Eventual Chemical Transformation of Metals and Chalcogens into Metal Chalcogenide Nanoplates through a Surface Nucleation-Detachment-Reorganization Mechanism

Gyeongbae Park,†,‡ Jiwoo Lee,‡ Sungmin Moon,‡ Heeseung Yang,‡ Anupam Giri,‡ Junghyeok Kwak,‡ Young-Kwang Jung,‡ Aloysius Soon,§,∥ and Unyong Jeong‡,†

†Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-Ro, Nam-gu, Pohang, North Gyeongsang 37673, Republic of Korea
‡Department of Materials Science and Engineering, Yonsei University, 50 Yonsei-Ro, Seodaemun-gu, Seoul 03722, Republic of Korea

ABSTRACT: Many studies have reported the synthesis of two-dimensional (2D) nanoplates and nanosheets of the layer-structured metal chalcogenides but also have reported various structures far from the 2D shape. In multicomponent compounds, the elemental concentrations keep changing during the reaction; hence, the reactions are considered to be nonstoichiometric from the nucleation and may include continuous changes in the structure and composition. The different shapes of the metal chalcogenides with the layered structure are attributed to the nonstoichiometric reactions. However, it has not been studied if such nonstoichiometric reactions eventually produce 2D nanoplates, and the mechanism involved in the transformation has not been understood. This study investigates a two-step chemical reaction as an extreme nonstoichiometric nucleation and growth. It reveals that the layer-structured metal chalcogenides \((M_nX_m, M = Sb and Bi, X = Se and Te)\) with the \(R\bar{3}m\) space group can be obtained by transforming premade pure chalcogen \((Se, Te)\) thick nanorods or metal microparticles \((Bi)\). By coupling our first-principles calculations with a shape-prediction thermodynamic model, we have also examined and rationalized the shape/aspect ratio of the \(M_nX_m\) nanocrystals under different experimental growth conditions. The tendency of anisotropic growth to form the 2D shapes during the transformations are discussed on the basis of experimental results and theoretical calculations.

INTRODUCTION

Strategies to control the dimension, shape, and elemental distribution of multicomponent nanocrystals have been developed extensively.1−4 Understanding the underlying principles of nucleation and growth of the nanocrystals is essential to achieve the rational synthesis of nanocrystals with specific dimension, shape, and elemental distribution. Although the classical nucleation and growth theory describes the formation of single-component nanocrystals,5,6 it fails to clearly elucidate the nucleation and growth of multicomponent nanocrystals synthesized by the coreduction process.7−12 The classical theory assumes that the chemical composition of the nuclei has the same composition with the product nanocrystals, so the whole nucleation and growth process is stoichiometric.13−15 However, even when the concentrations of the precursors are stoichiometric for the target nanocrystal, the elemental concentrations in the reactor keep changing because of the difference in reduction rates of the precursors. The solid−liquid−solid process where the reduced element redissolves into a solution also makes it difficult to keep the reaction stoichiometric.16−19 Such continuous change in the elemental concentrations may cause temporal variations of the crystal structure and chemical composition of the nanocrystals. Several papers have reported such nonstoichiometric nucleation and growth in the formation of bimetallic alloy nanocrystals and metal chalcogenides.9,20−22 This nonstoichiometric nanocrystal formation cannot be explained by the conventional nucleation and growth theory.

Recently, the oriented attachment was suggested as a nonclassical nucleation and growth mechanism to explain the formation of metal chalcogenide two-dimensional (2D) nanocrystals.23−26 In the oriented attachment, small nanocrystals orient their side edges to face the edge of a growing 2D crystal and reorganize to be a part of a large single crystal. This oriented attachment is possible because of the anisotropic bond strength between the strong covalent bond in the side edge and the weak van der Waals interaction in the thickness direction. The nanocrystals with the 2D layered structures are energetically favored compared to the nanocrystals with the dangling bonds on their surface.23−26 However, this nonclassical mechanism cannot explain the continuous change in the structure and composition of the nanocrystals during the growth process.27,28 Therefore, the nonclassical mechanism in the oriented attachment is not applicable to the nonstoichiometric nucleation and growth of the nanocrystals.29−31
Due to the intrinsically anisotropic bonding nature, metal chalcogenides grow preferentially into 2D structures. Among the metal chalcogenides 2D nanocrystals, synthesis of M₂X₃ (M = Sb and Bi, X = Se and Te) with the R₃m space group in the solution phases has been developed well. In M₂X₃, five atomic layers (X–M–X–M–X) are covalently bonded to form a quintuple layer (QL), and the quintuple layers are stacked through weak van der Waals interactions along the c-axis. Due to the intrinsically anisotropic bonding nature, metal chalcogenides grow preferentially into 2D structures. Unfortunately, there have been many articles reporting different shapes of nanocrystals (not 2D shapes) even when the reaction processes were very similar. Therefore, the M₂X₃ metal chalcogenides can be good model systems to investigate the general possibility of eventual formation of 2D nanocrystals. Herein, we present the chemical transformation from premade pure chalcogen particles or pure metal particles into metal chalcogenide 2D nanocrystals in solution-based reactions. These materials have drawn considerable attention due to their unique physical properties such as thermoelectric characteristics and being a topological insulator. Also very recently, small Bi₂Se₃ nanoparticles with 30–50 nm in lateral dimension have received interest for their photothermal effect, potential contrast agents for X-ray imaging, and photoacoustic imaging.

### RESULTS AND DISCUSSION

**Transformation of Pure Chalcogens into Metal Chalcogenide Nanoplates.** Owing to the linear chain-like molecular structure and the hexagonal close-packing of the molecules, the crystals of Se and Te preferentially grow along the c-axis; thereby, the formation of 1D nanowires (NWs) is thermodynamically preferred in nanocrystals of Se and Te. These 1D shapes are suitable for investigating whether the 1D shapes will evolve into the 2D nanocrystals during the chemical transformation into metal chalcogenides.

