

# Influence of Phosphoric Acid Treatment on the Photocatalytic Activity of Zinc Oxide

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## Abstract

Zinc oxide is often used as a white pigment for cosmetics; however, it exhibits photocatalytic activity that causes the decomposition of sebum on the skin when exposed to the ultraviolet radiation in sunlight. In this work, zinc oxide was reacted with various concentrations of phosphoric acid for several hours to synthesize a novel white pigment for cosmetics. The chemical composition, powder properties, photocatalytic activities, colors, and smoothness of these pigments were studied. The obtained materials exhibited x-ray diffraction peaks relating to zinc oxide and phosphate after phosphoric acid treatment. The ratio of zinc phosphate to zinc oxide was estimated from inductively coupled plasma results. The sample treated for 6 hours had a high P/Zn ratio, therefore this sample contained a larger amount of zinc phosphate. The concentration of phosphoric acid had less influence on the P/Zn ratio than the processing time. The particle size of the samples became larger with phosphoric acid treatment. The photocatalytic activity of the zinc oxide was inhibited by the phosphoric acid treatment. The obtained samples had enough high reflectance in the visible light region.

*Keywords:* Zinc oxide, phosphoric acid treatment, photocatalytic activity, particle size

## I. Introduction

Zinc oxide is used in cosmetic applications as a white pigment<sup>1</sup>. This oxide is well known for its photocatalytic activity<sup>2</sup>, causing a certain degree of decomposition of sebum on the skin in the presence of the ultraviolet radiation in sunlight. Several technical processes have been investigated and used to repress this effect: for example, the use of composite particles with silicon oxide<sup>3</sup>. However, these composite materials are too hard for use on a human face, where softer materials are required for use as white pigments. In addition, one study has reported that microfine zinc oxide is adsorbed through the skin<sup>4</sup>. A novel white pigment that is not adsorbed must be used.

Phosphates have been used in ceramic materials, catalysts, adsorbents, fluorescent materials, dielectric substances, biomaterials, metal surface treatments, fertilizers, detergents, food additives, fuel cells, pigments, and other applications<sup>5–8</sup>. Phosphate materials are well known to be bio-compatible. Therefore, phosphates are expected to be useful as novel white pigments in cosmetics.

When used as a cosmetic pigment, both the particle shape and size distribution of the phosphate particles are important. Homogeneous spherical particles are expected to spread well on the skin<sup>9</sup>, however, overly small particles are unsuitable because the pigments may enter the pores of the skin. Generally, sub-micrometer pigments are used. The standard size of white pigment particles used in cosmetics is difficult to determine because the pore sizes of

the skin are affected by factors such as age, gender, and climate<sup>10</sup>. Furthermore, overly large particles are inappropriate as their coatings may crack on the skin<sup>11</sup>. It is therefore important to control the particle sizes in pigments. In earlier studies<sup>12,13</sup>, we prepared zinc phosphate pigments with no catalytic activity. However, these zinc phosphates had particle sizes larger than 1  $\mu\text{m}$ . Because these particles were too large, a novel process was required to produce smaller particles as a white pigment. Despite showing no photocatalytic activity, the zinc phosphate particles were too large, while on the other hand, zinc oxide is capable of reaching smaller particle sizes but exhibits photocatalytic activity. In this work, we investigate zinc oxide particles with a zinc phosphate coating. The target particles have a core-shell structure, with a core of zinc oxide and a shell of zinc phosphate. Our purpose in this work was to obtain a novel white pigment of sub-micrometer size that did not exhibit photocatalytic activity.

In this work, zinc oxide was shaken with various concentrations of phosphoric acid for several hours. The chemical compositions, powder properties, photocatalytic activities, colors, and smoothness of the obtained precipitates and their thermal products were studied, with potential cosmetic applications in mind.

