超臨界流体を用いた機能性金属カルコゲナイド材料の環境適応型合成プロセス

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Title

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Chapter 1

It is ideal that metal chalcogenide materials used in renewable energy devices are synthesized by an inexpensive and safe synthetic process and have high performance. Hence, this study proposes a metal chalcogenide synthesis process for energy conversion devices using less toxic solid chalcogen sources (S_8, SeO_2 and Se) and metal oxide precursors under supercritical reductive conditions. Using simple and inexpensive staring materials is also excellent in environmental harmony.

$$S_8 + Se \text{ or } SeO_2 + MO_x \rightarrow MS_ySe_z$$
$$\text{(SCF reductive condition)}$$

This study is presently in the fundamental phase as shown in Fig. 1. It is necessary to understand the basic reaction process in SCFs and the effects of SCF on metal chalcogenide materials during chalcogenization. Therefore, in this study, we first demonstrate that metal sulfides, selenides and its solid solutions can be synthesized in SCF. Subsequently, we investigate what kind of chemical reactions in the SCF occurs during the chalcogenization, how this process affects to the crystal growth and mass transfer within the solid, and how are they be dispersed in the supercritical fluid after the chacogenizaion. Finally, metal chalcogenides synthesized by using this process is applied to hydrogen evolution catalyst and its characteristics are evaluated.

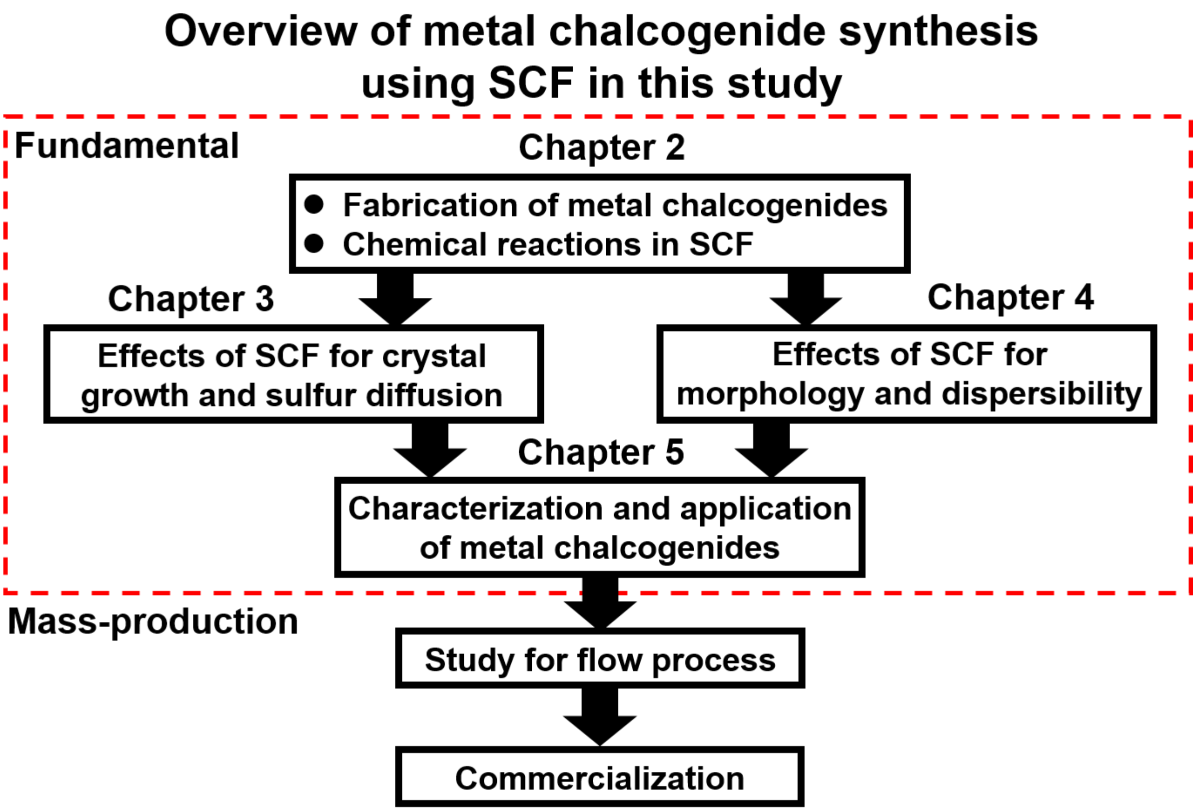

Fig. 1 Overview of this study

This paper consists of 6 chapters. The contents of each chapter are given below.

Chapter 1 describes the background and purpose of this research.

Chapter 2 clarifies the effectiveness of the proposed chalcogenization process and also describes the chemical reactions of sulfur and selenium in SCF.

Chapter 3 describes the effects of SCF for crystal growth and sulfur diffusion using ZnS and CZTS thin films as examples.

Chapter 4 describes formation of an edges-rich structure and dispersibility using layered materials as an example.

Chapter 5 shows detailed characterization of materials and the electrocatalytic activity of $Mo(S,Se)_2$ for hydrogen evolution reaction.

Chapter 6 summarizes this research and describes future prospects.

