1 Photocatalytic reduction of CO₂ over exposed-crystal-face-controlled TiO₂ nanorod having a
2 brookite phase with co-catalyst loading

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Abstract

Photocatalytic reduction of carbon dioxide (CO₂) was carried out using exposed-crystal-face-controlled titanium(IV) oxide (TiO₂) having a brookite phase. Methanol (CH₃OH) was detected as the main product, and trace amounts of formic acid, carbon monoxide, methane, and hydrogen were also detected in some cases. The prepared nanorod-shaped brookite TiO₂ with large {210} and small {212} exposed crystal faces showed larger CH₃OH generation than that of commercial brookite TiO₂ powder (Kojundo Chemical Laboratory Co., Ltd.). The activity of a brookite TiO₂ nanorod for CO₂ reduction depended on its aspect ratio because the {210} crystal faced worked as a reduction site, whereas an oxidation site was assigned to {212} crystal faces. Photodeposition of gold (Au) or silver (Ag) nanoparticles on the nanorod-shaped brookite TiO₂ induced a dramatic increase in CH₃OH production because the deposited metal particles work as reductive sites for multi-electron reduction of CO₂. Among the co-catalyst-loaded brookite TiO₂ nanorods, nanorod-shaped brookite TiO₂ loaded with Ag showed higher activity. The source of carbon of CH₃OH obtained by CO₂ reduction is discussed on the basis of results of a labeling experiment using ¹³CO₂.

Keywords: Exposed-crystal-face-controlled TiO₂; Brookite TiO₂ nanorod; Separation of reaction sites; Reduction of carbon dioxide

1. Introduction

Practical application of photocatalysts in converting solar light to chemical energy has been an attractive research field [1-11]. Water splitting over photoirradiated semiconductor photocatalysts has become an important issue world wide [12-20] because hydrogen is a promising alternative fuel when fossil fuels become depleted. In addition, CO₂ reduction to produce usable products is an important topic from the viewpoint of not only an environmental issue but also artificial photosynthesis. Although reduction of CO₂ using semiconductors such as TiO₂ as a photocatalyst

was reported by Fujishima [21], progress in this field has been very slow compared to the progress made in development of water splitting for hydrogen evolution. Photocatalytic reaction using semiconductor photocatalysts has been reported to have the potential to reduce CO₂ into hydrocarbons using water as an electron donor. For example, oxide semiconductor photocatalysts including titanium(IV) oxide (TiO₂) can produce formic acid (HCOOH), formaldehyde (HCHO), methanol (CH₃OH), and methane (CH₄) [22-34]. However, quantum yields for photocatalytic CO₂ reduction have been low. One reason for the low yields is that most of the reactions for CO₂ reduction employ a multi-electron process with relatively high redox potential, as shown below. In addition, back reaction on the surface of a semiconductor photocatalyst easily proceeded, resulting in retardation of CO₂ reduction, because many kinds of intermediates would be involved in this multi-electron reaction.

Therefore, control of reaction sites on the surfaces of photocatalysts is a promising strategy for improvement of CO₂ reduction. In order to control reaction sites on the surface of a TiO₂ photocatalyst, we developed technology for controlling exposed crystal faces of TiO₂ nanoparticles [35-43]. The exposed crystal surfaces worked as reduction sites and oxidation sites separately, resulting in improvement of photocatalytic activity for organic pollutant decomposition. These surface properties should be useful for improvement of a multi-electron reaction such as CO₂ reduction because back reactions on the surfaces of photocatalysts would be drastically retarded.

Kominami et al. prepared single-phase brookite TiO₂ powder for the first time by solvothermal synthesis in which oxobis(2,4-pentanedionato-*O,O'*)titanium was used as the TiO₂ precursor and sodium laurate was used as a reagent for controlling the crystal structure [44]. They subsequently investigated the photocatalytic activity of single-phase brookite TiO₂ [45, 46].

