



Preparation and photocatalytic activity of strontium titanate nanocube-dispersed mesoporous silica

Kiyofumi Katagiri^{a,*}, Yuki Miyoshi^a, Kei Inumaru^{a,b,*}

^aDepartment of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

^bAdvanced Catalytic Transformation Program for Carbon Utilization (ACT-C), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

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ABSTRACT

Strontium titanate (SrTiO₃) nanocube-dispersed mesoporous silica was prepared. Oleate-modified SrTiO₃ nanocubes with diameter of ca. 10 nm were synthesized by a hydrothermal process. The nanocubes were embedded into mesoporous silica, aided by the high affinity of surface oleyl groups with surfactants employed as templates of the mesoporous silica. Nanocubes within the nanocomposite maintained their shape and size without fusion or sintering, even after calcination at 1073 K. Oleate groups on the surface of SrTiO₃ nanocubes burned out together with CTAB during the calcination process. Nitrogen adsorption behavior of the nanocomposites was comparable to that of conventional mesoporous silica. The nanocomposite exhibited high photocatalytic activity in the decomposition of methylene blue because of the combination of preferential molecular adsorption by mesoporous silica and photocatalysis by SrTiO₃. The methylene blue decomposition rate by the nanocomposite was larger than that of the composite prepared with conventional SrTiO₃.

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1. Introduction

Recent progress in synthetic methodology for inorganic nanocrystals has facilitated their application as components for miniature devices [1–4]. Controlling nanocrystalline shape has been particularly challenging, but substantial progress has been made on the shape-controlled synthesis, e.g., triangles, rods, cubes, and tetrapods [5–7]. The synthesis of metal oxide nanocubes is of fundamental and technological interest, because their shape-dependent physical properties can be tuned with respect to particular applications. Synthetic methods for nanocube materials are continually being developed, and metal oxide nanocubes have been synthesized via several approaches. Liquid phase chemical processes, hydrothermal and solvothermal methods, and sol–gel and oxalate-based methods have been reported. The hydrothermal process is a versatile method for preparing colloidal metal oxide nanocrystals with a controlled shape and size and, is applicable to nanocubes [8–13]. Liu et al. used sodium dodecyl sulfate as a capping agent to obtain 25 nm Co₃O₄ nanocubes, by oxidizing freshly-reduced cobalt nanoparticles in the reaction system [8]. Li and Zang reported the synthesis of NaTaO₃ nanocubes by a

single-step hydrothermal method [9]. Nanocrystalline La₂Sn₂O₇ photocatalysts of cubic morphology were synthesized by Zeng et al. [10]. Ohara and Adschiri et al. prepared Fe₂O₃ and CeO₂ nanocubes via a supercritical hydrothermal process, in which long chain fatty acids were used as surface modifiers [11,12]. Nanocubes were covered with hydrophobic organic chains, and transparent nanocube dispersions in organic solvents were obtained. More recently, we reported the hydrothermal preparation of sub-10-nm monodisperse SrTiO₃ nanocubes, using the water-soluble titanium complex, titanium bis(ammonium lactate)dihydroxide (TALH), oleic acid, and hydrazine [14]. Dang et al. followed this approach [15] and extend it to preparation of BaTiO₃ [16]. Mimura et al. employed these nanocubes to obtain highly ordered nanocube assemblies by capillary force assisted solution self-assembly [17,18]. The piezoresponse of a mixed assembly of SrTiO₃ and BaTiO₃ nanocubes exhibited a non-linear curve and stepwise behavior at high poling field, which differed from that of ferroelectric BaTiO₃ and paraelectric SrTiO₃ nanocube assemblies [19]. In addition to its use in dielectric materials, SrTiO₃ can form nanosized particles which have widespread applications (as thermoelectric [20,21], semiconducting [22], and catalytic materials [23,24]). An important application of SrTiO₃ is in photocatalytic materials. Its conduction band minimum (CBM) is higher (more negative) than the H⁺/H₂ reduction potential (0 V vs. NHE), while the valence band maximum (VBM) is lower (more positive) than the O₂/H₂O oxidation potential (1.23 V vs. NHE) [25–27]. Doping SrTiO₃ with noble metals, such as Mn, Ru, Rh, Pd, Ir, and Pt, can further enhance its

* Corresponding authors. Address: Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan. Fax: +81 82 424 5494.

