FABRICATION OF SE NANOWIRES FROM SNSE USING CHEMICAL TRANSFORMATION METHOD

[1]HYUN JU, [2]JOOHEON KIM

[1,2]School of Chemical Engineering & Materials Science, Chung-AngUniversity, Seoul 06974, Republic of Korea
Email: [1]mohani@cau.ac.kr, [2]jooheonkim@cau.ac.kr

Abstract - Se nanorods with ~50 nm diameter are fabricated from SnSe bulk crystals via hydrothermal transformation procedure in oxalic acid solution, and the reaction mechanism for the chemical transformation is suggested. The oxalic acid and SnSe particle are reacted and then generated numerous Se nuclei, which crystallized into Se nanorods due to theintrinsic character of one-dimensional (1D) growth of Se.

Index Terms - Hydrothermal transformation, Tin selenide, Selenium, Nanorod

I. INTRODUCTION

Selenium (Se) is an attractive element in the chalcogenide group and have been widely studied in various researches including chemistry, medicine, ceramics, electronics, and metallurgy. Recent advances in nanotechnology enables to fabricate Se nanostructures viavarious synthesis techniques, and the research of nanostructured Se based semiconducting devices is highly required to develop future technology, because the low-dimensional nanostructures have unique characteristics with efficient electrical transport, which allow the nanomaterials to outperform bulk materials in various research areas [1,2].

Se nanostructures are fabricated by various synthetic techniques such as, hydrothermal synthesis, photocatalytic process, electrochemical method, vapor phase growth, template-assisted synthesis, and so on [3]. Chemical transformation is one of the strategies to achieveSe nanostructures, which can transform original material to desired material with changing composition, dimension, and morphology. Ion exchange [4] and Kirkendall effect [5] based transformation reactions are famous strategies, thus they have been mainly studied by many research groups to successfully obtain target materials. Especially, stabilizer-depleted transformation method enables to fabricate unary nanostructures from binary compounds, which is different from ion exchange and Kirkendall effect [6]. However, further research is necessary investigating stabilizer-depleted chemical transformation for pure and unary nanostructures because only few papers have been reported to date. Herein, we report on a prospective strategy for fabrication of unary Se nanostructures from SnSe bulk crystals via a chemical transformation procedure in oxalic acid solution. The formation of intermediate complex consisting of SnSe and oxalic acid, and oxidation of the complex facilitate the successful preparation of Se nanostructures. One-dimensional (1D) growth of Se nanostructures can be observed after the nucleation because of the intrinsic anisotropy of Se, resulting in the fabrication of Se nanorods (NRs).

II. DETAILED EXPERIMENTS

SnSe crystals (99.999%, Alfa Aesar) were ball-milled into small particles using zirconia balls in an inert atmosphere. The rotation speed of the planetary mill was set to 150 rpm to generate a rolling action of the balls, which applied shearing forces to the materials. 29 mg of SnSe powder was added to an aqueous solution containing 180 mg of oxalic acid ($C_2H_2O_4$) and 100 mL of DI water. After vigorous stirring, the mixture was transferred into a Teflon-lined autoclave and sealed. The vessel was then heated to 443 K for 2h to carry out the chemical transformation procedure. The resulting product was collected and washed several times with dilute HCl solution and ethanol, and dried in a vacuum oven. The resulting product was pressed for 10 min at 823 K under 50 MPa, yielding Se/SnSe samples.

