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SYNTHESIS AND CHARACTERIZATION OF MoO₃ NANO PARTICLE BY CONTROLLING VARIOUS GROWTH CONDITIONS IN SOLUTION COMBUSTION METHOD

In this paper, synthesize MoO₃ particles with various particle properties by control growth influence factors was mainly studied. The experimental conditions were established in molar ratio of Mo:urea and pH levels. The plate-type of MoO₃ particles were formed without proceeding any established conditions, but the rod-shape particles were formed by adjusting molar ratio of Mo:urea. Also, different ranges of the particle size were formed by adjusting experimental conditions. Through the results, it was confirmed that particles with a size in the range of 300 ~ 400 nm were obtained by adjusting precursor concentration and the micrometer size of particles were formed by increase pH levels. The properties of the particles formed accordingly by setting various factors that can affect the growth process of MoO₃ particle was analyzed as variables and the particle growth behavior was also observed.

Keywords: Molybdenum trioxide, Solution combustion method, Particle morphology, Nano-rod, Nanoparticle

1. Introduction

Molybdenum trioxide (MoO₃) is an oxide metal with chemical structures of distorted MoO₆ octahedra in an orthorhombic crystal [1,2]. In recent years, MoO₃ has been used to various applications with its outstanding properties such as high stable thermolability, photocatalytic, and corrosion resistance [3-5]. Therefore, MoO₃ is well using as catalytic material belonging to many types to reactions with the participation of hydrogen or oxygen [6-9]. Also, MoO₃ is inevitably using to produce molybdenum (Mo) metal and some of the researches have already revealed the various process to synthesize Mo particles from MoO₃ [10-14]. Despite of these properties, it is well known that the way of obtaining MoO₃ particles is very limited by refining from molybdenite as raw material, and it require such hard and complicated process conditions such as high-temperature annealing and auto-clave [15,16]. Furthermore, as the process is being complicated, controlling particle properties is being more complicated, and it directly effects to adapted MoO₃ applications by functional deterioration. Therefore, many types of research concerning on synthesize MoO₃ are actively underway [17-21], but there have been no studies to control and synthesize these grain growth factors and most methods have been used to control the general particle shape by using certain additives and surfactants.

Therefore, synthesized MoO₃ particles were demonstrated its properties in size and shape by various experimental conditions that affect particle growth such as molar ratio of additives and pH levels.

2. Experimental

2.1. Synthesis process of MoO₃

The Ammonium heptamolybdate tetrahydrate (AHM) powders [(NH₄)₆Mo₇O₂₄·4H₂O, DAEJUNG] were infused into 200 mL of distilled water in molar concentration of 0.2 M. Urea (CH₄N₂O, JUNSEI) was dissolved in distilled water separately, with same molar ratios from AHM concentrations. The separated solutions were combined by pouring, after that, the pH level was adjusted by adding acetic acid (CH₃COOH, DAEJUNG) to reaching acidic pH levels in 3. The contained solutions with different adjusted pH levels were stirred at 85°C for 2 hours to extracting precipitates, and then dried in 90°C until all the precipitates were completely dry. The obtained precipitates were annealed in twice by different temperatures of 250°C and 550°C to form final stable MoO₃ particles.

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2.2. Variable conditions

The molar ratios of Mo:urea was adjusted to 1:20, 1:8, and 1:4 from a fixed value of 1:1 and the different concentrations of organic additive were proceeding in 7:1, 13:1, and 70:1.

The pH levels also adjusted differently with ammonia water (NH_4OH , 25.0 ~ 28.0%, DAEJUNG), and sodium hydroxide (NaOH , DAEJUNG) to leach to basic levels in 7, and 10. To the acidic pH levels, hydrochloric acid (HCl , 35%, DAEJUNG) was used instead of acetic acid. Since the pH level of 5 was naturally formed without adding any solutions, the process was continued without the pH adjust step.

