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Preparation of Crystalline Tungsten Oxide Nanorods with Enhanced Photocatalytic Activity under Visible Light Irradiation

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Crystalline tungsten oxide (WO_3) nanorods with diameters of approximately 8 nm were prepared using SBA-15 mesoporous silica as a hard template and ammonium metatungstate as a tungsten source, which have larger surface area (ca. $90\,m^2\,g^{-1}$) than other WO_3 materials and, therefore, exhibit superior photocatalytic activity for the decomposition of acetic acid under visible light irradiation after Pt loading.

The development of visible light-driven photocatalysts is highly desirable for the efficient decomposition of environmental organic contaminants using sunlight or indoor fluorescent lights. Recently, much attention has been focused on tungsten(VI) oxide (WO_3) for the decomposition of organic compounds under visible light because it exhibits high photocatalytic activity when the surface is modified with nanoparticulate platinum (Pt),[1,2] palladium (Pd),[3] or copper oxide (CuO).[4–6]

In general, high photocatalytic activity requires both high crystallinity, that is, a low density of lattice defects, to reduce the recombination of the photoexcited electrons and holes required for the catalytic reaction, as well as a large surface area to increase the density of active surface sites where the photocatalytic reaction can take place.[7–9] Unfortunately, these two features are generally exclusive in the current preparation of photocatalytic semiconductors. High crystallinity is typically obtained by calcination at high temperatures for long periods, which generally results in lowered surface areas.

There is intense research to produce crystalline WO_3 with larger surface areas. Miyauchi[10,11] reported hydrothermal synthesis of WO_3 with surface area of ca. $25\,m^2\,g^{-1}$, and we[12,13] have reported three-dimentionally ordered macroporous WO_3 with surface area of $20–30\,m^2\,g^{-1}$. In order to enhance photocatalytic activity, crystalline WO_3 with much larger surface area is needed.

There have been several reports regarding the production of nanometer size WO_3 crystals using mesoporous silica templates.[14–19] All the reported methods have employed phosphotungstic acid, a Keggin-type tungsten–phosphorous mixed oxide cluster,[20] as a tungsten precursor. The Keggin-type phosphotungstic acid has a central PO_4 tetrahedron with 12 surrounding WO_6 octahedra. However, WO_3 materials prepared from phosphotungstic acid are not photocatalytically active, probably because of the presence of residual phosphorus impurities after calcination.[13]

We describe a method to produce pure crystalline WO_3 nanorods using SBA-15 as a mesoporous silica template and ammonium metatungstate as the tungsten source. Ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}$) is a Keggin-type tungsten oxide cluster that does not include phosphorus species,[20] is stable in water and polar solvents, and can be infiltrated in template voids.[13]

Ammonium metatungstate was impregnated into the pores of SBA-15, and tungsten oxide (WO_3) was formed by subsequent calcination at 873 K. The silica template was removed by HF treatment, and the WO_3 obtained was washed with water.[23]

Figures 1 and S1[23] show SEM and TEM images of the synthesized WO_3 material. The SEM image (Figure S1a[23]) of the WO_3 materials obtained after silica removal shows two types of particles, nanorod particles and large particles with diameters of several hundred nanometers. The nanorod particles have diameters of ca. 7 to 8 nm, which indicates that the SBA-15 pores acted as a successful template. The large submicron-sized particles were also observed before silica removal (Figure 1a), which indicates that they were formed outside of the SBA-15 template. To remove the large particles, the mixture was suspended in ethanol and centrifuged. The obtained supernatant was separated from the sedimented solid, and a yellow solid (34% yield) was obtained by drying the supernatant (Table 1, Entry 3).

The obtained yellow solid contains nanorod particles with diameters of ca. 7 to 8 nm and lengths of 20 to 50 nm (Figures 1b, 1c, and S1b).[23] No other particles were observed in the electron micrographs, which indicates the material exclusively contains nanorod particles. The lattice fringes were observed in each nanorod (Figure 1b), which implies that these are crystalline materials.

