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Kinetically Controlling Phase Transformations of Crystalline Mercury Selenidostannates through Surfactant Media

Wei-Wei Xiong,[†] Pei-Zhou Li,[‡] Tian-Hua Zhou,[§] Alfred Iing Yoong Tok,[†] Rong Xu,[§] Yanli Zhao,[‡] and Qichun Zhang*,[†]

[†]School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

[‡]Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

[§]School of Chemical & Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore

Supporting Information

ABSTRACT: Herein we report the surfactant-thermal method to prepare two novel one-dimensional mercury selenidostannates, $[DBUH]_2[Hg_2Sn_2Se_6(Se_2)]$ (**1**) and $[DBUH]_2[Hg_2Sn_2Se_7]$ (**2**), where DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, by applying PEG-400 as the reaction medium. It is worth noting that **1** is kinetically stable and can be transformed into thermodynamically stable phase **2** under a longer reaction time. Our strategy "growing crystalline materials in surfactants" could open a new door to preparing novel crystals with diverse structures and interesting properties.

Crystalline chalcogenides play an important role in the advancement of materials science because of their diverse structures, interesting properties, and wide applications.[1] The preparation of crystalline chalcogenides can be conducted in various conditions such as high-temperature solid-state reaction, solution processes, and hydrothermal/solvothermal/ionthermal environments.[2−4] It has been demonstrated that synthetic conditions strongly affect the structures and spatial arrangement of chalcogenides.[2−4] Thus, developing a new method to synthesize crystalline chalcogenides should make a great contribution in this field.

Recently, we have already shown that crystalline arsenochalcogenides can be prepared under surfactant-thermal conditions.[5] The reason for our choice of surfactants as reaction media is that surfactants have several advantages such as low cost, high thermal stability, negligible vapor pressure, and multifunctional properties (e.g., neutral, cationic, anionic, zwitterionic, acidic, or basic). More importantly, the success of surfactants in controlling the shape, size, and pores of micro/nanostructures makes us believe that surfactants could be promising media to direct the growth of crystalline materials.[6]

Although we have already demonstrated the possibility of growing chalcogenides in surfactant media, there is still a long way to understanding (1) how surfactants control the growth of crystalline chalcogenides, (2) whether the growth of crystalline chalcogenides in surfactant media is a thermodynamic or kinetic process, and (3) whether surfactants can be trapped in the structures of crystalline chalcogenides. The curiosity surrounding these questions strongly stimulated us to increase exploration of surfactant-based media systems.

Chalcogenidostannates have been widely studied mostly because of their varied structures and particular properties such as adsorption, fluorescence, ion exchange, and semiconductivity.[7] Herein, we try to use chalcogenidostannates as a model system to give an answer to question 2 above: the growth of crystalline chalcogenides in surfactant media is kinetically controlled. By using poly(ethylene glycol)-400 (PEG-400) as the solvent, we obtained two novel one-dimensional (1D) mercury selenidostannates, namely, $[DBUH]_2[Hg_2Sn_2Se_6(Se_2)]$ (**1**) and $[DBUH]_2[Hg_2Sn_2Se_7]$ (**2**), where DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. The reason for our choice of PEG-400 is because (1) PEG-400 is a liquid at room temperature and has been widely used as a surfactant in materials science (nano and bulk) and medicine chemistry and (2) PEG has a lot of oxygen atoms, which should have a strong ability to bind with metal atoms.

In our further study, we found that **1** is kinetically stable and can be converted into the more stable phase **2** with a longer reaction time under the same conditions. It is worth noting that only **2** was observed at various reaction times when the surfactant was removed, indicating that surfactant PEG-400 can kinetically direct the formation of **1** at relatively short time.

Compounds **1** (red rod crystals; Figure 1a) and **2** (yellow block crystals; Figure 1a) were synthesized under the same reaction conditions by heating a mixture of $HgCl_2$, Sn, Se, DBU, H_2O, and PEG-400 at 160 °C, differentiated by the reaction time (4 days for **1** and 20 days for **2**). Subsequent investigation of this system with different times indicates that **1** can be gradually transformed into **2** (Figure 1a). By control of the reaction time in the range of 2−4 days, pure red rod crystals of **1** were obtained. If the reaction time was increased to 5−8 days, some small yellow block crystals of **2** were found on the surface of the red rod crystals of **1**, but compound **1** was still the main phase. If the reaction time was extended to 12 days, yellow block crystals of **2** became the main phase and a small amount of red rod crystals of **1** remained. If we continued to heat this reaction for 20 days, a pure phase of **2** was obtained. More interestingly, there was no **1** and only pure **2** (Figure 1a) in the reaction systems if PEG-400

