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Synthesis of cuboid-type tungsten trioxide photocatalysts for oxygen evolution from water in the presence of silver(I) sulfate under visible light irradiation

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ABSTRACT

We synthesized various cuboid-type tungsten trioxide (WO_3) particles using a hydrothermal method followed by calcination at various temperatures between 200 and 500 °C. Visible-light photocatalysis of these particles was investigated for oxygen (O_2) evolution from water in the presence of sacrificial silver(I) sulfate. The calculated crystallite diameters increased with increasing calcination temperature, suggesting that the level of crystallinity increased with calcination temperature. The average specific surface area of the particles was almost the same for all calcination temperatures in the range 200–400 °C, but was decreased at 500 °C. The photocatalytic reaction rate of O_2 formation increased with increasing calcination temperature up to 400 °C, and then decreased as calcination temperature was further increased to 500 °C. We therefore concluded that the rate increased with calcination temperature up to 400 °C due to the increasing crystallinity, but then decreased due to the decreased specific surface area.

1. Introduction

Photocatalysts that split water into hydrogen (H_2) and oxygen (O_2) without the input of fossil fuel-derived energy have attracted much attention. Fossil fuel is currently a major source of consumed energy, but the future depletion of fossil fuels and the release of carbon dioxide pollution into the atmosphere are concerns to be addressed. The photocatalytic water-splitting reaction has the ability to resolve both of these problems because it can produce H_2 and O_2 from only sunlight and water. Of the two half-reactions of overall water splitting, namely, the formation of H_2 and the formation of O_2, the latter is considered more difficult to achieve since it has to occur mechanistically through several steps requiring both four positive holes and the formation of O—O bonds [1–3].

The use of semiconductor photocatalysts such as titanium(IV) oxide (TiO_2) to produce H_2 and O_2 has attracted much attention because these photocatalysts can contribute to the use of renewable resources for the clean and environmentally friendly production of energy. TiO_2 is a wide band gap photocatalyst (band gap = 3.2 eV) that can catalyze the evolution of H_2 from various compounds under ultraviolet (UV) light irradiation [4–7]. However, UV light accounts for only about 5% of total solar energy, whereas visible light accounts for about 50% of that energy. Therefore, the development of photocatalysts using visible light is an important topic from a practical point of view. Many efforts have been devoted to the synthesis of visible-light-responsive photocatalysts for various photocatalytic reactions, with these catalysts including TiO_2 doped with nitrogen [8] and sulfur [9] as well as TiO_2 modified with H_2PtCl_6 [10], Cu^{2+} [11], and Rh^{3+} [12].

A metal oxide MO_x that has a simple composition and structure and requires no additives to design a visible-light-responsive photocatalyst is a candidate for environmentally friendly photocatalysts. To our knowledge, among simple oxides, tungsten(VI) oxide (WO_3) has been reported to exhibit photocatalytic activity for the formation of O_2 from the oxidation of water under irradiation with visible light [13,14]. WO_3 is therefore a favorable material for carrying out water splitting in a clean manner, considering the benefit of being able to use the plentiful visible-light energy that is found in solar radiation.

Many reports have shown that the morphology, size, and crystallinity of WO_3 particles are significant factors influencing their photocatalytic activity [13,15–18]. In general, smaller particles exhibit higher photocatalytic activity because they have larger specific surface areas. Larger specific surface areas adsorb more reactants, which increases the rate of surface charge transfer and hence facilitates the photocatalytic reaction [19]. Furthermore, the diffusion length for

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photogenerated electron (e^-) and hole (h^+) pairs is shorter in fine particles [13]. For these reasons, fine particles are expected to show high activity. However, particles often grow large because they are highly crystalline, which can be expected to promote high photocatalytic activity. Crystal defects due to low crystallinity act as recombination centers of e^- and h^+, and therefore large particles resulting from high crystallinity would be expected to have a lower recombination probability. Thus, to synthesize WO_3 particles that have high activity for the evolution of O_2 from water, it is necessary to find out which of these factors has the predominant effect on photocatalytic activity.

In 2009, Hong et al. [14,20] reported that larger WO_3 particles have higher photocatalytic activity for water oxidation in the presence of silver nitrate ($AgNO_3$) as a sacrificial electron acceptor due to a resulting well-developed space-charge layer and high crystallinity. In 2013, Amano et al. [13,20] reported that the water oxidation activity of WO_3 with $AgNO_3$ as a sacrificial acceptor increased for particles with increasing diameters up to 200 nm because large particles with a low surface area suppress surface recombination of photogenerated electrons and holes. While these reports suggest that increasing the WO_3 particle size and crystallinity is effective for increasing photocatalytic activity, the WO_3 particle shape was not controlled for in these studies. The optimal reaction conditions are expected to depend on the particle shape. Moreover, studies on photocatalytic reactions of modified WO_3 using ${IO_3}^-$ as a sacrificial electron acceptor have reported the apparent quantum efficiency (AQE) [21–24], however, those of bare WO_3 using Ag^+ as the same acceptor have reported the amount and rate of O_2 formation, but not reported AQE [13,14,25,26].

In the present study, cuboid-type WO_3 (C-WO_3) photocatalyst particles were calcined at various temperatures between 200 and 500 °C, and the resulting samples were then investigated for their ability to photocatalyze water oxidation under visible light irradiation in the presence of sacrificial silver sulfate (Ag_2SO_4). The particles formed were found to be cuboid regardless of the calcination temperature, but the photocatalytic activity differed between samples. Thus, we set out to determine the main factor influencing the photocatalytic activity of the C-WO_3 particles prepared. We also determined the AQE value of C-WO_3 calcined at 400 °C.

