

CHAPTER 1

INTRODUCTION

Over past decade years, researchers and scientists have been focused on fabrication of one-dimensional (1D) inorganic nanomaterials such as nanowires, nanobelts, and nanotubes because those 1D inorganic materials exhibit chemical and physical properties which are difference from their bulk materials due to the reduced size and the large surface-to-volume ratios [1].

Layer inorganic materials such as TiO_2 , VO_x and MnS_2 , have attracted interest with regard to a number of their applications, resulting from their absorption and electrochemical properties. One of these material is molybdenum oxide (MoO_3), which is very interesting because of its catalytic, photochromic and electrochromic properties, and widely used in catalytic industries, display devices, sensors, smart windows, lubricants, and electrodes for batteries. MoO_3 has two basic poly-types: orthorhombic MoO_3 (α -type) being a thermodynamically stable phase, and the metastable monoclinic MoO_3 (β -type) with a ReO_3 -type structure. The most important structural characteristic of α - MoO_3 is its structural anisotropy, which is considered as a layered structure parallel to the (010) plane. Each layer is composed of two sub-layers, each of which is formed by corner-sharing octahedra along the [001] direction. An alternate stack of these layered sheets along the [010] direction would lead to the formation of α - MoO_3 , of which the van der Waals interaction would be the major binding force between the piled sheets. One might take advantage of the intrinsic

structural anisotropy of α -MoO₃ for tuning its properties by interlayer structural modification and annealing [2]. Moreover, α -MoO₃ is a wide-gap n-type semiconductor material (2.6 eV) and used as a catalyst for hydrogen evolution reaction [3-5].

The MoO₃ nanostructures have been synthesized by physical and chemical methods such as solid-state reaction and wet chemical method. Nevertheless, the product obtained from solid-state reaction is irregular morphologies, large particle-sized distribution, non-homogeneous phases and others. On the other hand, advanced wet chemical method has been successfully used to prepare highly purified metal oxides and superconductors with multiple cationic compositions [6]. They include the sol-gel method, co-precipitation method, hydrothermal method, reverse micelle soft-template method, microemulsion method, microwave-assisted synthesis, sonochemical method and so on. These methods can be produced better crystal quality, and at lower growth temperature than solid state reaction [7-9].

In this work, α -MoO₃ nanostructures will be synthesized using a hydrothermal process. Several reactions condition, such as reaction temperature, holding reaction time and kind of acid will be varied to study their influences on the phase, morphology and formation mechanism of α -MoO₃ nanostructures. The electrochemical for hydrogen evolution reaction and optical properties of product were investigated.

1.1 Molybdenum Oxide (MoO_3)

1.1.1 Physical Properties [10]

Synonyms	Molybdic anhydride, Molybdite, Molybdic trioxide
Molecular formula	MoO_3
Molecular weight	143.94 g/mol
Appearance	white solid
Melting point	795 °C
Boiling point	1155 °C
Solubility in water	0.1066 g/100 mL (18 °C), 2.055 g/100 mL (70 °C)

1.1.2 Structure

Molybdenum oxide has three crystal structure including Orthorhombic (figure 1.1) MoO_3 is composed of layers of distorted MoO_6 octahedra in an orthorhombic crystal. The octahedra share edges and form chains which are cross-linked by oxygen atoms to form layers. The octahedra have one short molybdenum-oxygen bond to a non-bridging oxygen [10]. Moreover, hexagonal and monoclinic (figure 1.2) are structure of MoO_3 .

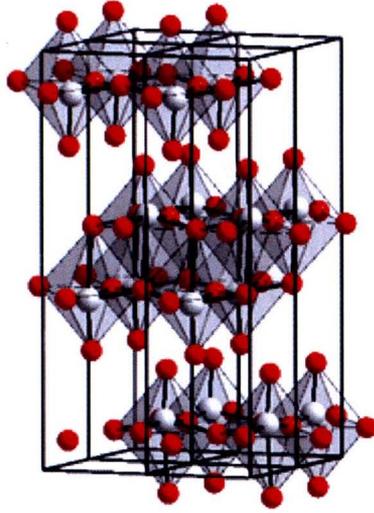


Figure 1.1 Orthorhombic crystal structure of MoO₃ [10]