2.3. Characterization

The morphology of as-prepared precipitates and MoO_3 was observed by field emission scanning electron microscope (FE-SEM, ZEISS, Gemini). Ultraviolet visible spectroscopy (UV-vis, SHIMADZU) analysis was conducted to observing behaviors from nucleus growth from every condition and the phase analysis was also conducted to confirming obtained particles phase property by X-ray diffraction (XRD, ULTIMA IV, Rigaku).

3. Result and discussion

During the reacting times from the process, the precipitates were extracted in solutions due to the ionic substitution between Mo ions and urea. Mo ions exist as Mo^{6+} when AHM dissolved into the distilled water, and the presence of NH_4^+ , and OH^- are being removed by hydrolysis reaction in water. Since the Mo^{6+} ions exist in the water, the added urea complex ions are starting to attach with Mo^{6+} and make strong interactions to

extracting Mo ions from the functional ionic group and forming precipitates as solid state. In addition, it is not limited to urea, but any of other organic additives such as EDTA or sorbitol also can be used, and it is known that the characteristics of the particles formed for each of these additive types are varied [22]. Based on this principle, XRD analysis was performed for each process to confirm the phases of formed particles. As shown in Fig. 1, the phases from precipitates are confirmed as ammonium tetramolybdate with many unidentified peaks which considered as organic matters from the used additive. As the process continued to the first annealing process, the peaks became more cleared as molybdenum oxide ammonia without any peaks of impurities or organic matters, and the stable formation of MoO_3 phase was formed by the second annealing process at 550°C . As a result, the formed particles from standard condition were confirmed with their plate-type shape with average size of 493 nm (± 66).

The particle formation behavior according to the change of precursor and additive concentration was analyzed. MoO_3 particles were formed with decreased precursor concentration of 1:20, 1:8, and 1:4 ratios from the conventional 1:1 molar ratio of Mo:urea. During the process, UV-vis absorbance analysis was performed to confirm the substitution reactivity of the precursor and the organic additive according to the reaction time. Since the AHM has its own absorbance peak of UV-vis analysis due to the charge transferring by UV-lights [23]. The size and height of the AHM-specific absorbance peak decreased according to the reaction time due to the decrease in the number of AHM ions by the substitution reaction between the precursor ions and the organic additives. Therefore, it was possible to grasp the tendency and activity of precursor ions through UV-vis absorbance analysis for various conditions. As shown in Fig. 2(a)-(c), the graph was plotted by pointing the highest peaks from the UV-vis absorption results by each of times, in order to confirming the

