



Research paper

Highly selective photocatalytic conversion of CO₂ by water over Ag-loaded SrNb₂O₆ nanorods



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ABSTRACT

Strontium niobates (SrNb₂O₆ and Sr₂Nb₂O₇) with regular nanostructures were synthesized by a facile flux method. Ag-loaded SrNb₂O₆ and Sr₂Nb₂O₇ exhibited different performances for the photocatalytic reduction of CO₂ in H₂O. Compared to Sr₂Nb₂O₇ nanoflakes and SrNb₂O₆ nanoparticles, SrNb₂O₆ nanorods exhibited higher photocatalytic activity and selectivity toward CO evolution. Stoichiometric amounts of CO (51.2 μmol h⁻¹) and H₂ (1.1 μmol h⁻¹) as the reduction products, in addition to O₂ (24.8 μmol h⁻¹) as the oxidation product, were obtained, indicating that H₂O serves as an electron donor in the photocatalytic conversion of CO₂. In addition, the effect of the Ag cocatalyst on the photocatalytic conversion of CO₂ was investigated.

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1. Introduction

Carbon dioxide (CO₂), which is one of the major contributors to the greenhouse gas effect, has become a worldwide environmental burden because of fossil fuel consumption [1–4]. As a result, supplementing the natural carbon cycle and addressing climate change are imperative. The conversion of CO₂ to other valuable chemical compounds, e.g. CO, HCOOH, HCHO, CH₃OH, and CH₄, under ambient temperature and pressure conditions has attracted considerable attention as a sustainable strategy to solve environmental and energy issues [5–9], especially conversion of CO₂ into CO, which is widely studied in recent years as an alternative route to produce syngas components [10,11]. Since the discovery of the photoreduction of CO₂ into organic compounds using various semiconductors by Inoue et al. [5,12], several studies on the semiconductor-based photocatalytic conversion of CO₂ using H₂O as an electron donor have been reported [13–18]. Nevertheless, the selective activation of CO₂ by electrons and suppression of H₂ evolution in an aqueous solution are difficult because the redox potential of H⁺/H₂ (–0.41 V vs. NHE, at pH 7) is more positive than that of CO/CO₂ (–0.51 V

vs. NHE, at pH 7) [19,20]. Previously, our group has reported high activity for Ag-loaded ZnGa₂O₄-modified Ga₂O₃ [21,22], La₂Ti₂O₇ [23], SrO-modified Ta₂O₅ [24], ZnGa₂O₄ [25], Sr₂KTa₅O₁₅ [26], and ZnTa₂O₆ [27] for the photocatalytic conversion of CO₂ by H₂O under UV irradiation. Ag cocatalysts are well known to be effective for the conversion of CO₂ to CO in aqueous solutions [12,28,29]. However, still only a few photocatalysts have been reported, which exhibit high activity and selectivity for the photocatalytic conversion of CO₂ by H₂O, even with the modification of a Ag cocatalyst. Hence, it is imperative to develop highly efficient photocatalysts for CO₂ reduction using water as the electron donor.

Niobium-containing materials, e.g., SrNb₂O₆ and Sr₂Nb₂O₇, have been reported as promising candidates for water splitting because of their attractive layered crystal structures, containing the [NbO₆] octahedra that can be distorted, and the high energy of the Nb 4d orbitals [30–34]. These structural advantages of niobium-based materials also make them promising for the photocatalytic reduction of CO₂. Nevertheless, only a few studies have reported the photocatalytic performance of niobium-based photocatalysts for CO₂ reduction, and the reported activities and selectivities were not satisfactory [35–37]. An inerratic nanostructure for a photocatalyst has been reported to not only increase active sites for the photocatalytic reduction of CO₂ in the presence of H₂O but also promote the separation of oxidation and reduction sites because of its anisotropic effect [12,26,38,39].

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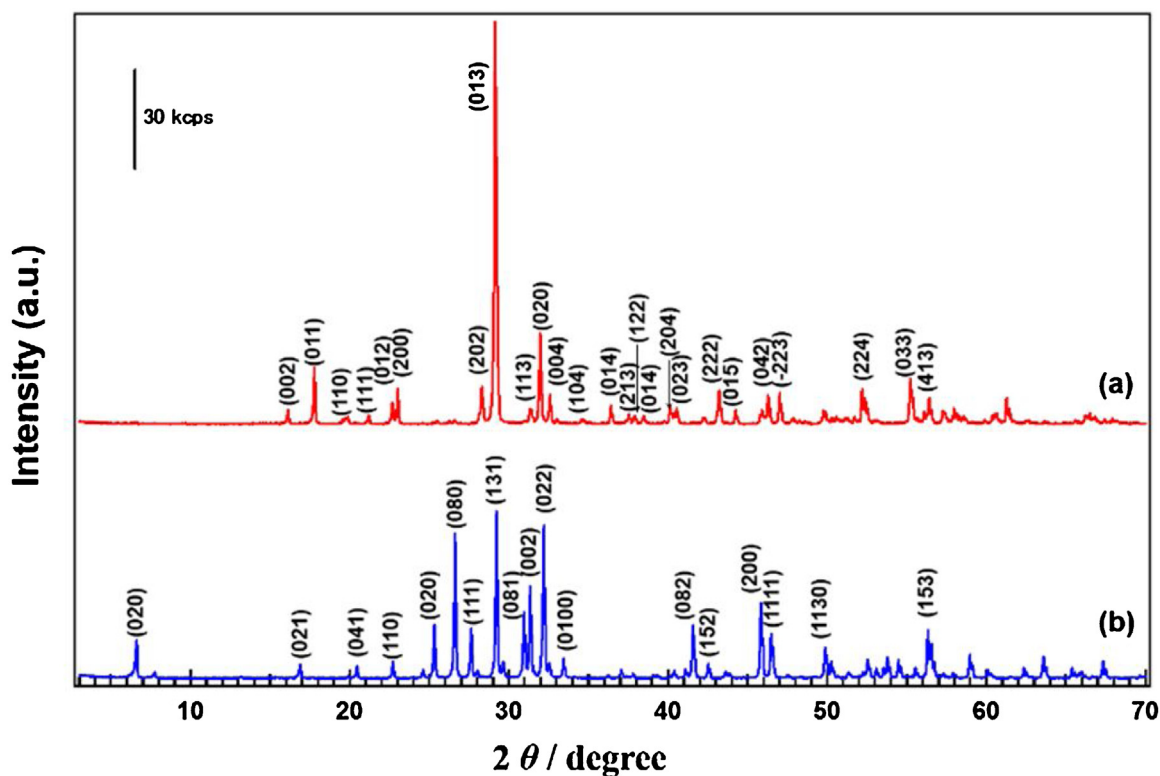


