Syntheses, crystal structures and applications of novel crystalline metal chalcogenides

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**SYNTHESES, CRYSTAL STRUCTURES AND
APPLICATIONS OF NOVEL CRYSTALLINE METAL
CHALCOGENIDES**

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Nanyang Environment & Water Research Institute

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APPLICATIONS OF NOVEL CRYSTALLINE METAL
CHALCOGENIDES**

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Abstract

Crystalline metal chalcogenides have been a research focus in materials science for a long time due to their abundant structural chemistry and physicochemical properties in the field of photoelectric, ion-exchange, photocatalysis, nonlinear optics, and lithium/sodium-ion batteries (LIBs/SIBs). The chalcogenide chemistry has gained sustainable development by exploring new synthetic methods, designing novel structures and exploiting particular properties. In this dissertation, a series of novel metal chalcogenides have been successfully synthesized through a new synthetic strategy (namely the surfactant-thermal method) and fully characterized. Besides, their semiconductor photocatalytic properties and energy storage performances have been investigated respectively.

Two novel manganese thioantimonates, $[\text{MnSb}_2\text{S}_4(\text{N}_2\text{H}_4)_2]$ (**MAS-1**) and $[\text{Mn}(\text{tepa})\text{Sb}_6\text{S}_{10}]$ (**MAS-2**), and two new silver thioantimonates, $(\text{NH}_4)\text{AgSb}_4\text{S}_7 \cdot \text{H}_2\text{O}$ (**SAS-1**) and $(\text{NH}_4)\text{AgSb}_2\text{S}_4$ (**SAS-2**), have been prepared and used as efficient photocatalysts for crystal violet (CV) and rhodamine B (RhB) degradation. Two manganese thioantimonates possess neutral layered structure while two silver thioantimonates are constructed with ammonium ions acting as counterions and structure-directing agents. The optical band gaps are estimated to be ~ 1.97 eV for **MAS-1**, ~ 2.12 eV for **MAS-2**, ~ 1.70 eV for **SAS-1** and ~ 1.85 eV for **SAS-2**, bespeaking the semiconductor properties for visible light adsorption.

Three novel crystalline metal chalcogenides, $[\text{NH}(\text{CH}_3)_2][\text{Sb}_4\text{S}_5(\text{S}_3)]$ (**ASS**), $(\text{H}_3\text{O})_2(\text{enH}_2)\text{Cu}_8\text{Sn}_3\text{S}_{12}$ (**CTS**) and $(\text{NH}_4)\text{InSb}_2\text{S}_5\cdot\text{phen}$ (**IAS**), have been explored as anode materials for LIBs/SIBs. Compound **ASS** is constructed by one dimensional neutral ribbons and dimethylamine molecules are located in interchain space. Single crystal $(\text{H}_3\text{O})_2(\text{enH}_2)\text{Cu}_8\text{Sn}_3\text{S}_{12}$ (**CTS**) possesses an open framework, in which the interconnected micro-channels (diameter of 1 nm) overall distributed and both of H_2en^{2+} and H_3O^+ cations located in the micro-channels. **ASS** and **CTS** have been explored as electrode materials for LIBs. One attractive feature of $(\text{NH}_4)\text{InSb}_2\text{S}_5\cdot\text{phen}$ (**IAS**) is that NH_4^+ ions and *phen* molecules not only act as counterions but as structure-directing agents or templates. Molecular *phen* can act as both channels and reservoirs for reversible charging and discharging processes and accommodate the possible volume expansion during cycling. **IAS** has been explored as an anode material of LIBs and SIBs.

In summary, a family of novel crystalline metal chalcogenides have been exploited as photocatalysts for dye degradation and anode materials for LIBs/SIBs.

Contents

Acknowledgments.....	I
Abstract.....	III
Contents	V
Lists of Figures	IX
Lists of Tables	XV
Abbreviations	XVII
Chapter 1	1
Introduction.....	1
1.1 Background	1
1.1.1 Charming Properties of Crystalline Metal Chalcogenides.....	1
1.1.2 Applications of Crystalline Metal Chalcogenides.....	4
1.1.2.1 Applications in Dye Degradation.....	5
1.1.2.2 Application in Lithium/Sodium Storage	6
1.2 Objectives	8
1.3 Scope.....	10
1.4 Organization.....	11
Chapter 2.....	13
Synthetic Methods of Crystalline Metal Chalcogenides.....	13
2.1 High Temperature Solid-State Method	13
2.2 Hydro(solvo)thermal Method	14

