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亜酸化ナノ粒子の合成と触媒特性評価

Synthesis of Suboxide Nanoparticles
and Their Catalytic Properties Febrigia Ghana
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成 果 の 概 要

1. Background

In the past decade, tungsten oxide (WO_3) nanoparticles have attracted much attention as an efficient material for photocatalysis, phototherapy, and electrochemical applications, due to their favorable physical and chemical properties. Their relatively narrow band gap of 2.6–3.0 eV allows for excitation by visible wavelengths, which is desirable for photocatalysis applications. The favorable surface interaction between tungsten oxide and organic dye molecules also makes it a good adsorbent. The interaction between dye molecules and WO_3 nanosheet surfaces has been reported previously. WO_3 nanoparticles in the form of films or nanosheets were used as adsorbents, and exhibited selective adsorption properties, though the amount of adsorbed material was not high. Another report proposed the structuration of WO_3 nanoparticles to enhance their surface area, which improved their

adsorption properties and photocatalytic performance. A nonstoichiometric phase of WO_3 known as tungsten blue oxide (WO_x) nanoparticles has recently received much interest. The presence of oxygen vacancies within its structure provides several advantages compared to WO_3 (Song J. et al., 2015; Ghosh S. et al., 2015). For example, oxygen vacancies in the transition-metal oxide figuratively act as dopants, which decreases the band gap in a way similar to the addition of Pt onto TiO_x nanoparticles (Arif A.F. et al., 2017; Rinaldi F.G. et al., 2017). Hence, an intrinsic semiconductor can be converted to a hypothetically extrinsic semiconductor with a donor activation energy at 0.01 eV. WO_x nanoparticles also have the ability to generate free electrons ($N \sim 10^{21} \text{ cm}^{-3}$). Numerous approaches have been developed for synthesis of WO_x nanoparticles, including approaches based on supercritical fluid, sol gel, hydrothermal, and chemical vapor deposition methods. WO_x particles can reportedly be produced by heating ammonium paratungstate

for several hours, which is feasible for industrial-scale applications. The use of WO_x particles in various forms and morphologies, such as Ag/WO_x nanorods, $\text{WO}_x\text{-TiO}_2$ composites, WO_x/C nanocomposites, and WO_x nanorods, for photocatalytic application has been previously reported. Such reports have shown that other than the presence of an additional dopant or cocatalyst, increasing the amount of oxygen vacancies inside the crystal structure could improve the photocatalytic performance. However, most resulting products were reportedly larger than 100 nm. Nanosized particles (i.e., smaller than 100 nm) are preferred because higher specific surface area gives them higher activity. To the best of our knowledge, there are still no reports on synthesis of WO_x nanoparticles smaller than 100 nm via thermal reduction methods at reduction temperatures in the range of 300–700°C. Furthermore, there are also no reports regarding the effect of reduction temperature on their catalytic performances under dark condition and light irradiation for organic dye degradation.

In this study, WO_x nanoparticles were synthesized from plasma-synthesized WO_3 nanoparticles via a thermal reduction process under 100% H_2 gas inside an electric furnace. The effect of the reduction temperature on the physicochemical properties of the resulting WO_x nanoparticles was investigated systematically. The degradation of rhodamine B (RhB) under dark conditions and visible light irradiation was studied to evaluate the adsorption and photocatalytic performance of the as-synthesized WO_x nanoparticles.

2. Experimental

WO_x nanoparticles were synthesized from plasma-synthesized WO_3 nanoparticles (used as received from Nisshin Engineering Inc., Japan without any additional treatment) with an average particle size of 6 nm. In a typical process, 0.5 g of plasma-synthesized WO_3 nanoparticles were loaded into ce-

ramic boats, which were placed in the center of the furnace. The reduction temperature was varied from 100 to 700°C, with a heating rate of 10°C min⁻¹, and reduction was carried out for 1 h. Throughout the entire process, high-purity H_2 gas was flown into the furnace chamber at a rate 1 L min⁻¹. A photoreactor system equipped with a solar simulator was used as the visible light source. In a typical degradation experiment, 100 mg of WO_x nanoparticles was dispersed in 200 mL of RhB solution (12 mg L⁻¹). The adsorption process was monitored under dark conditions for 3 h before starting the photocatalytic activity measurements. The photocatalytic activity was observed for 2 h under visible light irradiation. For this analysis, a UV–vis absorption spectrophotometer was used to obtain the absorption spectra of samples at given times.