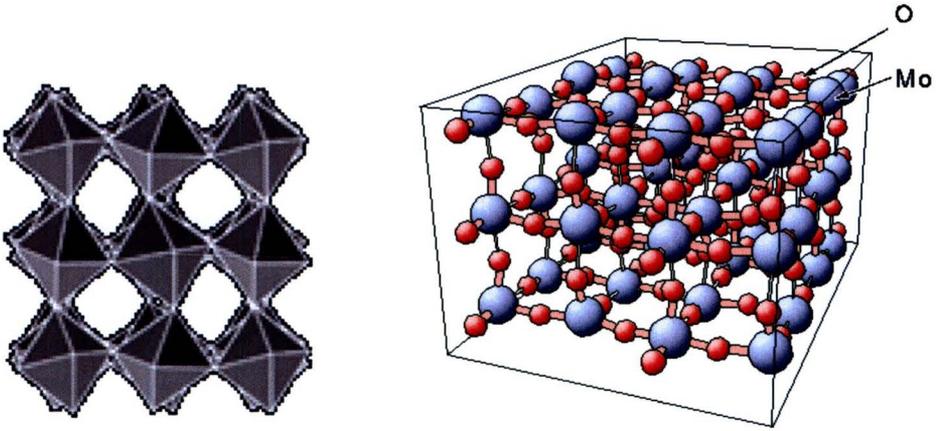


Figure 1.2 Monoclinic crystal structure of MoO₃

1.1.3 Application of MoO₃

Molybdenum oxide is very interesting because of its catalytic, photochromic and electrochromic properties, and widely used in catalytic industries, display devices, sensors, smart windows, lubricants, and electrodes for batteries. Moreover, α -MoO₃ is a wide-gap n-type semiconductor material (2.6 eV) and used as a catalyst for hydrogen evolution reaction [3-5]. There are a number of reports on the preparation of 1D MoO₃ nanomaterial which shows a better of both chemical and physical properties than other morphologies such as α -MoO₃ nanorods, a promising cathode material in reversible lithium-ion batteries. MoO₃ nanobelts films are excellent field emitters. MoO₃ nanorods have been found to be a valuable candidate for use as gas sensor devices owing to their sensitivity to nitrogen dioxide, and anhydrous ammonia and used as sensors for carbon monoxide and methanol at a working temperature of 200 °C and a relative humidity of about 40% [11].

1.2 Powder Preparation

1.2.1 Hydrothermal method

The hydrothermal method is one of the most promising solution techniques for advanced materials processing. In the usual hydrothermal process, the starting chemicals are dissolved in water. This solution is placed in a reactor (Figure 1.3) and the chemical reaction is carried out in closed systems under high pressure and elevated temperature, which allow for greater solubility of solids for the reaction process, and the desired compounds can be synthesized at lower temperature, as compared to the solid-state reaction method. This method has several advantages over the other conventional processes, such as energy saving, simplicity, cost effectiveness, better nucleation control, pollution control (since the reaction is carried out in a closed system), higher dispersion, higher rate of reaction, better shape control, and lower temperature operation in the presence of an appropriate solvent. The hydrothermal technique has a lot of advantages in accelerating interaction between solid and fluid species - pure phase and homogeneous materials can be achieved. Reaction kinetics can be enhanced. The hydrothermal fluids offer higher diffusivity, lower viscosity, enhance the facility of mass transport and higher dissolving power. For the most important, the chemical environment were suitably limited and controlled [12].

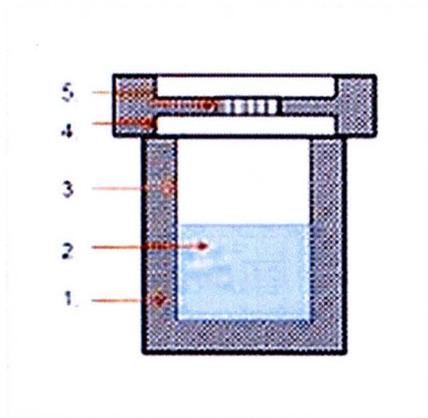


Figure 1.3 Equipment of hydrothermal method 1) Stainless steel autoclave, 2) Precursor solution, 3) Teflon liner, 4) Stainless steel lid, 5) Spring [12].

For the method of this technique, firstly, Temperature-difference method

The most extensively used method in hydrothermal synthesis and crystal growing. The supersaturation is achieved by reducing the temperature in the crystal growth zone. The nutrient is placed in the lower part of the autoclave filled with a specific amount of solvent. The autoclave is heated in order to create two temperature zones. The nutrient dissolves in the hotter zone and the saturated aqueous solution in the lower part is transported to the upper part by convective motion of the solution. The cooler and denser solution in the upper part of the autoclave descends while the counterflow of solution ascends. The solution becomes supersaturated in the upper part as the result of the reduction in temperature and crystallization sets in. Secondly, temperature-reduction technique, in this technique crystallization takes place without a temperature gradient between the

growth and dissolution zones. The supersaturation is achieved by a gradual reduction in temperature of the solution in the autoclave. The disadvantage of this technique is the difficulty in controlling the growth process and introducing seed crystals. For these reasons, this technique is very seldom used. Metastable-phase technique is based on the difference in solubility between the phase to be grown and that serving as the starting material. The nutrient consists of compounds that are thermodynamically unstable under the growth conditions. The solubility of the metastable phase exceeds that of the stable phase, and the latter crystallize due to the dissolution of the metastable phase. This technique is usually combined with one of the other two techniques above [13].

