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Preparation of porous titanium phosphate glass-ceramics for NH_3 gas adsorption with self-cleaning ability

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Abstract

Porous glass-ceramics with a skeleton of γ-$Ti(HPO_4)_2 \cdot 2H_2O$ crystals are derived from glasses in the Li_2O–CaO–TiO_2–P_2O_5 system by utilizing spinodal-type phase separation, crystallization and subsequent acid treatment of the resulting glass-ceramics. The glass-ceramics have both micro-sized (1–2 μm) and nano-sized pores (5–30 nm), and they adsorb polar molecules. In the present work, porous TiO_2 layers of 200–500 nm thickness were successfully deposited on the surfaces of the glass-ceramics by an infiltration of $Ti(OCH(CH_3)_2)_4$ and water vapor treatment at 100 °C under 100% relative humidity. X-ray diffractometry and laser Raman spectroscopy revealed the formation of anatase crystals. The resulting anatase-modified porous glass-ceramics show high activities for NH_3 adsorption as well as for photodecomposition of the adsorbed NH_3 molecules.

Keywords: Glass-ceramic; Sol–gel processes; TiO_2

1. Introduction

Porous glasses and glass-ceramics utilizing spinodal-type phase separation have advantages over porous ceramics prepared by conventional powder-sintering methods. This process is relatively simple, and crystalline phases with an active function can be also precipitated as the skeleton of the porous materials. Our group has developed a series of porous glass-ceramics in the titanium phosphate system.[1,2] Porous glass-ceramics with a skeleton of $LiTi_2(PO_4)_3$ or $LiTi_2(PO_4)_3$:Al show excellent cation exchange properties. These crystals have so-called Nasicon-type structure,[3] in which PO_4 tetrahedra share their corners with TiO_6 octahedra to form a three-dimensional network. Since Li^+ ions are located in two different sites of the conduction channel, $LiTi_2(PO_4)_3$ shows high Li^+ conductivities with chemical stability.[4,5]

Porous glass-ceramics with a skeleton of γ-$Ti(HPO_4)_2 \cdot 2H_2O$ crystal (denoted by THP glass-ceramics, hereafter) which have a two-dimensional layered structure can be prepared by crystallization of glasses in the Li_2O–CaO–TiO_2–P_2O_5 system and subsequent acid treatment of the resulting glass-ceramics at temperatures higher than 60 °C. The porous glass-ceramics adsorb polar molecules such as NH_3 or monoalkylamines due to the strong interaction between the P–OH groups located at the interlayers in the THP and the polar molecules.[6]

Various types of adsorbents modified with photocatalytic materials have been widely investigated since they can be used for applications to air- and/or water-purification, antifouling protection and bleaching.[7,8] Among them, hydroxyapatite (HAp)/TiO_2 composites show good adsorption and photodecomposition properties for polluting materials such as bacteria and toxic chemical compounds.[9–13] However, the chemical degradation of HAp under acidic conditions limits the industrial application of the HAp/TiO_2 composites. Fluorine-substituted HAp and TiO_2 composites have been investigated to improve the chemical degradation of HAp.[14]

In the present work, chemically stable porous THP glass-ceramics coated with anatase TiO_2 microcrystals were prepared by an infiltration sol–gel process. Precursors of TiO_2 were infiltrated into the THP glass-ceramics, followed by water vapor treatment to precipitate anatase crystals. Their structures and the photodecomposition activities of adsorbed NH_3 molecules under UV irradiation are discussed.

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2. Experimental procedure

2.1. Preparation of porous THP glass-ceramics

A nominal composition of the mother glass was $11.7Li_2O·3.3Al_2O_3·26.7TiO_2·33.3P_2O_5·25CaO$ in mol%. The batch mixture was prepared using raw materials of reagent grade Li_2CO_3, $Al(OH)_3$, $CaCO_3$, TiO_2 and H_3PO_4 (85% liquid). The mixture was put into a Teflon beaker with a small amount of water and stirred well to make a slurry. After the slurry was dried, the resulting product was melted in a platinum crucible at 1350 °C for 2 h in air. The melt was poured onto a stainless plate to obtain the mother glass.

