



# Highly active aggregate photocatalyst with hierarchically porous structures synthesized by using a hydroxyapatite template

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## ARTICLE INFO

### Article history:

Received 6 January 2016

Received in revised form 2 May 2016

Accepted 4 May 2016

Available online 4 May 2016

### Keywords:

A. Ceramics

A. Nanostructures

B. Sol-gel chemistry

B. Phase transitions

D. Catalytic properties

## ABSTRACT

Crystalline meso-/macroporous  $\text{TiO}_2$  aggregate was synthesized by using a hydroxyapatite template. The hydroxyapatite could be removed by treating it with hydrochloric acid even after it was heated at  $800^\circ\text{C}$ . The aggregate included macropore with sizes of  $1\text{--}5\ \mu\text{m}$  in diameter and longer than  $5\ \mu\text{m}$  in length, penetrating into the aggregate, with walls that consisted of nanoparticles. Based on the results of  $\text{N}_2$ -BET and X-ray diffraction measurements, decline in specific surface area and anatase-rutile phase transformation during heating were suppressed by the addition of the hydroxyapatite. That is, the aggregate had higher specific surface area and higher anatase phase ratio than the control sample obtained without using the hydroxyapatite. Photocatalytic activity evaluated by a photo-decomposition of methylene blue dye increased with increasing heating temperature. The aggregate heat-treated at  $800^\circ\text{C}$  had three times higher photocatalytic activity and twenty times larger aggregate diameter than the commercial ST-01  $\text{TiO}_2$  powder.

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## 1. Introduction

Many studies have been performed on the application of titanium dioxide ( $\text{TiO}_2$ ) photocatalyst to environmental purification because  $\text{TiO}_2$  can photodecompose organic matter under UV irradiation [1,2]. Preparation of a highly active  $\text{TiO}_2$  photocatalyst is one of the most attractive topics. Some papers demonstrated that the photocatalytic activity was correlated with its bulk and surface properties such as crystalline phase [3], specific surface area [4], crystallinity [5] (or density of  $\text{Ti}^{3+}$  defects [6]), and density of surface hydroxyls [7]. Although it is difficult to reveal clearly the relationship between one of these effective factors and photocatalytic activity by an experimental work, it is widely accepted that an anatase-type  $\text{TiO}_2$  with a high specific surface area and with a high crystallinity (or a low density of defects) have a high photocatalytic activity. In fact, most commercial  $\text{TiO}_2$  photocatalysts mainly consist of crystalline anatase nanoparticles. However, the use of nanoparticles often results in problems in such as handleability and collectability. Moreover, nanoparticles are suggested to be harmful because they affect biological behavior

at cellular levels [8,9], and there are moves to tighten the regulation of nanomaterials. Therefore, the  $\text{TiO}_2$  nanoparticles are practically fixed on a substrate to prevent the inhalation.

Particle aggregation, for example by a spray-drying technique, can improve handleability and collectability of nanoparticles [10,11]. It can also reduce an inhalation volume of nanoparticles to human body by preventing powder scattering. While at the same time, in case of a common aggregation technique, photocatalytic activity is usually declined by the aggregation due to a formation of complicated diffusion pathway in the aggregate. During recent years, meso-/macroporous materials have attracted continuous research attention as some studies suggest that an introduction of interior macropore structure could enhance mass transport in the aggregate with accessible diffusion pathways [12,13]. So far, several approaches to prepare meso-/macroporous  $\text{TiO}_2$  materials have been developed using templates such as surfactants [14], latex spheres [15,16], polymer gels [16,17], woods [18], and  $\text{SiO}_2$  crystals [19]. They combine benefits of the mass transport of macropore with the high specific surface area of mesopore. However, the porous material obtained by using organic template is usually amorphous or low-crystalline phases because the heating temperature is limited to the decomposition temperature of the organic template; in many

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case they are lower than 600 °C. Although inorganic templates such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are not decomposed by the heating at high temperature, most of them have difficulty in removability because of their low solubility in acid or basic solutions, especially after they are heated at high temperature.

This work, for the first time, reports the synthesis of meso-/macroporous TiO<sub>2</sub> aggregate by using hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) particles as the template. The hydroxyapatite is an environmentally-friendly inorganic material that is highly soluble in an acid solution. The hydroxyapatite/TiO<sub>2</sub> composites were heat-treated at 500–800 °C, and the samples obtained after an acid treatment were investigated in terms of their particle morphology, size, crystalline phase, specific surface area and photocatalytic activity.

## 2. Material and methods

### 2.1. Synthesis

The hydroxyapatite template was obtained by the same synthesis process as that described in the preceding paper for the synthesis of macroporous silicon oxide [20]. Commercially available NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (1.2 g) and Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (4.1 g) were dissolved in distilled water (160 ml), and the pH value of the solution was adjusted to 10 using a 29 mass% NH<sub>4</sub>OH aqueous solution. After stirring for 3 h at room temperature, the powder precipitated was collected by filtration and dried at 110 °C. The morphology of the hydroxyapatite particle was cylindrical with cylinders of 200–300 nm in length and 20–30 nm in diameter [20]. The hydroxyapatite powder (250 mg) was ultrasonically dispersed in titanium tetraisopropoxide (TTIP, 5 g). After 2 h of hydrolysis reaction, the composite powder was collected by a centrifugation. Then, the composite powder (0.2 g) was heat-treated at respectively 500, 600, 700, 800 °C for 1 h, and subsequently acid-treated in a 1.0 mol/L hydrochloric acid solution (10 ml) for 10 min. After that, the powder was centrifuged six times with distilled water. The resulting powder is referred to here as the HA-temp sample. To obtain a control sample, the same synthesis process was carried out without using the hydroxyapatite template, and the obtained sample is referred to here as the No-temp sample.