As the first example of transformation of chalcogens into metal chalcogenides, the transformation of the Se NWs into Bi₂Se₃ nanoplates was investigated (Figure 1A–D). The t-Se NWs (Figure 1A) were synthesized in ethanol by converting amorphous Se (a-Se) particles into NWs. The dimensions of the Se NWs were tens of microns in length and 150–300 nm in thickness. For the chemical transformation, the Se NWs were redispersed in ethylene glycol, poly(vinyl pyrollidone) (PVP), acetic acid, and NH₃·H₂O were dissolved in the solution. At the reaction temperature of 150 °C, Bi nitrate precursor solution...
(in ethylene glycol) was quickly injected through a syringe. To obtain time-resolved samples, a small amount of solution (1 mL) was taken from the reaction batch. The reaction of the sample was immediately quenched in an ice bath. The solution turned from brick red to black in a few minutes, indicating Bi was reacting with the Se NWs.

Figure 1B shows the structural change after 2 min. 2D nanoplates were observed although their shapes were not well-defined. Small particles with irregular shapes were produced simultaneously. The surface of the Se NWs became roughened (inset in Figure 1B), indicating that the reaction with Bi took place at the surface. After 10 min, most of the small particles disappeared and the Se NWs were still observed but rarely found (Figure 1C). After 45 min, all the Se NWs disappeared and well-defined hexagonal nanoplates were obtained (Figure 1D).

As the second chemical change of chalcogens into metal chalcogenides, the transformation of the Te NWs into Bi$_2$Te$_3$ nanoplates was studied (Figure 1E–H). The t-Te NWs were synthesized by a polyol process reported in a previous study. The dimension was 10 nm-thick and several micrometers long (Figure 1E). Temperature of the Te NW dispersion in diethylene glycol was increased to 165 °C in the presence of Bi precursor (BiCl$_3$), PVP, and NaOH. It is notable that the Te NWs in the solution without Bi precursor had no change at the temperature during 1 day. After 4 h, most of the Te NWs disappeared and aggregates of small nanoparticles were observed (Figure 1F). The nanoplates were Te–Bi compounds (Figure 1G). The inset is a blow-up image of a remaining Te NWs whose surface turned rough and porous. The overall thickness of the NWs increased to ∼25 nm. The rough NWs contained a considerable amount of Bi (Figure S3), indicating the formation of Te–Bi compound. The small nanoparticles are considered to detach from the surface of the Te–Bi compound NWs because of the large mechanical stress by the volume expansion during the reaction with Bi. The conversion of Te into stoichiometric Bi$_2$Te$_3$ causes a volume increase by 66.29%. After 8 h of the reaction (Figure 1G), the NWs disappeared and the 2D nanoplates grew through the reorganization of the nanocrystals attached to the edge of the growing nanoplates. After 1 day of reaction (Figure 1H), only well-defined hexagonal nanoplates were observed.

As the third example of the transformation of chalcogens into metal chalcogenides, the chemical transformation of Te nanorods (NRs) into hexagonal Sb$_2$Te$_3$ nanoplates was investigated (Figure 1I–L). We used the thick Te NRs (180–300 nm in thickness) to check the possibility of the thermodynamic chemical transformation into the 2D nanoplates instead of from the thin NWs (Figure 1I). The Te NRs were dispersed in ethylene glycol; then, Sb precursor (SbCl$_3$), PVP, and NaOH were dissolved in the solution. The temperature was raised to 195 °C for the reaction. After 2.5 h of reaction, the surface on the Te NRs was roughened by the reaction with Sb and the aggregates of small nanoparticles were shown (Figure 1J). The chemical compositions of the NRs and the small nanoplates are found in Figures S4 and S5. The inset image implies that the nanoparticles detached from the NRs. After 3.5 h of reaction, nanoplates were observed together with the small nanoplates and the NRs (Figure 1K). After 8 h, all the small nanoparticles and the NRs disappeared, and only the hexagonal nanoplates were observed (Figure 1L).

Structural analysis of the 2D nanoplates obtained by the chemical transformation of the chalcogens is shown in Figure 2. Figure 2A–C exhibits the Bi$_2$Se$_3$ nanoplates transformed from
the Se NWs. A TEM image (Figure 2A) shows that the nanoplates have sharp and clear edges with a lateral dimension of 890 nm. The defect observed in the upper region of the plate is the screw-dislocation.14 The hexagonal lattice fringes with a uniform spacing of 0.207 nm coincide well with the spacing between (110) planes of R3m Bi2Se3 (Figure 2B). The electron diffraction spots (inset in Figure 2B) taken from the whole area of the nanoplate clearly indicates that the product Bi2Se3 is a single crystal. The peaks in the powder X-ray diffraction (Figure 2C) of the product Bi2Se3 were indexed to the R3m crystal structure (blue line). However, a few peaks were indexed to the (101), (421), (521), and (710) planes of the Pbmm crystal structure (red line) (JCPDS 77-0216), indicating a small fraction of the nanoparticles has the Pbmm structure. The existence of the Pbmm structure is not clearly understood at this stage. The rhombohedral Bi2Se3 is known to undergo phase transition to orthorhombic structure under high pressure (2–4.3 GPa) and at 500 °C.15 The reaction temperature is not high enough for complete transition to the orthorhombic structure.

The structural analysis of the Bi2Te3 nanoplates transformed from the t-Te NWs is shown in Figure 2D–F. The TEM image shows that the nanoplates are relatively uniform in size (Figure 2D). An average size of the nanoplates was 270 nm. The high resolution-TEM (HR-TEM) image taken at the edge of the nanoplate demonstrates a well-ordered crystal structure with the lattice spacing of 0.218 nm which corresponds to a lattice distance between (110) planes of R3m Bi2Se3 (Figure 2E). The selected-area electron diffraction (SAED) in the inset exhibits distinct six-folded spots, indicating the nanoplates are single crystalline. X-ray diffraction peaks (Figure 2F) are indexed with the R3m crystal structure of Bi2Te3 (JCPDS 15-0863).

