Monolithic SrTiO₃/titanate nanotube/TiO₂ nanocomposite toward enhanced photocatalytic activity

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Photocatalytic monoliths with hierarchical pores ranging from nm to µm, consisting of titanate nanotubes (TNTs), SrTiO₃ nanoparticles, and TiO₂ nanoparticles, are prepared by a hydrothermal reaction of a porous TNT/TiO₂ monolith with Sr(OH)₂. The precursory TNT/TiO₂ monolith is composed of TNTs and TiO₂ (anatase) nanoparticles where the frameworks of the monolith are constructed from interconnected and entangled TNTs. The SrTiO₃ nanoparticles and TNTs in the porous monolith is considered to benefit an enhancement of photocatalytic activity due to an effective suppression of the electron–hole recombination at the heterojunction.

Key-words: Photocatalyst, SrTiO₃, Heterojunction, Titanate nanotube, Monolith

1. Introduction

Monolithic materials are preferable for particular applications including heterogeneous catalysts and absorbates compared to powdery materials because they are more easily handled and separated from a solution.¹,² Hierarchically porous monoliths with wide distributions of pore size ranging from nm to µm are highly desirable in those applications because nm-scale mesopores increase the accessible surface area and µm-scale macropores enhance molecular diffusion inside the materials.³–⁷ Porous monoliths consisting of photocatalytic compounds are expected to be used as photocatalytic reactors, filters, and pellets.⁸–¹¹ To date, the most porous photocatalytic monoliths were prepared by a molecular-based sol–gel strategy combined with soft-templates.¹²–¹⁵ In this method, inorganic frameworks are constructed with oxides or hydroxides from molecular precursors like metal alkoxides through a sol–gel reaction, while the µm-scale macropores and nm-scale mesopores formed after the removal of the soft-templates. This strategy allows for the fabrication of porous photocatalytic monoliths composed of metal oxides such as TiO₂, ZrO₂, SrTiO₃.¹⁶–²⁰ Although the well-developed method allows to control the pore structures, a heat treatment process at high temperature is generally required to remove the soft-templates and to obtain the monolith with higher crystallinity, which causes a decrease of specific surface area and a collapse of the monolithic shape due to a shrinkage during the crystallization process of the inorganic networks. In addition, this process is unavailable for the thermodynamically-unstable crystalline phase like metal hydroxides at high temperature.

An alternative approach has been recently developed by assembling one-dimensional nanomaterials.²¹–²³ The inorganic frameworks are fabricated by the interconnection of the crystalline one-dimensional nanomaterials in which pores form between each nanomaterial. This method is free from a heat treatment process at high temperature because the frameworks are formed by the crystalline one-dimensional nanomaterials without any soft-templating agents, allowing for high accessible surfaces for the catalytic reaction. As an additional advantage of this procedure, porous monoliths composed of thermodynamically-unstable metal hydroxides are possible to be fabricated.²⁴,²⁵ Metal hydroxide-based monoliths are of interest for catalytic supports because metal hydroxides have highly reactive surfaces for post-modification.²⁶–³³ Recently, we have reported the fabrication of a titanate nanotube (TNT)-based macroporous monolith.³⁴ TNT is a tubular one-dimensional nanomaterial synthesized by the hydrothermal treatment of TiO₂ in NaOH aqueous solution. The wall of nanotube is composed of protonated titane with a layered structure that exhibits ion-exchange ability.³⁵–³⁷ The TNT-based monolith is impossible to be fabricated by the sol–gel strategy because protonated titane is a thermodynamically-unstable phase.³⁸,³⁹ Our approach is based on the interconnection of the elongated TNTs during the conversion process from TiO₂. The resultant monolith is shown to have a hierarchical architecture of nanopores and macropores. The monolith exhibits a faster rate and a higher capacity of Li⁺ exchange than simply-compact
TNTs thanks to the hierarchical porous architecture. Also, the monolith is reusable for multiple times without a lack of the exchange ability.