1 Recently, other groups have also reported single-phase brookite TiO₂ having several kinds of
2 characteristic structures, e.g., nanorods and nanotubes [47-51]. Among the three kinds of crystal
3 structure of TiO₂, brookite TiO₂ show the highest reduction ability from evaluation of conduction
4 band potential [52]. These properties are advantageous for CO₂ reduction. Therefore, we
5 developed exposed-crystal-face-controlled brookite TiO₂ for CO₂ reduction.

6 In addition, metal co-catalyst loading on semiconductor photocatalysts is frequently carried
7 out to enhance quantum yield and selectivity from CO₂ reduction into these products because
8 appropriate co-catalysts work as reduction sites and enhance multi-electron reduction as a result of
9 capturing electrons on metal particles [53-59, 31, 32, 34].

10 As mentioned above, we developed shape-controlled TiO₂ with specific exposed crystal
11 faces in order to improve photocatalytic efficiency [35-43]. Utilization of the shape-controlled
12 TiO₂ enhanced photocatalytic activity for decomposition of an organic compound because spatial
13 separation of redox sites was induced by different kinds of exposed crystal faces [35-43].
14 Moreover, this property has advantages in co-catalyst loading by a photodeposition method, and
15 site-selective co-catalyst loading on reduction faces by the photodeposition technique, which
16 possibly decreases the recombination rate in co-catalyst particles, enhances photocatalytic activity
17 by retarding back reactions. Actually, metal particles on reduction faces were observed in the
18 shape-controlled TiO₂ [35-43].

19 In the present study, we confirmed the advantage of photocatalytic CO₂ reduction by
20 exposed-crystal-face-controlled brookite TiO₂. Moreover, the effect of co-catalyst loading on the
21 exposed-crystal-face-controlled brookite TiO₂ on activity for photocatalytic reduction of CO₂ was
22 examined. Labeling experiments using ¹³CO₂ were also carried out in order to elucidate the
23 carbon source of CH₃OH as a main product for CO₂ reduction on exposed-crystal-face-controlled
24 brookite TiO₂ with co-catalyst loading.

25 26 27 2. Experimental Section

2.1. Materials

A titanium precursor (titaniumethoxide) was purchased from Sigma-Aldrich. Hydrogen peroxide (30%), ammonia, glycolic acid, polyvinyl alcohol (PVA), and polyvinyl pyrrolidone (PVP) were purchased from Wako Pure Chemical Industries, Ltd. Glycolic acid was used to control the crystallinity and morphology of brookite TiO₂ particles. Commercial brookite TiO₂ powder was obtained from Kojundo Chemical Laboratory Co., Ltd. Other chemical reagents used in the present study were commercial products without further treatment.

2.2. Procedure for preparation of brookite TiO₂ nanorods without a polymer

Morphology-controlled brookite TiO₂ with {210} and {212} exposed crystal faces was prepared by hydrothermal synthesis [52, 60-62].

The procedure for preparation of morphology-controlled TiO₂ without an aspect ratio control reagent such as PVA is as follows. Milli-Q water (3.0 cm³) was added to 10 cm³ of titanium(IV) ethoxide and 50 cm³ of ethanol with vigorous stirring, and the mixture was stirred for 30 min at room temperature. The resulting precipitate was centrifugally separated from the solution and dried under reduced pressure. The obtained amorphous titanium hydroxide particles (12.5 mmol) were dispersed in 30% hydrogen peroxide (40.0 cm³). Then 25% ammonia (10.0 cm³) and glycolic acid (18.75 mmol) were added, and yellow peroxo titanate acid (PTA) solution was obtained. After stirring the solution at ca. 60 °C for 6 h to remove excess amounts of hydrogen peroxide and ammonia, an orange gelled compound was obtained. The gelled compound was dispersed in Milli-Q water (3.0 cm³) and pH of the solution was adjusted to 10 by addition of ammonia. Then the volume of the solution was adjusted (50.0 cm³) by addition of Milli-Q water, and the solution in a Teflon bottle sealed with a stainless jacket (Sanaikagaku Co., HU-100) was heated at 200 °C for 48 h in an oven. After hydrothermal treatment, the residue in the Teflon bottle was washed with Milli-Q water until ionic conductivity of the supernatant was <10 μS cm⁻¹. The particles were dried under reduced pressure at 60 °C for 12 h.