The structural characterization of the Sb2Te3 nanoplates transformed from the t-Te NRs is displayed in Figure 2G–I. The nanoplates possessed a symmetric hexagonal shape as shown in the TEM image (Figure 2G). An average size of the nanoplates was 850 nm. The uniform lattice spacing was 0.213 nm, corresponding to a lattice spacing of (110) plane of R3m Sb2Te3 crystal structure (Figure 2H). The inset shows a SAED pattern taken from the whole region of the sample, indicating a single crystalline characteristic. The XRD pattern also reveals that the Sb2Te3 nanoplates are pure Sb2Te3 with R3m space group (JCPDS 71-0393) (Figure 2I).

Figure 3. AFM images and corresponding height profiles of (A) Bi2Se3, (B) Bi2Te3, and (C) Sb2Te3 nanoplates transformed from the chalcogen NWs and NRs. (D) DFT calculated surface energies of the stoichiometric (001), (015), and (110) surfaces for Bi2Se3, Bi2Te3, and Sb2Te3. (E–G) Predicted Gibbs-Wulff equilibrium crystal structures (ECS) for the experimentally observed nanoplate exposing only the (001) and (110) facets. The aspect ratios (r) of the lateral dimension (d) versus the thickness (h) are computed on the basis of the predicted ECS.

The reaction temperature is not high enough for complete transition to the orthorhombic structure. The calculated surface energy (γ) changes of Bi2Se3, Bi2Te3, and Sb2Te3, with a clear trend of γ(001) < γ(015) < γ(110) for each material, are shown in Figure 3D. When the anion (Se) in Bi2Se3 is replaced by Te, we find that γ(001) increases while γ(015) and γ(110) decrease. On the other hand, when the cation (Bi) in Bi2Te3 is replaced by Sb, there is no significant change in γ(001) while γ(015) and γ(110) decrease. According to Gibbs-Wulff theorem,16 an equilibrium crystal shape (ECS) of material can be determined by considering the relative ratios of the material’s surface energies. From our DFT calculations using eq S1, the ratios of γ(001) to γ(015) to γ(110) are 1:2.71:3.79, 1:2.09:2.85, and 1:1.81:2.57 for Bi2Se3, Bi2Te3, and Sb2Te3, respectively. This implies that (001) is the most abundant facet on the ECS. The lateral plane can be either the (015) facet or the (110) facet. The nanoplates with the (015) lateral facet have an inclined angle of 58° with the (001) basal plane which can be detectable in AFM or TEM. A recent paper has reported that the Bi2Te3 with the (015) lateral plane can have a thick truncated hexagon or a thin triangle.17 Meanwhile, the nanoplate with the (110) facet has a well-defined thin hexagon and thickness is uniform in the whole surface. The nanoplates in this study are considered to have the (110) lateral
plane from the thin and uniform thickness with the well-defined hexagonal structure. To mimic and study our experimentally observed ECS, we have also constructed a constrained ECS with the (110) lateral facet by simply restricting our choice of crystal planes (110) as suggested from our experimental data (Figure 3E–G). The aspect ratio (r) calculated for both the DFT-predicted ECSs correctly captures the relative trend observed in our experiments. Bi$_2$Se$_3$ has the highest tendency to adopt the morphology of thin nanoplates while Sb$_2$Te$_3$ has the lowest tendency to do so, yielding thicker nanoplates. It is notable that the same trend was obtained even when we removed the contraints, that is, including both (110) and (015) for the calculation. The result is shown in Figure S6.

**Transformation of Bi Particles into Metal Chalcogenide Nanoplates.** To investigate the chemical transformation of metals into 2D metal chalcogenide nanoplates, we synthesized Bi microparticles (MPs) and converted them into Bi$_2$Se$_3$ and Bi$_2$Te$_3$ nanoparticles. Bi MPs were prepared by modifying a literature process that produces Bi nanoparticles in tetraethylene glycol. The Bi precursor (Bi(OH)$_3$) was prepared by reacting Bi(NO$_3$)$_3$·5H$_2$O with NaOH in DI water, using the following reaction Bi$^{3+}$ + 3OH$^-$ → Bi(OH)$_3$. To stimulate the forward reaction, an excess amount of NaOH was used. Upon introducing Bi(NO$_3$)$_3$·5H$_2$O to the aqueous NaOH solution, white Bi(OH)$_3$ precipitate was formed immediately. The precipitate was collected and dried. The dry powder of Bi(OH)$_3$ was dispersed in tetraethylene glycol with the aid of mild ultrasonication, and the temperature was raised to 285 °C. The size of the Bi MPs ranged from 200 nm to 1 μm (Figure 4A). The large and broad size distribution is attributed to the slow reduction rate at 285 °C. Faster reduction at 314 °C led to more uniform distribution in size. The large dimension of the particles is appropriate in this study to investigate the thermodynamic possibility of the chemical transformation into 2D nanoplates.

The as-synthesized Bi MPs (20.9 mg) were dispersed in diethylene glycol (5 mL), and the temperature was raised to 200 °C. A precursor (H$_2$SeO$_4$) solution in diethylene glycol of molar equivalent amount was injected quickly to the Bi MP solution. The color of the solution immediately changed from dark gray to dark yellow and then dark red. The appearance of yellow and red color indicates the formation of Bi$_2$Se$_3$. After 3 min of reaction (Figure 4B), a large amount of irregular particles was observed and also nanoplates were protruding from the surface of spherical particles (marked with an arrow). EDX analysis was carried out for two different regions marked with black dashed circles in Figure 4B. The elemental analysis indicated that the spherical particles (Region 1) were Bi-rich (Bi:Se = 86.7:13.3) (Figure S7), and the irregular particles (Region 2) were a-Se (Bi:Se = 4.9:95.1) (Figure S8). The results imply that Se reacted at the surface of the Bi MPs. It is well-known that the a-Se dissolves in the solution at high temperature. The dissolved Se atoms react with the Bi MPs. After 55 min of the reaction (Figure 4C), the Bi MPs and the a-Se disappeared. It was readily observed that nanoparticle of 100~150 nm in diameter was attached to the edges of the growing nanoplates as shown in the inset of Figure 4C. The nanoplates are considered as Bi–Se compound particles. The preferential attachment to the side edges is because of the higher surface energy of the edges compared to those of the basal surfaces. The reaction completed after 12 h (Figure 4D). The small particles disappeared completely through the reorganization, and the nanoplates turned into well-developed hexagonal ones.