The BET surface area of the obtained material was $89\,m^2\,g^{-1}$ (Table 1, Entry 3), which is similar to the calculated value,[21] and support that the obtained material is exclusively composed of nanometer-sized particles.

Figure 2 shows XRD patterns of WO_3 particles obtained from ammonium metatungstate with and without the SBA-15 template. Peaks attributed to monoclinic WO_3 (JCPDS 43-1035) were observed, and all peaks were broad; the crystallite size estimated from the Scherrer equation using the (120) diffraction was ca. 10 nm. This result together with electron microscopy observations and surface area measurement confirms that the obtained material is exclusively composed of crystalline WO_3 nanorods.

Table 1 summarizes the yield, surface area, and nitrogen contents of the crystalline WO_3 nanorods prepared after different calcination temperatures. Calcination temperatures between 773 and 1073 K were suitable for the production of crystalline WO_3 nanorods without detectable nitrogen content (Entries 2, 3, 4, and 5, and Figure S2c[23]). The sedimented WO_3 solids obtained after centrifugation have smaller surface area, because they contain both nanorods and large crystals (Table S1, Figures S1c

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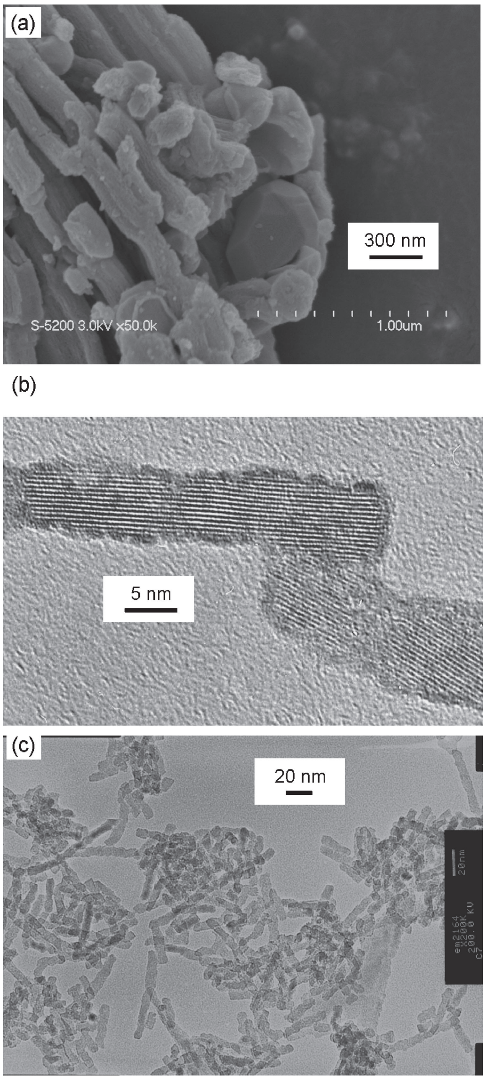

Figure 1. SEM and TEM images of WO_3 materials prepared using SBA-15 as a template. (a) WO_3 materials before SBA-15 removal. (b) and (c) WO_3 nanorods separated by centrifugation.

and S1d).[23] The presence of large crystals was also confirmed by powder XRD with sharper peaks (Figure S2b[23]). Nanorod materials with large surface area could be obtained even at 1073 K, which is not possible with organic templates.[13,22] However, only large crystals were obtained at calcination temperature of 1273 K (Table 1, Entry 6 and Table S1, Enrty 6),[23] which indicates that sintering of the WO_3 crystals occurred even in the presence SBA-15 template at such a high temperature (Figures S2a and S2b).[23]

Diffuse reflectance UV–vis spectra indicate that WO_3 nanorods have more intense adsorption in a range of 500–800 nm (Figure S3[23]), which indicate reduction of W in the nanorod materials. Detailed investigation is now underway in our group.