2.3. Procedure for preparation of brookite TiO₂ nanorods with a polymer as an aspect ratio control reagent

Milli-Q water (3.0 cm³) was added to 10 cm³ of titanium(IV) ethoxide and 50 cm³ of ethanol with vigorous stirring, and the mixture was stirred for 30 min at room temperature. The resulting precipitate was centrifugally separated from the solution and dried under reduced pressure. The obtained amorphous titanium hydroxide particles (25.0 mmol) were dispersed in 30% hydrogen peroxide (40.0 cm³). Then 25% ammonia (10.0 cm³) and glycolic acid (50.0 mmol) were added, and yellow peroxo titanic acid (PTA) solution was obtained. An aqueous solution containing an appropriate amount of PVA or PVP was added to the PTA solution. After stirring the solution at room temperature for 6 h to remove excess amounts of hydrogen peroxide and ammonia, an orange gelled compound was obtained. The gelled compound was dispersed in Milli-Q water (3.0 cm³) and pH of the solution was adjusted to 10 by addition of ammonia. Then the volume of the solution was adjusted (50.0 cm³) by addition of Milli-Q water, and the solution in a Teflon bottle sealed with a stainless jacket (Sanaikagaku Co., HU-100) was heated at 200 °C for 48 h in an oven. After hydrothermal treatment, the residue in the Teflon bottle was washed with Milli-Q water until ionic conductivity of the supernatant was <10 μS cm⁻¹. The particles were dried under reduced pressure at 60 °C for 12 h.

2.4. Photodeposition of Au or Ag co-catalyst on brookite TiO₂ particles

For photodeposition of Au, an aqueous suspension consisting of brookite TiO₂ particles (200 mg) and 50 mL of an ethanol solution (8 vol %) containing an appropriate amount of hydrogen tetrachloroaurate(III) tetrahydrate was photoirradiated with a light-emitting diode (Nichia, NCCU033), which emitted light at a wavelength of ca. 365 nm and an intensity of 0.3 mW cm⁻², under a nitrogen atmosphere with vigorous magnetic stirring for 24 h. For photodeposition of Ag, an aqueous suspension consisting of TiO₂ particles (200 mg) and 50 mL of Milli-Q water containing an appropriate amount of silver nitrate was photoirradiated under the same conditions. After irradiation, photodeposited samples were obtained by washing with water several times and drying.

1 The net amount of Au or Ag on the TiO₂ surface was estimated by analysis of the filtrate with
2 inductively coupled plasma optical emission spectroscopy (ICPOES; Shimadzu, ICPS-8000). ICP
3 analysis revealed that the net molar amounts of Au and Ag compounds photodeposited on the
4 brookite TiO₂ by photodeposition were more than 99% of the provided molar amounts of Au and
5 Ag.

7 2.5. Characterization of prepared samples

8 Crystal structures of the TiO₂ powders were characterized by using an X-ray diffractometer
9 (Rigaku, MiniFlex II) with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). Primary particle sizes of the
10 prepared samples were estimated from peaks at 37° which are attributed to brookite {121} in XRD
11 patterns using the Scherrer equation: $d = 0.9\lambda/\beta\cos\theta$, where λ is the wavelength of X-rays, θ is the
12 Bragg angle and β is the full width at half maximum. β was estimated by fitting the XRD patterns
13 with a superposition of Lorentz functions for peaks attributed to brookite. Diffuse reflectance (DR)
14 spectra were measured using a UV-VIS spectrometer (Shimadzu, UV-2500PC and 2600) equipped
15 with an integrating sphere unit (ISR-240A and ISR-2600plus). Specific surface area (S_{BET}) of the
16 particles was determined with a surface area analyzer (Quantachrome, Nova 4200e) by using the
17 Brunauer–Emmett–Teller equation. The morphology of prepared TiO₂ particles was observed by
18 using a scanning electron microscope (SEM; JEOL, JSM-6701FONO) and a transmission electron
19 microscope (TEM; Hitachi, H-9000NAR). X-ray photoelectron spectroscopy (XPS) spectra were
20 obtained by using Kratos AXIS NOVA equipped with an Al K α X-ray source of the dual anode.
21 The shift of binding energy was corrected using the C 1s level at 284.6 eV as an internal standard.
22 The net amounts of Au or Ag compounds on the hybrid photocatalysts were estimated by analysis
23 of the filtrate with inductively coupled plasma optical emission spectroscopy (ICP-OES; Shimadzu,
24 ICPS-8000).