### 2.2. Characterization

Powder X-ray diffraction (XRD) measurements were performed using a Philips X'Pert diffractometer with monochromated Cu K $\alpha$  radiation (45 kV, 40 mA). Scanning electron microscopy (SEM) images were obtained using a FE-SEM (FEI Sirion) at an acceleration voltage of 10 kV. The bulk chemical compositions were determined by X-ray fluorescence (XRF) analysis (XGT-5000Horiba). The specific surface areas were measured by a single-point N<sub>2</sub>-BET method (CHEMBET-3000 Yuasa) using powder samples dried at 150 °C for 1 day before the measurements.

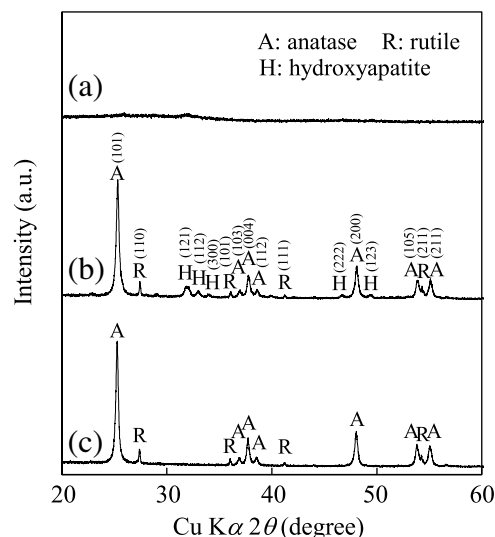
The photocatalytic activity was evaluated by measuring the photo-decomposition rate of methylene blue (MB) dye under UV irradiation [21]. The TiO<sub>2</sub> powder sample (10 mg) was dispersed ultrasonically for 10 min in 20  $\mu$ M MB solution (50 ml) and stirred for 24 h in the dark. The resulting suspension was irradiated by a UV (365 nm) light at the intensity of 0.50 mW/cm<sup>2</sup>. The samples were collected from the suspension after the UV irradiation for 15, 30, 45, and 60 min, respectively. The absorbance at a wavelength of 664 nm of the suspension sample centrifuged was measured by a UV-vis spectrometer (UV-3100PC Shimadzu) to determine the MB concentration. The photocatalytic activities of the samples were compared with the commercial TiO<sub>2</sub> powder, ST-01 Ishihara Sangyo, which is an anatase-type TiO<sub>2</sub> nanopowder with a specific surface area of 300 m<sup>2</sup>/g.

## 3. Results and discussion

XRD patterns of the hydroxyapatite/TiO<sub>2</sub> composite sample obtained after hydrolysis reaction of TTIP, the composite sample heat-treated at 800 °C, and the sample subsequently acid-treated (the HA-temp 800 °C sample) are shown in Fig. 1. No XRD peaks were detected in the composite sample before the heating (Fig. 1(a)). This indicates that the TiO<sub>2</sub> structure formed by the hydrolysis reaction of TTIP was amorphous, and the composite contained a small amount of low-crystalline hydroxyapatite. In contrast, sharp XRD peaks were detected in the composite sample after the heating at 800 °C (Fig. 1(b)). The peak assignments indicated that the sample composed of anatase (JCPDS 89-4921), rutile (JCPDS 89-4920), and hydroxyapatite (JCPDS 84-1998), and that the hydroxyapatite structure was maintained even after the heating at 800 °C. After an acid treatment in a 1.0 mol/L hydrochloric acid solution (Fig. 1(c)), the XRD peaks of the hydroxyapatite were not detected. The results of XRF analyses also confirmed the disappearance of hydroxyapatite. The bulk Ca/Ti atomic ratio of the powder sample was reduced from 0.050 to 0.006 by the acid treatment. It was thus inferred that hydroxyapatite has high acid solubility enough to be removed by the acid treatment with hydrochloric acid at room temperature.

Typical SEM images of the HA-temp 600–800 °C samples are shown in Fig. 2. Macroporous structures were observed in all the samples, and their pore sizes were mainly 1  $\mu$ m to 5  $\mu$ m. The difference between the pore sizes and the particle sizes of the hydroxyapatite template (200 nm to 300 nm [20]) was probably caused by the aggregation of the hydroxyapatite particles during the heating. The aggregation might also cause the nonuniformity of the macroporous structures. Further observation shows that most of the macropore was oriented parallel to each other within one aggregate. The mean volume diameter of the aggregates estimated by observing hundreds of aggregates in the SEM images were, respectively, 40  $\mu$ m (HA-temp 600 °C), 82  $\mu$ m (HA-temp 700 °C), and 76  $\mu$ m (HA-temp 800 °C). They were 10–20 times larger than that of the commercial ST-01 TiO<sub>2</sub> powder (4  $\mu$ m). In fact, the HA-temp samples could be easily collected by their gravity, filtration, or centrifugation.

Interestingly, the macropore walls in the aggregates composed of spherical nanoparticles. Primary particles with size of approximately 50 nm, for example in the HA-temp 700 °C sample, were



**Fig. 1.** XRD patterns of (a) the TiO<sub>2</sub>/hydroxyapatite composite obtained after the hydrolysis reaction of TTIP, (b) the composite heated at 800 °C for 1 h, and (c) the HA-temp 800 °C sample.

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