Protonated titanate is known to be a n-type semiconducting material showing photocatalytic ability similar to TiO$_2$ (anatase). Another interesting feature of protonated titanate is a topochemical conversion into titanate-based perovskites such as CaTiO$_3$, SrTiO$_3$ and BaTiO$_3$ by the hydrothermal treatment of cation-intercalated titanate. The perovskites prepared via the topochemical reaction have bonded interfaces like coherent and heteroeptifacial interfaces with protonated titanate. Such bonded interfaces are important for the enhancement of catalytic activities. For examples, a generation of heterojunction structures of TiO$_2$ and SrTiO$_3$ with good photocatalytic properties was reported. The valence and conduction band edges of SrTiO$_3$ are slightly negative than those of TiO$_2$ but also transfer of hole from the valence band of TiO$_2$ to that of SrTiO$_3$. Consequently, the improved separation between photogenerated electrons and holes can improve the photocatalytic activity of TiO$_2$. The valence and conduction band edges of protonated titanate are reported to be slightly positive than those of TiO$_2$ (anatase), indicating those of SrTiO$_3$ are also negative than those of protonated titanate similarly to anatase. Thus, the heterojunction structures of protonated titanate and SrTiO$_3$ with good interfaces are expected to exhibit the enhanced photocatalytic properties than pure protonated titanate.

Herein, we synthesized monoliths mainly composed of SrTiO$_3$ and TNTs where interconnected TNTs contributed to the formation of the frameworks on which SrTiO$_3$ nanoparticles were formed with close contact. A hydrothermal reaction of TNT-based macroporous monoliths with Sr(OH)$_2$ resulted in the formation of SrTiO$_3$ nanoparticles on TNTs maintaining the macroporous structures. The resultant SrTiO$_3$/TNT-based monolith exhibited higher efficiency on the photocatalytic degradation of rhodamine B (RhB) in comparison with the TNT-based monoliths.

2. Experimental

2.1 Preparation of TNT/TiO$_2$ monolith

The TNT/TiO$_2$ monolith was prepared by following the method described in a previous report. 0.40 g of anatase powder (ST-21, Ishara Sangyo, Co., Ltd., Japan) was dispersed in 2 mL of 5 M aqueous NaOH. The suspension was added in a polytetrafluoroethylene container (diameter: 30 mm, height: 40 mm). The container was sealed in a stainless-steel autoclave, and heated at 130°C for 36 h. After the reaction, the monolithic product in the bottom of the container was collected and washed with aqueous HCl (pH 3) for 24 h. The products were slowly dried at 40°C for 48 h.

2.2 Preparation of STO/TNT/TiO$_2$ monolith

The conversion from the TNT/TiO$_2$ monolith into STO/TNT/TiO$_2$ monolith was performed as follows. The TNT/TiO$_2$ monolith (0.562 g) was soaked into the conversion solution prepared by adding 1.31 g of Sr(OH)$_2$·8H$_2$O in a mixture of 12 mL of water, 4 mL of ethanol, 4 mL of 2.5 M aqueous NaOH, and 4 mL of polyethylene glycol solution (PEG, MW 300, 0.8 wt% in water). The polyethylene glycol was used as a potential growth modifier. The TNT/TiO$_2$ monolith in the conversion solution was transferred into the polytetrafluoroethylene container. The container was sealed in a stainless-steel autoclave, and heated at 100°C for 1–3 h. After the reaction, the monolithic product was collected and washed with water at least three times, 1 M acetic acid and ethanol. Then, the products were slowly dried at 40°C for 12 h. The washing process with 1 M acetic acid is to exchange intercalated cation from Sr$^{2+}$ to H$^+$ in the interlayer of TNT.

2.3 Characterization

Macrostructures and nanostructures were observed by a field emission scanning electron microscope (SEM) (S-4800, Hitachi, Japan) and transmission electron microscope (TEM) (JEM-2000FX, JEOL, Japan), operated at 200 kV. Crystal structures were characterized by X-ray diffraction (XRD), using Cu K$_\alpha$ radiation (λ = 0.154 nm) on a Rigaku diffractometer (SmartLab, Rigaku, Japan). Brunauer–Emmett–Teller (BET) surface areas were determined from N$_2$ sorption measurements (BELSORP-mini II; Bel Japan Inc., Japan). Before the measurement, the samples were degassed under vacuum at 150°C. Specific surface areas were estimated by the BET method.

2.4 Measurement of photocatalytic activity

The monolithic catalyst (40 mg) was placed at the bottom of a cell [for ultraviolet–visible (UV–Vis) spectrophotometer, optical path length: 10 mm] filled with 3 mL of RhB aqueous solution (0.01 mM). The monolithic catalyst was illuminated by light (500 W xenon arc lamp, SX-UID500, USHIO, Japan) through a quartz glass. Before photolirradiation, the photocatalyst was stored in the RhB aqueous solution for 1 h in order to exclude the effect of adsorption of dyes. The concentration of RhB in the solution was monitored with a spectrophotometer (UV–Vis; V-670 spectrophotometer, JASCO Corp., Japan) at λ = 553.5 nm. At prescribed intervals of illumination, the cell was directly analyzed with the spectrophotometer.

