Reviews—New development of inorganic ion exchanger

Preparation, Hydrothermal Treatment and Photocatalytic Activity of $\text{Zr}(\text{HPO}_4)_2/\text{TiO}_2$ Nanocomposites

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Abstract

α -type zirconium hydrogenphosphate (α -ZrP)/ TiO_2 nanocomposite was fabricated by the intercalation of titanium tetraisopropoxide into butylamine-intercalated α -ZrP in ethanol medium and followed by photocatalytic decomposition of organic compounds with UV irradiation. Prior to the photocatalytic decomposition, hydrothermal treatment was conducted in the temperature range of 100–250°C. All materials were characterized by X-ray diffractometry, SEM, TG-DTA, chemical analyses, FTIR, ^{31}P MAS NMR, UV-VIS absorption spectroscopy, and photocatalytic hydrogen evolution from an aqueous methanol solution. On the basis of the SEM observation, no significant deformation of the bulk samples occurred after hydrothermal treatment and UV-irradiation whereas delamination of host materials was caused by the intercalation of butylamine. ^{31}P MAS NMR and FTIR revealed that no chemical bonding between TiO_2 and phosphate groups of the host material. TiO_2 in zirconium hydrogenphosphate could be crystallized to anatase by the hydrothermal treatment. The hydrothermal treatment was effective for the photocatalytic decomposition of organic compounds. Complete decomposition was obtained in shorter UV irradiation time by the hydrothermal treatment due to the existence of anatase phase. Hydrothermally untreated α -ZrP/ TiO_2 exhibited negligible photocatalytic activity due to amorphous TiO_2 . The photocatalytic activity of α -ZrP/ TiO_2 was enhanced by the hydrothermal treatment whereas the activity was decreased with an increase in the hydrothermal temperature. α -ZrP/ TiO_2 hydrothermally treated at 100°C exhibited the highest photocatalytic activity and showed large blue-shift in UV absorption spectra due to the quantum-size effect.

Keywords: TiO_2 ; zirconium hydrogenphosphate; intercalation; hydrothermal treatment; photocatalyst

1. Introduction

Semiconductor photocatalytic reaction due to its low cost, ease of handling, and high resistance to photoinduced decomposition, TiO_2 is one of the most studied semiconductors for these photocatalytic reactions^{1–10}. The effectiveness of TiO_2 as a photocatalyst depends on its crystal phase, crystallite size, and crystallinity^{11–13}. TiO_2 fine particles have attracted much attention because of their photocatalytic activity resulting from the quantum-size effect^{14–16}. Intercalation of TiO_2 into layered compounds such as clay has been done using TiO_2 sol to synthesize ex-

tremely fine TiO_2 particles. TiO_2 -intercalated clay having microporous structure and high surface areas is expected to exhibit interesting photocatalytic activities^{17–21}. However, since intercalated TiO_2 in clay synthesized was amorphous or very poor crystalline state, the activity was lower than that of the crystalline TiO_2 such as anatase. Ooka et al applied hydrothermal treatment on TiO_2 -intercalated montmorillonite and found that TiO_2 crystallized to anatase in the interlayer spacing and the photocatalytic activity was enhanced by the hydrothermal treatment²².

TiO_2 can be readily intercalated into clay materials using

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TiO₂ sol, since the expandable clay materials are readily delaminated to homogeneous solution. However, it is not easy to intercalate TiO₂ into other layered materials since they do not easily swell in TiO₂ sol. Except clay materials, there are a few TiO₂-intercalated materials have been reported. Sato *et al* reported that TiO₂-intercalated H₄Nb₆O₁₇ and H₂Ti₄O₉ have been prepared from pre-expanded samples by propylamine using TiO₂ sol followed by photocatalytic decomposition of propylamine with UV irradiation^{23,24}. Although α -type zirconium hydrogenphosphate (α -ZrP) is one of typical layered materials, TiO₂-intercalated α -ZrP has not been reported so far, whereas alumina and chromia intercalated α -ZrP were prepared^{25,26}. We attempted intercalation of TiO₂ into pre-expanded α -ZrP with butylamine using TiO₂ sol, however, TiO₂ could not intercalate and butylamine was eluted to convert hydrogen form of α -ZrP, since α -ZrP is a weak acid type inorganic ion-exchangers.