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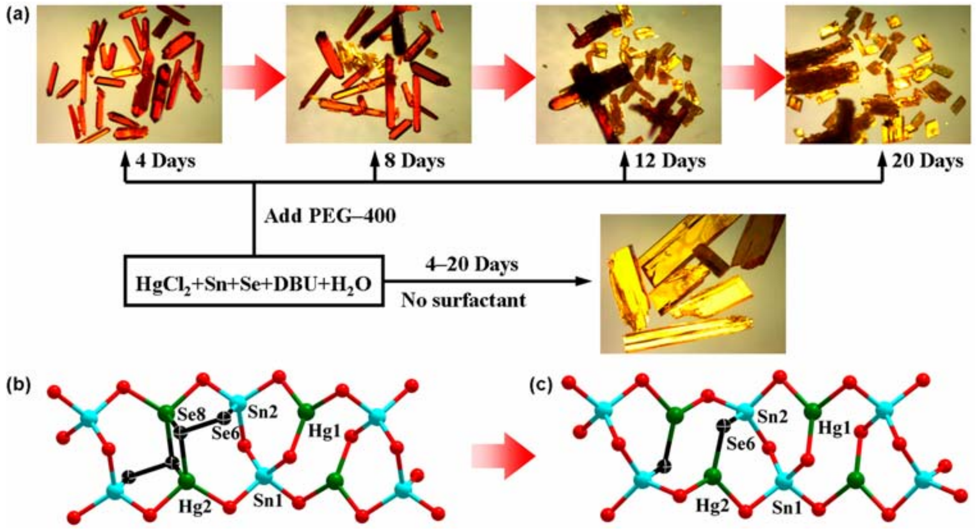

Figure 1. (a) With PEG-400 as the surfactant, a kinetically induced phase transformation was observed between **1** (red rod crystals) and **2** (yellow block crystals), while only **2** was obtained under the same reaction conditions without PEG-400. (b) View of the anionic $[Hg_2Sn_2Se_6(Se_2)]^{2-}$ ribbon of **1**. (c) View of the anionic $[Hg_2Sn_2Se_7]^{2-}$ ribbon of **2**.

was removed and the same reaction was performed under the same reaction conditions whatever the reaction time. Our results further confirmed that surfactants can kinetically control the growth of crystalline chalcogenides.

Single-crystal X-ray analysis revealed that compound **1** crystallizes in the space group $P2_1/c$ (Table S1 in the Supporting Information). Structural analysis indicates that **1** consists of 1D anionic $[Hg_2Sn_2Se_6(Se_2)]^{2-}$ ribbons, which are balanced by DBU cations (Figure 1b). The asymmetric unit of **1** has two crystallographically independent Hg^{2+} ions, two Sn^{4+} ions, six Se^{2-} ions, one Se_2^{2-} ion, and two $DBUH^+$ cations. Sn1 is coordinated with four Se^{2-} ions to generate a $[(Sn1)Se_4]$ tetrahedron, while Sn2 adopts a tetrahedral geometry by bonding to three Se^{2-} ions and one Se_2^{2-} ion to form a $[(Sn2)Se_3(Se_2)]$ unit. $[(Sn1)Se_4]$ and $[(Sn2)Se_3(Se_2)]$ are bridged together through one selenium to form a $[(Sn1)(Sn2)Se_6(Se_2)]$ unit. The Hg1 ion connects to three Se^{2-} ions to form a slightly distorted $[(Hg1)Se_3]$ trigonal plane, while the Hg2 ion tetrahedrally coordinates to two Se^{2-} ions and two Se_2^{2-} ions to produce a $[(Hg2)Se_2(Se_2)_2]$ unit. Pairs of such mercury units connect to each other via edge sharing to generate a $[(Hg2)_2Se_4(Se_2)_2]$ unit. The $[(Sn1)(Sn2)Se_6(Se_2)]$ unit connects to one $[(Hg2)_2Se_4(Se_2)_2]$ unit and two $[(Hg1)Se_3]$ trigonal planes in an opposite orientation by sharing Se^{2-} and Se_2^{2-} ions along the *a* axis and alternately forms an infinite $[Hg_2Sn_2Se_6(Se_2)]^{2-}$ anionic ribbon. The Se6−Se8 bond length is 2.356(2) Å, which is comparable with those reported in the literature.[1c,8]Single-crystal X-ray analysis reveals that compound **2** belongs to the space group $P\bar{1}$ (Table S1 in the Supporting Information) and contains 1D anionic $[Hg_2Sn_2Se_7]^{2-}$ ribbons and $DBUH^+$ cations. The asymmetric unit of **2** contains two crystallographically independent Hg^{2+} ions, two Sn^{4+} ions, seven Se^{2-} ions, and two $DBUH^+$ cations (Figure 1c). Tetrahedral $Sn1Se_4^{4-}$ and $Sn2Se_4^{4-}$ are connected together to form a $[(Sn1)(Sn2)Se_7]$ unit through corner sharing. Hg1 and Hg2 adopt a $[HgSe_3]$ trigonal-planar coordination geometry. The $[(Sn1)(Sn2)Se_7]$ unit links the adjacent $[(Hg1)Se_3]$ and $[(Hg2)Se_3]$ trigonal planes through the sharing of Se^{2-} ions to generate an infinite anionic $[Hg_2Sn_2Se_7]^{2-}$ ribbon along the *c* axis.