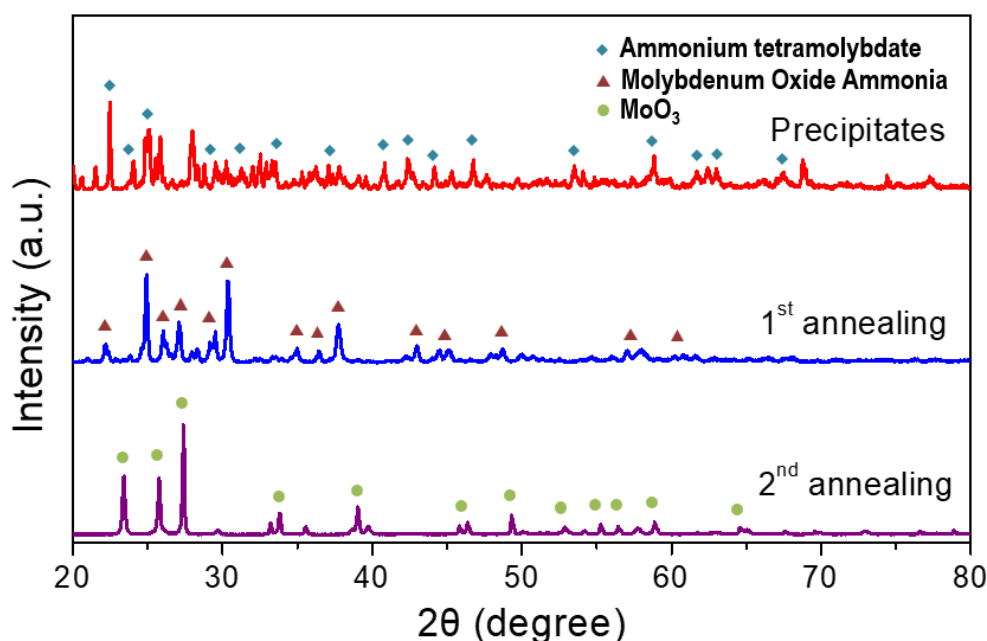


Fig. 1. XRD analysis result from the steps of synthesis process

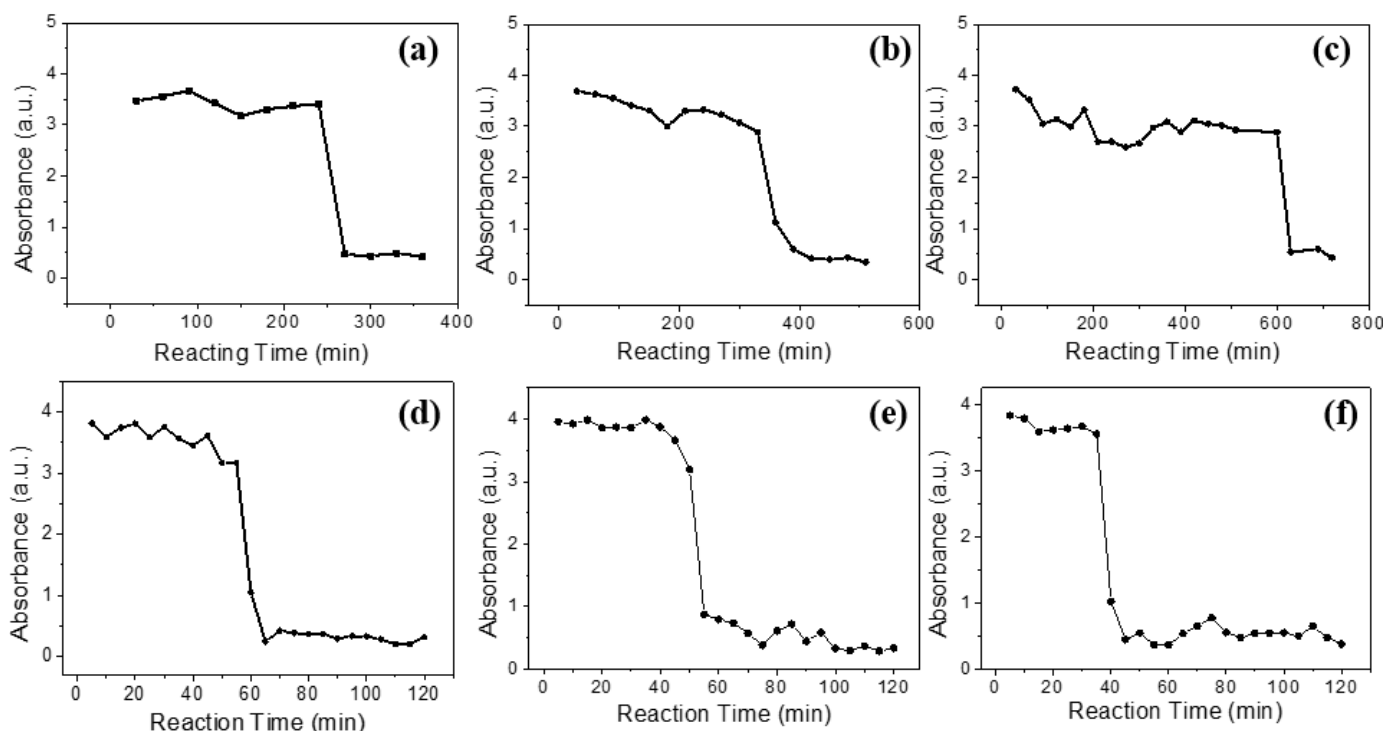


Fig. 2. UV-vis results in different ratios of Mo:urea, (a) 1:4, (b) 1:8, (c) 1:20 and different additive ratio of (d) 7:1, (e) 13:1, (f) 70:1

rate of change in absorbance of the precursor ions according to the reaction time. As the precursor concentration decreases, the ionic reactivity and precipitate formation rate was significantly decreased. Unlike, the previous MoO_3 from conventional 1:1 molar ratio, the formed MoO_3 particles were having a distinctly different shapes in nano-rod from 1:8 ratio, and when the molar ratio is changed to 1:20, the formed particles were had micron-size. In particle size and shape analysis through FE-SEM analysis (Fig. 3(a-c)), it was confirmed that the size of the particles

increased as the relative concentration of the precursor decreased to 432 nm, 349 nm, and 318 nm, respectively.

