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MORPHOLOGY MODIFICATION OF MoO_3 POWDERS BY HYDROGEN REDUCTION AND RE-OXIDATION PROCESS

An optimum route to fabricate the MoO_3 nanoparticles with modified morphology was investigated. Microstructure analysis for the MoO_3 powder prepared by high-energy ball milling process for 25 h showed that the plate-shaped raw powders are mostly converted into equiaxed fine particles, but exist as large agglomerates. However, the powder fabricated by the hydrogen reduction at 775°C of raw powder and re-oxidation at 450°C exhibits equiaxed fine particles with a size of about 260 nm and relatively small agglomerates. Additionally, the re-oxidized particles show a unimodal particle size distribution with measured values ranging from 0.18 to 0.42 μm. These results indicated that the reduction and re-oxidation process can significantly decrease the particle size and modify the powder morphology into an equiaxed shape.

Keywords: MoO_3 powder; morphology modification; ball milling; re-oxidation

1. Introduction

Molybdenum trioxide (MoO_3) has received considerable attention in recent years because of its potential applications in catalysts, electrochromic surface, gas sensor and electrodes of battery [1,2]. Crystalline MoO_3 phases exist in orthorhombic α-MoO_3, monoclinic β-MoO_3 or hexagonal structures, which are essentially built up of corner-sharing MoO_6 octahedra. The combination of these phases or the appropriate distribution of Mo ions with different oxidation states can result in unique materials with superior electrical and optical properties, as well as non-toxicity, cost-effectiveness, and good chemical stability [3]. In this field, the interest in the synthesis of nano-sized MoO_3 particles is emphasized

Several processes have been developed to synthesize MoO_3 nanoparticles with specific morphology, size and crystal structure using various synthesis techniques such as sol-gel, solution combustion, hydrothermal synthesis and chemical vapor deposition [4-6]. However, most of the synthesized MoO_3 particles have a unique agglomerated and layered structure along a specific crystallographic direction. Motivated by an interest in morphology modification, we focus on the preparation of equiaxed MoO_3 nanoparticles via high-energy ball milling or reduction/re-oxidation routes using commercial powder. In addition, the dependence of the particle characteristics on fabrication process is discussed.

2. Materials and methods

Commercial MoO_3 powder (99.9%, <5 μm, Kojundo) was used as starting material. Two different processes were applied to modify the powder morphology and particle size. In the first method, the milling of MoO_3 powder was carried out in a planetary ball mill with a ball-to-powder weight ratio of 15:1 up to 25 h. The ball and jar were made of stainless steel. The second used a hydrogen reduction and re-oxidation process of the raw powder. Reduction was performed in a hydrogen atmosphere (purity 99.999%) for 2 h by heating to 775°C at a heating rate of 5°C/min, and the reduced powder was re-oxidized in air at 450°C and 550°C for 5 h, respectively.

Phase identification of the powders was carried out by X-ray diffraction (XRD, Dmax 2500, Rigaku) analysis. The powder morphology was examined using field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL). Size distributions of powders were measured by dynamic light scattering using nano SAQLA (Otsuka Denshi).

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3. Results and Discussion

High-energy ball milling of commercial MoO_3 powder was carried out to modify its morphology and size. Fig. 1 shows typical morphology of the raw powder and the powders ball-milled for 2 and 25 h, respectively. As can be clearly seen in the SEM images, the plate-shaped raw powders due to a layered structure of MoO_3 crystal were changed into an equiaxed powders with a reduced size through ball milling. However, as shown in Fig. 1(b) and (c), particles with plate shape were observed in the case of milling for 2 h, and they still existed even when the milling time was increased to 25 h. To solve the limitations of controlling the powder shape in the ball milling process, reduction and re-oxidation processes were attempted.

Fig. 2(a) and (b) show SEM images of raw powder reduced by hydrogen at 775°C and re-oxidized at 550°C, respectively. The reduced powders had an equiaxed shape with smaller particle size than the raw powder and formed some agglomerates. Addition-