2.3 Ionothermal Method.....	15
2.4 Surfactant-thermal Method	17
Chapter 3	27
Crystalline Metal Chalcogenides for Photocatalytic Degradation.....	27
3.1 Literature Review.....	27
3.2 Experimental Section	33
3.2.1 Syntheses.....	33
3.2.2 Single Crystal X-ray Crystallography.....	36
3.2.3 Photocatalysis	38
3.3 Fundamental Principles of Semiconductor Photocatalyst.....	39
3.4 Results and Discussion	41
3.4.1 Crystal Structure Analyses	41
3.4.2 Characterization	49
3.4.2.1 EDS Analyses.....	50
3.4.2.2 PXRD Analyses	50
3.4.2.3 Optical Properties.....	51
3.4.2.4 Thermal Analyses.....	53
3.5 Photocatalytic Activities	54
3.6 Summary.....	58
Chapter 4.....	61
Crystalline Metal Chalcogenides for Lithium/Sodium-ion Batteries	61

4.1 Literature Review.....	61
4.2 Experimental Section	65
4.2.1 Syntheses.....	66
4.2.2 Single Crystal X-ray Crystallography.....	67
4.3 ASS for Lithium Storage.....	68
4.3.1 Electrochemical Measurements	68
4.3.2 Crystal Structure Analysis.....	69
4.3.3 Characterization	72
4.3.4 Electrochemical Lithium Storage	74
4.3.5 Summary	76
4.4 CTS for Lithium Storage	77
4.4.1 Electrochemical Measurements	77
4.4.2 Crystal Structure Analysis.....	78
4.4.3 Characterization	80
4.4.4 Electrochemical Lithium Storage	82
4.4.5 Summary	86
4.5 IAS for Lithium/Sodium Storage.....	87
4.5.1 Electrochemical Measurements	87
4.5.2 Crystal Structure Analysis.....	88
4.5.3 Characterization	91
4.5.4 Electrochemical Lithium Storage	91

4.5.5 Electrochemical Sodium Storage	98
4.5.6 Summary	99
Chapter 5	101
Conclusions and Future Work	101
5.1 Conclusions	101
5.2 Future Work	103
Appendixes	105
Atomic Coordinates of As-prepared Compounds	105
Publications during Ph.D. Candidate	109
References	111

Lists of Figures

Figure 1.1. Wavelengths of solar energy transmitted and absorbed by the atmosphere.	6
Figure 1.2. A schematic illustration of the working principles of a C ₆ /LiCoO ₂ lithium-ion cell. During charge process, lithium ions diffuse from LiCoO ₂ structure (the cathode) into graphite (C ₆) structure (the anode) with concomitant redox of the two electrodes, respectively. The reverse process occurs during discharge.	7
Figure 2.1. Structure of the compound [Sb ₇ S ₈ Br ₂](AlCl ₄) ₃ . ⁶⁷	16
Figure 2.2. Surfactants used in the surfactant-thermal method for chalcogenides preparation.	18
Figure 2.3. (a) The discrete clusters (0D); (b) Anionic chains (1D); (c) Anionic layer (2D) and (d) Open framework (3D) of thioarsenates firstly obtained through surfactant-thermal method. ³⁶	19
Figure 2.4. (a) The anionic [Hg ₂ Sn ₂ Se ₆ (Se ₂)] ²⁻ ribbon of 1; (b) The anionic [Hg ₂ Sn ₂ Se ₇] ²⁻ ribbon of 2. ⁸⁶	20
Figure 2.5. (a) The nanochannels of inorganic layers are threaded by extended PEG chains; (b) The single PEG chain in [DBNH] ₂ [Sn ₃ Se ₇]·PEG. ³⁸	21

