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Photocatalytic reduction of carbon dioxide by strontium titanate nanocube-dispersed mesoporous silica

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ABSTRACT

Strontium titanate nanocube-dispersed mesoporous silica (STO(NC)-MPS) nanocomposite was examined as a photocatalyst for the photoreduction of CO_2. Copper (Cu) was examined as a co-catalyst, and the results showed that it was effective for the production of CO under a flow of CO_2 and UV irradiation in water. As confirmed by gas chromatography–mass spectrometry, ^{13}CO was produced in the presence of $^{13}CO_2$, thus demonstrating that CO was generated upon photoreduction of CO_2. Simultaneous formation of O_2 suggested that water acted as a reductant in the photocatalysis process. Moreover, Cu supported on STO(NC)-MPS showed higher selectivity toward CO_2 reduction when compared with Cu-supported composite prepared from mesoporous silica and $SrTiO_3$ that was synthesized by conventional solid state reaction. Thus, the current findings highlight the characteristics and advantages of $SrTiO_3$ nanocubes and their nanocomposites with mesoporous silica as photocatalysts for CO_2 photoreduction.

1. Introduction

Nanocrystals are important materials owing to their properties, such as shape, size, crystal structure, and crystallinity, that can be controlled by tuning their preparation conditions [1–3]. They are expected to have large surface areas because of their small size and to expose particular crystal planes. Accordingly, nanocrystals are expected to find promising application in various fields including heterogeneous catalysis and photocatalysis [1,4,5].

Nanostructural control of composite materials to achieve enhanced functions has been of great interest in the fields of catalyst and photocatalyst design [6,7]. In addition to nanocrystals, various nanomaterials have been investigated, including nanofibers [8,9] and nanoporous materials [10–15]. Nanocomposite structures have also been of importance in recent studies on photocatalysts. For example, composite photocatalysts of TiO_2 and mesoporous silica exhibit molecule-selective photocatalytic activity toward the decomposition of organic molecules in water [13–15].

The photocatalytic reduction of CO_2 is both challenging and important in chemistry and technology as a means of energy conversion and environmental protection. Metal oxide semiconductor photocatalysts have been extensively studied for this reaction [16–24]. To prove the occurrence of "artificial photosynthesis", it is very important to confirm that the carbon source of the product is CO_2 and that the reductant is H_2O [25]. Some studies have reported the successful reduction of CO_2 over metal oxide semiconductor photocatalysts using H_2O as the reductant like a natural photosynthesis process [18,21,22–24].

We have previously reported that the composite material constituting strontium titanate nanocubes and mesoporous silica show promising performance as a photocatalyst [5]. The individual nanocubes are separated by mesoporous silica moiety, thereby inhibiting the sintering and fusion of the nanocubes and consequently promoting their stability at high calcination temperatures. Complete removal of carbon contamination by calcination is essential for CO_2 photoreduction experiments because the contaminants often act as carbon sources to produce compounds such as CO and CH_4 [25]. Thus, the high stability of a material is an important advantage for photocatalytic CO_2 reduction. Furthermore, the exposure of particular crystal planes, such as the (100) plane, may contribute to characteristic photocatalytic properties.

In this study, we prepared a nanostructure in which well-crystallized $SrTiO_3$ nanocubes were surrounded by mesoporous silica matrix. The nanocomposite was subsequently examined as a photocatalyst for the photocatalytic reduction of CO_2.

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2. Experimental

2.1. Sample preparation and characterization

Strontium hydroxide octahydrate and tetraethylorthosilicate were purchased from Sigma-Aldrich. Tetramethylammonium hydroxide (TMAOH), oleic acid, hydrazine monohydrate, tetrahydrofuran, hexane, ethanol, and ammonium chloride were obtained from Nacalai Tesque, Inc. (Tokyo, Japan). Hexadecyltrimethylammonium bromide was purchased from Tokyo Chemical Industry (Tokyo, Japan). Ammonia water (28% (w/w)) and $Sr(NO_3)_2$ were purchased from Kishida Chemical Co., Ltd. (Tokyo, Japan). All reagents were used as received. Deionized water was used in all experiments and was obtained from a Millipore Milli-Q system.

Detailed sample preparation procedures of oleate-modified $SrTiO_3$ nanocubes can be obtained from a previous report [26]. Briefly, aqueous solutions of titanium(IV) bis(ammonium lactato)dihydroxide (1.25 mmol) were prepared according to the reports by Kakihana et al. [27]. H_2TiO_3 was used as a source material instead of Ti metal. The solution of the Ti complex and strontium hydroxide octahydrate (1.25 mmol) was mixed in deionized water. Hydrazine monohydrate (2.0 mmol) and oleic acid (5.0 mmol) were then added. The solution pH was adjusted to 13.5 by adding TMAOH. The total volume of the solution was fixed at 50 mL. The reaction mixture was then introduced into a polytetrafluoroethylene vessel. The vessel was sealed and placed in a stainless steel autoclave, which was heated in an oven at 473 K for 24 h. The products were obtained by centrifugation and washed with saturated aqueous solution of ammonium chloride to remove $SrCO_3$ by-product. The products were then extracted with hexane, precipitated by adding ethanol, and finally collected by centrifugation.

A nanocomposite of $SrTiO_3$ nanocube-dispersed mesoporous silica was prepared as follows [5]: oleate-modified $SrTiO_3$ nanocubes were dispersed in tetrahydrofuran at a concentration of 250 mg mL^{-1}. The dispersion was then injected into an aqueous solution of hexadecyltrimethylammonium bromide (60 mmol L^{-1}; 23 mL), and the pH of the mixture was adjusted to 11.8 with ammonia water. Tetraethylorthosilicate (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 1 day. The obtained product was calcined at 1073 K for 6 h in air to obtain $SrTiO_3$ nanocube-dispersed mesoporous silica. The final content of $SrTiO_3$ in the nanocomposite was 34% (w/w). The nanocomposite is referred as STO(NC)-MPS.