## II. Experimental

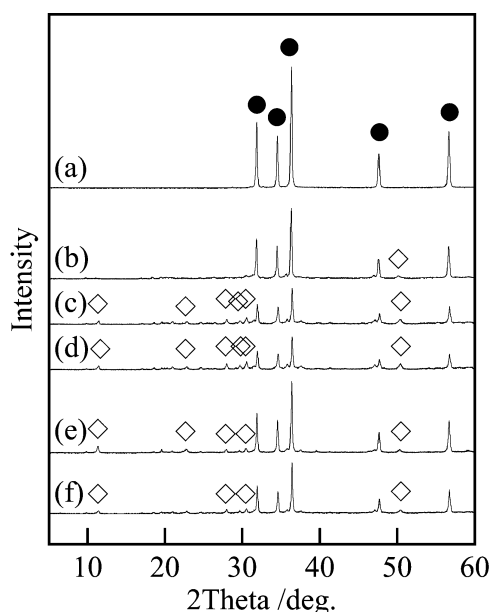
Zinc oxide was added to 0.1 mol/L of phosphoric acid solution (50 mL) in a glass tube at a molar ratio of P/Zn = 1/1 and 1/2, then shaken in water at 80 °C for 1, 3, and 6 hours. The 0.2 and 0.5 mol/L phosphoric acid was also used for

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1 hour. The powder samples were decanted, washed with water, and dried. Then, the precipitates were heated to 100 °C under atmospheric conditions to removed the adsorbed water. All chemicals were purchased from Wako Chemical Industries Ltd. (Osaka Japan), of commercial purity, and used without further purification.

The chemical compositions of these materials were analyzed using x-ray diffraction (XRD) and infrared (IR) spectra. The XRD patterns were recorded on an x-ray diffractometer (MiniFlex, Rigaku Corp.) using monochromatic CuK $\alpha$  radiation. The IR spectra of samples were recorded on a HORIBA FT-IR 720 (Horiba Ltd.) using the KBr disk method. Parts of samples were dissolved in a hydrochloric acid solution, and the ratios of phosphorus to zinc in the precipitates were calculated based on the inductively coupled plasma (ICP) results of these solutions using an SPS1500VR from Seiko Instruments, Inc.

The shapes and sizes of the thermal products were estimated from scanning electron microscopy (SEM) images and particle size distributions. SEM images of the sample powders were observed using a JSM-5510LV (JEOL). The particle size distributions were measured using a centrifugal precipitation particle-size distribution analyzer (SACP3L, Shimadzu Corp.).



**Fig. 1:** XRD patterns of samples prepared in various conditions ( $P/Zn = 1/2$ ), (a) pristine ZnO, (b) 0.1 mol/L, 1h, (c) 0.1 mol/L, 3 h, (d) 0.1 mol/L, 6 h, (e) 0.2 mol/L, 1 h, and (f) 0.5 mol/L, 1 h,  $\bullet$ ; ZnO,  $\diamond$   $Zn_3(PO_4)_2 \cdot 4H_2O$ .

The cosmetic properties investigated were photocatalytic activity, color, and smoothness. The photocatalytic activity of the samples was estimated by measuring the decomposition of methylene blue under 365 nm radiation<sup>14,15</sup>. The samples (0.01 g) were placed in 4 mL of methylene blue aqueous solution ( $1.0 \times 10^{-5}$  mol/L), and then this solution was radiated. The decrease in absorption at 660 nm was estimated over the course of 120 min. The color of the phosphate pigments was estimated using ultraviolet-visible (UV-Vis) reflectance spectroscopy with a spectrometer (UV2100; Shimadzu Corp., reference compound was BaSO<sub>4</sub>). The whiteness was also estimated with a TES135 plus

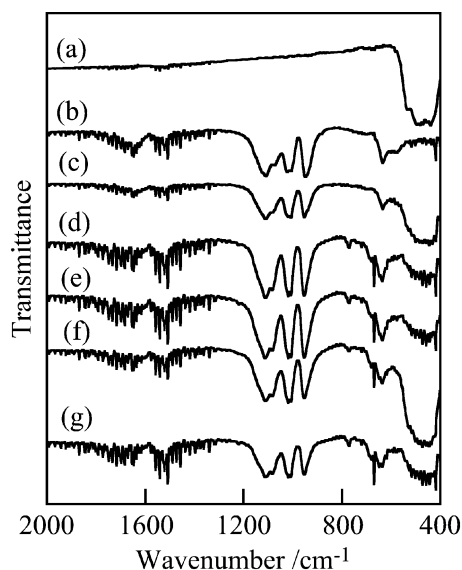
color analyzer (TES Electrical Electronic Corp). Particle smoothness was measured on artificial leather via objective evaluation of surface friction using a KES-SE (Kato Tech Co. Ltd.). Sample powders (approx. 50 mg) were spread onto the leather, and a sensor was then run over the powders (scan speed: 1 mm/s, area scanned: 3 cm<sup>2</sup>). The terms MIU and MMD represent the slipping resistance ( $\mu$ , average value in a distance of 20 mm) and the roughness of the powders (fluctuation of average frictional coefficient), respectively. The values of MIU and MMD are dimensionless because these values are related to the coefficients of friction and scattering, respectively. The dispersions of the MIU and MMD values were 0.03 and 0.002, respectively, with measurements carried out in triplicate.