The plate-shaped glass was heated at 580 °C for 20 h for nucleation and subsequently heated at 690 °C for 8 h for crystal growth. These temperatures were determined from the results of differential thermal analysis (DTA) and thermogravimetry (TG).

The resulting glass-ceramic was put into 1 M HCl aqueous solution at 100 °C for 3 days to obtain a porous $Ti(HPO_4)_2·2H_2O$ glass-ceramic (HCl treatment). Finally, the glass-ceramic was washed with deionized water.

2.2. Surface modification with anatase layers

The porous THP glass-ceramic was dried at 100 °C under vacuum, followed by immersion into a $Ti(OCH(CH_3)_2)_4$ (IPT) and isopropyl alcohol (IPA) mixture (the weight ratio of IPT:IPA = 1:3) under vacuum for 15 min. To precipitate anatase crystal, the IPT coated THP glass-ceramic was exposed to water vapor at 100 °C under 100% relative humidity for 10 h in a temperature-humidity controlled chamber (HIRAYAMA, HASTEST PC-304 R8).

2.3. Characterization

Crystalline phases were examined by X-ray diffraction (XRD) and the microstructure was observed by scanning electron microscopy (SEM). The pore structures of samples were measured using a nitrogen gas sorption analyzer. Laser raman spectra (LRS) was measured using the 514.5 nm line of an Ar^+ laser as the exciting beam.

The plate-shaped porous glass-ceramic covered with anatase layers was exposed to ammonia vapor at room temperature for 30 min in a tightly sealed vessel with 28% ammonia water for adsorption of NH_3 molecules, and then the sample was irradiated with UV light (black light, 365 nm). The photocatalytic decomposition of the adsorbed NH_3 molecules after UV irradiation was evaluated by Fourier transform infrared (FT-IR) spectroscopy (KBr technique).

3. Results and discussion

3.1. Preparation of porous THP glass-ceramics and surface modification with anatase

Fig. 1 shows XRD patterns of the $Li_2O–CaO–TiO_2–P_2O_5$ glass-ceramic before and after being treated with 1 M HCl. The glass-ceramic before HCl treatment consists of $LiTi_2(PO_4)_3$:Al and β-$Ca_3(PO_4)_2$ (denoted as LTP and β-TCP, respectively). After the HCl treatment, almost all of the LTP and β-TCP phase disappeared, and new crystal phases of $Ti(OH)PO_4$ and THP were observed. Fig. 2(a) and (b) shows SEM images of the glass-ceramics before and after the HCl treatment. The surface morphology of the glass-ceramic was drastically changed after the HCl treatment. The skeleton of the glass-ceramic was converted to a sponge-like structure with 1–2 μm diameter pores.

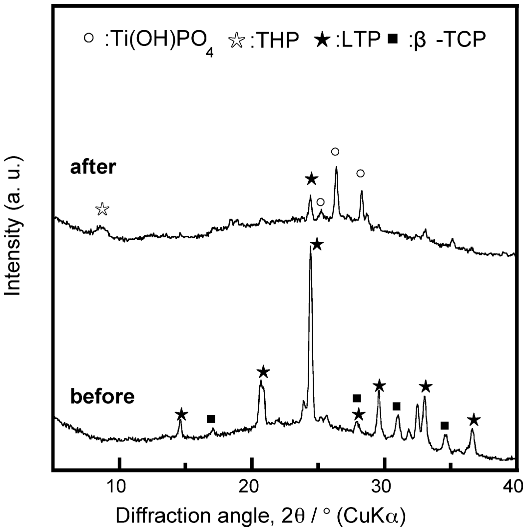

Fig. 1. XRD patterns of the glass-ceramics before and after treatment with 1 M HCl aqueous solution at 100 °C for 3 days.