26 2.6. Photocatalytic reduction of CO₂

27 Before evaluation of the photocatalytic activity, each sample was irradiated with UV light

using black light (UVP, XX-15BLB) in order to remove organic compounds on the sample. Photocatalytic reduction of CO₂ was carried out under ambient pressure. A light-emitting diode (Nichia, NCCU033), which emitted light at a wavelength of ca. 365 nm and an intensity of 0.3 mW cm⁻², was used as the light source for photocatalytic evaluation, and a test tube containing 5 mg of TiO₂ and 5 mL of 0.2 mol L⁻¹ KHCO₃ aqueous solution saturated with CO₂ was photoirradiated with stirring for 24 h. Reaction products in liquid and gas phases were analyzed by gas chromatography (Hitachi G-3500, FID detector) with DB-WAXETR columns, gas chromatography (GL Science 490-GC, micro TCD detector) with MS-5A columns, and ion chromatography (Dionex, ICS-900) with IonPac AS-12A columns. Spherical shaped brookite TiO₂ was used as commercial brookite TiO₂ powder.

Apparent quantum efficiency (QE) was defined by the following equation because of a 6-hole process for production of CH₃OH as a main product from CO₂ reduction.

$$\begin{aligned} \text{QE} &= \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100 \\ &= \frac{\text{Number of generated CH}_3\text{OH molecules} \times 6}{\text{Number of incident photons}} \times 100 \end{aligned}$$

2.7. Reactivity evaluation of exposed crystal faces by photodeposition of Pt and lead(IV) oxide (PbO₂) on brookite TiO₂ nanorods

Photodeposition of Pt and PbO₂ were carried out to determine reduction and oxidation sites on TiO₂ particles, respectively [63]. For determination of reduction sites, exposed crystal surface photodeposition of Pt was performed. An aqueous brookite TiO₂ nanorod suspension (2 g L⁻¹) containing 0.52 M 2-propanol and 1 mM hexachloroplatinic acid (H₂PtCl₆·6H₂O) was irradiated with a 300 W mercury UV lamp (WACOM Model XDS-501S) for 24 h. N₂ gas was vigorously purged through the suspension prior to UV irradiation. The light intensity was about 1 mW cm⁻². After irradiation, the color of the powder changed from white to silver, and the suspension was centrifuged and washed with distilled water and then collected as powder after drying for 5 h at 60

°C under reduced pressure.

PbO₂ nanoparticles were deposited as a result of Pb²⁺ ion oxidation in order to identify oxidation sites on the surface of brookite TiO₂ nanorods. This reaction was carried out in an aqueous brookite TiO₂ nanorod suspension (2 g L⁻¹) containing 0.1 M Pb(NO₃)₂ under an aerated condition. The pH of the solution for this reaction was adjusted to 1.0 by the addition of nitric acid according to the literature [63]. After photoreaction for 24 h using a 500 W Hg lamp (USHIO Co. Ltd., SX-UI501HQ), the color of the powder changed from white to brown, indicating that PbO₂ had been deposited on the surface. The light intensity was about 0.1 W cm⁻². Pt and PbO₂ particles deposited on TiO₂ were observed in SEM, EDX and TEM images.

3. Results and Discussion

3.1. Characterization

Figure 1 shows an XRD pattern of the prepared TiO₂. The structure of prepared sample was attributed to single-phase brookite TiO₂. Figure 2 shows a TEM image of the prepared TiO₂. Rod-like morphology with a length of 115 nm and width of 35 nm, which were agreed with the primary particle size estimated from the XRD pattern. Assignment of these exposed crystal faces was confirmed by SEM (Fig. 3), TEM (Fig. 2) and selected area electron diffraction (SAED) analyses. The prepared TiO₂ showed a nanorod shape with large {212} and small {210} exposed crystal faces, indicating that the nanorod-shaped particles were single crystals. S_{BET} of the prepared TiO₂ was 45 m² g⁻¹.