### III. Results and Discussion

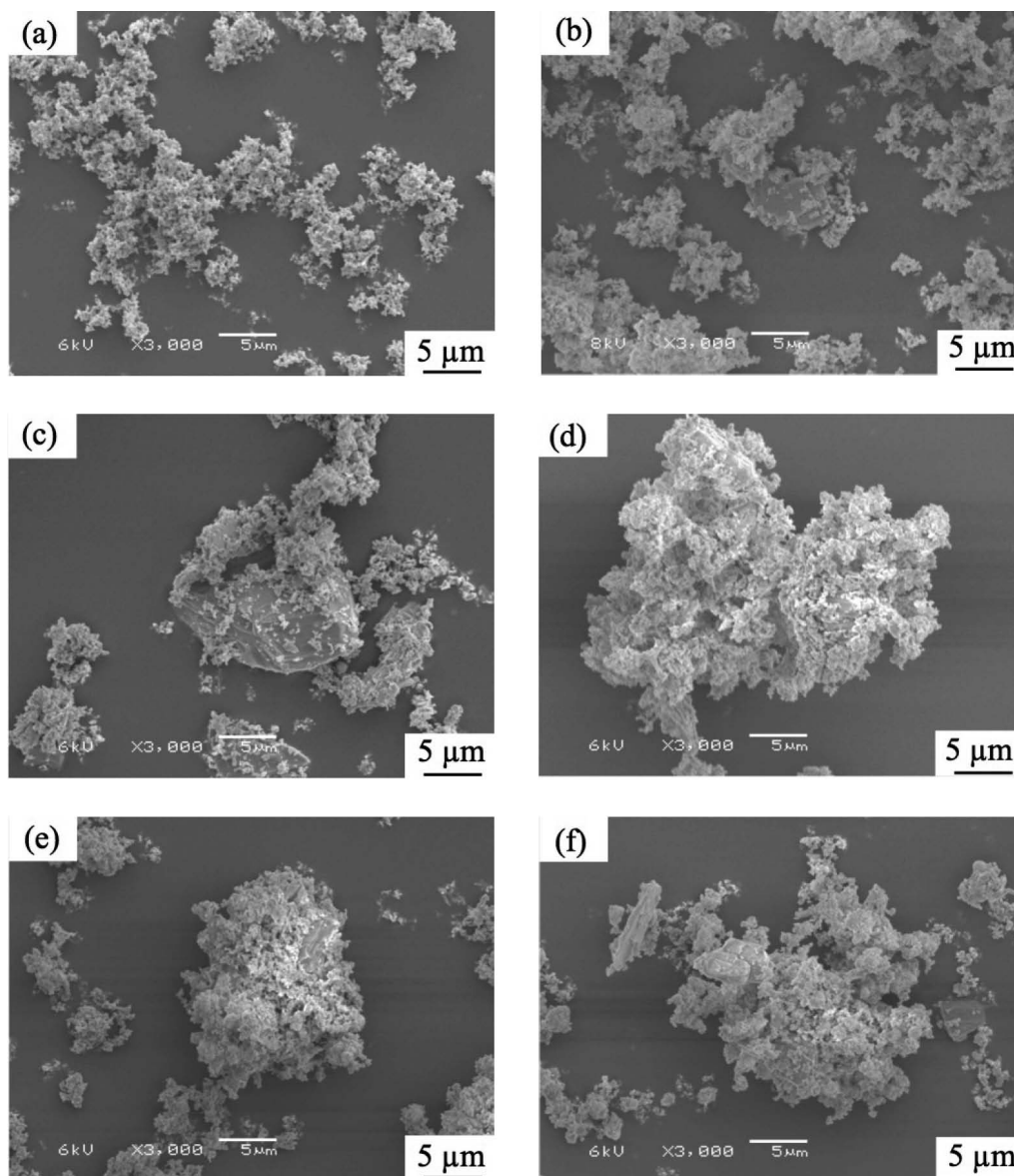
#### (1) Chemical Composition

Fig. 1 shows XRD patterns of samples prepared in various conditions and then heated to 100 °C ( $P/Zn = 1/2$ ). Phosphoric acid treatment resulted in the appearance of zinc phosphate peaks. Samples treated for 6 hours had stronger zinc phosphate peaks than other samples. On the other hand, peaks related to zinc oxide became smaller after treatment with phosphoric acid, with the sample treated for 6 hours showing particularly weak zinc oxide peaks. This confirms that zinc oxide was converted to zinc phosphate by treatment with phosphoric acid.