E-mail addresses: kktgr@hiroshima-u.ac.jp (K. Katagiri), inumaru@hiroshima-u.ac.jp (K. Inumaru).

photocatalytic activity [27,28]. However, the potential of 10 nm scale SrTiO₃ nanocubes as photocatalysts has not been reported.

In the present study, we have developed a nanocomposite material of SrTiO₃ nanocubes and mesoporous silica. We have recently reported a nanocomposite from surfactant-templated mesoporous silica and TiO₂ crystalline particles larger than the silica pore diameter [29–31]. The nanocomposite exhibited highly active and molecular-selective photocatalysis toward the decomposition of mixed alkylphenols because of the combination of preferential molecular adsorption by mesoporous silica and photocatalysis by TiO₂. Modifying the TiO₂ nanocrystals by the surface grafting of alkyl groups yielded efficient nanocomposite formation, where particles were completely surrounded by mesoporous silica. Therefore, oleate-modified SrTiO₃ nanocubes [14] were suitable for the current study. Surface oleyl groups have a high affinity toward surfactant micelles that act as templates of mesoporous silica, similar to the case of TiO₂ modified with alkyl groups. These oleyl groups can be removed together with surfactants by calcination. A common problem during the calcination of nanocrystals is fusion and sintering. Important characteristics such as the large surface area and specific crystalline faces of nanocubes are often lost upon fusion and sintering. We expected that mesoporous silica acts not only as an adsorbent but also as a matrix to prevent fusion and sintering of SrTiO₃ nanocubes during the calcination process. The nanocomposite consisting of SrTiO₃ nanocubes and mesoporous silica was characterized by powder X-ray diffraction (XRD), nitrogen adsorption isotherms, and transmission electron microscopy (TEM). Photocatalytic properties of the nanocomposite were investigated by the decomposition of an aqueous solution of methylene blue (MB). The capability of the nanocomposite to act as an adsorbent and photocatalyst was investigated by comparison with calcined SrTiO₃ nanocubes, pure mesoporous silica, and the composite material formed with conventional SrTiO₃ and mesoporous silica.

2. Experimental procedure

2.1. Materials

TALH, strontium hydroxide octahydrate, and tetraethylorthosilicate (TEOS) were purchased from Sigma–Aldrich. Tetramethylammonium hydroxide (TMAOH), oleic acid, hydrazine monohydrate, tetrahydrofuran (THF), hexane, ethanol, and MB were obtained from Nacalai Tesque, Inc. Hexadecyltrimethylammonium bromide (CTAB) was purchased from Tokyo Chemical Industry. Ammonia water (28% (w/w)) and SrTiO₃ powder were purchased from Kishida Chemical Co., Ltd. *N*-Octadecyltrichlorosilane was obtained from Shin-Etsu Chemical Co., Ltd. All reagents were used as received. All water used was deionized with a Millipore Milli-Q system.

2.2. Preparation of oleate-modified SrTiO₃ nanocubes

Detailed sample preparation procedures were described in a previous report [14]. Aqueous solutions of TALH (1.25 mmol) and strontium hydroxide octahydrate (1.25 mmol) were mixed in deionized water. The pH of the solution was adjusted to 13.5 by adding TMAOH. Hydrazine monohydrate (2.0 mmol) and oleic acid (5.0 mmol) were added. The total volume of the solution was fixed at 50 mL. The reaction mixture was placed in a polytetrafluoroethylene (PTFE) vessel. The vessel was sealed and placed in a stainless steel autoclave, which was heated in an oven for 24 h at 473 K. Products were obtained by centrifugation and washed with saturated aqueous solution of ammonium chloride to remove SrCO₃

by-product. The products were extracted with hexane, precipitated by the addition of ethanol, and finally collected by centrifugation.