When the ion substitution reaction between the Mo ions dissolved in the precursor and the functional groups of the organic additive is formed, the lower the concentration of the precursor Mo ions, the slower the ionic reaction proceeds, as shown by UV-vis analysis. Therefore, the formation and growth rate of the formed precipitates was slower compared to before, and this is thought to be a result of the decrease in the collision

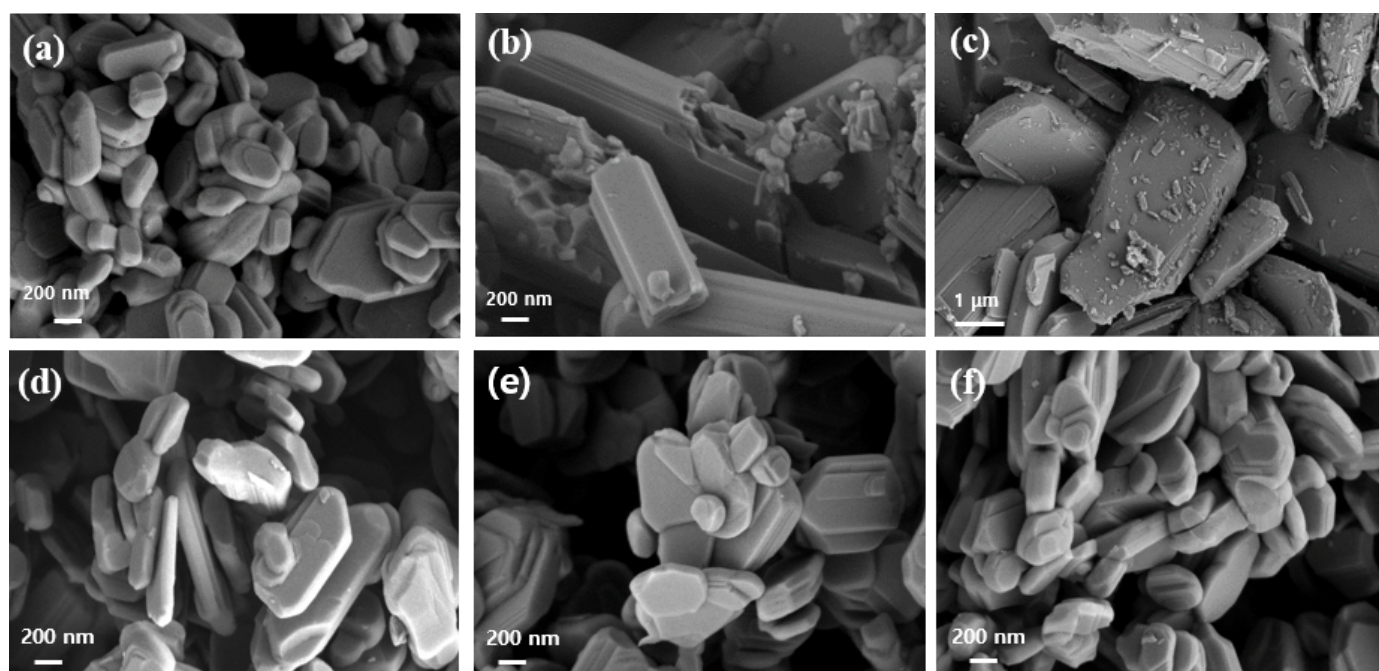


Fig. 3. FE-SEM images of MoO_3 particles in different Mo:urea ratio (a) 1:4, (b) 1:8, (c) 1:20 and different additive ratio of (e) 7:1, (f) 13:1, (g) 70:1