The photocatalytic decomposition of acetic acid was evaluated after loading the WO_3 samples with Pt as a co-catalyst.[23] Figure 3 shows the generation of CO_2 during the gas-phase decomposition of acetic acid over Pt-loaded WO_3 nano-

Table 1. Yield, surface area, nitrogen contents, and relative photocatalytic activity of the obtained crystalline WO_3 nanorods

Entry	Calcd temp/K	Yield /%	Surf. area /$m^2\,g^{-1}$	N cont. /wt %	Relative CO_2 evolution rate[a]
1	673	1		0.26	
2	773	14	88	0	
3	873	34	89	0	1.7
4	973	30	86	0	1.5
5	1073	28	83	0	1.7
6	1273	0			
7	3DOM WO_3 prepared PMMA sphere (diameter: 181 nm)[b]		11		1.0
8	3DOM WO_3 prepared PMMA sphere (diameter: 86 nm)[b]		23		1.3

[a] Photocatalytic activity (CO_2 evolution rate) was compared to CO_2 evolution rate of three-dimensionally ordered macroporous (3DOM) WO_3 prepared using poly(methyl methacrylate) (PMMA) sphere (PMMA diameter: 181 nm) at 873 K of calcination temperature. [b] Data from ref 13.

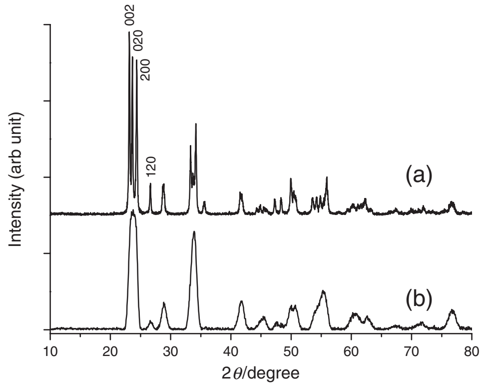

Figure 2. XRD patterns of (a) WO_3 prepared by calcination of ammonium metatungstate without a template at 1273 K and (b) WO_3 nanorods prepared using SBA-15 as a template and calcined at 873 K.

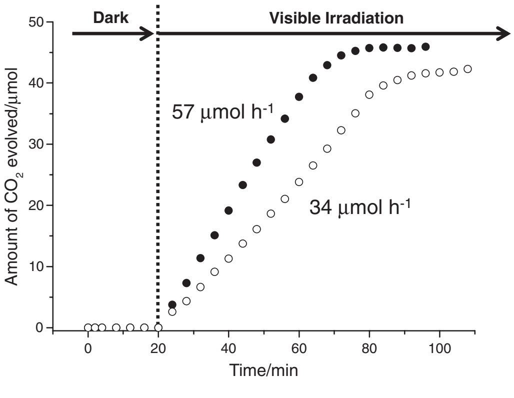

Figure 3. Time course of CO_2 evolution over Pt-loaded WO_3 prepared using SBA-15 as a template (●) and using PMMA spheres (diameter: 181 nm) (○). Calcination temperature was 873 K.

rods and 3DOM WO_3 prepared using the PMMA colloidal crystal template (at a calcination temperature of 873 K). CO_2 generation was observed immediately upon irradiation for all samples, without an appreciable induction time. The rate of CO_2 generation over the WO_3 nanorods was considerably higher than that for the corresponding 3DOM sample (Table 1), and this improvement is most likely due to the enlarged surface area. Further tuning of the crystal size and surface area to improve the catalytic activity is presently underway.

Crystalline WO_3 nanorods were successfully prepared using SBA-15 as a template and ammonium metatungstate as a tungsten source. The nanorods had diameters of ca. 8 nm and were 20 to 50 nm long with large surface areas. The photocatalytic activity of these materials was higher than that of our previously prepared 3DOM crystalline WO_3 because of its larger surface area.

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23 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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