In the present study, we have achieved the fabrication of α -ZrP/TiO₂ nanocomposite without using TiO₂ sol. Namely, intercalation of titanium tetraisopropoxide was done in ethanol medium without hydrolysis. Then hydrothermal treatment and photocatalytic decomposition of organic compounds were followed. The present paper describes the processing, characterization, and photocatalytic activity of α -ZrP/TiO₂ nanocomposites. The effect of the hydrothermal treatment on the photocatalytic activity was discussed from the standpoint of crystal phase, crystallinity and crystallite size of TiO₂.

2. Experimental

2.1 Materials

Zirconium (IV) oxychloride (ZrOCl₂•8H₂O), phosphoric acid (H₃PO₄), tetraisopropyl titanate (Ti(OPr)₄: Ti(OC₃H₇)₄), n-butylamine (C₄H₉NH₂) and hydrogen hexachloroplatinate hexahydrate (H₂PtCl₆•6H₂O) were GPR grade reagents (Nacalai Tesque).

2.2 Preparation of zirconium (IV) hydrogenphosphate

α -ZrP was prepared by the direct precipitation method using hydrofluoric acid (HF) as reported by A. Clearfield *et al.*²⁷ A 20 g of ZrOCl₂•8H₂O was dissolved in 100 cm³ of distilled water. The desired amounts of hydrofluoric acid and phosphoric acid were added successively with vigorous stirring to make the total volume of 130 cm³. The solution thus prepared was then allowed to warm in a thermostatic water bath for 48 h in order to decompose the fluoro-complex of zirconium. The white flaky product was separated by filtration, washed with distilled water and dried at 50°C

for 24 h.

2.3 Incorporation of titanium tetraisopropoxide in the α -ZrP

α -ZrP was converted to butylamine-intercalated α -ZrP (α -ZrP/BA) by stirring it (10 g) in 0.1 M butylamine aqueous solution (500 cm³) at 50°C for 72 h. The intercalation reaction was carried out in ethanol. A 5 g of α -ZrP/BA was added to the 100 cm³ of 0.5 M Ti(OPr)₄ ethanol solution at 25°C for 72 h. Then, the products were filtered off, washed with ethanol and dried at 50°C.

2.4 Hydrothermal treatment of α -ZrP/BA/Ti(OPr)₄

The resulting composite (2 g) and distilled water (100 cm³) were transferred into a PTFE-lined pressure vessel (200 cm³) and subjected to hydrothermal treatment at a constant temperature of 100, 150, 200, and 250°C for 16 h. The product was filtered off, washed with distilled water and ethanol, followed by air-drying at 50°C.

2.5 Photocatalytic decomposition of organic compounds and platinum loading on α -ZrP/BA/TiO₂ composite

Photocatalytic decomposition of organic compounds such as butylamine was carried out as follows; a 1 g of the portion of the samples was suspended in a 500 cm³ of 0.08 × 10⁻³ M H₂[PtCl₆] aqueous solution and irradiated with UV light from a 400 W high-pressure mercury lamp at room temperature for 5 h. Simultaneously, photochemical deposition of Pt particles on the TiO₂ was carried out using decomposed organic compounds as a sacrificial reagent. PtCl₆²⁻ anion was reduced to Pt metal with hydrogen derived from decomposition of organic compounds. Platinum on the TiO₂ particles is a promoter for hydrogen evolution from aqueous methanol solution.

2.6 Analysis

Powder X-Ray diffraction (XRD) patterns were recorded on a Rigaku Roterflex RU-300 RAD diffractometer using CuK α radiation (35 kV and 50 mA) and a scan speed of 2° min⁻¹ in 2 θ . The divergent and scattering slits were set at 0.5°, and the receiving slit was 0.3°. Scanning electron microscopy (SEM) studies were carried out with a Hitachi S-800 electron microscope, operating at 15 kV. The chemical compositions of the products were determined by inductively coupled plasma atomic emission spectroscopy (Seiko SPS-1500R) after dissolving the samples in 5 M HF. TG-DTA analysis was carried out using a Rigaku Corporation TAS 200 TG-DTA analyzer. The sample in platinum pan was heated at a heating rate of 5°C/min in static air. IR spectra of samples in KBr matrices were recorded on a Perkin-Elmer Spectrum 1000 FT IR spectrometer in the range of 4000–450 cm⁻¹. ³¹P MAS NMR spectra were

obtained on a Fourier-transform pulsed NMR spectrometer (Varian INOVA 500) with CPIMS probe. A measurement of UV-visible absorption spectra (UV-VIS) were recorded on a Hitachi 340 spectrophotometer equipped with an integrating sphere. The band-gap energies of the products were determined from the onset of UV-VIS absorption spectra of the powders.