To better understand the reaction mechanism, we carried out the transformation at a lower temperature of 150 °C. The slow reaction enables one to monitor the structural changes during the reaction. Figure 4E shows an SEM image taken after 2 h of reaction at 150 °C. Bi MPs with large cracks were readily observed. The cracks are attributed to the stress accumulated by the chemical transformation. Small particles detached from the surface of the MPs as shown in the TEM image (Figure 4F) with a wide range of elemental compositions. It cannot be excluded that a small fraction of Bi atoms were dissolved due to the surface energy increase caused by the sharp curvature at the rough surface and the cracks. The dissolved Bi atoms are expected to join in the fine adjustment of the chemical composition of the nanoplates.

The structural characterization of the nanoplates transformed from the Bi MPs is shown in Figure 5A–C. TEM image demonstrates that the as-synthesized nanoplates were hexagons with the average distance of 2.9 μm between opposite corners (Figure 5A). In the HR-TEM image (Figure 5B), the lattice distance was uniform with a spacing of 0.207 nm, which is well matched with the spacing between (110) planes of Bi$_2$Se$_3$. The distinct SAED pattern in the inset could be indexed to (110) and (030) planes of Bi$_2$Se$_3$ with [001] zone axis, demonstrating...
that the product was a single crystal. The XRD result shows good agreement with the \( R3m \) phase of \( \text{Bi}_2\text{Se}_3 \) (JCPDS: 33-0214) (Figure 5C).

We extended the same procedure to obtain \( \text{Bi}_2\text{Te}_3 \) nanoplates by adding the Te precursor (\( \text{Na}_2\text{TeO}_3 \)) instead of the Se precursor (\( \text{H}_2\text{SeO}_3 \)). The reaction followed the same mechanism with the Se precursor shown in Figure 4, but the reaction was completed within 2 h. After injection of the \( \text{Na}_2\text{TeO}_3 \) solution, the color of the reacting solution turned black within a few minutes whereas it took 30 min for \( \text{H}_2\text{SeO}_3 \). The as-synthesized \( \text{Bi}_2\text{Te}_3 \) nanoplates were smaller (100–300 nm) than the \( \text{Bi}_2\text{Se}_3 \) nanoplates (Figure 9). This large size difference between \( \text{Bi}_2\text{Se}_3 \) and \( \text{Bi}_2\text{Te}_3 \) nanoplate through the same procedure is attributed to higher reduction potential of \( \text{TeO}_3^{2-} \) (\( E^o = 0.827 \) V) than that of \( \text{H}_2\text{SeO}_3 \) (\( E^o = 0.740 \) V), resulting in a burst nucleation and growth at the same reaction conditions. Figure 5D–F exhibits the \( \text{Bi}_2\text{Te}_3 \) nanoplates synthesized from Bi MPs. The TEM image shows hexagonally well-developed \( \text{Bi}_2\text{Te}_3 \) nanoplates with 260 nm in lateral dimension (Figure 5D). The uniform lattice fringes with the distance of 0.218 nm corresponding to the lattice spacing of (110) planes of \( \text{Bi}_2\text{Te}_3 \) were confirmed by HR-TEM (Figure 5E). The inset shows a distinct electron diffraction pattern of \( \text{Bi}_2\text{Te}_3 \) nanoplates, which demonstrates that obtained \( \text{Bi}_2\text{Te}_3 \) nanoplates possess single and high crystallinity. The XRD pattern of dried \( \text{Bi}_2\text{Te}_3 \) powder is well matched with the \( R3m \) phase of \( \text{Bi}_2\text{Te}_3 \) (JCPDS 15-0863) (Figure 5F).

The average thicknesses of the \( \text{Bi}_2\text{Se}_3 \) and \( \text{Bi}_2\text{Te}_3 \) nanoplates transformed from the Bi MPs were 91 nm (±10 nm) and 25 nm (±6 nm) (Figure S10), so the ratios of the lateral dimension versus the thickness were \( r = 31.9 \) and \( r = 10.4 \), respectively. Regardless of the starting materials, the \( \text{Bi}_2\text{Se}_3 \) nanoplate has a larger ratio \( r \) of the lateral dimension versus the thickness compared to the \( \text{Bi}_2\text{Te}_3 \) nanoplate \( r = 101.1 \) for \( \text{Bi}_2\text{Se}_3 \) and \( r = 24.5 \) for \( \text{Bi}_2\text{Te}_3 \) when the starting materials are chalcogen nanowires). To rationalize the differences in the aspect ratios found in both \( \text{Bi}_2\text{Se}_3 \) and \( \text{Bi}_2\text{Te}_3 \) nanostructures, we perform additional DFT calculations for both the (001) and (110) surfaces of these chalcogenides where low-energy surface defects (for both the cation and anion) are taken into consideration. It has been reported that these surface defects generally have a rather low defect formation energy (\( \Delta H \)). By taking into account these low-energy surface vacancies and specific growth conditions, we model and examine the crystal morphology of the \( \text{Bi}_2\text{Se}_3 \) and \( \text{Bi}_2\text{Te}_3 \) nanoplates experimentally observed and determine their corresponding aspect ratios. Using the \textit{ab initio} atomistic thermodynamics \((\text{aiAT}) \) model\textsuperscript{46,47-49} we perform surface energy calculations (using eq S2) for the nonstoichiometric (001), (110), and (015) surfaces with different concentrations of surface cation and anion vacancies, where the nonstoichiometric structures are denoted as “(pristine surface) + defect”. Given that our experimental conditions may be far from the ideal thermodynamically equilibrated state or the role of surfactants and ligands may kinetically hinder the growth of certain crystal facets, we propose a constrained ECS that neglects the (015) surface (which is not observed in the TEM experiments in Figure 5A,D).

