Research Article

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^2g^{-1} . Samples synthesized at $\text{NH}_3/\text{W} = 3.2$ 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 $\ln(C_0/C)$ (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 $12.4\text{ h}^{-1}\text{g}^{-1}$ at $\text{NH}_3/\text{W} = 3.2$ and $13.9\text{ h}^{-1}\text{g}^{-1}$ at $\text{NH}_3/\text{W} = 12.9$ 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 valance 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_2O_3 [10], Co^{2+} -doped TiO_2 [11, 12], SnO_x ($x = 1, 2$) [13], MgO-ZnO [14], and YMO_4 ; Eu^{2+} ($M = \text{V}, \text{P}$) [15]) through facile wet process, so-called NANometer-sized Crystal Formation in Alcoholic Solutions method (NAC-FAS), 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 ($<100^\circ\text{C}$) 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 $>98\%$,

FIGURE 1: XRD patterns of as-prepared samples at various NH_3/W mole ratios: (a) 3.2, (b) 6.5, (c) 12.9, (d) 25.7, and (e) 52.4 (mol/mol), respectively.

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-filtrated $\text{Cu-K}\alpha$ 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 $8^\circ/\text{min}$. The crystallite size was calculated from the half-peak width at half height for the WO_3 ($2\theta = 25^\circ$) 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 WO_3 nanocrystals. Particle size of WO_3 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 Quantochrome Quantsorb using the Brunauer-Enarmett-Teller (BET) method after samples were dried at 120°C . UV-visible spectra for WO_3 nanocrystals were measured by a spectrophotometer U-4000 (Hitachi Co., Ltd., Hitachi, Japan). Photocatalytic activity of WO_3 nanocrystals for the photo oxidation degradation of gaseous acetaldehyde was measured at room temperature by gas chromatography

FIGURE 2: XRD patterns of samples heat treated at 400°C for 2 hours at various NH_3/W ratios: (a) 3.2, (b) 6.5, (c) 12.9, (d) 25.7, and (e) 52.4 (mol/mol), respectively.

(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 $\lambda_{\text{ex}} > 450 \text{ nm}$ was $3.50 \text{ mW}\cdot\text{cm}^{-2}$.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns for as-prepared samples at the different NH_3/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 H_2WO_4 crystal were identified at $\text{NH}_3/\text{W} = 3.2$ mole ratio and in other samples prepared at the range of $\text{NH}_3/\text{W} = 6.5$ –52.4 mole ratio, the crystalline peaks of $(\text{NH}_4)_6\text{W}_{12}\text{O}_{39}$ were observed. Meanwhile, after heat treatment at 400°C , only WO_3 peak in all samples was observed as demonstrated in Figure 2. The main peak of XRD patterns which was laid around $2\theta = 25^\circ$ was broad in the case of sample prepared at $\text{NH}_3/\text{W} = 3.2$ mole ratio, but this peak became sharper for other samples over $\text{NH}_3/\text{W} = 6.5$ mole ratio. From the calculation using Scherrer equation, the crystalline size of WO_3 at $\text{NH}_3/\text{W} = 3.2$ mole ratio was estimated to be 6 nm and it became over 20 nm beyond $\text{NH}_3/\text{W} = 6.5$ mole ratio. As a result, at the higher NH_3/W mole ratio, it might be possible to synthesize the nanometer-sized WO_3 particles with high crystallinity using this NAC-FAS method.

The results of TG-DTA measurement for as-prepared samples at $\text{NH}_3/\text{W} = 12.9$ 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

FIGURE 3: TG-DTA curves of as-prepared sample at $\text{NH}_3/\text{W} = 12.9$ ratio (mol/mol).

FIGURE 4: FT-IR spectra of samples prepared at $\text{NH}_3/\text{W} = 12.9$ ratio (mol/mol).