The hydrothermal processing of materials is a part of solution processing and it can be described as super heated aqueous solution processing. Figure 1.4 shows the pressure temperature map of various materials processing techniques [14]. When the production processing goes out of ambient temperature to higher or lower temperature and pressure condition to higher or lower pressure directions, particularly to vacuum, environmental loads would increase. In this regard, we cannot depend only on the high-technology industry for materials processing. On the other hand, solution processing is located in the p-T range characteristics of ambient conditions where all lives are living on the earth. Thus, solution processing should be the most environmentally friendly and should be used more as a low-energy process for producing even various artificial materials [15]. According to this, the hydrothermal processing of advanced materials can be considered as environmentally benign.

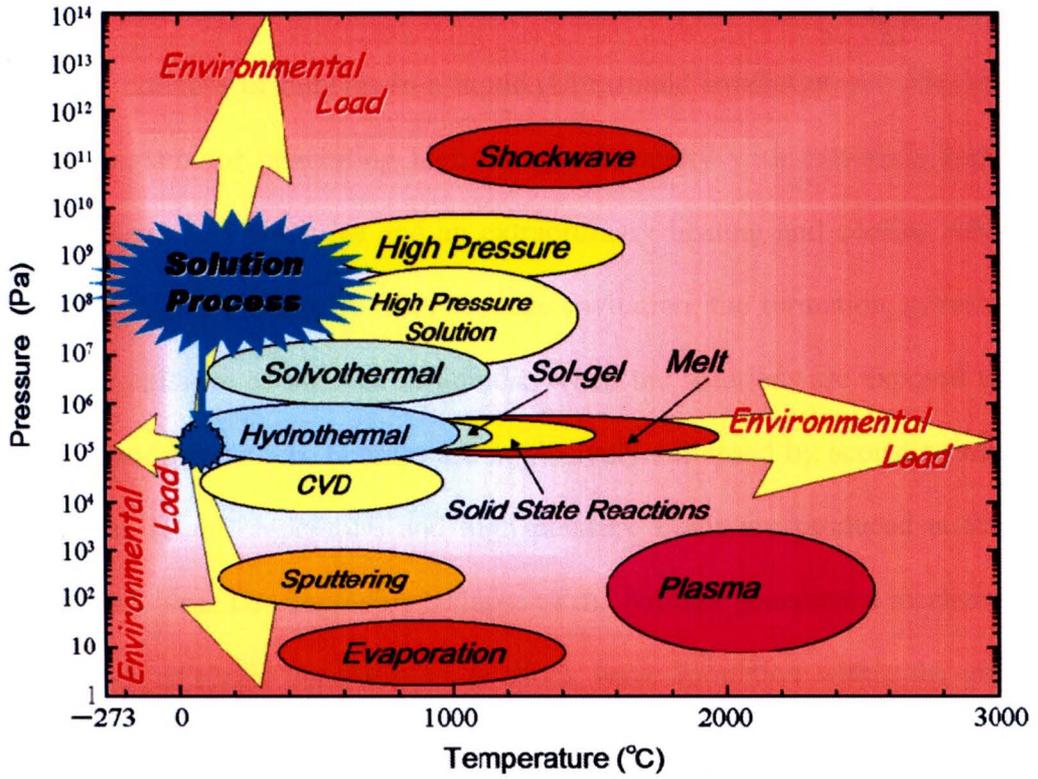


Figure 1.4 Pressure temperature map of materials processing techniques [14].