2.3. Preparation of SrTiO₃ nanocube-dispersed mesoporous silica

A nanocomposite of SrTiO₃ nanocube-dispersed mesoporous silica was prepared as follows: Oleate-modified SrTiO₃ nanocubes were dispersed in THF at a concentration of 250 mg mL⁻¹. This dispersion was injected into an aqueous solution of CTAB (60 mmol dm⁻³; 23 mL), and the pH of the mixture adjusted to 11.8 with ammonia water. TEOS (1.8 mL) was quickly added under vigorous stirring. After aging for 1 h, the precipitate was filtered, washed with water, and dried at 343 K for one day. The materials were calcined at 1073 K for 6 h under an O₂ stream to obtain SrTiO₃ nanocube-dispersed mesoporous silica. The final content of SrTiO₃ in the nanocomposite was 34% (w/w). For comparison, a composite material formed with conventional SrTiO₃ and mesoporous silica was also prepared. Commercial SrTiO₃ powder purchased from Kishida Chemical Co., Ltd. was hydrophobized by modification using *n*-octadecyltrichlorosilane. The composite material was then prepared according to the same procedure as that for the nanocube-dispersed mesoporous silica. The final composition of SrTiO₃ in this composite was also adjusted to 34% (w/w). Pure mesoporous silica without SrTiO₃ was also prepared in a similar manner. In addition, oleate-modified SrTiO₃ nanocubes in the absence of silica were calcined at 1073 K for 6 h under O₂.

2.4. Characterization

The phase compositions of precipitates were determined by XRD (D8 Advance, Bruker AXS, Germany) using Cu K α radiation. Particle size and distribution were evaluated by dynamic light scattering (DLS), using a Photal ELS-Z2 instrument (Ohtsuka Electronics Co. Ltd.). TEM images were captured with a JEOL JEM-2010 microscope operated at 200 kV. Samples were prepared by depositing a droplet of the dispersion on carbon-coated copper grids covered with polyvinyl formal film or elastic carbon film and drying in air overnight. Scanning electron microscopy (SEM) images were captured with a Hitachi S-4800 microscope. Fourier transform infrared (FT-IR) spectra were collected with a JASCO FT/IR-4200 spectrometer fitted with a Universal ATR polarization accessory and recorded over the range 2500–400 cm⁻¹. Nitrogen adsorption isotherms were measured at 77 K using a Belsorp-mini (Japan Bel Co. Ltd., Osaka, Japan).

2.5. Photocatalytic testing

The photocatalytic activity of SrTiO₃ nanocube-dispersed mesoporous silica was investigated by decomposition of MB in aqueous solutions. 30 mL of aqueous solution of MB (1.0 \times 10⁻⁵ mol dm⁻³) was loaded in a vial. After incubation for 120 min, 10 mg of SrTiO₃ nanocube-dispersed mesoporous silica was added. After further incubation for 180 min, 3.0 mL of the solution was transferred to a quartz spectrophotometer cell. The cell was irradiated with ultraviolet (UV) light using a black light bulb (λ = 252 nm). These experiments were carried out in a dark box to prevent any direct degradation of MB. Changes in concentrations of MB in the aqueous solution were interpreted from absorption spectra measured on a UV-Vis spectrophotometer (PerkinElmer Lambda 900) after several time intervals. As controls, the same experiments were carried out for the composite formed with commercial SrTiO₃ and mesoporous silica, pure mesoporous silica (without SrTiO₃), and calcined SrTiO₃ nanocubes (without mesoporous silica). These experiments were normalized by the amount of mesoporous silica moiety and/or SrTiO₃ components.

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