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 cm^{-1} was assigned to the stretching vibration of N-H bond and the one around 1400 cm^{-1} was attributed to the rotational vibration of N-H bond, respectively. However, after heat treatment at 400°C , these peaks disappeared and the absorption peak's intensity attributed to the stretching vibration of 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 WO_3 crystal in the as-prepared samples by the heat treatment at 400°C .

Figure 5 shows TEM images of WO_3 nanocrystalline particles prepared at various different NH_3/W mole ratios, which was 3.2, 6.5, 12.9, 25.7, 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 nm, while, the average particle size of synthesized WO_3 powder in this work was observed to be in the range of 5–20 nm even though it showed the slight aggregation. In addition, the surface area of commercial WO_3 powder was measured to be $3.0\text{ m}^2\text{g}^{-1}$, while that of WO_3 powder prepared by NAC-FAS method at the different NH_3/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 WO_3 product and 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 WO_3 nanocrystalline

FIGURE 5: TEM images of WO_3 nanocrystalline particles prepared at various NH_3/W ratios: (a) 3.2, (b) 6.5, (c) 12.9, (d) 25.7, (e) 52.4 (mol/mol), and (f) commercial product, respectively.

FIGURE 6: UV-visible spectra of WO_3 nanocrystalline particles: (a) 3.2, (b) 12.9 NH_3/W ratio (mol/mol), and (c) commercial product.

FIGURE 7: Change in acetaldehyde concentration against irradiation time under visible light ($I = 3.5 \text{ mWcm}^{-2}$): (a) 3.2, (b) 12.9 NH_3/W ratio (mol/mol), and (c) commercial product.

particles prepared at $\text{NH}_3/\text{W} = 3.2$ and 12.9 mole ratio showed the red shifting comparing to commercial WO_3 product and had an absorption edge in the visible light range. Therefore, the impurity energy level owing to oxygen deficiency might be formed in from the result that new absorption peak appeared below 600 nm wavelength [16]. Next, we investigated the property of the photocatalytic degradation of gaseous acetaldehyde for these samples.

Figure 7 shows the photocatalytic degradation against gaseous acetaldehyde of commercial WO_3 powder and WO_3 nanocrystalline one prepared at $\text{NH}_3/\text{W} = 3.2$ and 12.9 mole ratio. It is very clear that all WO_3 sample had a photocatalytic activity of the visible light from the result that the acetaldehyde concentration decreased by the photoirradiation time.

Meanwhile, when $\ln(C_0/C)$ (C_0 : 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 $12.4 \text{ h}^{-1}\text{g}^{-1}$ at $\text{NH}_3/\text{W} = 3.2$ and $13.9 \text{ h}^{-1}\text{g}^{-1}$ at $\text{NH}_3/\text{W} = 12.9$ ratio (mol/mol), respectively, and they showed higher value than that of commercial WO_3 product, which value was $7.80 \text{ h}^{-1}\text{g}^{-1}$. These results reveal that the surface area and the crystallinity of WO_3 powder have a strong effect on the photodegradation of gaseous acetaldehyde.

4. CONCLUSIONS

Nanometer-sized WO_3 particles have been successfully 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 $13.70 - 32.50 \text{ m}^2\text{g}^{-1}$ and showed the high crystallinity at the higher NH_3/W mole ratio. Especially, samples synthesized at $\text{NH}_3/\text{W} = 3.2$ 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 WO_3 products, and experimental results reveal that the surface area and the crystallinity of those powders had a strong effect on the photodegradation.