Chapter 2

To clarify the effectiveness of the SCF process, we focused on the chalcogen-introduction step for fabrication of metal chalcogenides. To discuss the reaction in fluids and solid separately, we chose a thin-film system, and demonstrated SCF selenization, sulfurization and simultaneous sulfurization and selenization (chalcogenization) of Cu–In and Cu–Zn–Sn oxide precursor films using low-cost selenium and sulfur sources, (SeO_2, elemental selenium and elemental sulfur), at 400 °C, for 25–70 min. As mentioned in 1.3, prepared CIS and CZTS is well-known materials for solar cells, and we can compare SCF chalcogenization process with other conventional processes. In addition, to investigate the chemical reactions of sulfur and selenium in SCF, analyses for the solvent and generated gas after SCF chalcogenization are carried out and the chemical reaction species and the reaction scheme are determined. As the results, EDS, XRD, Raman spectroscopy analyses and absorption spectra measurements revealed that the atomic composition can be tuned by varying the ratio of selenium and sulfur sources. EtOH enables sufficient supply of SeO_2 and sulfur to reaction field due to its high solubility, and in high temperature condition reduces SeO_2 and sulfur to form Se^{2-} and S^{2-}. It was concluded that Se^{2-} and S^{2-} react to metal oxide precursors with oxygen reduction process caused by ethanol in SCF chalcogenization.

Chapter 3

We focus on how this process affects crystal growth and mass transfer within a solid. The dependences of SCF solvents indicated that both high solubility and the reducibility of supercritical ethanol were important for chalcogenization. This suggests that reduction of the metal oxide is expected to proceed simultaneously with the supply of sulfur in the solid. Hence, we adopted SCF sulfurization of ZnO films as a simple model system and analyzed the progress of crystal growth and the degrees of sulfur in-diffusion and oxygen out-diffusion. Finally, the same process was carried out with a Cu-Zn-Sn oxide to fabricate a CZTS thin film. As the results, the crystal growth and sulfur diffusion of ZnS and CZTS were analyzed by XRD and depth profile analyses. Crystal growth and sulfur diffusion progressed as the ethanol density increased. It is supposed that the reduction of metal oxide is the driving force. As the ethanol density was larger, its reduction was promoted and an oxygen concentration gradient was generated in the film. As a result, according to Fick's first law, oxygen diffused outward. S^{2-} reacted with the reduced metal oxide. The continuous supply of S^{2-} at a high concentration resulted in its gradual diffusion from the top to the bottom due to the concentration gradient.

Chapter 4

The effects of the morphology and dispersibility of the samples were investigated by varying the solvent and the ethanol density. The affinity between the supercritical fluid and metal chalcogenide is an important factor determining the morphology and dispersibility. To compare the affinity between ethanol and metal chalcogenide in each condition, the Hansen solubility parameter is used. The correlation between the morphology of the synthesized sample and the value of the solubility parameter is discussed. MoS_2 was used as model sample and the effects of SCFs for the morphology and dispersibility of MoS_2 were investigated by varying the solvent and the ethanol density conditions. As the results, almost similar affinity between SC EtOH and SCW was found under the condition that MoS_2 with edge-exposed structure was synthesized. In addition, it was found that as the ethanol density increased edges-exposed MoS_2 was synthesized. It means that as ethanol density increases, the affinity between SC EtOH and MoS_2 increases. Therefore, regardless of any solvent, If MoS_2 is synthesized under a reductive condition and equivalent HSP value to this experiment, edge-exposed MoS_2 can be synthesized using SCF sulfurization.

Chapter 5

We explore the possibility that metal chalcogenides synthesis process in SCF can be applied to produce highly-active hydrogen evolution catalyst. We demonstrate a one-pot synthesis process for not only MoS_2 but also composition-controlled $MoS_{2-x}Se_x$ with an edge-rich structure and a thin-layered $Mo(S,Se)_2$/rGO composite using a moderate temperature for a short processing time. The synthesis was achieved using environmentally friendly starting materials and reductive supercritical conditions without an annealing process for the synthesized samples. As the results, the synthesis of composition-controlled edge-rich $MoS_{2-x}Se_x$ with a thickness of 1–10 layers and a corresponding $MoS_{0.9}Se_{1.1}$/rGO composite were demonstrated by using SCF chalcogenization process. The electrocatalytic HER activity increased with increasing Se concentration and was further improved by complexing with rGO. In particular, $MoS_{0.9}Se_{1.1}$/rGO showed a very low overpotential of 160 mV (vs. RHE) and a low Tafel slope of 44 mV/dec. at a cathodic current density of 10 mA/cm^2. Such good HER performance is due to the edge-rich structure and the conductive paths formed between $MoS_{0.9}Se_{1.1}$ and rGO. The HER activity values can be categorized into the highest-activity group of the previously reported molybdenum dichalcogenide and its composite. From the above, it was demonstrated that the metal chalcogenide materials synthesized by SCF chalcogenization process shows sufficiently high properties as a hydrogen evolution catalyst as compared with the metal chalcogenide material synthesized by other processes.

Chapter 6

In this study, it was found that SCFs with high solubility and reducibility are suitable for synthesis of functional metal chalcogenide materials using less-toxic solid chalcogen sources and metal oxide precursors. The utilization of SCF reductive condition for the synthesis of metal chalcogenides has a lot of advantages such as shorter reaction time, lower reaction temperature, the proceeding of crystal growth, the promotion of sulfur diffusion in oxide precursors and improvement of dispersibility of a few-layered materials. This SCF processes studied in this work can open sustainable chemistry to the fabrication of other metal chalcogenides.