3. Result and discussion

Fig. 1 shows X-ray diffraction (XRD) patterns of the plasma-synthesized WO_3 nanoparticles and WO_x nanoparticles synthesized under reduction temperatures ranging from 100 to 700°C for 1 h. The XRD pattern of the pale green WO_3 nanoparticles could be assigned to the monoclinic crystal structure based on PDF no. 43-1035. The main diffraction peaks at $2\theta = 24.2, 26.7,$ and 34.0° corresponded to the (020), (200), and (202) planes, respectively. Similar XRD patterns were observed for the WO_x nanoparticles reduced at 100–300°C. However, the color of the WO_x nanoparticles gradually changed from green to bluish green to teal blue. The change in color was caused by oxygen loss within the crystal structure, which led to a change in the W valence state. During reduction, some of the initial W^{6+} were reduced to W^{5+} and W^{4+} , which were responsible for the color change of the nanoparticles. $\text{WO}_{2.9}$ nanoparticles with a navy-blue color were obtained when the WO_3 nanoparticles were reduced at 400°C. The XRD pattern was consistent with PDF no. 05-0386 of the monoclinic $\text{WO}_{2.9}$ crystal structure. As discussed

Fig. 1 XRD patterns of the WO_3 nanoparticles and WO_x nanoparticles reduced at different temperatures for 1 h under a H_2 gas atmosphere.

above, the darkening of the WO_x nanoparticle color was associated with an increase in the amount of oxygen deficiencies. More oxygen vacancies within the crystal structure resulted in darker particles. When the reduction temperature was increased to 500°C, the dominant phase the WO_x nanoparticles was WO_3 monoclinic crystal structure. A weak peak of $\text{WO}_{2.9}$ monoclinic crystal structure was still observed, as well as new broad peaks at 2θ of 40–55°.

The color of the WO_x (500°C) nanoparticles was peacock blue violet. The broad peaks could be assigned to a set of complex structures of different phases of WO_x nanoparticles that were hard to distinguish. WO_3 monoclinic peaks were observed because the nanoparticles had a very active surface, which rapidly oxidized when exposed to the atmosphere. When reduced at 700°C, nanoparticles with a black color were obtained. The XRD pattern showed that the WO_x (700°C) nanoparticles were pure W metal, and that the WO_3 nanoparticles had been over reduced.

Fig. 2 TEM images of the (a) WO_3 nanoparticles and WO_x nanoparticles synthesized under different reduction temperatures for 1 h. **Fig. 2a** shows the pristine WO_3 nanoparticles, which had an average diameter (d_p) of 6 nm. Increasing the reduction temperature from 100 to 500°C yielded monodisperse WO_x nanoparticles with d_p values of 7–11 nm, respectively, as shown in **Fig. 2b–f**. **Fig. 2g** shows a TEM image of the sample prepared at 700°C, in which the nanoparticles were sintered with a d_p of approximately 20 nm. WO_3 nanoparticles reportedly readily sinter at annealing temperatures higher than 300°C.

Fig. 2 shows transmission electron microscopy (TEM) images of the WO_3 nanoparticles and WO_x nanoparticles synthesized under different reduction temperatures for 1 h. **Fig. 2a** shows the pristine WO_3 nanoparticles, which had an average diameter (d_p) of 6 nm. Increasing the reduction temperature from 100 to 500°C yielded monodisperse WO_x nanoparticles with d_p values of 7–11 nm, respectively, as shown in **Fig. 2b–f**. **Fig. 2g** shows a TEM image of the sample prepared at 700°C, in which the nanoparticles were sintered with a d_p of approximately 20 nm. WO_3 nanoparticles reportedly readily sinter at annealing temperatures higher than 300°C.

Fig. 3 shows the degradation of RhB solution as a function of time over the WO_3 nanoparticles and WO_x nanoparticles reduced at different temperatures. The degradation process of RhB, which includes adsorption and photocatalysis processes, is shown in **Fig. 3a**. **Fig. 3b** shows a plot of their corresponding $-\ln(C/C_0)$ values against the visible light

Fig. 3 (a) Degradation profiles of RhB over the WO_3 nanoparticles and WO_x nanoparticles (b) $-\ln(C/C_0)$ versus irradiation time plots.

irradiation time. C and C_0 represent the concentration of RhB solution at any given time and its initial concentration, respectively.

Fig. 3a shows that the adsorption–desorption equilibriums of RhB in dark conditions over the WO_3 nanoparticle and WO_x (300°C) nanoparticle surfaces occurred after approximately 10 min. The RhB concentration after measurement for 3 h in dark conditions and 2 h under visible light irradiation over the WO_x (300°C) nanoparticles decreased only slightly from that over the WO_3 nanoparticles. The corresponding RhB concentrations were 93 and 96%. The rate constant (k) for the photodecomposi-

tion of RhB under visible light irradiation by each sample was evaluated using simplified Langmuir–Hinshelwood kinetics, and the results are shown in **Fig. 3b**. The WO_x (400°C) nanoparticles showed higher adsorption and photocatalytic performance, with remaining RhB concentrations of 74 and 66% after measurement in dark conditions for 3 h and under visible light irradiation for 2 h, respectively. The k value for this sample was $1.48 \times 10^{-3} \text{ min}^{-1}$. The degradation of RhB increased significantly when the WO_x nanoparticles were reduced at 425°C. The remaining RhB concentrations for these nanoparticles were approximately 30 and 19% after measurements in dark conditions and under visible light irradiation, respectively, and the k value was $7.5 \times 10^{-3} \text{ min}^{-1}$. This k value was 93 times higher than that for the WO_3 nanoparticles. The above results indicated that the amount of RhB adsorbed on the particle surface increased as the reduction temperature increased.

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外部発表成果

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