2.7 Photocatalytic reaction

Photocatalytic reaction was carried out at 30°C in a Pyrex reactor attached to an inner radiation type 400 W high-pressure mercury lamp. The photocatalytic activity over platinized α -ZrP/TiO₂ was determined by measuring the volume of gas evolved during the irradiation of the catalyst (0.3 g) suspensions in an aqueous methanol solution (500 cm³, CH₃OH:H₂O volume ratio = 1:4). The production of hydrogen was confirmed by a gas chromatography (GL-science GC-320) using a Molecular Sieve 13X column.

3. Results and Discussion

3.1 Preparation of α -ZrP/TiO₂

A direct intercalation of Ti(OPr)₄ into α -ZrP/BA was tried in ethanol medium without hydrolysis of titanium tetraisopropoxide followed by the photocatalytic decomposition of butylamine. XRD patterns of the α -ZrP (a), α -ZrP/BA (b), α -ZrP/BA/Ti(OPr)₄ (c), the composite

hydrothermally treated at 100°C (d) and succeeding UV irradiation (e) are shown in **Fig. 1**. The structure of α -ZrP has been elucidated by Clearfield *et al.*^{28,29} The interlayer spacing and thickness of α -ZrP are 0.76 and 0.63 nm, respectively, and the distance between hydroxyl groups of PO₄ in the ZrP plane is 0.53 nm. In the XRD pattern for ZrP/BA (b), three harmonic peaks were observed and the lowest angle peak corresponding to (020) of α -ZrP shifted to lower 2θ values compared to α -ZrP, indicating the expansion of interlayer by intercalation of butylamine. The gallery height of α -ZrP/BA determined by subtracting the α -ZrP layer thickness of 0.63 nm is 1.26 nm which is in agreement with the previously reported results³⁰. Since the molecular length of butylamine is ca 0.7 nm, it seems that bilayer of butylamines are inclined to the layers of the α -ZrP by ca 64°. The XRD pattern of α -ZrP/BA/Ti(OPr)₄ (c) is almost same as that of α -ZrP/BA, indicating that Ti(OPr)₄ is incorporated into the butylamine bilayers.

It is well known that amorphous TiO₂ has low photocatalytic activity compared with crystalline TiO₂ such as rutile and anatase³¹. We have found that TiO₂ prepared by the hydrothermal treatment revealed the higher photocatalytic activity than commercial TiO₂³². To obtain an active TiO₂, the hydrothermal treatment was conducted to ZrP/BA/Ti(OPr)₄ in the temperature range of 100–250°C. The XRD pattern of the composite hydrothermally treated at 100°C (d) is shown in **Fig. 1**. After hydrothermal treatment, basic layered structure was maintained, indicating that organic compounds such as butylamine could not be decomposed by the hydrothermal treatment. Besides, anatase phase was recognized in the XRD patterns after the hydrothermal treatment, titanium tetraisopropoxide was hydrolyzed to titanium hydroxides and crystallized to anatase phase.

The XRD pattern of the sample after UV-irradiation for 5 h prior to hydrothermal treatment at 100°C for 16 h are shown in **Fig. 1**(e). In the case of the hydrothermally untreated product, two peaks were observed at 1.81 and 0.84 nm, where the peak at 1.81 nm remained indicates that photocatalytic decomposition of butylamine was not completed even after UV-irradiation for 24 h. On the other hand, only one peak of 0.84 nm was observed for the hydrothermally treated sample, indicating that it takes less than 5 h to remove organic compounds completely. Rapid photocatalytic decomposition can be achieved by UV irradiation after the hydrothermal treatment. Accordingly, hydrothermal treatment is more effective to decompose the organic compounds due to the crystallization of anatase. The peak at 0.84 nm can be attributed to the TiO₂ interca-

Fig. 1 Powder X-ray diffraction patterns of (a) zirconium hydrogenphosphate (ZrP), (b) butylamine intercalated ZrP (ZrP/BA), (c) titanium tetraisopropoxide intercalated ZrP/BA (ZrP/BA/Ti(OPr)₄), (d) ZrP/BA/Ti(OPr)₄ hydrothermally treated at 100°C for 16 h, and (e) followed by UV irradiation for 5 h. Closed circle represents the peak attributable to anatase.