3. Results and discussion

The SrTiO$_3$/TNT-based monolith (STO/TNT/TiO$_2$ monolith) was synthesized via a reaction of the TNT-based monolith (TNT/TiO$_2$ monolith) with Sr(OH)$_2$. The TNT/TiO$_2$ monolith is composed of TNTs and TiO$_2$ (anatase) nanoparticles where the frameworks of the monolith were constructed from interconnected and entangled TNTs with residual anatase nanoparticles as reported in our previous report. The TNTs in the frameworks were reacted with Sr(OH)$_2$ to form SrTiO$_3$ nanoparticles. Figure 1 shows a resultant STO/TNT/TiO$_2$ monolith. Although a few cracks were observed, monoliths of centimeter scale could be
fabricated with sufficiently robust frameworks as it could be handled without special care. The monolith possessed macropores of which diameters are ranging from 1 to 10 μm as seen in the SEM image. The macropores in the monolith play an important role for enhanced photocatalytic activity of the monolith because reactants can diffuse inside the material. The formation of SrTiO$_3$ nanoparticles with around 50 nm in diameter was observed on the interconnected and entangled TNTs (Fig. 2). The specific surface area of the STO/TNT/TiO$_2$ monolith was as high as 82.14 m$^2$/g derived from the nanostructured SrTiO$_3$ and the nanotubular protonated titanate (Fig. S1). It should be noted that the monolith could be obtained by a simple drying process without supercritical drying which is generally required to obtain porous monoliths.

The μm- and nm-scale structures of the STO/TNT/TiO$_2$ monolith were compared with those of the TNT/TiO$_2$ monolith (Fig. 3). Before the formation of SrTiO$_3$, the TNT/TiO$_2$ monolith was constructed from TNTs and TiO$_2$ nanoparticles where TNT/TiO$_2$ secondary particles of a few micrometers were bridged by entangled/interconnected TNTs [Figs. 3(a) and 3(b)]. Macropores with a range from 1 to 10 μm were formed by the concentration fluctuation of TNT. These results consisted with our previous report.$^{34}$ After the reaction of the TNT/TiO$_2$ monolith with Sr(OH)$_2$ for 1 h under a basic hydrothermal condition, SrTiO$_3$ nanoparticles with around 50 nm homogeneously formed on the TNT-based frameworks [Figs. 3(c) and 3(d)]. The formation of SrTiO$_3$ with the presence of protonated titanate (H$_2$Ti$_6$O$_8$·H$_2$O) and TiO$_2$ (anatase) was confirmed by XRD measurement (Fig. 4). The presence of TiO$_2$ (anatase) in the TNT/TiO$_2$ secondary particles was confirmed by TEM (Fig. S2). The peaks attributed to SrTiO$_3$ were located at slightly lower angle than those of the standard SrTiO$_3$ (JCPDS 35-0734). Similar peak shift attributed to perovskite (BaTiO$_3$) toward lower angle was reported in H$_2$Ti$_6$O$_8$·H$_2$O/BaTiO$_3$ system.$^{43}$ The conversion from protonated titanate into SrTiO$_3$ is considered to take place via a two-step solvothermal topochemical process as reported so far.$^{50,51}$ In the first step, Sr$^{2+}$ are intercalated into the interlayer space of protonated titanate by the cation-exchange process from H$^+$ into Sr$^{2+}$. Then, the intercalated Sr$^{2+}$ reacts with the TiO$_6$ octahedra of protonated titanate to form SrTiO$_3$ nanocrystals. The SrTiO$_3$/TNT nanocomposite, that TNTs are partly converted into SrTiO$_3$ nanoparticles, can be synthesized under an optimal reaction time in this process. This process resulted in the direct formation of SrTiO$_3$ nanoparticles on TNTs with close contact. The formation of SrTiO$_3$ nanoparticles did not lead to the obvious change of the macropores. While, in the nanometer-scale structures, a break of TNT bridges was partly observed due to the formation of SrTiO$_3$ nanoparticles on the TNT bridges. Less dense TNT bridges were considered to be broken by the conversion of the elongated TNTs into the spherical SrTiO$_3$ nanoparticles (Fig. 5). The partial break of TNT bridges might cause the crack formation in the monolith. However, most TNT bridges still remained after the formation of SrTiO$_3$ nanoparticles on them as observed in Fig. 3(e), resulting in the centimeter-scale monolith enough strong for handling and the use for applications. Longer reaction time of the TNT/TiO$_2$ monolith with Sr(OH)$_2$ resulted in the promotion of...
the conversion from TNT to SrTiO₃ and the growth of the SrTiO₃ nanoparticles (Fig. S3). The molar ratios of SrTiO₃ to TNT for the samples prepared in 1 and 2 h were 0.30 and 0.36, respectively, which was calculated from XRD patterns with a calibration curve (Fig. S4). After 3 h reaction time, the frameworks of the monolith were mainly composed of cubic SrTiO₃ nanoparticles with a few hundred nm in a diameter, which made the monolith brittle because of little TNT bridges.