To better understand the experimental results that show a clear dependence of the initial growth conditions, we choose to vary the limits of the chemical potential of the anions in question to compare with the conditions in the experiments. Namely, as a first-step approximation, bulk phases of Se and Te are chosen to represent the chemical reservoirs for Se and Te NWs, respectively, while molecular dimers (\( \text{Se}_2 \) and \( \text{Te}_2 \)) are used to approximate that of the Se and Te elements. Given that the chemical potentials of the anion and cation cannot be considered independently, the chemical potential of Bi is then determined from eq S3 where the enthalpy of formation for each compound is taken as its bulk value.

Specifically, the bulk limits are taken as \( \mu_{\text{Se}} = -3.70 \) eV and \( \mu_{\text{Te}} = -3.45 \) eV, while the molecular limits are set to \( \mu_{\text{Se}} = -2.93 \) eV and \( \mu_{\text{Te}} = -2.44 \) eV to mimic the precursors used (see Figure 6A,B). As shown, when the chemical potential of the anion increases, the surface energy of the (110) surface structures decreases dramatically, favoring the (110) surface structures with more Bi surface vacancies, while that of (001) remains constant until the (001) + \( V_{\text{Bi}} \) surface becomes more
we infer that, when using the bulk phases of Se and Te as their surface seems marginal, especially closer to the bulk limit. Thus, (110) surface for both compounds. The in aspect ratios to the presence of surface Bi vacancies in the decreasing trend. Here, we may attribute this drastic change in ratio varies between 1.12 ≤ r ≤ 2.70, showing a similar decreasing trend. Here, we may attribute this drastic change in the aspect ratios to the presence of surface Bi vacancies in the (110) surfaces, which largely lowers the surface energies of the (110) surface for both compounds. The influence of the (001) surface seems marginal, especially closer to the bulk limit. Thus, we infer that, when using the bulk phases of Se and Te as their aspect ratios are much larger when compared to that when referencing their molecular phases. In comparison to the experiments, aspect ratios of 101.1 and 24.5 are found for Bi₂Se₃ and Bi₂Te₃ when Se(Te) NWs are used, while much smaller aspect ratios of 31.9 and 10.4 are determined when the molecular precursors are used. This corroborates well with our experimental findings.

From these predicted constrained morphologies, one may draw two conclusions. Depending on the source of our chemical reservoirs, the aspect ratio may be varied and controlled (e.g., Bi₂Se₃ or Bi₂Te₃ nanoplates have larger r when the reference state of anion is in the bulk phase rather than the molecular precursor phase). Under all growth conditions in this model, the Bi₂Te₃ nanoplate has a smaller r than the Bi₂Se₃ nanoplate, corroborating well with the experimental results.

The overall reaction mechanisms are illustrated in Scheme 1. When starting materials are chalcogens and the metal precursors are added, the reduced metal elements react at the surface of the chalcogens, causing the surface of the chalcogens to roughen and form irregular nanoparticles on the chalcogen surfaces. The irregular particles detach from the surface of chalcogens because of the stress accumulation caused by the volume increase by the chemical transformation. The irregular particles attach to the edges of the growing nanoparticles and rearrange to form single crystal nanoparticles. When the starting materials are the metal particles and the chalcogen precursors are added, some fraction of the chalcogen elements react with the metal particles at the surfaces to form the nanoparticles, but many fractions nucleate homogeneously to form the chalcogen particles. The chalcogens redissolve in the solution and join the transformation of the metal MPs into compound materials.

Small irregular nanoparticles detach from the MPs. The irregular nanoparticles attach to the growing nanoparticles and form single irregular nanoparticles via rearrangement processes.

**CONCLUSIONS**

Single crystal 2D nanoplates of various metal chalcogenides (Bi₂Se₃, Bi₂Te₃, and Sb₂Te₃) have been synthesized by chemically transforming pure chalcogens (Se nanowires, Te nanowires, Te nanorods) and pure metal microparticles (Bi). This two-step process enabled us to investigate the extreme nonstoichiometric nucleation and growth process. We revealed that stoichiometric metal chalcogenides can be obtained.

![Scheme 1. Schematic Illustration of Reaction Mechanisms](image)

Figure 6. Calculated surface free energy of the nonstoichiometric (001) and (110) surfaces (with low-energy surface defects) of (A) Bi₂Se₃ and (B) Bi₂Te₃ (as a function of the chemical potential of the anions, Se and Te). Surfaces with the cation and anion vacancies (i.e., V⁺, V⁻, and Vₓ, accordingly) are considered, where the coefficients 2 and 3 are designated as the number of surface vacancies per unit surface cell. (C and D) The aspect ratio of the constrained Gibbs-Wulff equilibrium crystal structures (ECS) for the experimentally observed nanoparticles, exposing only the (001) and (110) facets. The aspect ratios (r) of the lateral dimension (d) versus the thickness (h) are computed on the basis of the predicted ECS (as presented in Figure 3G).

stable near the molecular limit for both compounds. This has a considerable impact on the aspect ratios of their constrained ECS (Figure 6C,D). For Bi₂Se₃, the aspect ratio is found to reduce by almost half (i.e., 3.52 ≤ r ≤ 1.59) with increasing values of the Se chemical potential, and for Bi₂Te₃, the aspect ratio varies between 1.12 ≤ r ≤ 2.70, showing a similar decreasing trend. Here, we may attribute this drastic change in the aspect ratios to the presence of surface Bi vacancies in the (110) surfaces, which largely lowers the surface energies of the (110) surface for both compounds. The influence of the (001) surface seems marginal, especially closer to the bulk limit. Thus, we infer that, when using the bulk phases of Se and Te as their

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Formal thermodynamic chemical reservoir, the predicted aspect ratios are much larger when compared to that when referencing their molecular phases. In comparison to the experiments, aspect ratios of 101.1 and 24.5 are found for Bi₂Se₃ and Bi₂Te₃ when Se(Te) NWs are used, while much smaller aspect ratios of 31.9 and 10.4 are determined when the molecular precursors are used. This corroborates well with our experimental findings.