Fig. 2 Powder X-ray diffraction patterns of the products from ZrP/BA/Ti(OPr)₄ treated at various hydrothermal temperatures for 16 h and followed by UV irradiation for 5 h. Hydrothermal temp: (a) 100°C, (b) 150°C, (c) 200°C, and (d) 250°C.

lated ZrP. Subtracting the thickness of α -ZrP, gallery height can be estimated to be 0.6 nm, suggesting TiO₂ fine particles (or thin plates) exist in the interlayer of α -ZrP.

The XRD patterns of the samples hydrothermally treated at various temperatures and followed by UV irradiation are shown in **Fig. 2**. The peaks of the anatase phase became more intense after the hydrothermal treatment at higher temperature, suggesting that the crystallite size increased with an increase in hydrothermal temperature. The crystallite size of anatase phase was calculated from (010) peak in XRD patterns. The crystallite size increased from 0.76 to 1.28 nm with an increase in hydrothermal temperature range of 100–250°C. However, a shoulder peak of 1.33 nm was observed in the patterns treated at 200°C or higher, which suggests that the existence of the interlayer constructed with thicker TiO₂ pillars.

3.2 Characterization

Fig. 3 shows SEM images of the ZrP (a), ZrP/BA/Ti(OPr)₄ (b), hydrothermally treated at 100°C (c) and UV irradiated (d), respectively. As shown in **Fig. 3(a)**, the grains are prismatic with smooth surfaces. It was found that the material was delaminated by the intercalation of butylamine (**Fig. 3(b)**). However, no significant deformation of the bulk samples occurred after hydrothermal treatment (**Fig. 3(c)**) and UV-irradiation (**Fig. 3(d)**). No serious fracture of the ZrP is seen, and the shape and size of the observed are close to those before hydrothermal treatment.

TG-DTA curves for the ZrP/BA (a), ZrP/BA/Ti(OPr)₄ (b), hydrothermally treated at 100°C (c) and UV

Fig. 3 Scanning electron micrographs of (a) ZrP, (b) ZrP/BA/Ti(OPr)₄, (c) product of (b) hydrothermally treated at 100°C for 16 h, and (d) UV-irradiated sample of (c) in aqueous medium for 5 h.

Fig. 4 TG-DTA curves for (a) ZrP/BA, (b) ZrP/BA/Ti(OPr)₄, (c) product of (b) hydrothermally treated at 100°C for 16 h, and (d) UV-irradiated sample of (c) in aqueous medium for 5 h.

irradiated (d) were shown in **Fig. 4**. In the DTA curve for ZrP/BA, three endothermic peaks and one exothermic peak were observed at 100, 230, 270 and 300°C, respectively. The first endothermic peak can be ascribed to the dehydration and the other peaks might be attributable to the decomposition of butylamine. In the DTA curves for ZrP/

Table 1 Chemical composition of the products at each process

	Zr (wt%)	P (wt%)	Ti (wt%)	Wt loss (%)	P/Zr	Ti/Zr
found for						
α -ZrP	28.2	18.7	—	13.3	2.0	—
α -ZrP/BA	19.6	13.0	—	40.1	2.0	—
α -ZrP/BA/Ti(OPr) ₄	8.0	6.1	10.7	33.9	2.0	2.6
Hydrothermally treated α -ZrP/BA/Ti(OPr) ₄	14.0	9.0	16.9	27.7	1.9	2.3
α -ZrP/TiO ₂ (UV irradiated)	17.5	11.3	20.2	13.7	1.9	2.2
calculated for						
Zr(HPO ₄) ₂ •H ₂ O	30.3	20.6	—	12.0	2.0	—
Zr(HPO ₄) ₂ •H ₂ O•2(C ₄ H ₉ NH ₂)	20.4	13.9	—	40.7	2.0	—
Zr(HPO ₄) ₂ •H ₂ O•2(C ₄ H ₉ NH ₂)•2.6Ti(OPr) ₄	7.8	5.3	10.7	61.5	2.0	2.6
Zr(HPO ₄) ₂ •H ₂ O•2(C ₄ H ₉ NH ₂)•2.3TiO ₂	14.5	9.9	17.6	28.4	2.0	2.3
Zr(HPO ₄) ₂ •H ₂ O•2.2TiO ₂	17.9	12.2	20.7	13.5	2.0	2.2

^aContents of Zr, P, Ti were analysed using ICP atomic emission method from dissolved solution of the samples. ^bWeight loss was estimated from TG curves in the temperature range upto 600°C.