III. RESULTS AND DISCUSSION

The schematic mechanism for the transformation procedure of SnSe to Se NR is shown in Fig. 1. The aqueous solution consisting of ball-milled SnSe particles and oxalic acid is reacted under hydrothermal condition. The oxalic acid attacks the SnSe particle, and they form complex intermediate, as presented in equation (1).

$$C_2H_2O_4 + SnSe \rightarrow SnSe(C_2O_4)^{2-} + 2\,H^+ \qquad (1)$$

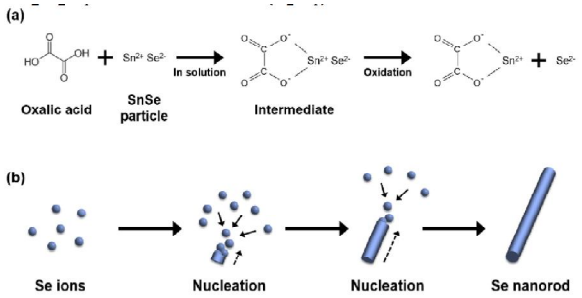

Fig. 1. Schematic mechanism for the transformation procedure of SnSe to Se nanorod. (a) Generation of Se ions from SnSe with oxalic acid, and (b) anisotropic growth of Se nanorod from Se ions.

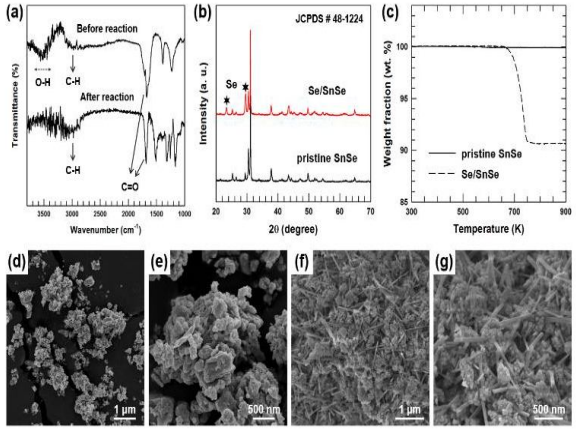

Fig. 2. (a) FT-IR spectra of aqueous solutions including oxalic acid before and after the reaction. (b) XRD patterns and (c) TGA thermograms of the pristine SnSe powder and Se/SnSe sample. (d) Low- and (e) high-magnifications of FE-SEM images of SnSe powder. (f) Low- and (g) high-magnifications of FE-SEM images of Se/SnSe sample.

Then, the metastable intermediate is oxidized by O_2 according to equation (2), leading to many Se nuclei in solution.

$$2\,SnSe(C_2O_4)^{2-} + O_2 + 2\,H_2O \rightarrow 2\,Sn(C_2O_4)^{2-} + 2\,Se + 4\,OH^- \quad (2)$$

Fig. 1b shows the scheme for fabrication of Se NR from Se ions, which obviously occurs through nucleation and following 1D growth because of the intrinsic nature of Se to grow anisotropic 1D structure [3]. To prove the proposed mechanism described above, Fourier transform-infrared (FT-IR) analysis was performed to characterize the structure of oxalic acid in solution. Fig. 2a shows the FT-IR spectra of aqueous solutions before and after the reaction. A large peak at ~3400 cm^{-1} from solution before the reaction indicates the O-H vibrations of oxalic acid [7]. However, it reduces after the transformation reaction because the O-H bonds of oxalic acid are broken during the reaction, resulting in that the oxalic acid forms complex with Sn^{2+} ion, as described in Fig. 1a. X-ray diffraction (XRD) and thermogravimetric analysis (TGA) results further confirmed the transformation process of SnSe. Fig. 2b shows the XRD patterns of the SnSe powders before (pristine SnSe) and after the reaction (Se/SnSe). Pristine SnSe powder reveals the typical diffraction pattern from the orthorhombic Pnma crystal structure (JCPDS # 48-1224) [8], and there are no other peaks in the XRD result, denoting the pure phase of SnSe. Two samples have diffraction peaks with the same positions but the sample after the reaction contains additional peaks different from the pristine SnSe, implying that transformed Se particles are present in the product. Fig. 2c shows the TGA thermograms for the pristine SnSe and Se/SnSe sample. The pristine SnSe exhibits outstanding thermal stability up to a temperature of 900 K because it contains SnSe as the only component. However, the Se/SnSe sample reveals a thermal degradation at ~700 K, which might be attributed to the transformed Se crystals. This result is well supported by the previous discussion of XRD analysis. The result of field-emission scanning electron microscopy (FE-SEM)images further identifies the chemical transformation of