From these predicted constrained morphologies, one may draw two conclusions. Depending on the source of our chemical reservoirs, the aspect ratio may be varied and controlled (e.g., Bi₂Se₃ or Bi₂Te₃ nanoplates have larger r when the reference state of anion is in the bulk phase rather than the molecular precursor phase). Under all growth conditions in this model, the Bi₂Te₃ nanoplate has a smaller r than the Bi₂Se₃ nanoplate, corroborating well with the experimental results.

The overall reaction mechanisms are illustrated in Scheme 1. When starting materials are chalcogens and the metal precursors are added, the reduced metal elements react at the surface of the chalcogens, causing the surface of the chalcogens to roughen and form irregular nanoparticles on the chalcogen surfaces. The irregular particles detach from the surface of chalcogens because of the stress accumulation caused by the volume increase by the chemical transformation. The irregular particles attach to the edges of the growing nanoparticles and rearrange to form single crystal nanoparticles. When the starting materials are the metal particles and the chalcogen precursors are added, some fraction of the chalcogen elements react with the metal particles at the surfaces to form the nanoparticles, but many fractions nucleate homogeneously to form the chalcogen particles. The chalcogens redissolve in the solution and join the transformation of the metal MPs into compound materials. Small irregular nanoparticles detach from the MPs. The irregular nanoparticles attach to the growing nanoparticles and form single irregular nanoparticles via rearrangement processes.

**CONCLUSIONS**

Single crystal 2D nanoplates of various metal chalcogenides (Bi₂Se₃, Bi₂Te₃, and Sb₂Te₃) have been synthesized by chemically transforming pure chalcogens (Se nanowires, Te nanowires, Te nanorods) and pure metal microparticles (Bi). This two-step process enabled us to investigate the extreme nonstoichiometric nucleation and growth process. We revealed that stoichiometric metal chalcogenides can be obtained.

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Starting materials are chalcogen NWs and metal MPs. The elements reduced from the precursors react at the surfaces of the starting materials to form nuclei. The nuclei detached from the surfaces and attached to the edges of growing nanoparticles. Reorganization of the atoms forms hexagonal single crystal nanoplates.
regardless of the starting composition and dimension. To understand our experiments, we have also calculated the surface energies and examined the expected nanoshapes of Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$. Using a first-principles thermodynamic model, we have provided the constrained nanomorphologies of Bi$_2$X$_3$ (X = Se, Te) under different growth conditions. The nonstoichiometric chemical transformation was accomplished by the surface nucleation of the metal chalcogenides at the surface of the pure chalcogens or metals, detachment of the nuclei from the surface, and then attachment and reorganization of the nanocrystals into large single crystal nanoplates. This study also reports that the tendency to form 2D structures (high aspect ratio) depends on the chemical species of the metal chalcogenides, in the order of Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmate.

Experimental section, characterization, computational details, supplementary TEM and SEM images, EDX spectrum of intermediate compound, and equilibrium crystal structures (PDF)

**AUTHOR INFORMATION**

*Corresponding Authors*
*E-mail: aloysius.soon@yonsei.ac.kr.*
*E-mail: ujeong@postech.ac.kr.*

**ORCID**

Aloysius Soon: 0000-0002-6273-9324

Unyong Jeong: 0000-0002-7519-7595

**Author Contributions**

*G.P. and J.L. contributed equally to this work.*

**Notes**

The authors declare no competing financial interest.

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Supporting information

Eventual Chemical Transformation of Metals and Chalcogens into Metal Chalcogenide Nanoplates through a Surface Nucleation-Detachment-Reorganization Mechanism

Gyeongbae Park,† Jiwoo Lee,‡ Sungmin Moon,† Heeseung Yang,‡ Anupam Giri,† Junghyeok Kwak,† Young-Kwang Jung,‡ Aloysius Soon,*‡ Unyong Jeong*,†

†Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-Ro, Nam-gu, Pohang, 37673, Republic of Korea

‡Department of Materials Science and Engineering, Yonsei University, 50 Yonsei-Ro, Seodaemun-gu, Seoul 03722, Republic of Korea

* Address of correspondence: aloysius.soon@yonsei.ac.kr, ujeong@postech.ac.kr

# These authors contributed equally to this work.
Experimental section

Materials. The chemicals used in this study were selenium dioxide (SeO₂, 99.8%, Aldrich), selenous acid (H₂SeO₃, 99%, Aldrich), telluric acid (Te(OH)₆, 98%, Aldrich), sodium tellurite (Na₂TeO₃, 99%, Aldrich), bismuth nitrate (Bi(NO₃)₃·5H₂O, Aldrich), bismuth chloride (BiCl₃, ≥ 98%, Aldrich), antimony chloride (SbCl₃, ≥ 99.0%, Sigma-Aldrich), poly(vinyl pyrrolidone) (PVP, Mw ~ 55,000, Aldrich), sodium hydroxide (NaOH, 93~100%, Duksan), hydroxyl amine solution (NH₂OH, 50wt% in H₂O, Aldrich), β-cyclodextrin (≥ 97%, Sigma), L-ascorbic acid (reagent grade, Sigma), deionized water (DI water, 18.2MΩ, VIVAGEN EXL3 system), ethylene glycol (EG, > 99%, J. T. Baker), diethylene glycol (DEG, > 99%, Daejung), tetraethylene glycol (TEG, > 98%, Daejung), acetic acid (glacial) (≥ 99.5%, Daejung), ethanol (95%, Daejung), and acetone (≥ 99.5%, Daejung)