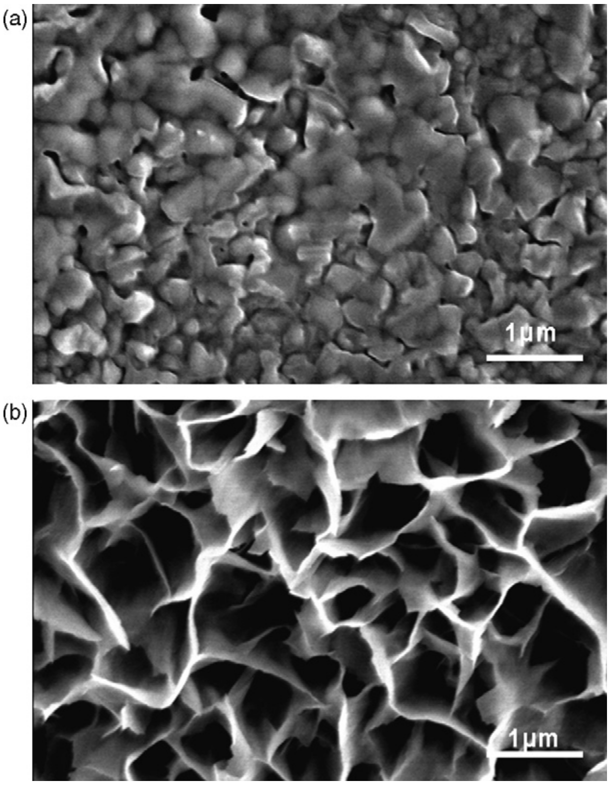

Fig. 2. SEM images of the glass-ceramics (a) before and (b) after treatment with 1 M HCl aqueous solution at 100 °C for 3 days.

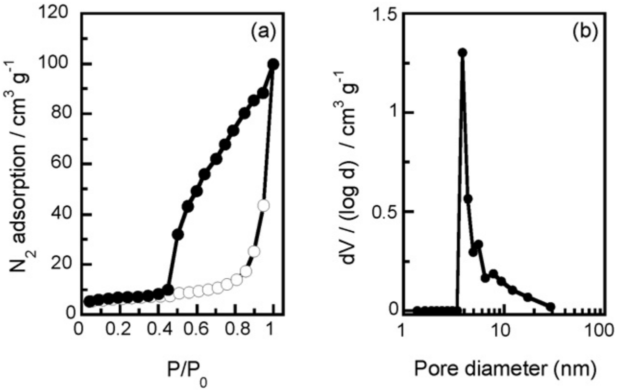

Fig. 3. (a) Nitrogen gas sorption and desorption isotherm for the porous THP glass-ceramic. Open and closed symbols indicate the adsorption and desorption branches, respectively. (b) Pore size distribution curve, determined by a BJH method using the desorption branch of (a).

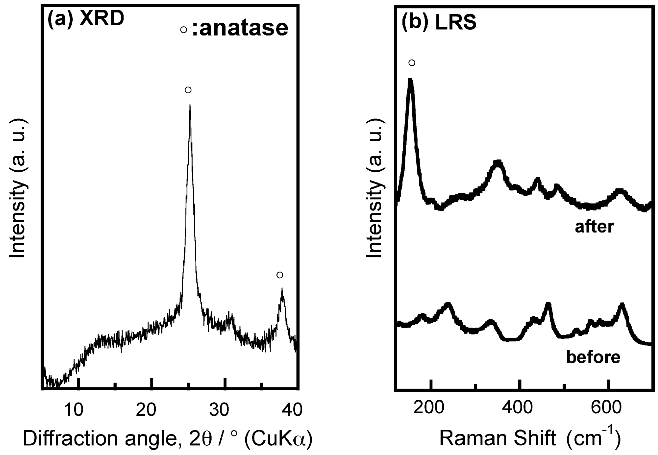

Fig. 4. (a) XRD pattern of the TiO_2-coated porous THP glass-ceramic after the water vapor treatment. (b) LRS of the TiO_2-coated porous THP glass-ceramic before and after the water vapor treatment.