Fig. 2 shows the IR spectra of samples prepared in various conditions and then heated to 100 °C ( $P/Zn = 1/2$ ). Samples prepared in this work exhibited same absorption peaks with those of zinc phosphate at 1120–940 cm<sup>-1</sup>. The peak at 630 cm<sup>-1</sup> was also due to zinc phosphate. Wide absorption at 540–400 cm<sup>-1</sup> was observed in the IR spectra of samples treated at 0.1 and 0.2 mol/L for 1 hour (Fig. 2(c)(f)). Because this adsorption is due to zinc oxide, these samples had a large amount of zinc oxide. These results corresponded with the XRD peak intensity of zinc oxide in Fig. 1.



**Fig. 2:** IR spectra of samples prepared in various conditions ( $P/Zn = 1/2$ ), (a) pristine ZnO, (b) commercial  $Zn_3(PO_4)_2 \cdot 4H_2O$ , (c) 0.1 mol/L, 1 h, (d) 0.1 mol/L, 3 h, (e) 0.1 mol/L, 6 h, (f) 0.2 mol/L, 1 h, and (g) 0.5 mol/L, 1 h.



**Fig. 3:** SEM images of samples prepared in various conditions ( $P/Zn = 1/2$ ), (a) pristine ZnO, (b) 0.1 mol/L, 1 h, (c) 0.1 mol/L, 3 h, (d) 0.1 mol/L, 6 h, (e) 0.2 mol/L, 1 h, and (f) 0.5 mol/L, 1 h.

**Table 1:** P/Zn ratio in samples treated in various conditions.

Shaking time /hour	$H_3PO_4$ conc. /mol L <sup>-1</sup>	Preparation condition P/Zn	
		1/1	1/2
1	0.1	0.45	0.23
3	0.1	0.59	0.38
6	0.1	0.63	0.41
1	0.2	0.52	0.22
1	0.5	0.55	0.30

Table 1 shows P/Zn ratios in samples prepared in various conditions, as calculated from ICP measurements. The mixing ratio in preparation,  $P/Zn = 1/1$  or  $1/2$ , had a considerable influence on the P/Zn ratio in precipitates. Samples treated for 6 hours were observed to have a slightly higher P/Zn ratio than others. Longer processing time was

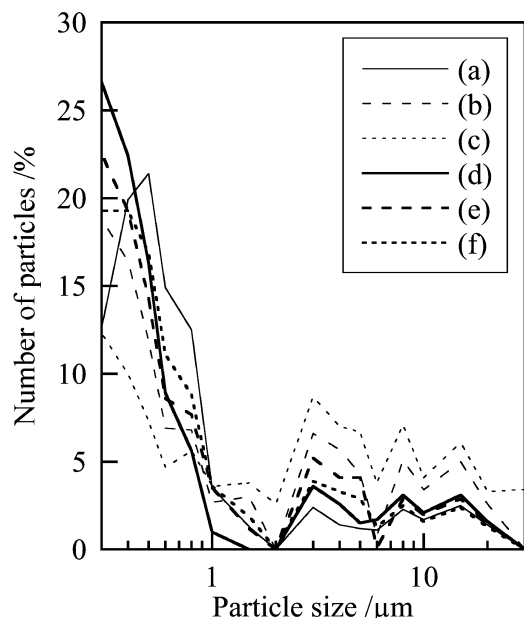
effective in the reaction between zinc oxide and phosphoric acid than the concentration of phosphoric acid. When zinc oxide and phosphate were mixed in a molar ratio of  $ZnO/Zn_3(PO_4)_2 = 1/3$ , the P/Zn ratio observed was  $3/5$ , while the molar ratios of  $ZnO/Zn_3(PO_4)_2 = 2/1$  and  $7/1$  resulted in  $P/Zn = 2/5$  and  $1/5$ , respectively.