BA/Ti(OPr)₄ and hydrothermally treated samples, broad and sharp exothermic peaks were observed at 250 and 350 °C, which are attributable to the decomposition of butylamines whereas the peaks shifted to higher temperatures compared with those of ZrP/BA. An another exothermic peak around 500°C was observed only in the DTA curve for the ZrP/BA/Ti(OPr)₄ sample. This might be due to the decomposition of Ti(OPr)₄³³. In the DTA curve for UV-irradiated sample (Fig. 4(d)), an exothermic peak was observed at 180°C, which seemed to be the remained organic compounds after UV-irradiation. The total weight losses increased as the following order: α -ZrP/TiO₂ < α -ZrP/BA/TiO₂ < α -ZrP/BA/Ti(OPr)₄ < α -ZrP/BA. The chemical composition and weight losses for the products at each process are summarized in **Table 1** together with the estimated chemical compositions of each product. On the basis of Ti content, Ti(OPr)₄ intercalated into the ZrP/BA with molar ratio of Ti/Zr (ca. 2.6), part of which was released from the interlayer of α -ZrP/BA during the hydrothermal treatment (12%) and UV-irradiation (4%).

FTIR spectra for the ZrP/BA, ZrP/BA/Ti(OPr)₄, hydrothermally treated at 100°C and UV irradiated were shown in **Fig. 5** in the range of 3500–2000 and 1500–400 cm⁻¹. Three bands in the range of 3000–2800 cm⁻¹ and two bands at 1210 and 1140 cm⁻¹ can be assigned to the (CH)_n and CN bands, respectively^{34,35}. The intensity of these bands was weakened after intercalation of Ti(OPr)₄. However, the intensity was recovered after hydrothermal treatment presumably due to the hydrolysis of bulky Ti(OPr)₄. Eventually, after UV irradiation, the intensity of the bands decreased again due to the decomposition of butylamines.

Fig. 5 FTIR spectra of (a) ZrP/BA, (b) ZrP/BA/Ti(OPr)₄, (c) product of (b) hydrothermally treated at 100°C for 16 h, and (d) UV-irradiated sample of (c) in aqueous medium for 5 h.

³¹P MAS NMR is a useful tool for studying phosphorus environment since the chemical shift of the phosphate group is remarkably sensitive to its coordination number. The ³¹P MAS NMR spectra for α -ZrP (a), α -ZrP/BA (b), α -ZrP/BA/Ti(OPr)₄ (c) and α -ZrP/TiO₂ (d) are shown in **Fig. 6**. In the spectrum of α -ZrP, there is a single resonance at -20 ppm indicating the presence of only one kind of phosphorus environment in the structure which is corresponding to monohydrogen phosphate, (ZrO)₃POH³⁶. In contrast, the spectrum of α -ZrP/BA showed two different resonances at -16.2 and -20.5 ppm. The downfield shift can be caused by the weakening of the interaction between P atoms due to the enlargement of the

Fig. 6 ^{31}P MAS NMR spectra of (a) ZrP, (b) ZrP/BA, (c) ZrP/BA/Ti(OPr) $_4$, (d) product of (c) hydrothermally treated at 100°C for 16 h and followed by UV-irradiated in aqueous medium for 5 h. Peaks marked with an asterisk are spinning sidebands.

Fig. 7 UV-VIS absorption spectra of (a) ZrP/BA, (b) ZrP/BA/Ti(OPr) $_4$ hydrothermally treated at 100°C for 16 h, followed by UV-irradiated in aqueous medium for 5 h, and (c) bulk anatase powders.

interlayer spacing. Upon intercalation of alkylamines, linear alkylchain primary amines produced downfield shifts. The spectrum of α -ZrP/BA/Ti(OPr) $_4$ was not significantly changed from that of α -ZrP/BA. The spectrum of α -ZrP/TiO $_2$ shows one broad signal at -22.5 ppm, indicating that there is no crosslinking like P-O-Ti-O-P which signal appears at -30 ppm as Q 4 unit³⁷. Accordingly,

Fig. 8 Cumulative amounts of gas evolved from 500 cm 3 of an aqueous methanol solution at 30°C over 0.3 g of ZrP/BA/Ti(OPr) $_4$ hydrothermally treated at various temperatures exposed to irradiation from 400 W mercury lamp. Hydrothermal temp.: (Δ) untreated, ($\circ$) 100°C, ($\bullet$) 150°C, ($\square$) 200°C, and ($\blacksquare$) 250°C.

there is no chemical bonding between TiO $_2$ and phosphate groups of the host material.