1.2.2 Sonochemical method

Sonochemistry arises from acoustic cavitation, the formation, growth, and implosive collapse of bubbles in a liquid. Ultrasound irradiation provides an unusual mechanism for generating high energy chemistry with extremely high local temperatures and pressures and an extraordinary heating and cooling rate. Sonochemistry drives principally from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in liquids. When the solutions are exposed to strong ultrasound irradiation, bubbles are implosively collapsed by acoustic field in the solution. High temperature and high pressure fields are produced at the center of the bubbles. The implosive collapse of the bubbles generates a localized hotspot through adiabatic compression or shock wave formation within the gas phase of the collapsing bubbles. The conditions formed in these hotspots have been experimentally determined, with high temperature (>5000 K), pressure (>20 MPa) and heating and cooling rates ($>10^{10}$ K/s), with nanosecond lifetimes [16-17]. Therefore, the average temperature in the system is still near room temperature. These extreme conditions can drive chemical reactions such as oxidation, reduction, dissolution and decomposition, which have been employed to prepare nanoparticles. Sonication of the precursor in the presence of support materials provides an alternative means of trapping the produced nanoparticles [18]. In addition, due to the rapid heating and cooling rates inside the bubble, sonochemistry is also useful for making amorphous nano-phase particles. The following sonochemical effects can be observed in chemical reactions and processes: increase in reaction speed, increase in reaction output, more efficient

energy usage, sonochemical methods for switching of reaction pathway, performance improvement of phase transfer catalysts, avoidance of phase transfer catalysts, use of crude or technical reagents, activation of metals and solids, increase in the reactivity of reagents or catalysts, improvement of particle synthesis, and coating of nanoparticles [19].

1.3 Ag Composite

In the last decade, the concept of superhard nanocomposite materials consisting of two or more mutually immiscible phases, induced numerous research teams to undertake studies focused on the synthesis and properties of these materials, particularly in the thin film form. Beside already classical nanocomposite structures where a hard phase like metal nitrides (TiN, VN, W₂N) coexists with the amorphous matrix (Si₃N₄) [17-19], there is a second group of nanocomposites, where the crystallite size reduction of a nitride (TiN, CrN, ZrN) or carbide (TiC) phase has been achieved by an addition of soft metals (Cu, Ag). They are immiscible with the nitride phase and do not create stable nitrides [20]. Although nitrides of copper (Cu₃N and CuN₃) and silver (AgN₃) are known, their thermal stability is very limited and they easily decompose into free metals.

Although this approach would unavoidably increase the cost due to the expensive Ag, it is a meaningful process because it was found that there was remarkable improvement in the high rate capability and outstanding tolerance to over-charging and over-discharging irrespective of their moderate specific capacity and utmost stable cycling [20-22].

1.4 Polyol Process: Reduction by Propylene Glycol

The polyol process has been proposed as a simple and versatile method for nanoparticles synthesis. Propylene glycol in this process acts as a solvent as well as a reducing agent. It has been reported that spontaneous reduction of Ag(I) species by ethylene glycol can take place at room temperature [23-24]. However, the reaction kinetics is slow that the formation of silver particles takes several hours. An increase in the reaction temperature contributes to shorter reaction time due to the reduction in the thermodynamic potential gap between the solvent oxidation and reduction of the metallic species [25]. In this process, a metallic compound is dissolved in a liquid polyol (usually ethylene glycol), then the experimental conditions are adjusted to achieve the reduction of the metallic precursor by the polyol, atomic metal nucleation and metal particle growth. A rigorous control of the different reaction parameters such as temperature, type, amount and order of addition of reactants, allows control of the size, shape and size distribution of the particles. Each metal synthesis is therefore a special case that requires specific conditions for its optimization. In spite of its wide application for the synthesis of finely divided metals, the fundamentals of the polyol process are poorly understood. A better understanding of the various phenomena involved in this process are needed for delineating the fundamental mechanisms of particle formation and for extending the use of this process to new metal synthesis. Since the polyol process is based on a redox reaction between the metallic precursor and the solvent, the electrochemical aspects of this reaction must be known. The present investigation was undertaken to determine the oxidation potential of propylene glycol and the reduction potential of various

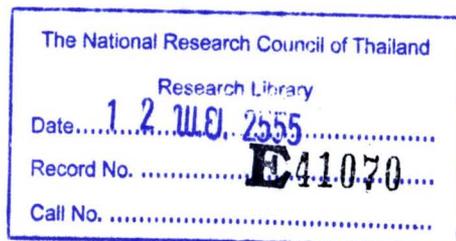


noble metal precursors in propylene glycol. Linear sweep voltammetry was used for this purpose, and the effect of temperature on the measured potentials was investigated [23].

1.5 Literature review

Song et al.[1] prepared one-dimensional molybdenum oxide nanostructures using commercial bulk MoO_3 crystals as Mo source and layered mesostructures and cetyltrimethylammonium bromide (CTAB) as controlling morphology by hydrothermal process. X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectrometry, and thermal analysis were used to characterize these as-obtained MoO_3 nanomaterials. By using CTAB as the structure-directing template, novel molybdenum oxide nanofibers with triple interlayer distances of 2.84, 2.66, and 2.46 nm have been synthesized. The nanofibers have diameters of 20-100 nm and length up to 20 μm . The growth of multilamellar molybdenum oxide nanofibers can be interpreted by the combination of surfactant/inorganic self-assembly process and host/guest intercalation chemistry.