Synthesis of t-Se nanowires (NWs). We modified the procedure reported in a literature.¹ Selenium dioxide (0.5 g) and β-cyclodextrin (0.5 g) were dissolved in DI water (100 mL) for 10 min under magnetic stirring. The aqueous solution was added into a L-ascorbic acid aqueous solution (0.5 g in 100 mL of DI water) under continuous magnetic stirring at room temperature. The color of the mixture solution changed immediately from colorless to yellow, and gradually changed to red, indicating the nucleation of amorphous Se (α-Se). After 4 h, the solution was centrifuged at 10000 rpm for 5 min, and washed three times with DI water and ethanol. The precipitate was re-dispersed in ethanol (300 mL) and aged for 1 day without magnetic stirring. A color changed red to brick-red, indicating the growth of t-Se NWs. The t-Se NWs were collected by centrifuge (3500 rpm, 5 min) and washed with excess ethanol three times, and dried under vacuum at room temperature for 12 h. The Se NWs were dried and stored in inert environment (Ar gas) to prevent possible oxidation in the air.
Synthesis of thin t-Te NWs and thick t-Te nanorods (NRs). We followed the procedure in a literature.² Telluric acid (0.69 g), PVP (0.6 g), and sodium hydroxide (0.4 g) were dissolved in 50 mL of EG, separately. Those solutions were poured into a round-bottom flask at room temperature under magnetic stirring for 10 min. A hydroxyl amine aqueous solution (50 wt% in H₂O, 4.8 mL) was added to the mixture solution. The temperature of the solution was raised to 160 °C under nitrogen atmosphere. After reacting for 2 h, the solution was cooled in the air to room temperature. The precipitate was collected by centrifuge and washed three times with DI water and acetone. The product was dried under vacuum at 60 °C for 12 h. To obtain thick t-Te NRs, the thin t-Te NWs (38.28 mg) and NaOH (200 mg) were dispersed in EG (10 mL) and the temperature was raised to 195 °C. The thin t-Te NWs retracted to thick t-Te NRs. The resultant t-Te NRs were collected by centrifuge.

Synthesis of Bi microparticles (MPs). We modified the procedure in a literature.³ Bismuth nitrate powder (0.485 g) was added into sodium hydroxide aqueous solution (0.4 g in 40 mL of DI water) to form bismuth hydroxide. The product was collected by centrifuge (3500 rpm, 5 min) and washed several times with excess amount of DI water to remove residual sodium hydroxide. Then the white precipitate was dried under vacuum for 12 h. The dried bismuth hydroxide (1.04 g) was dispersed in TEG (200 mL) by ultrasonication. The solution was heated up to 285 °C under nitrogen atmosphere. While heating, the color gradually changed from milky white to dark gray, indicating the thermal decomposition of bismuth hydroxide and the formation of bismuth particles. After 4 h of reaction, the solution was cooled to room temperature in the air. The product was collected by centrifuge (12000 rpm, 10 min) and washed with DI water (100 mL) and ethanol (300 mL). The precipitate was dried under vacuum for 12 h.
Transformation of the $\tau$-Se NWs into Bi$_2$Se$_3$ nanoplates. The as-prepared $\tau$-Se NW powder (17 mg), PVP (150 mg), acetic acid (3.6 mL), and hydroxyl amine solution (0.36 mL) were introduced in EG (13.5 mL) in a round-bottom flask under magnetic stirring. The temperature of the solution was raised to 150 °C under nitrogen atmosphere. Bismuth nitrate solution (72 mg in 3mL of EG) was quickly injected into the solution. After injection, the color of the solution changed to dark brown, which indicates the nucleation of Bi$_2$Se$_3$. The reaction was stopped after 45 min by quenching the reaction temperature. The product was centrifuged (12000 rpm, 10 min) and washed three times with DI water (30 mL) and acetone (240 mL).

Transformation of the $\tau$-Te NWs into Bi$_2$Te$_3$ nanoplates. The as-prepared $\tau$-Te NW powder (38.28 mg), PVP (100 mg), sodium hydroxide (200 mg), and bismuth chloride (63 mg) were dissolved in 10 mL of DEG under magnetic stirring. Then the temperature of the solution was raised to 165 °C under nitrogen atmosphere. The color of the solution slowly changed from dark blue to black. After 24 h, the solution was cooled in the air. The product was centrifuged (12000 rpm, 10 min) and washed with DI water (20 mL) and acetone (160 mL).

Transformation of Synthesis of $\tau$-Te NRs into Sb$_2$Te$_3$ nanoplates. The as-prepared $\tau$-Te NR powder (38.28 mg), PVP (100 mg), sodium hydroxide (200 mg), and antimony chloride (45.6 mg) were fully dissolved in 10 mL of EG under magnetic stirring. The solution was heated to 195 °C under nitrogen atmosphere. The color of the solution gradually changed from gray to shiny gray. The reaction took 8 h to be completed. The suspension was cooled in the air. The product was centrifuged (12000 rpm, 10 min) and washed with DI water (20 mL) and acetone (160 mL).

Transformation of Bi MPs into Bi$_2$Se$_3$ and Bi$_2$Te$_3$ nanoplates. The dried Bi MPs powder (20.9 mg) and PVP (100 mg) were dispersed in DEG (5 mL). The solution was heated to 200 °C
(10 °C/min) under nitrogen atmosphere with continuous magnetic stirring. For the synthesis of Bi$_2$Se$_3$ nanoplates, a selenous acid solution (19.347 mg in 20 mL of DEG) was rapidly introduced through a syringe into the Bi MPs solution. The reaction was allowed to proceed for 12 h and cooled in the air. The product was centrifuged (10000 rpm, 5 min) and washed three times with DI water (60 mL) and acetone (480 mL). For the synthesis of Bi$_2$Te$_3$ nanoplates, a sodium tellurite solution (33.239 mg in 20 mL of DEG) was injected in the Bi particle solution. The other process was the same for the synthesis of Bi$_2$Se$_3$ nanoplates.

**Characterization.** The samples were analyzed by scanning electron microscopy (SEM, HITACHI S-4800), energy dispersive X-ray spectroscopy (EDX, HORIBA EMAX x-stream 2), transmission electron microscopy (TEM, JEOL JEM-2100F) operated at 200 kV, and X-ray diffraction (XRD, RIGAKU D/MAX-2500/PC) with Cu Kα radiation (λ = 0.1542 nm). The topologies of the samples were investigated with atomic force microscopy (AFM, BRUKER Nanoscope V).