REFERENCES

- [1] T. Shimamoto and B. Ohtani, "Evaluation and control of photocatalytic activities of suspended semiconductor photocatalysts through action spectrum analyses," *Journal of Surface Science Society of Japan*, vol. 24, no. 1, pp. 39–45, 2003.
- [2] G. R. Bamwenda and H. Arakawa, "The visible light induced photocatalytic activity of tungsten trioxide powders," *Applied Catalysis A*, vol. 210, no. 1-2, pp. 181–191, 2001.
- [3] Y. T. Kwon, K. Y. Song, W. I. Lee, G. J. Choi, and Y. R. Do, "Photocatalytic behavior of WO_3 -loaded TiO_2 in an oxidation reaction," *Journal of Catalysis*, vol. 191, no. 1, pp. 192–199, 2000.
- [4] H. Tada, A. Kokubo, M. Iwasaki, and S. Ito, "Deviation of the TiO_2 photocatalyst by coupling with WO_3 and the electrochemically assisted high photocatalytic activity of WO_3 ," *Langmuir*, vol. 20, no. 11, pp. 4665–4670, 2004.
- [5] T. Tatsuma, Y. Ohko, and A. Fujishima, "Mechanism and applications of energy storage photocatalyst," *Journal of the Surface Science Society of Japan*, vol. 24, no. 1, pp. 13–18, 2003.
- [6] H. I. S. Nogueira, A. M. V. Cavaleiro, J. Rocha, T. Trindade, and J. D. Pedrosa de Jesus, "Synthesis and characterization of tungsten trioxide powders prepared from tungstic acids," *Materials Research Bulletin*, vol. 39, no. 4-5, pp. 683–693, 2004.
- [7] M. Iwasaki, Y. Inubushi, and S. Ito, "New route to prepare ultrafine ZnO particles and its reaction mechanism," *Journal of Materials Science Letters*, vol. 16, no. 18, pp. 1503–1505, 1997.
- [8] Y. Inubushi, R. Takami, M. Iwasaki, H. Tada, and S. Ito, "Mechanism of formation of nanocrystalline ZnO particles through the reaction of $[\text{Zn}(\text{acac})_2]$ with NaOH in EtOH ," *Journal of Colloid and Interface Science*, vol. 200, no. 2, pp. 220–227, 1998.

- [9] M. Iwasaki, M. Hara, and S. Ito, "Facile synthesis of nanocrystalline anatase particles from titanyl sulfate," *Journal of Materials Science Letters*, vol. 17, no. 20, pp. 1769–1771, 1998.
- [10] M. Iwasaki, M. Hara, and S. Ito, "Synthesis of nanometer-sized hematite single crystals through NAC-FAS method," *Journal of Materials Science*, vol. 35, no. 4, pp. 943–949, 2000.
- [11] M. Iwasaki, M. Hara, H. Kawada, H. Tada, and S. Ito, "Cobalt ion-doped TiO_2 photocatalyst response to visible light," *Journal of Colloid and Interface Science*, vol. 224, no. 1, pp. 202–204, 2000.
- [12] M. Iwasaki, M. Hara, H. Kawada, H. Tada, and S. Ito, "Preparation of co-doped TiO_2 fine particles by NAC-FAS method and their photocatalytic activities," *Material Technology*, vol. 18, no. 1, pp. 35–40, 2000.
- [13] M. Iwasaki, T. Matsui, H. Matsui, M. Hara, H. Tada, and S. Ito, "Synthesis of nanometer-sized SnO_x particles by NAC-FAS method and their electric conductivity," *Journal of the Japan Society of Colour Material*, vol. 73, pp. 535–540, 2000.
- [14] S. Ohshiro, M. Iwasaki, M. Hara, and S. Ito, "Low-temperature synthesis of nanometer-sized single crystals in MgO-ZnO solid solution," *Journal of the Japan Society of Colour Material*, vol. 75, no. 7, pp. 327–329, 2002.
- [15] M. Iwasaki, N. Yamashita, M. Taguchi, S. Karuppucharmy, S. Ito, and W. Park, "Blue emission of $\text{YMO}_4\text{:Eu}^{2+}$ ($M = \text{V}, \text{P}$) nanocrystals prepared through facile wet process," in *Nanophotonic Materials III*, vol. 6321 of *Proceedings of SPIE*, pp. 1–9, San Diego, Calif, USA, August 2006.
- [16] T. J. Tate, M. Garcia-Parajo, and M. Green, "Ion implantation effects in polycrystalline WO_3 thin films," *Journal of Applied Physics*, vol. 70, no. 7, pp. 3509–3511, 1991.