3.2. Effect of PVA or PVP as an aspect ratio control reagent (T = 48 h, pH 7)

To determine the role of PVA or PVP in the reaction, we conducted a series of syntheses by varying the concentration of PVA or PVP. TEM and SEM images showed that addition of the PVA or PVP polymer resulted in control of the shape of TiO₂ nanorods. Figure 2 (a - b) shows TEM images of brookite TiO₂ nanorods obtained after hydrothermal treatment with different PVA

1 or PVP concentrations. TEM images without a polymer (Figure 2c) showed a rod-like shape with an
2 aspect ratio of **2.7** and single crystalline quality of the brookite TiO₂ nanorod.

3 The aspect ratio of brookite TiO₂ nanorods was decreased by addition of PVA or PVP.
4 The effect of aspect ratio control for a brookite TiO₂ nanorod by addition of PVA was greater than
5 that by addition of PVP as shown in Fig. 2 (a – b). These results indicate that addition of 50 mg of
6 PVA was sufficient to prepare brookite TiO₂ particles with a small aspect ratio (Figure S1). The
7 aspect ratio of a brookite TiO₂ nanorod with specific exposed crystal faces is sensitive to
8 photocatalytic activity for CO₂ reduction, as discussed in a later section. The ratio of exposed
9 reduction sites to oxidation sites on the surface of a brookite TiO₂ nanorod should be controlled in
10 order to improve CO₂ reduction. Under the optimized conditions, reduction sites on the surface of
11 a brookite TiO₂ nanorod should be predominantly exposed.

13 3.3. Photodeposition of Pt and PbO₂ for determination of reduction and oxidation sites

14 In order to determine reactivity such as oxidation or reduction on the exposed crystal
15 surface of brookite TiO₂, photodeposition of Pt and PbO₂ was carried out. The colors of TiO₂
16 powder after UV irradiation in the presence of H₂PtCl₆ and Pb(NO₃)₂ aqueous solutions changed to
17 gray and brown, respectively [63]. These color change in brookite TiO₂ suggested that Pt and
18 PbO₂ were deposited on the TiO₂ surface. Furthermore, the presence of Pt and Pb elements was
19 confirmed by XPS analysis. Pt particles were efficiently deposited on the exposed crystal surface
20 assigned to reduction site because of Pt⁴⁺ reduction. The oxidation site of exposed crystal surface
21 was assigned to PbO₂ deposition because Pb⁴⁺ was oxidized to produce PbO₂ nanoparticles.
22 Figure 4 shows TEM images of Pt- and PbO₂-deposited brookite TiO₂ nanorods that were prepared
23 by 48 h of hydrothermal treatment with PTA solution containing glycolic acid without a polymer.
24 Small particles were observed on the specific exposed face of the brookite TiO₂ nanorod. Small
25 particles were assigned by TEM with EDX analysis to Pt or PbO₂ deposited on the reductive or
26 oxidative crystal surface of the brookite TiO₂ nanorod (Fig. 4). Pt nanoparticles of ca. 10 nm in
27 size were mainly observed on the {210} face of a brookite TiO₂ nanorod, while large PbO₂ particles

with sizes of more than 100 nm were deposited on the {212} face of a brookite TiO₂ nanorod. These smaller particles were not observed on TiO₂ particles before the photodeposition procedure (Fig. 4).

As described in a later section, a correlation was found between photocatalytic activity and surface structure of TiO₂ particles, and photocatalytic activity increased with increase in the aspect ratio of brookite TiO₂ nanorods, which indicate the ratio of {210} to {212} exposed crystal faces. This result suggests that brookite TiO₂ nanorods with a small surface area of {212} and large surface area of {210} are suitable for photocatalytic CO₂ reduction. The highest photocatalytic activity of a brookite TiO₂ nanorod prepared by 48 h of hydrothermal treatment in the absence of a polymer was mainly due to the larger surface areas of reduction sites on the nanorod TiO₂ structure with the largest aspect ratio.