2. Material and methods

2.1. Synthetic procedures

C-WO_3 was synthesized by a previously reported method [27]: To synthesize C-WO_3, $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ (Wako Pure Chemical Industries) was kept at 80 °C and added drop by drop into HNO_3 (Wako Pure Chemical Industries, 69–70 wt% assay) which was kept at 75 °C, and then the mixture were stirred for 1 day at room temperature. After the reaction was completed, the resulted product was centrifuged to obtain the precursor of H_2WO_4. After the precursor was transferred into distilled water and the pH was controlled to 1.5, it was stirred for 1 day at room temperature. Then, the suspension was processed hydrothermally at 160 °C for 14 h. The collected product was dried at 100 °C and calcined to obtain the final product of C-WO_3. Here, various final calcination temperatures between 200 and 500 °C were used.

2.2. Characterization of C-WO_3 particles

The shapes of C-WO_3 particles calcined at various temperatures were observed by scanning electron microscopy (SEM; S-4800, Hitachi). X-ray diffraction (XRD) patterns of C-WO_3 were recorded using an Ultima-IV instrument (Rigaku), and the data were standardized with NiO ($2\theta = 43.3°$, JCPDS No. 00-044-1159), which was mixed with C-WO_3 at a concentration of 33 wt%. The specific surface area was measured using a BELSORP-mini II (BEL JAPAN) at liquid nitrogen temperature. The samples were pretreated at 120 °C for 1 h. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were obtained using a spectrophotometer (UV-3101PC, Shimadzu) with barium sulfate as the reference material. Photoluminescence (PL) spectra were obtained using a fluorescence spectrometer (JASCO FP-6500) with an excitation wavelength at 270 nm and a UV-35 (350 nm) cut-off filter.

2.3. Photocatalytic reactions

The photocatalytic activities of the samples were examined by measuring the molar amount of evolved O_2 from an aqueous Ag_2SO_4 solution (20 mmol L^{-1}) subjected to irradiation with visible light from a 49 m Wcm^{-2} blue LED ($\lambda = 472$ nm). Ag_2SO_4 (Wako Pure Chemical Industries) was used as a redox reagent (an electron scavenger) in this O_2 evolution reaction. The C-WO_3 powder (50 mg) and the Ag_2SO_4 solution (5.0 mL) were put into a 35-mL test tube, and the air in the test tube was replaced with argon. Ag nanoparticles that were deposited on the WO_3 particles by the photocatalytic reaction were observed by using transmission electron microscopy (TEM; JEM-2100F, JEOL), and the amounts of Ag nanoparticles were determined by using atomic absorption spectrometry (AAS; AA-6200, Shimadzu) after dissolving the Ag particles with 16 molL^{-1} HNO_3 (Wako Pure Chemical Industries, 69–70 wt% assay). In addition, AAS (A-1000, Hitachi) was used to determine the amounts of Ag^+ adsorbed on the C-WO_3 particles without the photocatalytic reaction after stirring the same suspension in a test tube for 5 h in the dark, which was done in order to check the relation between the amount of Ag^+ and the specific surface area described above. The amount of evolved oxygen was analyzed by gas chromatography (Shimadzu GC-8A, TCD detector, MS-5A column, argon carrier gas).

The AQE for O_2 evolution was measured using the same experimental setup, except for the light irradiation condition, and an action spectrum was obtained. Here, we irradiated a sample with eight wavelengths of monochromatic light: 309, 360, 437, 467, 489, 542, 594, and 644 nm. The widths of the wavelengths of light centered at 437, 489, 542, 594, and 644 nm were ± 15 nm, and those of the other wavelengths of light were ± 20 nm. The AQE values at the eight wavelengths of light were calculated using Eq. (1) [28].

$$\text{AQE} = \frac{4 \times \text{Rate of } O_2 \text{ evolution}}{\text{Rate of incidence of photons}} \times 100 \tag{1}$$

3. Results and discussion

Fig. 1 shows SEM images of C-WO_3 calcined at various temperatures. The C-WO_3 particles were cuboid regardless of the calcination temperature, but the corners of the cuboids were slightly rounded when the calcination temperature was 500 °C. Also note that the cuboids had already been formed before calcination (Fig. S1). The particle sizes were 50–300 nm. Small particles were observed on the surface of large particles in the images shown in Fig. 1a–c, but the number of small particles was decreased in the image shown in Fig. 1d, probably due to the small particles having grown and aggregated into large ones at a calcination temperature of 500 °C.

Fig. 2 shows XRD patterns for the C-WO_3 calcined at various temperatures. Every pattern was assigned to monoclinic WO_3 (JCPDS No. 01-083-0950), and the triclinic WO_3 (JCPDS No. 00-032-1395) peaks were not observed at $2\theta = 33.00°$, 34.49°, and 40.95° as shown by the dotted lines. Fig. S2 shows XRD patterns for the C-WO_3 before calcination, indicating that C-WO_3 was monoclinic before calcination. The crystallite diameters based on the diffraction peaks from the (002), (020), and (200) planes were estimated using the Scherrer equation as shown in Table 1. The diameter calculated from each of these diffraction peaks increased with increasing calcination temperature. Large crystalline particles generally have higher crystallinity, so the samples calcined at high temperatures were expected to have high crystallinity. Moreover, the intensities of the peaks in the range of 33°–34.5° were