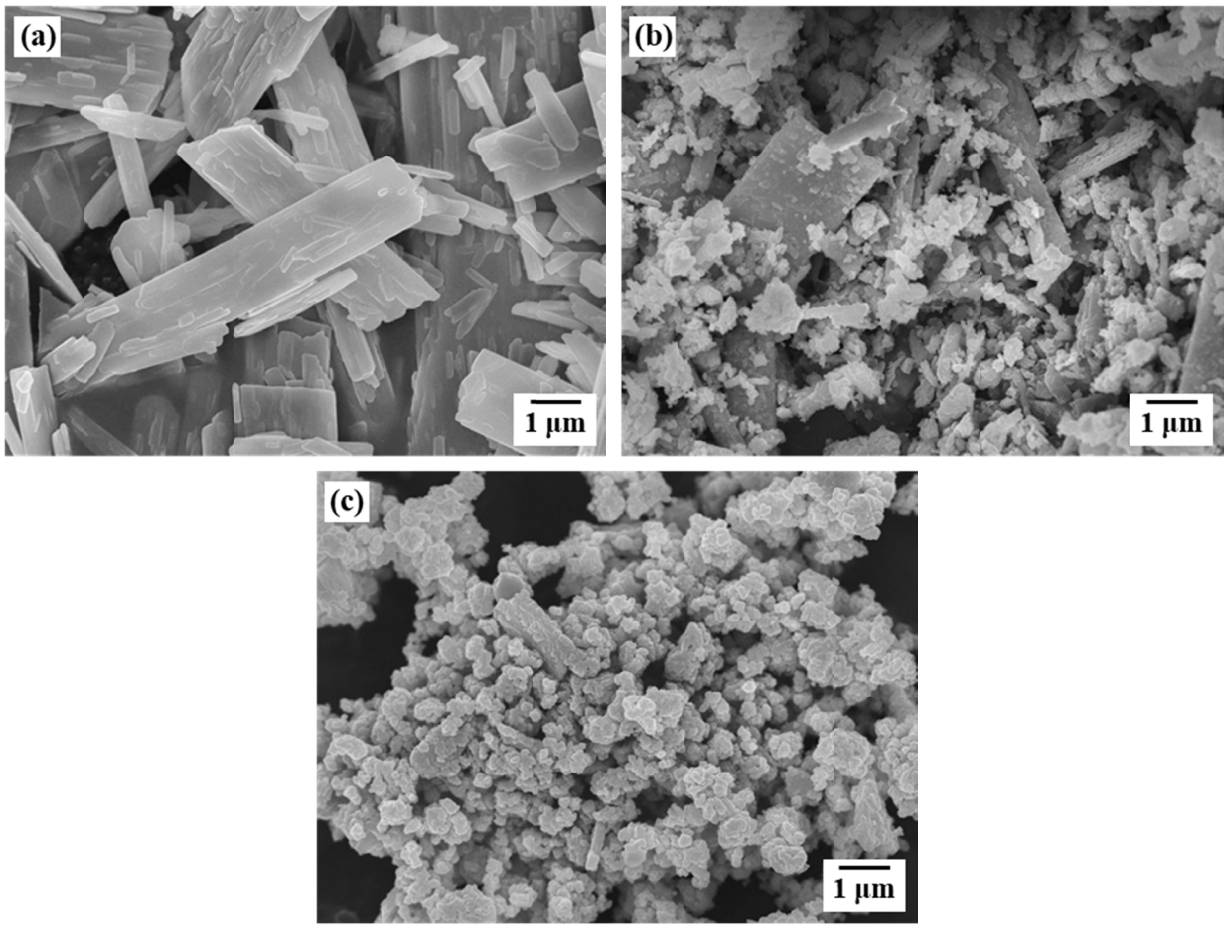

Fig. 1. SEM morphologies of MoO_3 powder: (a) raw, (b) ball-milled for 2 h and (c) ball-milled for 25 h