3.4. Photocatalytic activity for CO₂ reduction over a brookite TiO₂ nanorod with exposed crystal surfaces

In this study, amounts of the gas phase products are a trace (under the detection limit of Gas chromatography) over photoirradiation of co-catalyst loaded brookite TiO₂. When bare brookite TiO₂ was used, amounts of H₂, CO, CH₄ products are about 8, 3, 0 nmol, respectively. And amount of HCOOH is 35 nmol under ionic chromatography. Eventually, CH₃OH is a main product for the CO₂ reduction by using prepared brookite TiO₂ photocatalysts without co-catalyst. Photocatalytic reductions of CO₂ in our systems were performed in an aqueous suspension of prepared brookite TiO₂ at pH 7.3. Under the condition, the ionic forms of CO₂ in aqueous media should be a mixture of HCO₃⁻, H₂CO₃. Redox potentials of CO₃²⁻, H₂CO₃ are +0.209, +0.044 V vs NHE for methanol formation from CO₂ reduction, respectively [64]. In addition, redox potentials of HCO₃⁻ might be placed between +0.209 and +0.044 V vs NHE. Figure 5 shows CH₃OH generation for the prepared brookite TiO₂ nanorod and commercial brookite TiO₂, which are non shape-controlled particles with S_{BET} of 27 m² g⁻¹. CH₃OH production by the prepared brookite TiO₂ nanorod was 2-times greater than that by spherical shaped commercial brookite TiO₂. This result indicated that a

1 shape-controlled brookite TiO₂ nanorod with exposed crystal phases has higher activity for CO₂
2 reduction than non shape-controlled commercial brookite TiO₂, presumably due to separation of
3 oxidation and reduction sites. Moreover, larger {210} and smaller {212} exposed crystal faces
4 may be an ideal surface structure for a multi-electron process for CO₂ reduction.

5 As described above, the aspect ratio of a brookite nanorod was decreased by addition of
6 PVA or PVP as an aspect control reagent to the reaction solution during hydrothermal treatment.
7 Aspect ratio dependence of the photocatalytic activity of a brookite TiO₂ nanorod with exposed
8 crystal surfaces for CO₂ reduction was observed. The photocatalytic activity of a brookite TiO₂
9 nanorod for CO₂ reduction was decreased when the aspect ratio of the brookite TiO₂ nanorod
10 became lower by using PVA or PVP as an aspect ratio control reagent. Enlargement of {210}
11 assigned to reduction sites is an important strategy for improvement of photocatalytic CO₂
12 reduction over a brookite TiO₂ nanorod under UV light.

14 3.5. Effect of co-catalyst loading on photocatalytic activity

15 For further improvement of photocatalytic activity for CO₂ reduction, Au or Ag particles as
16 co-catalysts were loaded on the prepared brookite TiO₂ nanorod by the photodeposition method. It
17 was expected that the co-catalysts would be deposited on {210} exposed crystal faces of the
18 prepared brookite TiO₂ nanorod because reduction reaction ($\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}^0$, $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}^0$)
19 predominantly proceeds over {210} faces of a brookite TiO₂ nanorod. Actually, loaded co-catalyst
20 particles were observed mainly on {210} exposed crystal faces of the samples with larger amounts
21 of Au and Ag loading as shown in Fig. 6.