## (2) Powder properties

Spherical particles are the preferred shape for particles used in cosmetic applications. Fig. 3 shows SEM images of samples prepared in various conditions and then heated to  $100\text{ }^\circ\text{C}$  ( $P/Zn = 1/2$ ). Samples prepared in this work had large aggregates over  $10\text{ }\mu\text{m}$  in diameter. Samples treated with phosphoric acid had larger particles than pristine zinc oxide.

Fig. 4 shows the particle size distributions of samples prepared in various conditions and then heated to  $100\text{ }^\circ\text{C}$  ( $P/Zn = 1/2$ ). The ultrasonic treatment before the measure-

ment of the particle size distributions resulted in smaller particle sizes for all samples than those observed via SEM. Samples prepared in this work had a higher ratio over  $1\ \mu\text{m}$  than pristine ZnO. Especially, the sample treated for 3 hours had large particles (Fig. 4(c)). From the ICP results, this sample had a large amount of zinc phosphate (Table 1), which affected the particle size distribution because zinc phosphate consists of particles larger than  $1\ \mu\text{m}$ <sup>12,13</sup>.



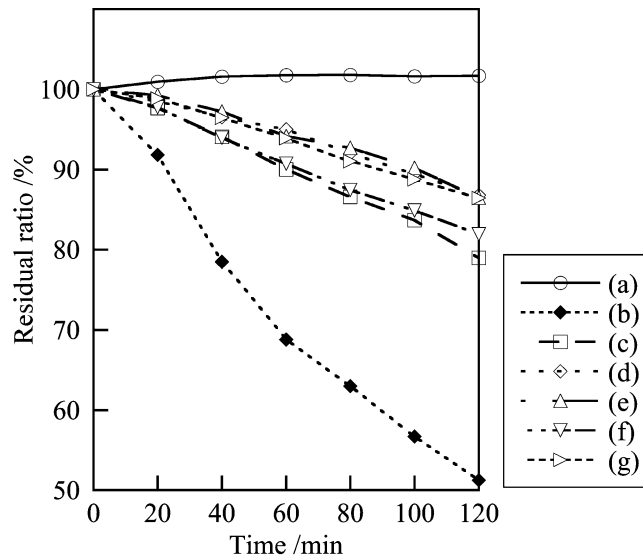
**Fig. 4:** Particle size distributions of samples prepared in various conditions ( $P/Zn = 1/2$ ), (a) pristine ZnO, (b) 0.1 mol/L, 1 h, (c) 0.1 mol/L, 3 h, (d) 0.1 mol/L, 6 h, (e) 0.2 mol/L, 1 h, and (f) 0.5 mol/L, 1 h.

### (3) Cosmetic properties

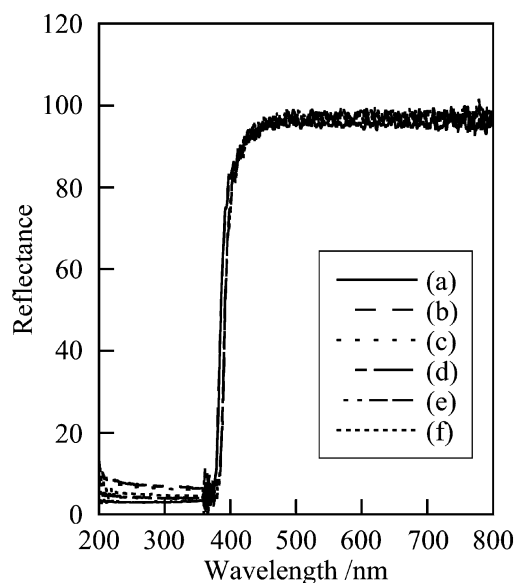
Fig. 5 shows the photocatalytic activity of samples prepared in various conditions, and then heated to  $100\ ^\circ\text{C}$  ( $P/Zn = 1/2$ ). Methylene blue was decomposed by zinc oxide under UV radiation (Fig. 5(b)), but this photocatalytic activity was inhibited by the phosphoric acid treatment (Fig. 5(c) – (g)). Samples treated for 3 and 6 hours and with 0.5 mol/L for 1 hour indicated weaker photocatalytic activity than those prepared with 0.1 and 0.2 mol/L for 1 hour. The photocatalytic activity of zinc oxide was suppressed by the formation of zinc phosphate, which has no photocatalytic activity<sup>12,13</sup>. If the zinc phosphate shell was perfectly formed on the zinc oxide core, the particles had no photocatalytic activity. Therefore, the particles obtained in this work were assumed to have some cracking of the zinc phosphate shell. These results corresponded with IR and ICP results.