Fig. 3(a) shows the nitrogen gas adsorption and desorption isotherm for the porous THP glass-ceramic. The hysteris is clearly observed, and the isotherm is considered to be of the Type V in the IUPAC classification.[15] The pore size distribution curve calculated using the BJH method based on the result of the nitrogen gas desorption measurement is shown in Fig. 3(b). The sharp peak at 3.8 nm in diameter was also obtained using the result of the nitrogen gas adsorption branch. Note that, in addition to the micro-sized pores as shown in the SEM images, the THP glass-ceramic has nano-sized pores. A porous glass-ceramic with both micro- and nano-sized pores was prepared after the HCl treatment of the Li_2O–CaO–TiO_2–P_2O_5 glass-ceramic. Similar pore structures with bimodal pore sizes have been developed[16] and applied for the column of high performance liquid chromatography (HPLC).[17,18]

The TiO_2-modified glass-ceramic composites were prepared for a self-cleaning adsorbent. Anatase crystal can be obtained by heat treatment of a TiO_2 gel above 400 °C.[19] However, dehydration of THP was observed at around 280 °C, leading to decomposition of the pore structure. The Ti–O–Ti network is hydrolyzed when the TiO_2 gel is placed in hot water, followed by precipitation of anatase crystals at temperatures lower than 100 °C.[20] The crystallization of TiO_2 gel films by water vapor was also reported.[19] In the present work, water vapor treatment of TiO_2 gel was adopted. The porous THP glass-ceramic was immersed into $Ti(OCH(CH_3)_2)_4$ (IPT) and 2-propanol (IPA) mixture solution under vacuum, followed by water vapor treatment at 100 °C and 100% relative humidity. Fig. 4(a) shows the XRD pattern of the IPT-infiltrated porous THP glass-ceramic after the water vapor treatment. Two peaks attributed to anatase crystal are clearly observed at the diffraction angle 2θ of ∼25° and ∼38°. The formation of anatase crystal after the water vapor treatment is also seen in the LRS spectra. As shown in Fig. 4(b), a typical Raman band attributed to anatase crystal is observed at around 150 cm^{-1} after the water vapor treatment. Fig. 5 shows the SEM image of the anatase-coated porous THP glass-ceramic. Note that the skeleton surfaces of the THP glass-ceramic are well-coated with the TiO_2 layer. Thickness of the anatase layers, roughly estimated to be 200–500 nm from the SEM image, varied with the concentration of IPT in the 2-propanol mixture. The specific surface area, calculated from the result of the nitrogen gas sorption measurement, slightly decreased after the deposition of anatase layers (from 20 to 16 m^2/g), suggesting that the sol–gel-derived anatase layers are porous, which allow gas adsorption.

3.2. *Photocatalytic decomposition of adsorbed NH_3 molecules*

We previously reported that the porous THP glass-ceramic of 5 mg can absorb ammonia gas of about 200 ppm within 5 min.[6] The photocatalytic decomposition of the adsorbed NH_3 molecules with UV irradiation was evaluated by FT-IR spectroscopy. Fig. 6(a) and (b) shows the FT-IR spectra for the unmodified THP and anatase-coated THP glass-ceramics, respectively, before and after UV irradiation. The band at around 1400 cm^{-1} assigned to the N–H stretching mode of adsorbed NH_3 molecules is clearly observed not only for unmodified THP glass-ceramic but also for the anatase-coated THP glass-ceramics. Note that the absorbance of the peak for the anatase-coated THP decreases with increasing the UV irradi-

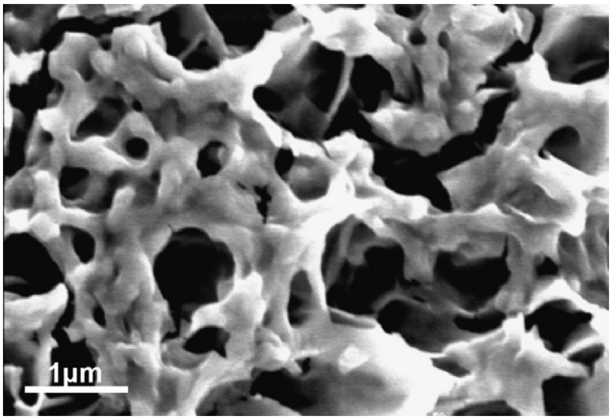

Fig. 5. SEM image of the anatase-coated porous THP glass-ceramic.