frequency and probability between ions due to the influence of the decreased amount of precursor. Also, this result could be occurred from when there are excessive number of functional groups, aggregation is occurred between the template additives, thereby influence the aggregation and larger particle size tendency of the formed particles [22]. Therefore, this result has a tendency to form similar particles from the previous sample with the ratio of 1:4, but below that, the precipitates with many agglomerations were confirmed through the high-temperature process, and formed plate and rod-shape of MoO_3 particles. Following particle growth and characterization according to the ratio of Mo:urea, analysis in decreased concentration of organic additives to be added was also conducted. The concentration of urea to be used was configured under the conditions under Mo:urea molar ratio of 7:1, 13:1, and 70:1 and the precursor was maintained as before. With the nucleation behavior through UV-vis analysis, there was no significant difference from the previous experiment conducted with the established ratio of 1:1 due to the concentration of the precursor that was maintained as it was, and ionic substitution occurred at a similar time period and precipitates were formed as shown in Fig. 2(d)-(f). The difference in particle size and shape according to the change in the concentration of organic additives was expected, but only a small difference in size decrease was found at 0.01 M, but no significant difference was observed at generally. This result is believed to occurred because the concentration of the additive that can be substituted is too low compared to the fixed precursor ion concentration, so the substitution reaction between ions and additives occurred with similar tendency to that of the standard conditions. In the observation of the shape through the FE-SEM analysis, as shown in Fig. 3(d)-(f), it was confirmed that most of them had a plate shape similar to the previous reference concen-

tration, and the particle sizes were measured at about 346 nm, 348 nm, and 247 nm, based on 7:1, 13:1, and 70:1, respectively.

In the case of molybdenum trioxide particles, which were reacted under the existing acidic condition of pH 3, a rapid particle formation reaction proceeded due to high reactivity of functional groups from urea [24]. In general, as the level of particle growth by concentration according to pH increases, the rate of ion reaction and precipitate formation decreases significantly. This is due to the presence of OH^- groups that increase proportionally as the pH level reaches a higher level, thereby interfering with the ion substitution reaction, and due to the strong attraction of the formed particles, precipitates are not formed despite a relatively long reaction time [22,25]. Therefore, in the molybdenum trioxide particle formation experiment, after drying all the solutions that did not precipitate to obtain AHM precipitates, which annealed to form MoO_3 particles. As a result of, synthesizing particles for each level of pH 3, 5, 7, and 10, all plate-shaped particles were produced as shown in Fig. 4(a)-(c), and the sizes based on the diameter of the particles were 265 nm, 283 nm, 587 nm, and 720 nm, respectively, found that as the pH level increased, the length of the particles also increased. In the case of nitrogen functional groups present in urea, the formation of hydroxyl functional groups that increase as the pH concentration of the base is reached interrupts the substitution of precursor and organic additive ions. Therefore, the reaction in basic conditions decreases the activity of ions, thus does not form precipitates even after a long period of time as a result of UV-vis. Since the annealing process was conducted with the precipitates that obtained by drying all solutions, it was confirmed that the high frequency of aggregation was occurred during the steps of extraction by drying. Therefore, the ionic strength can be changed according to the change in the activity of the ions, and