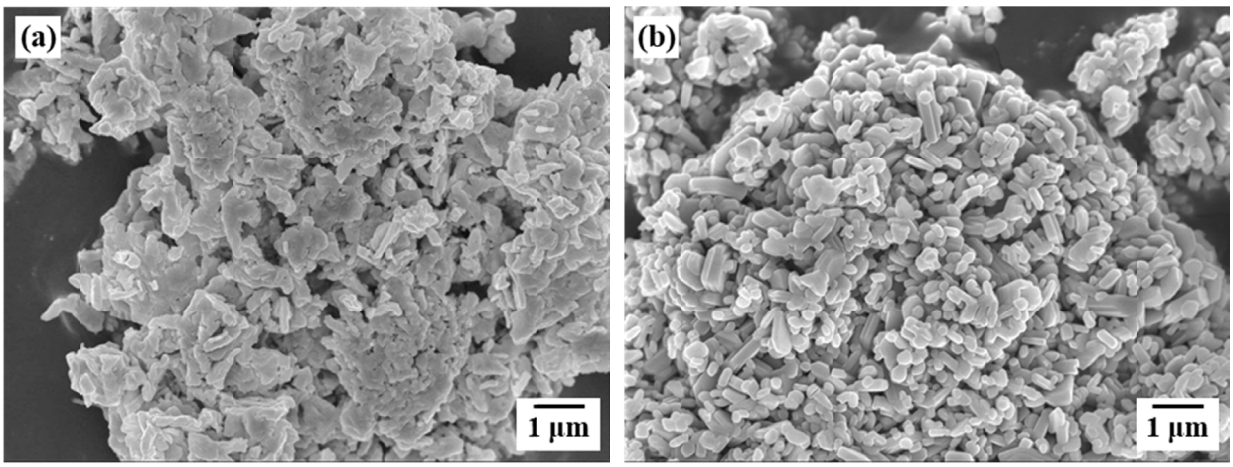

Fig. 2. SEM images of MoO_3 powders at different stages of processing; (a) after hydrogen reduction at 775°C for 2 h and (b) re-oxidation at 550°C for 5 h in air

ally, XRD analysis in Fig. 3(b) reveals that the reduced powder was composed entirely of Mo phase without any unreduced phase. It is generally known that hydrogen reduction of MoO_3 proceeds in two stages: $MoO_3 \rightarrow MoO_2$ in the temperature range of 350-600°C, and $MoO_2 \rightarrow Mo$ in 600-800°C [7]. Additionally, it has been reported that increasing hydrogen concentration in a reducing atmosphere and high-temperature reduction helps in the refinement of reduced particles and formation of equiaxed particles due to the direct reduction of MoO_3 to metallic Mo and the increase in nucleation rate [8,9]. Therefore, the formation of agglomerates composed of Mo nanoparticles shown in Fig. 2(a) can be interpreted as being due to the neck growth caused by a relatively high reduction temperature and the use of a high-purity hydrogen atmosphere, which are the conditions of this experiment.

To fabricate shape-modified MoO_3 powder, the reduced Mo was thermally re-oxidized by annealing in air at 550°C. As shown in Fig. 2(b), the re-oxidized particles were mainly equiaxed and partially plate-shaped. Considering the reported literature that α-MoO_3 can be formed by annealing Mo thin film in air at 400°C [10], the observed particles are considered to be MoO_3 phase. However, because the re-oxidized powder in Fig. 2(b) showed relatively coarse particles and agglomerates, re-oxidation at low temperature was attempted for refinement of particles.

Fig. 3(a) shows typical microstructure of MoO_3 powder re-oxidized at 450°C in air for 5 h. Comparison with the powder re-oxidized at 550°C in Fig. 2(b) indicated that the marked refinement of particles and agglomerates can be achieved by re-oxidation at 450°C. As clearly seen in magnified image of Fig. 3(a), fine particles of about 260 nm in size were observed in the re-oxidized powder. Meanwhile, as shown in the XRD profiles of Fig. 3(b), the re-oxidized powders have a main peak corresponding to the α-MoO_3 phase in the spectrum, and the β-MoO_3 peak also appears as a trace phase. The presence of β-MoO_3 phase in the powder is mainly attributed to the relatively low re-oxidation temperature [11].

The particle size distributions of the raw and reduced/re-oxidized MoO_3 powders are shown in Fig. 4(a) and (b), respectively. The raw powder exhibited relatively large particle size, and the bimodal distribution of particle size varied between 0.40 and 53.4 μm due to the platelet morphology and large agglomeration as shown in Fig. 1(a). In contrast, it can be clearly seen in Fig. 4(b) that the re-oxidized powder after hydrogen reduction existed in a unimodal distribution with measured values rang-