Accurate analysis of the differences in the structures of **1** and **2** is very helpful for us to understand why there is phase transition between them. As shown in Figure 1b,c, the structural difference in the inorganic ribbon between **1** and **2** is that **1** has Se_2^{2-} species while **2** only has Se^{2-} ions. Probably the Se···Se bond was not stable and decomposed to a Se^{2-} ion with longer heating in surfactant media. It is worth noting that a high reaction temperature (e.g., 190 °C) only gave **2** even a reaction time of 2 days. These results confirmed that **1** is kinetically stable while **2** is thermodynamically stable. The formation of a kinetically stable phase of **1** may attribute to the numerous oxygen atoms in the PEG chains, which have strong interaction with the metal center and confined the crystal growth of compound **1** in the PEG chains. In addition, the active oxygen atoms may have some interactions with Se_2^{2-} species via hydrogen bonds, which will result in the formation of kinetically stable **1**. With a prolonged reaction time, the crystals of **1** grew bigger (this tendency has been observed by controlling the reaction time in the ranges of 1−4 days), and then it would be difficult to confine the crystal growth within the PEG chains. Then the interactions between the oxygen atoms of the PEG chains and Se_2^{2-} species became weak, the Se_2^{2-} species decomposed to Se^{2-} ions, and this led to the formation of phase **2**.

When we replaced PEG-400 by using other kinds of surfactants, we found that suberic acid has an effect similar to that of PEG-400 to obtain compound **1** and observe the transformation from **1** to **2**, but the yields of **1** and **2** were significantly lower compared with those when PEG-400 was used as the surfactant. When using poly(vinylpyrrolidone) (PVP) as the surfactant, a very small amount of yellow crystals of **2** were obtained. Some other surfactants (such as oleylamine, tetradecylamine, and sodium dodecyl sulfate) have also been used under the same reaction conditions, but no crystals were obtained. It was worth noting that only yellow crystals of **2** could be obtained if PEG-400 and water were replaced by some conventional organic solvents such as *N*,*N*-dimethylformamide, methanol, and acetonitrile.

As shown in Figure 2, the optical absorption spectra of **1** and **2** exhibit sharp absorption edges at 2.17 and 2.43 eV, respectively, which are consistent with their colors. The band gap of **1** show a

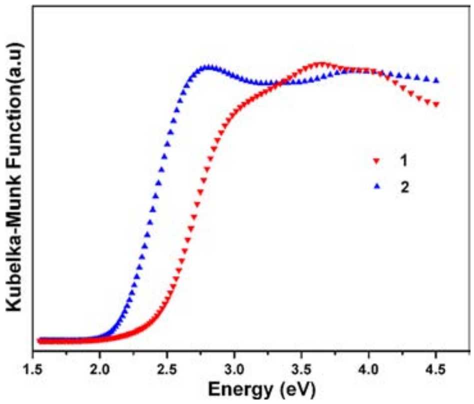

Figure 2. Solid-state optical absorption spectra of **1** and **2**.

red shift compared with that of **2** owing to their structural difference.

Thermogravimetric analysis (TGA) was used to examine the thermal stabilities of **1** and **2** in the range of 30−600 °C under a N_2 atmosphere (Figure S1 in the Supporting Information). Both TGA curves of **1** and **2** display only one main weight loss between 30 and 600 °C. Compound **1** undergoes a weight loss of 64.1% (theoretical value of 64.8%), corresponding to the loss of two DBU (19.3%), two HgSe (35.5%) and two Se (10.0%) per formula unit. Compound **2** exhibits a weight loss of 62.7% (theoretical value of 62.9%), which is attributed to the loss per formula unit of two DBU (20.3%), two HgSe (37.3%), and one Se (5.3%).

In summary, by using surfactants (PEG-400) as reaction media, two novel 1D mercury selenidostannates have been synthesized. Interestingly, **1** was found to be kinetically stable and could be converted into **2** under the same conditions with a longer treatment time. If the surfactant was removed and the reaction was performed under the same conditions, only **2** was obtained. Structural analysis of **1** and **2** makes us believe that Se···Se units play an important role in the phase transformation. The optical absorption spectra of **1** and **2** exhibit sharp absorption edges at 2.17 and 2.43 eV, respectively, which are consistent with their colors. Our research not only demonstrated that the surfactant-thermal condition is a promising method for synthesizing new crystalline chalcogenides but also confirmed that the growth of crystalline chalcogenides is kinetically controlled. We believe that our synthetic strategy could offer more chances to synthesize novel crystalline chalcogenides with various structures and interesting properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, powder X-ray diffraction patterns, TGA curves, perspective views of structures **1** and **2**, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: qczhang@ntu.edu.sg.

Notes

The authors declare no competing financial interest.

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