Figure 3.1. Schematic illustration of the fundamental principles of photocatalysis: (I) the generation of exciton by a photon; (II) the exciton recombination to liberate heat or light; (III) the reductive reaction conducted by a CB electron; (IV) the oxidative reaction conducted by a VB hole; (V) the further pollutants degradation to produce mineralization products; (VI) the trapping of a CB electron and (VII) a VB hole at the semiconductor surface. ¹³⁰	41
Figure 3.2. (a) Coordination environment of Mn^{2+} ion in compound MAS-1; (b) The $[\text{SbS}_2]_n^{n-}$ chain formed by $[\text{Sb}^{\text{III}}\text{S}_3]^{3-}$ clusters; (c) The 2D layered structure of compound MAS-1 viewed along the <i>c</i> -axis. H atoms are omitted for clarity.....	43
Figure 3.3. The layered structure of compound MAS-2 further stacks into a 3D structure through weak Mn–S interaction. The weak interaction between Mn-S2 [3.686(8) Å] is indicated as blue dashed lines. The disordered tepa molecules are not shown for clarity.	44
Figure 3.4. (a) The neutral layered structure $[\text{MnSb}_6\text{S}_{10}]$ in compound MAS-2 viewed along the <i>a</i> -axis; (b) the sizes of the 8-membered window and (c) the 24-membered window in MAS-2. H atoms are omitted for clarity.	45
Figure 3.5. (a) Asymmetric unit of compound SAS-1; (b) 24-membered ring labelled with the longest two-atom distance; (c) view of the open-framework architecture of SAS-1 along <i>a</i> axis with one 24-membered ring circled. H atoms are omitted for clarity.	47
Figure 3.6. (a) A packing view of compound SAS-2 along the <i>b</i> axis displaying the	

interlayer space where ammonium ions are located; (b) the $[\text{AgSb}_2\text{S}_5]_n^{3n-}$ ribbons and	
(c) 2D anionic layers $[\text{AgSb}_2\text{S}_4]_n^{n-}$. H atoms are omitted for clarity.....	49
Figure 3.7. The energy dispersive X-ray spectroscopy of (a) MAS-1; (b) MAS-2; (c)	
SAS-1 and (d) SAS-2.....	50
Figure 3.8. PXRD patterns of compound (a) MAS-1; (b) MAS-2; (c) SAS-1 and (d)	
SAS-2.....	51
Figure 3.9. Solid-state optical absorption spectra of compounds (a) MAS-1; (b) MAS-	
2; (c) SAS-1 and (d) SAS-2. Insets in (a) to (d) are the photographs of crystals of MAS-	
1, MAS-2, SAS-1 and (d) SAS-2, respectively.....	52
Figure 3.10. TGA curves for compounds (a) MAS-1; (b) MAS-2; (c) SAS-1 and (d)	
SAS-2.....	54
Figure 3.11. Photocatalytic degradation of CV over compounds (a) MAS-1; (b) MAS-	
2; (c) SAS-1 and (d) SAS-2 monitored as the normalized change in concentration as a	
function of illumination time. The insets in (a) to (d) showed the temporal changes of	
CV solutions.....	55
Figure 3.12. PXRD patterns of compounds (a) MAS-1; (b) MAS-2; (c) SAS-1 and (d)	
SAS-2 before and after the CV photodegradation.	56
Figure 3.13. Photocatalytic degradation of RhB over compounds (a) MAS-1; (b) MAS-	
2; (c) SAS-1 and (d) SAS-2 monitored as the normalized change in concentration as a	
function of illumination time. The insets in (a) to (d) showed the temporal changes of	
RhB solutions.....	57

Figure 3.14. PXRD patterns of compounds (a) MAS-1; (b) MAS-2; (c) SAS-1 and (d) SAS-2 before and after the RhB photodegradation.	58
Figure 4.1. (a) Asymmetric unit of compound ASS; (b) alternately arranged two rings, $[\text{Sb}_3\text{S}_3]$ and $[\text{Sb}(\text{S}_3)]$; (c) view of the infinite $[\text{Sb}_4\text{S}_5(\text{S}_3)]_n$ chains and dimethylamine molecules along the a -axis.....	70
Figure 4.2. The pseudo-2D network of ASS viewed along the b direction. H-bonding interactions are shown in dotted lines.	71
Figure 4.3. Packing diagram of ASS viewed along the c direction. H-bonding interactions are shown in dotted lines.	71
Figure 4.4. Characterization of compound ASS. (a) XRD pattern; (b) SEM image of the as-obtained crystalline product; (c) SEM image of grinding product (the inset is a typical TEM image); (d) SAED pattern.....	73
Figure 4.5. TGA curve for compound ASS.....	73
Figure 4.6. (a) AFM scans of $[\text{NH}(\text{CH}_3)_2][\text{Sb}_4\text{S}_5(\text{S}_3)]$ nanosheets; (b) the corresponding cross-sectional thickness.	74
Figure 4.7. Electrochemical characterization of ASS anode. (a) Cyclic voltammograms between 0.01 and 3.0 V measured at a scan rate of 0.1 mV s^{-1} ; (b) the charge and discharge curves at a current density of 0.1 A g^{-1} ; (c) the charge-discharge curves at different current densities; (d) rate performance at different rates; (e) capacity as a function of cycle numbers at a current density of 0.1 A g^{-1}	76

