Synthesis of Nanometer-Sized WO$_3$ Particles by Facile Wet Process and Their Photocatalytic Properties

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Nanometer-sized WO$_3$ particles were prepared from alkaline alcohol-water mixture with WCl$_6$ and NH$_3$ under reflux. The resultant particles at various NH$_3$/W mole ratios were well crystallized ranging 5–20 nm in diameter and the surface area was in the range of 13.70–32.50 m$^2$/g. Samples synthesized at NH$_3$/W = 3.2 and 12.9 ratio (mol/mol) had an absorption edge in the visible light range and showed the photocatalytic activity under the irradiation of visible light, and the surface area and the crystallinity of those powders had a strong effect on the photocatalytic degradation. When ln($C_0/C$) (where $C_0$: initial concentration of acetaldehyde, $C$: final concentration of acetaldehyde after irradiation) was plotted against photoirradiation time, the degradation velocity constant ($k$) against acetaldehyde estimated from the slope of lines was $12.4\ h^{-1}g^{-1}$ at NH$_3$/W = 3.2 and $13.9\ h^{-1}g^{-1}$ at NH$_3$/W = 12.9 ratio (mol/mol), respectively.

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1. INTRODUCTION

In recent, a semiconductive photocatalyst like titanium oxide (TiO$_2$) has a great attention in the viewpoint that its clean and infinite photo energy can decompose the versatile volatile organic compounds (VOCs) such as NO$_x$ and SO$_x$. TiO$_2$ as the representative semiconductor photocatalyst, in which the electric potential of valance band is +3.0 eV [1], has a strong oxidation function by a hole produced owing to electron’s transition from valence band to conduction band. However, its energy band gap has a high value of 3.2 eV and its absorption edge is laid on the UV light region. Therefore, the photocatalytic property of TiO$_2$ can exhibit outdoors but not indoors.

Meanwhile, tungsten oxide (WO$_3$), in which the electric potential of valence band is +3.1 eV [2], has almost the same oxidation capability as TiO$_2$. Moreover, its energy band gap of 2.7 eV is relatively small and its absorption edge locates on the visible region. Thus it is anticipated to exhibit the photocatalytic ability even indoors. Also, TiO$_2$/WO$_3$ composite materials have been reported as fascinating ones: high active photocatalyst [3], photocatalytically inactive materials [4], energy storage photocatalyst [5]. At present, a thermal decomposition of tungsten acid has been reported as a general method to prepare WO$_3$ particles [6]. However, the method has some problems that the high quantum efficiency was not expected because its particle size was over submicron order. On the contrary, if synthesis of nanometer-sized WO$_3$ particle could be accomplished, it will be used as a photocatalytic material in enormous applied fields.

We have already reported the low-temperature synthesis of nanocrystalline metal oxides particles (ZnO [7, 8], TiO$_2$ [9], Fe$_2$O$_3$ [10], Co$^{2+}$-doped TiO$_2$ [11, 12], SnO$_x$ (x = 1, 2) [13] MgO-ZnO [14], and YMO$_4$: Eu$^{2+}$ (M = V, P) [15]) through facile wet process, so-called NAnometer-sized Crystal Formation in Alcoholic Solutions method (NACFAS), in which an alcohol-water mixture with metal salts is refluxed without the deliberate addition of surfactants or adsorbing ligands. In this report, the low-temperature (<100°C) preparation of nanometer-sized WO$_3$ single crystals using the NAC-FAS method was investigated and its visible photocatalytic properties were estimated.

2. EXPERIMENTAL PROCEDURES

WO$_3$ nanoparticles were prepared as follows. Tungsten chloride (WCl$_6$; TEOKA Chemical Co. Inc.), purity >98%,
5.04 mmol was dissolved in 50 mL of ethanol. Under refluxing at 70°C, the mixture of ammonia water and ethanol, which concentration varied in the range of 0.016–0.26 mol/L, was dropwise added for 1 hour and subsequently refluxed for 1 hour. After this operation, the mixture was cooled to room temperature while stirring the mixture. Precipitates in the reaction mixture were isolated by the centrifugal separation at a rotating rate of 13 000 r.p.m., washed with methanol, dried at room temperature overnight in a vacuum. Prepared samples were heat treated at 400°C for 2 hours under atmosphere. Powder X-ray diffraction (XRD: RIGAKU MiniFlex) was carried out using Ni-filtered Cu-Kα radiation for determining the crystal structure of products. The normal condition was set at 30 kV-15 mA in the range of 5°–105° with 8°/min. The crystallite size was calculated from the half-peak width at half height for the WO3 (2θ = 25°) diffraction peaks using the Scherrer equation. TG-DTA measurement (RIGAKU Thermal analyzer TG 8010 D) for investigating the temperature dependences of samples was carried out, and FT-IR spectrometer (Nippon Bunkou, FT/IR-470 plus) was used to investigate the ammonium salt and the absorbed water that remained as impurities on the surface of the as-prepared WO3 nanocrystals. Particle size of WO3 nanocrystals was observed using a transmission electron microscope (TEM: JEOL JEM-3010) at an acceleration voltage of 300 kV. Specific surface area was measured by Quantchrome Quantors using the Brunauer-Enarmett-Teller (BET) method after samples were dried at 120°C. UV-visible spectra for WO3 nanocrystals were measured by a spectrophotometer U-4000 (Hitachi Co., Ltd., Hitachi, Japan). Photocatalytic activity of WO3 nanocrystals for the photo oxidation degradation of gaseous acetaldehyde was measured at room temperature by gas chromatography (Shimatsu GC-9A, FID detector) and the light source was Xenon lamp (Wacom Co. HX-500) with a cut-off filter and the light intensity of λex > 450 nm was 3.50 mW·cm⁻².

3. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns for as-prepared samples at the different NH3/W mole ratio, which was 3.2, 6.5, 12.9, 25.7, and 52.4, respectively, and XRD patterns of samples heat treated at 400°C were demonstrated in Figure 2. As shown in Figure 1, diffraction peaks attributed to H2WO4 crystal were identified at NH3/W = 3.2 mole ratio and in other samples prepared at the range of NH3/W = 6.5–52.4 mole ratio, the crystalline peaks of (NH4)6W12O39 were observed. Meanwhile, after heat treatment at 400°C, only WO3 peak in all samples was observed as demonstrated in Figure 2. The main peak of XRD patterns which was laid around 2θ = 25° was broad in the case of sample prepared at NH3/W = 3.2 mole ratio, but this peak became sharper for other samples over NH3/W = 6.5 mole ratio. From the calculation using Scherrer equation, the crystalline size of WO3 at NH3/W = 3.2 mole ratio was estimated to be 6 nm and it became over 20 nm beyond NH3/W = 6.5 mole ratio. As a result, at the higher NH3/W mole ratio, it might be possible to synthesize the nanometer-sized WO3 particles with high crystallinity using this NAC-FAS method.

The results of TG-DTA measurement for as-prepared samples at NH3/W = 12.9 mole ratio were shown in Figure 3. The endothermic peak around 70°C was attributed to the evaporation of absorbed water and the exothermic peak in the range between 320°C and 370°C was owing to the remained organic component. Another exothermic peak was observed around 400°C and it is accompanied with
the abrupt weight decrease due to the decomposition of \((\text{NH}_4)_6\text{W}_{12}\text{O}_{39}\).

Meanwhile, Figure 4 demonstrated FT-IR spectra of the above same sample. In this figure, the absorption peak around \(3000\ \text{cm}^{-1}\) was assigned to the stretching vibration of \(\text{N–H}\) bond and the one around \(1400\ \text{cm}^{-1}\) was attributed to the rotational vibration of \(\text{N–H}\) bond, respectively. However, after heat treatment at \(400^\circ\text{C}\), these peaks disappeared and the absorption peak’s intensity attributed to the stretching vibration of \(\text{W–O}\) bond became stronger. From these FT-IR and TG-DTA results, it was clear that \((\text{NH}_4)_6\text{W}_{12}\text{O}_{39}\) decomposed and transformed to \(\text{WO}_3\) crystal in the as-prepared samples by the heat treatment at \(400^\circ\text{C}\).

Figure 5 shows TEM images of \(\text{WO}_3\) nanocrystalline particles prepared at various different \(\text{NH}_3/\text{W}\) mole ratios, which was \(3.2, 6.5, 12.9, 25.7, \) and \(52.4\), and commercial products, respectively. The average particle size of commercial product as shown in Figure 5(f) was found to be about \(100\ \text{nm}\), while, the average particle size of synthesized \(\text{WO}_3\) powder in this work was observed to be in the range of \(5–20\ \text{nm}\) even though it showed the slight aggregation. In addition, the surface area of commercial \(\text{WO}_3\) powder was measured to be \(3.0\ \text{m}^2\text{g}^{-1}\), while that of \(\text{WO}_3\) powder prepared by NAC-FAS method at the different \(\text{NH}_3/\text{W}\) mole ratios, which were \(3.2, 6.5, 12.9, 25.7, \) and \(52.4\), was measured to be \(32.50\ \text{m}^2\text{g}^{-1}, 12.40\ \text{m}^2\text{g}^{-1}, 18.20\ \text{m}^2\text{g}^{-1}, 13.70\ \text{m}^2\text{g}^{-1}, 16.80\ \text{m}^2\text{g}^{-1}\), respectively, and it showed higher values of 4–10 times comparing to that of commercial product.

Figure 6 demonstrates the UV-visible spectra of commercial \(\text{WO}_3\) product and \(\text{WO}_3\) nanocrystalline particles prepared at \(\text{NH}_3/\text{W} = 3.2\) and \(12.9\) mole ratio. Crossing point of two dotted lines in the figure indicates the original location of absorption edge at \(\text{NH}_3/\text{W} = 12.9\) mole ratio assuming that the impurity is not present in the sample. As a result, the basic absorption edge of \(\text{WO}_3\) nanocrystalline...
3.2, (b) 12.9 NH3/W ratio (mol/mol), and (c) commercial product.

Nanometer-sized WO3 particles have been successfully prepared from alkaline alcohol-water mixture with WCl6 and NH3 under reflux. The resultant particles at various NH3/W mole ratios were well crystallized ranging 5–20 nm in diameter and the surface area was in the range of 13.70 – 32.50 m2g−1 and showed the high crystallinity at the higher NH3/W mole ratio. Especially, samples synthesized at NH3/W = 3.2 and 12.9 (mol/mol) had an absorption edge in the visible light range and showed high photocatalytic activity under the irradiation of visible light comparing to the commercial WO3 products, and experimental results reveal that the surface area and the crystallinity of those powders had a strong effect on the photodegradation of gaseous acetaldehyde.

4. CONCLUSIONS

Meanwhile, when ln (C0/C) (C0: initial concentration of acetaldehyde, C: final concentration of acetaldehyde after irradiation) was plotted against photoirradiation time, a linear relation was made for all samples. The degradation velocity constant (k) against acetaldehyde estimated from the slope of lines was 12.4 h−1g−1 at NH3/W = 3.2 and 13.9 h−1g−1 at NH3/W = 12.9 ratio (mol/mol), respectively, and they showed higher value than that of commercial WO3 product, which value was 7.80 h−1g−1. These results reveal that the surface area and the crystallinity of WO3 powder have a strong effect on the photodegradation of gaseous acetaldehyde.

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