The photocatalytic activity of the STO/TNT/TiO₂ monolith was investigated by monitoring the photocatalytic degradation of RhB, which was compared with that of the TNT/TiO₂ monolith. The monolith (40 mg) placed at the bottom of a container filled with RhB aqueous solution was illuminated by light (500 W xenon arc lamp). At prescribed intervals of illumination, the concentration of the RhB aqueous solution was analyzed with the spectrophotometer. As shown in Fig. 6, both the TNT/TiO₂ monolith and the STO/TNT/TiO₂ monolith showed photocatalytic activity for the degradation of RhB. The STO/TNT/TiO₂ monolith exhibited better photocatalytic activity than the TNT/TiO₂ monolith as the rate constants was almost doubled (STO/TNT/TiO₂ monolith: 5.6 × 10⁻³ min⁻¹, TNT/TiO₂ monolith: 2.6 × 10⁻³ min⁻¹), although the specific surface area of the STO/TNT/TiO₂ monolith (82.14 m²/g) was lower than that of the TNT/TiO₂ monolith (116.24 m²/g). This result indicated that the photocatalytic activity of the TNT/TiO₂ monolith was improved by the formation of SrTiO₃ particles. The enhancement of the photocatalytic activity is probably due to the formation of SrTiO₃/protonated titanate heterojunction as similarly reported for the SrTiO₃/TiO₂ heterostructure system. The valence and conduction band edges of protonated titanate are reported to be positive than those of SrTiO₃ (Fig. S5). Both protonated titanate and SrTiO₃ were excited under photoirradiation (Fig. S6). The generated electrons in SrTiO₃ as well as holes in protonated titanate are immigrated to the conduction band of protonated titanate and the valence band of SrTiO₃, respectively. The heterojunction is considered to improve the separation of photogenerated electrons/holes pairs in the SrTiO₃/protonated titanate heterostructure, which effectively suppresses the electron–hole recombination. As a result, the improved separation between photogenerated electrons

Fig. 3. SEM images of the TNT/TiO₂ monolith (a, b) and the STO/TNT/TiO₂ monolith (c, d).

Fig. 4. XRD patterns of the TNT/TiO₂ monolith and the STO/TNT/TiO₂ monolith.
and holes is considered to improve the photocatalytic activity of the TNT/TiO$_2$ monolith by the formation of SrTiO$_3$ nanoparticles on the TNTs with close contact. However, the STO/TNT/TiO$_2$ monolith prepared at longer reaction time (2 h) with Sr(OH)$_2$ was found to exhibit lower photocatalytic activity than the TNT/TiO$_2$ monolith (Fig. S7). As mentioned above, the longer reaction time led to a further conversion from protonated titanate to SrTiO$_3$ and the growth of the SrTiO$_3$ nanoparticles, which decreased the accessible active surface of the TNTs (Fig. S3). Although the SrTiO$_3$/protonated titanate heterojunction suppresses the electron–hole recombination, SrTiO$_3$ itself is reported to be less effective as photocatalyst,$^{48,52}$ which resulted in a decrease of the photocatalytic activity of the STO/TNT/TiO$_2$ monolith prepared at longer reaction time. It should be mentioned that the hardness of the monoliths remained even after the photocatalytic investigation because the monolith is collectable from the solution.

4. Conclusions

Porous monoliths consisting of TNTs, SrTiO$_3$ nanoparticles, and TiO$_2$ nanoparticles were fabricated from a porous TNT/TiO$_2$ monolith by reacting with Sr(OH)$_2$. The obtained monolith possessed macropores (from 1 to 10 μm). The SrTiO$_3$ nanoparticles formed on TNTs with close contact. The photocatalytic activity of the TNT/TiO$_2$ monolith was improved by the formation of SrTiO$_3$ nanoparticles on TNTs. This is probably considered to be due to the effective suppression of the electron–hole recombination by the SrTiO$_3$/protonated titanate heterojunction structure.

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