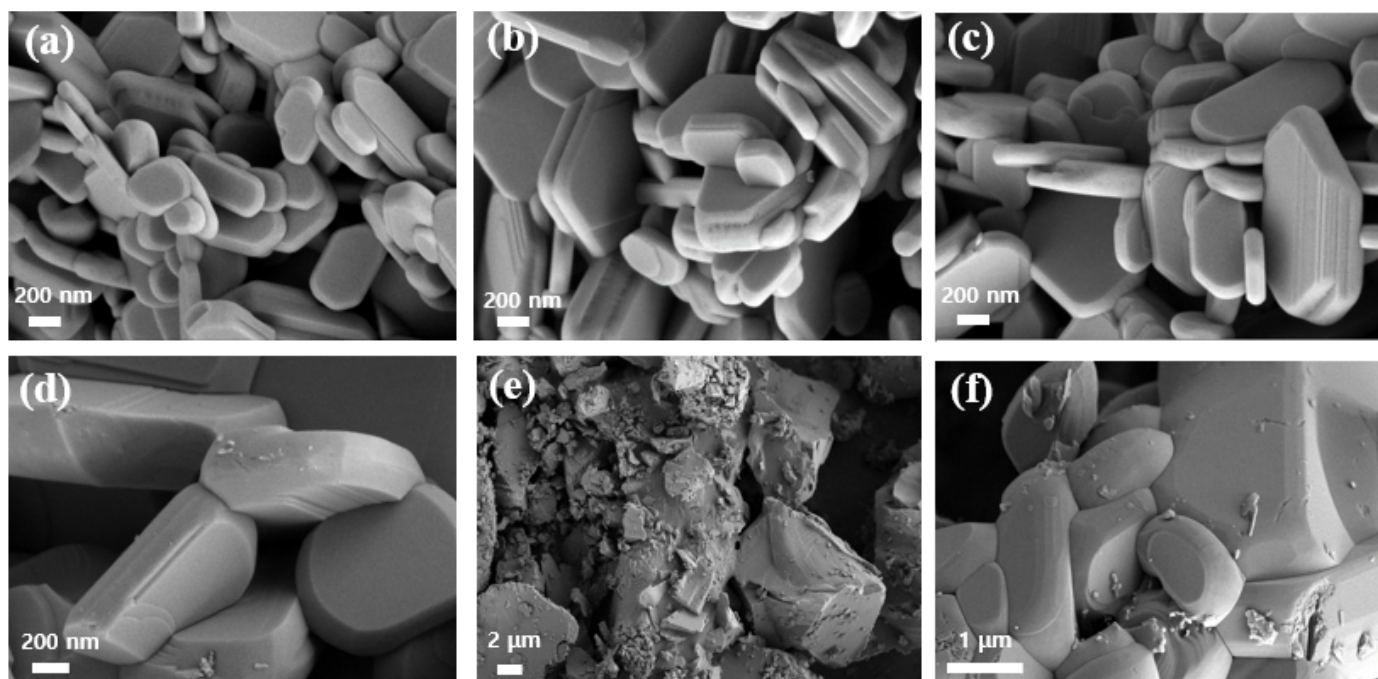


Fig. 4. FE-SEM images of MoO_3 particles from different pH levels, (a) pH 5, (b) pH 7, (c) pH 10 and different solutions of (d) HCl (pH 3) (e) NaOH (pH 7), (f) NaOH (pH 10)

resulted in incremental particle size as the pH levels increased. In addition, to find out the difference according to the type of solution for pH adjustment, proceed as in the previous experiment, but the adjustment solution was performed using sodium hydroxide for basic and hydrochloric acid for acid. As shown in Fig. 4(d)-(f), compared with the previous conditions, under the condition of pH 3 adjusted with HCl solution, the particles were produced with an average of 3.5 μm . With the conditions of pH 7 and 11 by using NaOH and ammonia solution, particles with a rapid increased in particle size were identified due to the deep aggregation phenomenon. In the case of this result, the tendency of the chloride present from the HCl solution and the sodium component from NaOH to form a complex compound decreased the effect of the functional group of urea on the Mo ions, and the tendency of particle growth is increased instead of uniform nucleation.

4. Conclusion

MoO₃ powder was prepared through a solution combustion method using AHM as a precursor and applying an organic additive for chemical ion substitution reaction. By establishing various influencing factors that affect the process of growth of precursor ions, the properties of the final formed oxide particles are analyzed with various shapes, sizes, distributions. From the results, rod-shaped particles were formed by specific molar ratio of Mo:urea and the size of the particle could be controlled by adjusting organic additive concentration. Also, through the increasing levels of pH, the micrometer size of MoO₃ powder can be obtained in large-circle shape. As a result, the characteristics of the particles formed were controlled and analyzed by controlling various growth factors.

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