Fig. 6 shows the UV-Vis reflectance spectra of samples prepared in various conditions, and then heated to  $100\ ^\circ\text{C}$  ( $P/Zn = 1/2$ ). In the visible region, all samples showed no difference compared to zinc oxide. In the ultraviolet region, samples prepared for 3 and 6 hours possessed higher reflectance than those prepared under other conditions. This was due to the high reflectance of zinc phosphate in the ultraviolet region<sup>12</sup>, and the high amount of zinc phosphate in this sample as measured based on the ICP results (Table 1). The colors of the powders were also estimated

using a  $L^*a^*b^*$  color space. Table 2 shows the whiteness of samples prepared using various conditions, from the  $L^*$  values in the  $L^*a^*b^*$  color space. The values of all the samples were high enough to qualify as white pigments ( $L^* > 95$ ). These results corresponded with the above UV-Vis reflectance spectra.



**Fig. 5:** Photocatalytic activities of samples prepared in various conditions ( $P/Zn = 1/2$ ), (a) blank, (b) pristine ZnO, (c) 0.1 mol/L, 1 h, (d) 0.1 mol/L, 3 h, (e) 0.1 mol/L, 6 h, (f) 0.2 mol/L, 1 h, and (g) 0.5 mol/L, 1 h.



**Fig. 6:** UV-Vis reflectance spectra of samples prepared in various conditions ( $P/Zn = 1/2$ ), (a) pristine ZnO, (b) 0.1 mol/L, 1 h, (c) 0.1 mol/L, 3 h, (d) 0.1 mol/L, 6 h, (e) 0.2 mol/L, 1 h, and (f) 0.5 mol/L, 1 h.

As described above, pigments with high smoothness spread well on the skin, meaning powder smoothness is important for cosmetics<sup>16</sup>. Table 3 shows the smoothness of samples prepared under various conditions. Generally, suitable MIU and MMD values for cosmetic applications are less than 0.6 and less than 0.04, respectively. All samples had sufficiently small MIU and MMD values. Samples prepared for 6 hours had smaller MIU values than other samples.

**Table 2:** Whiteness of samples treated in various conditions (ZnO; 96.1).

Shaking time /hour	H <sub>3</sub> PO <sub>4</sub> conc. /mol L <sup>-1</sup>	Preparation condition P/Zn	
		1/1	1/2
1	0.1	99.3	97.3
3	0.1	99.3	99.8
6	0.1	99.1	99.9
1	0.2	97.7	99.3
1	0.5	99.4	99.9

**Table 3:** Smoothness of samples treated in various conditions.

P/Zn (preparation)	Shaking time /hour	H <sub>3</sub> PO <sub>4</sub> conc. /mol L <sup>-1</sup>	MIU	MMD
			/-	/-
1/1	1	0.1	0.33	0.014
1/1	3	0.1	0.42	0.013
1/1	6	0.1	0.27	0.013
1/1	1	0.2	0.33	0.013
1/1	1	0.5	0.37	0.013
1/2	1	0.1	0.36	0.013
1/2	3	0.1	0.33	0.022
1/2	6	0.1	0.32	0.021
1/2	1	0.2	0.40	0.013
1/2	1	0.5	0.44	0.013
ZnO	-	-	0.50	0.016

#### IV. Conclusions

Zinc oxide was shaken in 0.1 mol/L of phosphoric acid for 1, 3, and 6 hours, and 0.2 and 0.5 mol/L of phosphoric acid for 1 hour. The obtained materials showed XRD peaks corresponding to zinc oxide and zinc phosphate after phosphoric acid treatment. The ratio of zinc oxide to phosphate was estimated from ICP results. The processing time had considerable influence on the reaction between zinc oxide and phosphoric acid compared to the concentration of phosphoric acid. The photocatalytic activity of zinc oxide became lower after treatment with phosphoric acid. All samples had enough high reflectance in the visible light range. After phosphoric acid treatment, the smoothness of samples improved. The novel white pigment for cosmetic applications was obtained by phosphoric acid treatment of zinc oxide.

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