Subba Reddy et al. [26] synthesized MoO_3 nanorods as cathodes for lithium batteries using polyvinyl pyrrolidone (PVP) as a surfactant by hydrothermal method. Scanning electron microscopy images revealed that MoO_3 nanorods have a diameter and length of 50–200 nm and 1–10 μm , respectively. In addition, X-ray diffraction technique, Fourier transformation infrared spectroscopy, thermogravimetric analysis and voltammetric measurement were used to characterize the structure, phase, atomic vibration and electrochemical



property of as-synthesized MoO_3 nanorods. They show that charge capacity of MoO_3 nanorods is 156 mA.h.g^{-1} during the initial discharge process.

Subba Reddy et al. [27] reported the synthesis of PEG-free MoO_3 nanomaterial from MoO_3 solution and PEG-added MoO_3 nanomaterial (pristine MoO_3 and aged MoO_3 nanobelts) using hydrothermal process. This research shows that the electrochemical property of PEG-added aged MoO_3 nanobelts has a higher specific charge capacity than the PEG-free MoO_3 and PEG-added pristine MoO_3 .

Dhage et al. [3] synthesized hexagon shaped h- MoO_3 nanorods - via the probe sonication route using ammoniummolybdate, urea and sodium dodecyl sulphate at 70°C . Pure metastable h- MoO_3 and α - MoO_3 were produced under the current synthetic conditions. The h- MoO_3 phase was transformed to α - MoO_3 phase at 400°C , while the hexagon shape rods structures of h- MoO_3 were collapsed and transformed to elongated particles of α - MoO_3 . The as-prepared products were also characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM).

Phuruangrat et al.[4] synthesized high aspect ratios (>200) MoO_3 nanowires by the decomposition of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ under a microwave-assisted hydrothermal method (microwave radiation heating), comparing to the conventional hydrothermal (electric heating) method. XRD and SEM reveal that the products are orthorhombic MoO_3 nanowires with 50 nm in diameter and 10–12 μm in length. Comparing to the conventional hydrothermal reaction, higher temperature and longer reaction times for producing one-dimensional MoO_3 were

carried out. Finally, the electrochemical testing of as-synthesized MoO_3 nanowires for hydrogen reaction evolution was tested in H_2SO_4 solution. By comparing the commercial MoO_3 and conventional hydrothermal MoO_3 , MoO_3 nanowires obtained by microwave-assisted hydrothermal method showed higher electrocatalytic activity for hydrogen reaction evolution than others.

Pereira et al. [28] prepared MoO_3 with nickel or cobalt doping by the polymeric precursor method. The powder precursors were characterized by TG/DTA, X-ray diffraction, infrared and Raman spectroscopy and scanning electron microscopy. Finally, $\alpha\text{-MoO}_3$ was produced after calcination at a low temperatures below $700\text{ }^\circ\text{C}$.

Fang et al. [29] synthesized MoO_3 at low temperature by hydrothermal approach. The influence of hydrothermal temperature, time, concentration of the peroxomolybdic acid solution, and additives on the morphology of the products has been investigated. It was found that the morphology of urchin-shaped microstructures of peroxo- modified molybdenum oxide hydrate can be controlled in the temperature range of $65\text{--}75\text{ }^\circ\text{C}$. The as-synthesized uniform microstructures, which were collected from the 0.9 mol/L molybdenum solutions after 14 h at $75\text{ }^\circ\text{C}$, are $35\text{--}40\text{ }\mu\text{m}$ in diameter, and they were constructed by nanoscale blocks of $300\text{--}400\text{ nm}$ in width and about 190 nm in thickness. The dimensions of microstructures and their building blocks were dramatically magnified when the molybdenum concentration was reduced, while those dimensions can be efficiently decreased by adding small quantities of HNO_3 or LiNO_3 into the precursor solution. By moderate calcination, $\alpha\text{-MoO}_3$ with a hierarchical microstructure can be achieved. The possible formation mechanism

of urchin-shaped microstructure was discussed using the results of UV–visible spectroscopy and electron microscopy.

1.6 Research objectives

1. To develop the synthesis of one-dimensional MoO_3 by hydrothermal method.
2. To study the effects of pH, concentration, reaction temperature and holding reaction time on the synthesis of one-dimensional MoO_3 by hydrothermal method.
3. To synthesized silver composite on molybdenum oxide nanobelts by a sonochemical method