22 After photodeposition, the color of the samples changed depending on the kind of loading
23 material and loading amount. The colors of Au-loaded and Ag-loaded samples immediately after
24 photodeposition were dark purple and pale henna, respectively. The colors of the samples
25 correspond to localized surface plasmon resonance (LSPR) absorption of Au and Ag [65-68], and
26 this implies that some of the Au and Ag particles were present as a metal state. However, the color
27 of Ag-loaded samples changed after pre-treatment for photocatalytic activity (UV irradiation for

removal of organic compounds on the sample), indicating that aggregation of Ag nanoparticles or oxidation of Ag to generate Ag₂O might have occurred [34]. Figure 7 shows DR spectra of the prepared brookite TiO₂ nanorod with Au or Ag loading just before photocatalytic evaluation. Absorption peaks around 550 nm and 500 nm, which correspond to LSPR of Au and Ag on TiO₂, were observed in Au-loaded and Ag-loaded TiO₂ samples, respectively [65-67]. This implies that some of the Au and Ag particles were presumably present as a metal state after the pre-treatment for photocatalytic activity. Actually, XPS measurements were carried out on the Au-loaded and Ag-loaded TiO₂ samples (Figure S2). XPS spectra showed that loaded Ag particles were present as a mixture of Ag and Ag₂O. In contrast, the XPS spectrum confirmed that loaded Au particles were present as metal without other oxidation states. This coincides with the unchanged color of Au-loaded samples after the pre-treatment for photocatalytic activity.

Figure 8 shows CH₃OH generation of the prepared brookite TiO₂ nanorod with Au or Ag loading. CH₃OH generation showed an optimum amount with co-catalyst loading in all cases. In photocatalytic reaction systems, CO₂ reduction usually competes with H₂ evolution as a result of H⁺ reduction. For instance, H₂ evolution predominantly occurs over Pt-loaded TiO₂ particles. On the other hand, Ag loading on the surface of a brookite TiO₂ nanorod induces predominant CO₂ reduction. Therefore, loading an optimum amount of a co-catalyst on the surface of brookite TiO₂ improves the selectivity between CO₂ reduction and H₂ evolution as well as the photocatalytic activity for CO₂ reduction. Although the key mechanism for highly selective CO₂ reduction on co-catalyst-loaded brookite TiO₂ is under investigation, preferential CO₂ adsorption on a co-catalyst loaded on the surface of TiO₂ particles might be one of the key steps for improving predominant CO₂ reduction.

Increase in CH₃OH generation on brookite TiO₂ loaded with a co-catalyst was presumably due to prevention of recombination and/or enhancement of selectivity for CH₃OH generation as a result of multi-electron reduction by electron capturing on metal particles. This effect was probably influenced by properties of co-catalyst particles, e.g., loading site, amount, particle size and dispersibility. Decrease in CH₃OH generation with an excess amount of the co-catalyst may

be due to the filter effect caused by photoabsorption and/or light scattering of co-catalyst particles. Actually, relative reflectance of the samples in the wavelength of more than 400 nm increased with an increase in loading amount (Fig. 8). Moreover, excess amount of co-catalyst loading may result in covering active sites or absorption sites of reactants and loss of appropriate properties as co-catalyst particles, such as dispersibility and particle size.

In order to elucidate the influence of particle size on CH₃OH generation, absorption peaks attributed to LSPR of Au and Ag particles were evaluated in UV-VIS spectra (Fig. 8). Figure 8 shows absorption wavelength of the peak (λ_p) attributed to LSPR of Au and Ag as a function of amount of co-catalyst loading. A red shift of LSPR peak was usually observed by particle size growing and aggregation state of metal particles [68-70].

The peaks of Au-loaded samples showed dependence on loading amount up to 0.1 wt%. This indicates that the decrease in CH₃OH generation by the 0.1 wt% Au-loaded sample was mainly caused by an increase in particle size and decrease in dispersion of Au particles. In contrast, the peaks of Ag-loaded samples were only slightly red-shifted with an increase in loading amount. This indicates that decrease in CH₃OH generation with a larger amount of Ag loading might be due to the filter effect.

Therefore, CH₃OH generation of the Au-loaded brookite TiO₂ nanorod was influenced by particle size and/or aggregation state in addition to the effect observed in the Ag-loaded sample.