For comparison, a composite formed from mesoporous silica and $SrTiO_3$ – prepared by conventional solid state reaction – was also prepared. Conventional $SrTiO_3$ powder was prepared by calcination of a mixture of $Sr(NO_3)_2$ and TiO_2 (P25, kindly supplied by Nippon Aerosil Co. Ltd., Tokyo, Japan) at 1073 K for 10 h in air [28]. The obtained $SrTiO_3$ was washed with HNO_3 aqueous solution. The composite material was then prepared using the same procedure as that used for preparing the $SrTiO_3$ nanocube-dispersed mesoporous silica. The final composition of $SrTiO_3$ in this composite was also adjusted to 34% (w/w). This composite is referred as STO(SR)-MPS.

Furthermore, Pt, Ag, and Cu were examined as co-catalysts. Pt and Ag were deposited on STO(NC)-MPS nanocomposite using electrochemical deposition as follows. STO(NC)-MPS (300 mg) was first dispersed in water (10 g). Then, the metal source ($H_2PtCl_6{\cdot}6H_2O$ or $AgNO_3$) and methanol (1.1 mL) were added to the dispersion, and the mixture was irradiated under a 500 W ultra high-pressure Hg lamp for 24 h. The metal loading was 0.3 wt.%. For deposition of Cu co-catalyst, the composite (STO(NC)-MPS or STO(SR)-MPS) was impregnated with an aqueous solution of $Cu(NO_3)_2$ and then calcined at 1073 K for 5.5 h under O_2 flow. The metallic Cu loading amount was adjusted to 0.3 wt.%. The co-catalyst-loaded samples are denoted as Pt/*x*, Ag/*x*, and Cu/*x*, where *x* refers to the nanocomposite (i.e., STO(NC)-MPS or STO(SR)-MPS).

X-ray powder diffraction (XRD) patterns were recorded on a D8 Advance diffractometer (Bruker AXS, Germany) using Cu Kα radiation. Transmission electron microscopy (TEM) images were captured on a JEOL JEM-2010 microscope (Tokyo, Japan), operating at 200 kV. For analysis, the samples were prepared by depositing a droplet of the sample dispersed in hexane on copper grids coated with polyvinyl formal film or elastic carbon film, followed by drying in air overnight. Scanning electron microscopy images were captured using a Hitachi S-4800 microscope. Nitrogen adsorption–desorption isotherms were measured at 77 K using a Belsorp-mini (Japan Bel Co. Ltd., Osaka, Japan).

2.2. Photocatalytic testing

Preliminary experiments were conducted, whereby the photocatalytic activities of Pt/STO(NC)-MPS, Ag/STO(NC)-MPS, and Cu/STO(NC)-MPS (metal loading = 0.3 wt.%) toward CO_2 reduction were examined. A low CO_2 reduction efficiency was observed over Pt/STO(NC)-MPS photocatalyst. The reduction of CO_2 to CH_4 over Ag/STO(NC)-MPS was detected, however, the activity was not high. In contrast, a high reduction efficiency to CO was detected for Cu/STO(NC)-MPS. Accordingly, the photocatalytic activity of Cu/STO(NC)-MPS was studied further. In the subsequent studies, the Cu loading was fixed to 1.0 wt.%.

The photocatalytic CO_2 reduction over Cu/STO(NC)-MPS was investigated using a flow reactor system. Prior to the photocatalytic activity tests, following calcination of the photocatalyst, the photocatalyst (210 mg) was promptly transferred to the photocatalytic reactor containing water (700 g). The glass flow reactor cell was equipped with a quartz water-cooling inner lamp jacket. The photocatalyst was then irradiated with a high-pressure Hg lamp (450 W) from the center of the cell through the jacket under O_2 flow (10 cm^3 min^{-1}) overnight. This procedure enabled removal of residual organic species on the photocatalyst via photocatalytic oxidation to CO_2. Subsequently, the gas flow was changed to He to eliminate O_2 in water. The gas flow was then changed to CO_2 (10 cm^3 min^{-1}), and the water in the reactor was saturated with CO_2 without photoirradiation. Finally, the lamp was lit again and the outlet gas flow was analyzed by an online gas chromatograph equipped with a BID detector (Shimadzu GC-2010, Kyoto, Japan).

2.3. $^{13}CO_2$ Isotope experiment

In the above photocatalytic experiment, $^{13}CO_2$ was used instead of $^{12}CO_2$. The outlet gas was analyzed using a gas chromatography–mass spectrometer (JEOL JMS-Q1050GC) equipped with an MS-5A capillary column. ^{13}CO and ^{12}CO were observed by monitoring signals associated with $m/z = 29$ and 28, respectively.

3. Results and discussion

3.1. Characterization of STO(NC)-MPS and STO(SR)-MPS nanocomposite photocatalysts

Fig. 1 shows TEM images of the $SrTiO_3$ nanocubes and STO(NC)-MPS composite. As determined from Fig. 1a, the cubes were approximately 10 nm in size. A mixture of dark and light features was also observed, suggesting that the cubes featured crystalline phases. Fig. 1b shows that the STO nanocubes were dispersed in the mesoporous silica matrix.

Fig. 2a shows the XRD pattern of STO(NC)-MPS at low- and high-angle regions. In the high-angle region, distinct diffraction peaks were observed. These peaks were similar to those of the nanocubes

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