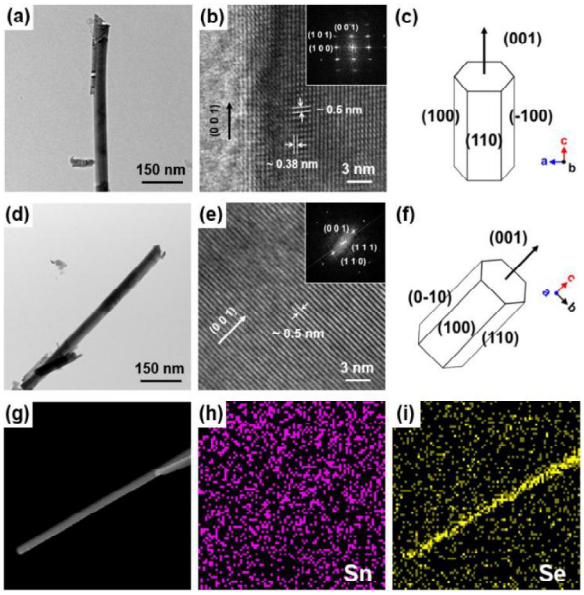

Fig. 3. (a, d) Low- and (b, e) high-magnifications FE-TEM images of single Se nanorods. Selected area electron diffraction patterns of the Se nanorods are in the insets of high-magnification FE-TEM images (b) and (e). (c, f) Schematic illustrations of crystal structures of individual Se nanorods shown in (b) and (e). (d) FE-SEM image Se nanorod and the corresponding EDS mappings of (e) Sn and (f) Se elements.

SnSe to Se NRs. Fig. 2d and 2e show the low- and high-magnifications of FE-SEM images of the SnSe powder, which show that ball-milled SnSe nanoparticles with ~200 to 500 nm in sizes are present. After the chemical transformation procedure, numerous particles comprising SnSe nanoparticles and 1D NRs that are randomly distributed in the low- and high-magnifications FE-SEM images of Se/SnSe sample, as shown in Fig. 2f and 2g.

The generated NRs via chemical transformation were further identified by following investigations. Fig. 3a and 3d show the FE-SEM and low-magnification field-emission transmission electron microscopy (FE-TEM) images of single NR, exhibiting 1D structure with a diameter of ~50 nm. The high-magnification FE-TEM image and the corresponding selected area electron diffraction (SAED) patterns shown in Fig. 3b and 3e indicate the distances between the lattice fringes are ~0.5 and ~0.38 nm, correspond to the (0 0 1) and (1 0 0) planes of the Se NR. The direction of (0 0 1) in the SAED is parallel to the axis of NR, resulting in that the fabricated NR is a single crystal along the (0 0 1) direction, which is in keeping with the highly anisotropic structure of Se shown in Fig. 1. The hexagonal crystal structures of individual Se NRs can be schematically illustrated by symmetric facets in Fig. 3c and 3f considering from the

above discussion. Fig. 3g–i indicate FE-SEM image and the corresponding energy-dispersive X-ray spectroscopy (EDS) mappings of Sn and Se atoms of Se NR, confirming that the fabricated NR is composed of only Se elements.

CONCLUSION

This study proposes the fabrication procedure for 1D Se NRs from SnSe crystals via a chemical transformation. Se NRs were chemically transformed from milled SnSe crystals with the aid ofoxalic acid solution. The oxalic acid attacked the SnSe particle under hydrothermal condition, and they formed complex intermediate, which were oxidized, resulting in the generation of Se nuclei in solution. Numerous Se nuclei got together and crystallized into Se NRs due to their intrinsic nature of 1D growth. Visual investigations identified that the resulting Se NRs exhibited 1D structure with a diameter of ~50 nm. This work highlights that the successful transformation of Se NRs from SnSe crystals through hydrothermal procedure in oxalic acid solution, which can develop research areas of nanoscale materials.

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