The UV-VIS absorption spectra of the α -ZrP/BA (a), α -ZrP/TiO $_2$ hydrothermally treated at 100°C (b), and commercial anatase powders (c) are shown in Fig. 7 in a wavelength region of 200–600 nm. The α -ZrP/BA is silent in the range of 200–600 nm, indicating that zirconium phosphate and butylamine have no absorption in this range. In comparison to the bulk anatase, the blue shift was observed in the spectrum of the α -ZrP/TiO $_2$ presumably due to the quantum size effect^{15,16}. The band gap was estimated to be 3.45 eV from the absorption edge (ca. 360 nm) which is bigger than that of the bulk anatase form (3.2 eV)³¹.

3.3 Photocatalytic activity of Pt-loaded ZrP/TiO $_2$

Photocatalytic activity was examined by the hydrogen evolution from an aqueous methanol solution. As proposed reaction mechanism in the aqueous methanol decomposition, holes generated by the light would oxidize methanol, formaldehyde and formic acid eventually to produce carbon dioxide while the electrons in the conduction band would simultaneously reduce protons in the solution to produce hydrogen¹⁰. Thus, hydrogen was produced in three consecutive redox reactions. No oxygen evolution was confirmed by the gas chromatography. The time courses of gas evolution over Pt-loaded α -ZrP/TiO $_2$ hydrothermally treated at various temperatures are shown in Fig. 8.

The untreated composite exhibits a low photocatalytic

Table 2 Hydrogen evolution rate, crystallite size and specific surface area of ZrP/TiO₂

Hydrothermal temp. (°C)	H ₂ evolution rate ^{a)} (cm ³ /h)	crystallite size ^{b)} (nm)	specific surface area ^{c)} (m ² /g)
untreated	6.5	—	67.3
100	69.0	7.7	77.3
150	61.6	8.3	73.6
200	51.5	9.6	71.4
250	33.7	12.8	64.0

^aCatalyst, 300 mg; H₂O, 500 cm³; light source, high-pressure mercury lamp (400 W); reaction cell, inner irradiation reaction Pyrex cell; temperature, 30°C. ^bCalculated from the (020) diffraction peak of anatase using the Scherrer equation. ^cCalculated from nitrogen adsorption isotherms using the BET equation.

activity due to the amorphous phase. The hydrothermally treated composites exhibit the constant hydrogen evolution without being deactivated. The hydrogen evolution rates calculated from the slope of the lines are summarized in **Table 2** together with the crystallite size of anatase phase and surface area of the composites. The hydrogen evolution rate of the composite decreased with the hydrothermal temperature, corresponding to the decrease in the crystallite size of anatase. The quantum-size effect arises in the photocatalytic activity of TiO₂ particles of size <10 nm^{14–16}). The crystallite size of the present TiO₂ was categorized in the quantum size except for the sample hydrothermally treated at 250°C. In the case of bulk TiO₂, crystallite sizes of the samples hydrothermally synthesized at 100 and 200°C were 19.7 and 27.6 nm, respectively³²). These values are larger than 10 nm and several folds as large as those of TiO₂ in the presence of ZrP. Accordingly, quantum-size TiO₂ powders can be prepared using the interlayer space of zirconium hydrogenphosphate.

The intercalation of TiO₂ into zirconium hydrogenphosphate was achieved by the direct reaction of titanium tetraisopropoxides in ethanol medium without hydrolysis followed by the photocatalytic decomposition of organic compounds. The following conclusions were made regarding its crystallinity and photocatalytic properties.

- (1) TiO₂ in zirconium hydrogenphosphate could be crystallized to anatase by the hydrothermal treatment.
- (2) The hydrothermal treatment was effective for the photocatalytic decomposition of organic compounds: Complete decomposition was obtained in shorter UV irradiation time by the hydrothermal treatment due to the existence of anatase phase.
- (3) Photocatalytic activity of the nanocomposites was

enhanced by the hydrothermal treatment, whereas the activity decreased with an increase in the hydrothermal temperature.

Since the photocatalytic activity was enhanced by relatively mild hydrothermal treatment, the proposed fabrication method can be applicable to other layered host materials.

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