.3 eV and that of TiO₂ pure was around 3.2 eV, which were listed in Table 1. The measured E_g of TiO₂ 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 TiO₂/HAp product was 3.6 eV which was larger than that of TiO₂ anatase, rutile, or brookite [9, 14]. As a result, the analyses indicated that the main phase of the TiO₂/HAp product was hydroxyapatite and the secondary phase was amorphous TiO₂ 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

TiO₂/HAp material was successfully synthesized by precipitating hydroxyapatite in the presence of TiO(OH)₂ gel in the hydrothermal system. XRD result revealed that TiO₂/HAp sample had hydroxyapatite phase, but there was no anatase

or rutile phase, even though TiO(OH)₂ gel could be changed to TiO₂ anatase after calcining up to 750°C. TEM image of TiO₂/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 TiO₂. The shifts of binding energy and band gap energy of TiO₂/HAp product compared to those of TiO₂ 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 TiO₂ 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.

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