3.6. Labeling experiments using ¹³CO₂ reduction of CO₂

We applied ¹H-NMR spectroscopy for analyzing the carbon source of CH₃OH. Labeling experiment by using ¹³CO₂ for CO₂ reduction was taken place over Au loaded brookite TiO₂ nanorod for 24 h under UV light irradiation. Before evaluation of the photocatalytic activity, each sample was irradiated with UV light using black light (UVP, XX-15BLB) for 1 day in order to remove organic compounds on the sample. Degas and purge ¹³CO₂ processes were shown in Fig. 9. Photocatalysts powder 5 mg were ultrasonically dispersed in deionized water (5 mL). After complete degassing the whole system by diaphragm pump (Process 1), ¹³CO₂ gas was bubbling for

15 min (Process 2). CO₂ photoreduction is performed for 24 h during UV irradiation (Process 3). After the reaction, the photocatalysts was removed by centrifugal separation. The aqueous samples (4 ml) for ¹H-NMR are dissolved in D₂O (1 ml). 3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt (SIGMA-ALDRICH) was used as an internal standard compound. In the ¹H-NMR of the same solution, a doublet ($J_{CH} = 142$ Hz) attributable to the proton coupled to the ¹³C of ¹³CH₃O[−] was observed at 3.34 ppm, but no singlet due to the proton of ¹²CH₃O[−] was detected (Figure 10). These results clearly show that the carbon source of CH₃OH is ¹³CO₂.

4. Conclusion

Brookite TiO₂ particles with specific exposed crystal faces were prepared by hydrothermal treatment. In addition, PVP or PVA was used as an aspect control reagent. The aspect ratio of the prepared brookite TiO₂ nanorod was controlled by addition of PVA or PVP.

Photocatalytic CO₂ reduction using brookite TiO₂ nanorods with large {210} and small {212} exposed crystal faces were carried out. CH₃OH was obtained as the main product for CO₂ reduction over a brookite TiO₂ nanorod under UV light. Photocatalytic activity of a brookite TiO₂ nanorod for CO₂ reduction is higher than that of spherical-shaped commercial brookite TiO₂. In addition, a brookite TiO₂ nanorod with larger aspect ratio showed higher photocatalytic activity than that with a smaller aspect ratio. This indicates that larger {210} and smaller {212} exposed crystal faces prevented back reaction and enhanced multi-electron reduction as a result of separation of redox sites. Au or Ag loading on the reduction crystal surface of the prepared brookite TiO₂ nanorod increased CH₃OH generation. The mechanisms of activity enhancement by the loading of metals might be different. Au loading increased selectivity for CH₃OH generation to some extent. On the other hand, loading of Ag with appropriate properties resulted in a larger increase in CH₃OH generation than that in the case of Au, though Ag has no selectivity for CH₃OH generation. The carbon source of CH₃OH, which is the main product of CO₂ reduction over a brookite TiO₂ nanorod, was confirmed by a labeling experiment using ¹³CO₂.

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Figure Captions

Figure 1. XRD pattern

Figure 2. TEM images of brookite TiO₂ nanorod (a) with PVA (b) with PVP and (c) without polymer

Figure 3. SEM images of the prepared brookite TiO₂ nanorod (a) with PVA (b) with PVP and (c) without polymer

Figure 4. TEM images and EDX analyses of Pt or PbO₂ loaded brookite TiO₂ nanorods (a) Pt (b) PbO₂

Figure 5. Amount of CH₃OH generated over several kinds of brookite TiO₂ (commercial brookite TiO₂, the prepared brookite TiO₂ with PVA, PVP and without polymer

Figure 6. TEM images of brookite TiO₂ nanorods (a) bare sample and (b) Au loaded brookite TiO₂ and (c) Ag loaded brookite TiO₂

Figure 7. DR spectra of metal co-catalysts loaded brookite TiO₂ nanorods (a) Au and (b) Ag

Figure 8. Amount of CH₃OH generated over the metal co-catalysts loaded brookite TiO₂ nanorods as a function of amount of co-catalysts (a) Au (b) Ag

Figure 9. Process of experiments reduction of CO₂ using ¹³CO₂.

Figure 10. ¹H-NMR spectra of Au-loaded brookite TiO₂ nanorod

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Figure 1

Figure 2

(a)

(b)

(c)

Figure 3

Figure 4

TEM

EDX

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10