**Computational details.** All calculations are performed using density-functional theory (DFT) for the bulk and surface properties of M$_2$X$_3$ (M = Bi, Sb and X = Se, Te) with the projector augmented wave (PAW)$^4$ method as implemented in Vienna *Ab initio* Simulation Package (VASP).$^5,6$ The generalized-gradient approximation (GGA) to exchange-correlation (xc) functional due to Perdew, Burke and Ernzerhof (PBE)$^7$ is used together with vdW corrections via the Grimme D2 scheme$^8$ (i.e. PBE + D2) to calculate all structural optimizations and surface energies. Agreeing well with experiments, it has been previously reported that the PBE + D2 approach provides an accurate description of the structural parameters for weakly bonded layered systems like Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$.$^9$
In this work, we have explicitly include the $5s^25p^3$ orbitals for Sb, the $5d^{10}6s^26p^3$ orbitals for Bi, the $4s^24p^4$ orbitals for Se, and the $5s^25p^4$ orbitals for Te as valence states in the PAW potentials. We have used a kinetic energy cutoff of 500 eV for the expansion of the Kohn Sham orbitals in a planewave basis, and the Brillouin-zone (BZ) integrations are performed using $k$-point Γ-centered grids of $12 \times 12 \times 1$, $4 \times 4 \times 1$, and $6 \times 3 \times 1$ for the (001), (015), and (110) surfaces, respectively. In addition, the slab models for each surface are constructed containing 25, 13, and 13 atomic layers for (001), (015), and (110), respectively. These are determined according to a previous theoretical report.\textsuperscript{10} The inner most 5, 3, and 3 atomic layers for (001), (015), and (110) are fixed in their bulk positions, accordingly with a vacuum region set to 15 Å to avoid the artificial interactions between repeating atomic slabs in the $z$-direction. Slab models with various surface cation and anion vacancies are also considered. We have relaxed all atomic structures until the total energies and forces do not change by more than $10^{-5}$ eV and $10^{-4}$ eV/Å, respectively.

The DFT-derived surface energies ($\gamma$) of the stoichiometric $M_2X_3$ compounds are calculated based on the equation as follows:

$$\gamma = \frac{1}{2A} \left( E^{\text{slab}} - N_{\text{f.u.}}^{\text{slab}} E^{\text{bulk}} \right),$$  

(S1)

where $E^{\text{slab}}$ is the total energy of the slab system, $N_{\text{f.u.}}^{\text{slab}}$ is the number of stoichiometric formula units in the slab system, $E^{\text{bulk}}$ is the total energy per formula unit of the bulk, and $A$ is the area of the surface. Based on these DFT-calculated surface energies (using eq S1), the equilibrium crystal shape (ECS) can be predicted via the Gibbs-Wulff theorem.\textsuperscript{11} Specifically, the ECSmorphologies are determined based on the summation of orientation-dependent surface energies with the aim at minimizing total energy of the crystal at a constant volume.
To calculate the surface energies under nonstoichiometric condition, we exploit the ab initio atomistic thermodynamics (aiAT) model. Based on this approach, environment-dependent surface energies, $\gamma(\mu_i)$ can be calculated as a function of the chemical potential of interest in the following manner,

$$
\gamma(\mu_i) = \frac{1}{A} \left[ G^\text{surf} - \sum_i N_i \mu_i(p_i, T) \right],
$$

where $G^\text{surf}$ is the Gibbs free energy of the surface, $N_i$ is the number of the species $i$, and $\mu_i$ is the chemical potential of the various species $i$ present in the system. In case of sufficiently large particles of $M_2X_3$ at ambient temperatures, bulk $M_2X_3$ could be considered as a thermodynamic reservoir where the surface is equilibrated. This assumption constrains the chemical potentials of $M$ and $X$ ($\mu_M$ and $\mu_X$) to the Gibbs free energy of $M_2X_3$ ($G^\text{bulk}_{M_2X_3}$) as defined by,

$$
G^\text{bulk}_{M_2X_3} = 2\mu_M + 3\mu_X.
$$

Consequently, eq S2 can be reformulated by eq S3 to express the surface free energy only as a function of $\mu_X$,

$$
\gamma(\mu_X) = \frac{1}{2A} \left[ G^\text{surf} - \frac{N_M}{2} G^\text{bulk}_{M_2X_3} - \left( N_X - \frac{3}{2} N_M \right) \mu_X \right].
$$

Here, the factor 1/2 is due to the use of our symmetric slab model. Thus, the thermodynamic stability of different surface orientations of $M_2X_3$ can be compared at a given chemical potential of $X$, using eq S4. In this work, we express the dependence of the surface energy on the change in the chemical potential of $X$. 
Figure S1. Time-dependent study of TEM images of aliquots extracted (A) in the middle of injection, and at (B) 1 min, (C) 5 min, and (D) 30 min after injection completed.

Figure S2. EDX spectrum and relative composition of Te-Bi compound nanoparticles shown in figure 1F.
**Figure S3.** EDX spectrum and relative composition of rough Te NWs containing Bi shown in figure 1F.

**Figure S4.** EDX spectrum and relative composition of Te NRs shown in figure 1J.

**Figure S5.** EDX spectrum and relative composition of Te-Sb compound nanoparticles shown in figure 1J.
Figure S6. DFT determined nanoplates exposing only the (001) and (015) facets for defect free (A) Bi$_2$Se$_3$, (B) Bi$_2$Te$_3$, and (C) Sb$_2$Te$_3$.

Figure S7. EDX spectrum taken at region 1 marked in figure 4B.
**Figure S8.** EDX spectrum taken at region 2 marked in **figure 4B**.

![EDX spectrum](image)

**Figure S9.** SEM image of Bi$_2$Te$_3$ nanoplates transformed from Bi MPs.

![SEM image](image)

**Figure S10.** AFM images and corresponding height profiles of (A) Bi$_2$Se$_3$ and (B) Bi$_2$Te$_3$ synthesized from Bi MPs.

![AFM images](image)

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