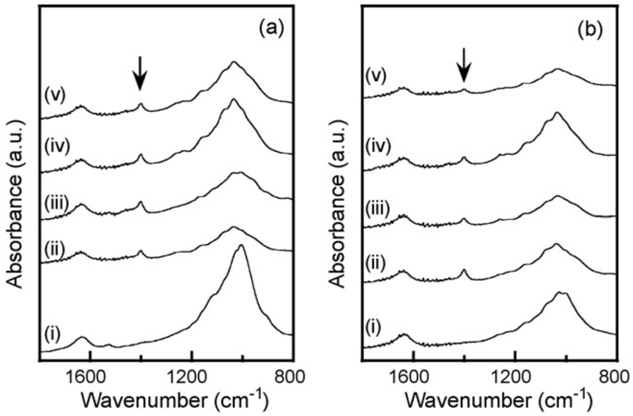

Fig. 6. FT-IR spectra for (a) unmodified THP glass-ceramic and (b) anatase-coated THP glass-ceramic with UV irradiation period: (i) before NH_3 adsorption; (ii) after NH_3 adsorption; (iii–v) after UV irradiation of the NH_3 adsorbed sample. UV irradiation periods of (iii–v) are 3, 12, and 24 h, respectively.

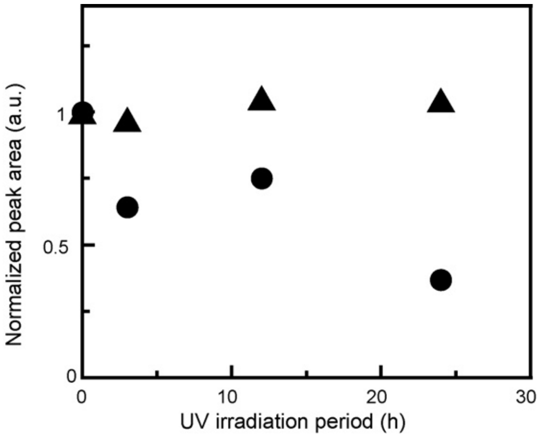

Fig. 7. Plots of the normalized peak area of N–H stretching mode at 1400 cm^{-1} for (▲) unmodified THP glass-ceramics and (●) anatase-coated THP glass-ceramic as a function of UV irradiation period.

ation period, whereas no significant changes are observed for the unmodified THP glass-ceramic. These results suggest that the adsorbed NH_3 molecules are photodecomposed by photocatalytic reaction of the anatase layers.

Changes in the peak area for the N–H stretching mode with UV irradiation period are plotted in Fig. 7, where the area is normalized by the value before UV irradiation. The peak area for the anatase-coated THP glass-ceramic gradually decreases with increasing the UV irradiation period. All of the NH_3 molecules, however, are not decomposed even after 24 h of UV irradiation. The ratio of the photodecomposed NH_3 molecules to the total absorbed NH_3 is estimated from the peak area to be about 65%. To improve the photocatalytic activity, investigations include using powdered samples, controlling the porosity and thickness of the anatase layers as well as analyzing the photocatalytic reaction products are in progress.

4. Summary

Porous glass-ceramics composed of THP crystal skeleton modified with anatase layers were prepared by an infiltration sol–gel process. Anatase crystals were formed after water vapor treatment at 100 °C and 100% relative humidity for 10 h. The modified THP glass-ceramics show a high activity for NH_3 absorption, and the adsorbed NH_3 molecules are gradually decomposed by UV irradiation.

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