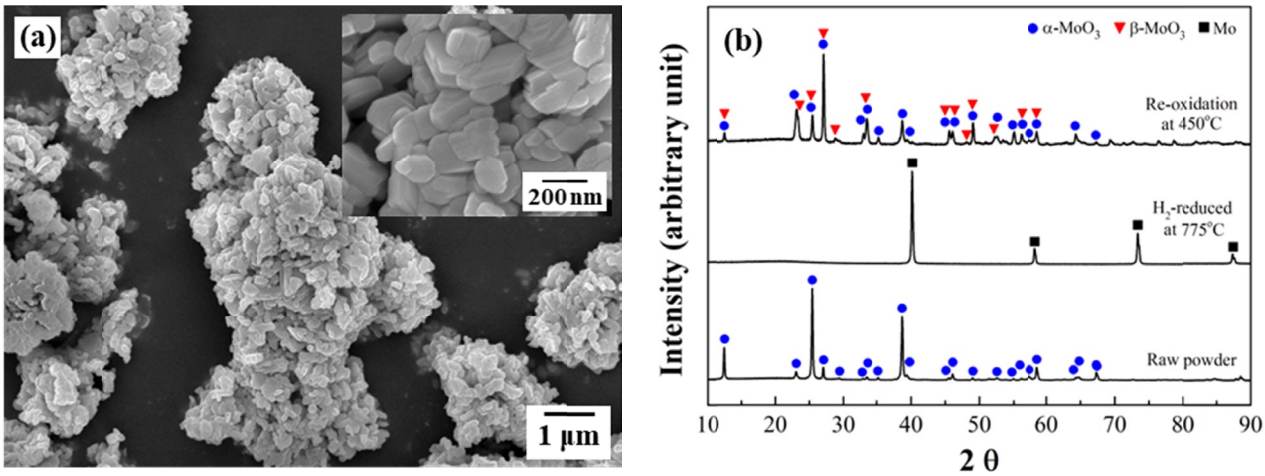

Fig. 3. Microstructure and phase analysis for prepared powders: (a) SEM image of MoO_3 powder after re-oxidation at 450°C for 5 h and (b) XRD profiles for different stages processing

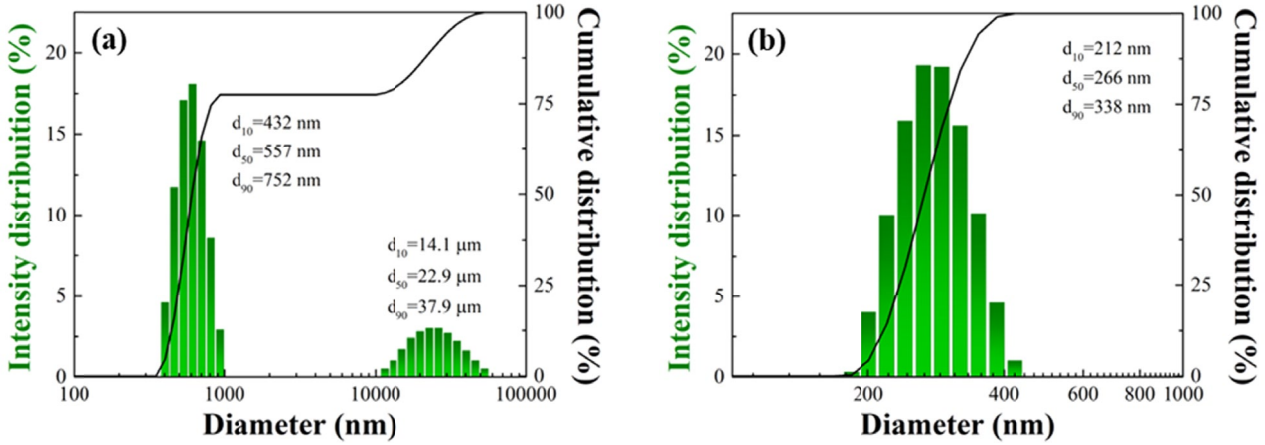

Fig. 4. Particle size distribution of (a) raw MoO_3 powder and (b) re-oxidation powder

ing from 0.18 and 0.42 μm. Therefore, these results indicated that the reduction and re-oxidation process can significantly decrease the particle size and modify the powder morphology into an equiaxed shape.

4. Conclusions

The present study focused on the refinement and morphology modification of commercial MoO_3 powders. Two methods, high-energy ball milling or reduction/re-oxidation routes, were attempted to prepare equiaxed MoO_3 nanoparticles. After ball milling for 25 h, most of the plate-shaped raw powders are changed into equiaxed particles with decreased size, but large agglomerates are formed and plate-shaped particles still exist. To overcome the limitations of powder characteristic control by the ball milling process, reduction and re-oxidation process was introduced. After hydrogen reduction at 775℃ and re-oxidation at 550℃, the powders exhibit large agglomerates composed mostly of an equiaxed MoO_3 particles. However, when re-oxidized at a relatively low temperature of 450°C, equiaxed fine particles with a size of about 260 nm are formed, and the size of the agglomerates is also significantly decreased. In addition, re-oxidized powders show a unimodal distribution of particle size. These results suggest that MoO_3 nanoparticles with modified morphology can be obtained by reduction and re-oxidation process.

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