Fig. 1. XRD patterns of (a) SrNb_2O_6 and (b) $\text{Sr}_2\text{Nb}_2\text{O}_7$ fabricated by a flux method.

In this study, two strontium niobates (e.g. SrNb_2O_6 and $\text{Sr}_2\text{Nb}_2\text{O}_7$) with regular nanostructures were synthesized by a flux method, and their performance in the photocatalytic conversion of CO_2 in H_2O was investigated. After modification with a Ag cocatalyst, SrNb_2O_6 with a nanorod structure exhibited higher photocatalytic activity and selectivity toward CO evolution compared to $\text{Sr}_2\text{Nb}_2\text{O}_7$ with a nanoflake structure and SrNb_2O_6 with a nanoparticle structure. In addition, the effects of the Ag cocatalyst on the photocatalytic conversion of CO_2 were discussed.

2. Experimental

2.1. Photocatalyst preparation

SrNb_2O_6 and $\text{Sr}_2\text{Nb}_2\text{O}_7$ were prepared by a flux method. To fabricate SrNb_2O_6 , 2 g of Nb_2O_5 powder (99.9%, Wako) and 6 g of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (99.9%, Wako) were ground in an alumina mortar for 5 min. $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ was used as the precursor and flux reagent. The mixture was calcined in air using an alumina crucible at 1173 K for 2 h. After calcination, the obtained powder was thoroughly washed three times with hot water (353 K) to remove the residual salt and dried at 353 K in an oven. The process of synthesizing $\text{Sr}_2\text{Nb}_2\text{O}_7$ was almost the same as that of synthesizing SrNb_2O_6 , except for the use of SrCO_3 (99.9%, Wako) as the precursor. Modification using a Ag cocatalyst was performed by chemical reduction (CR), impregnation (IMP), and photodeposition (PD) methods. For modification by CR method, the obtained SrNb_2O_6 or $\text{Sr}_2\text{Nb}_2\text{O}_7$ (1.5 g) was suspended into a 50 mL aqueous solution of AgNO_3 (0.1 M), followed by the dropwise addition of a NaPH_2O_2 (0.4 M) solution into the suspension. After stirring the mixture at 358 K for 1.5 h, it was filtered and dried at room temperature. For modification by IMP method, SrNb_2O_6 (1.5 g) was homogeneously dispersed in an aqueous AgNO_3 solution, followed by evaporation at 358 K to remove water and calcination at 723 K for 2 h in air. Modification by PD method was carried out in situ during the photocatalytic

conversion of CO_2 . The synthetic details have been reported in our previous studies [24,27]. Generally, 1.5 g of SrNb_2O_6 powder was dispersed in 1.0 L of ultra-pure water containing a required amount of AgNO_3 , and the dissolved air in the solution was completely degassed by a flow of Ar gas. The suspension was irradiated under a 400 W high-pressure Hg lamp with a quartz filter using an inner-irradiation-type reaction vessel with Ar gas flowing for 1.5 h, followed by filtration and dried at room temperature.

2.2. Characterization

The crystal phase and structure of the samples were observed by powder X-ray diffractometry (Rigaku Multiflex) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) at a scan rate of 4° min^{-1} . Sample morphologies were observed by field-emission scanning electron microscopy (FE-SEM, SU-8220, Hitachi High Technologies) and transmission electron microscopy (TEM, JEM-2100F). The Brunauer–Emmett–Teller surface areas of the photocatalysts were measured by their N_2 adsorption isotherms at 77 K using a volumetric gas adsorption apparatus (BELSORP-mini II, BEL Japan, Inc.). Prior to the measurements, each sample was evacuated at 473 K for 1 h using a pretreatment system (BELPREP-vacII, BEL Japan, Inc.). UV–vis diffuse-reflectance spectra were recorded on a UV–visible spectrometer (V-650, JASCO) equipped with an integrated sphere accessory.

2.3. Photocatalytic reaction

The photocatalytic conversion of CO_2 was carried out using a flow system with an inner-irradiation-type reaction vessel at ambient pressure. First, the synthesized photocatalyst (0.5 g) was dispersed in ultrapure water (1.0 L) containing 0.1 M NaHCO_3 . Second, CO_2 was bubbled into the solution at a flow rate of 30 mL min^{-1} . Third, the suspension was illuminated using a 400-W high-pressure mercury lamp with a quartz filter connected to a

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