Figure 4.8. Icosahedral $[\text{Cu}_8\text{S}_{12}]^{16-}$ cluster and its connectivity with six Sn^{4+} ions: (a) Ball and stick mode and (b) polyhedral mode.	79
Figure 4.9. View of the 3D Cu–Sn–S framework along bc direction	80
Figure 4.10. Characterization of CTS. (a) SEM image; (b) XRD pattern; (c) High-resolution TEM image; (d) SAED pattern.	81
Figure 4.11. TGA curve for compound CTS.....	82
Figure 4.12. Electrochemical characterization of CTS anode. (a) Cyclic voltammograms between 0.01 and 3.0 V measured at a scan rate of 0.1 mV s^{-1} ; (b) the charge and discharge curves of CTS at a current density of 0.1 A g^{-1} ; (c) rate performance at different rates; (d) Nyquist plots of CTS electrode before and after cycles, respectively. The inset is the equivalent circuit; (e) capacity as a function of cycle numbers at a current density of 0.1 A g^{-1}	86
Figure 4.13. (a) Asymmetric unit of IAS with labelled bond lengths of Sb–S and In–S; (b) the coordination of In atom and (c) Sb atom.....	89
Figure 4.14. View of the (a) 1D ribbon $[\text{InS}_4]_n^{5n-}$; (b) 2D layer $[\text{InSb}_2\text{S}_5]_n^{n-}$ and (c) double-layer $[\text{Sb}_2\text{S}_5]_n^{4n-}$ of IAS.	90
Figure 4.15. Stacking diagram of IAS viewed along a direction.....	90
Figure 4.16. (a) PXRD patterns of compound IAS; (b) TGA curve of IAS.	91
Figure 4.17. Electrochemical performance of IAS as anodes for LIBs. (a) CV profiles during the initial three cycles between 3.0 and 0.0 V at 0.2 mV/s . (b) Charge-discharge curves during the initial three cycles at 143 mAh g^{-1} . (c) Cycling performance and	

corresponding Coulombic efficiencies (CEs) at 143 mAh g ⁻¹ . (d) Rate performance and CEs at various current densities from 143 mA g ⁻¹ to 3.57 A g ⁻¹	95
Figure 4.18. Ultra-long cycling of IAS as anodes for LIBs. (a) Cycling and corresponding CEs of IAS at 2.5 A g ⁻¹ for 1000 cycles. (b) Voltage vs. time profiles of IAS at the 11 th . (c) Voltage vs. time profiles of IAS at the 1000 th	97
Figure 4.19. EIS profiles for IAS as an anode for LIBs.	98
Figure 4.20. (a) Electrochemical performance of IAS as anodes for SIBs. (a) Charge- discharge curves during the initial three cycles at 50 mAh g ⁻¹ . (b) Cycling performance and corresponding CEs at 50 mAh g ⁻¹ . (c) Long-term cycling and corresponding CEs at 143 mAh g ⁻¹	99

Lists of Tables

Table 2.1. Summary of crystalline metal chalcogenides prepared through surfactant-thermal method	22
Table 2.2. Summary of metal-organic frameworks and metal bromides prepared through surfactant-thermal method	23
Table 2.3. The advantages and disadvantages of different synthetic methods to prepare metal chalcogenides	24
Table 3.1. Summary of metal chalcogenide nanocrystals as photocatalysts for organic pollutants degradation	28
Table 3.2. Summary of crystalline metal chalcogenides as photocatalysts for organic pollutants degradation	32
Table 3.3. Crystallographic data and structure refinements for compounds MAS-1 and MAS-2.....	37
Table 3.4. Crystallographic data and structure refinements for compounds ASS-1 and SAS-2	38
Table 4.1. A survey of electrochemical properties of Tin-based materials for LIBs.....	63
Table 4.2. A survey of electrochemical properties of sulfides for LIBs.....	64
Table 4.3. Crystallographic data and structure refinements for compounds ASS, CTS and IAS	68

Table A1. Atomic coordinates and displacement parameters of non-hydrogen atoms for MAS-1.....	105
Table A2. Atomic coordinates and displacement parameters of non-hydrogen atoms for MAS-2.....	105
Table A3. Atomic coordinates and displacement parameters of non-hydrogen atoms for SAS-1	105
Table A4. Atomic coordinates and displacement parameters of non-hydrogen atoms for SAS-2	106
Table A5. Atomic coordinates and displacement parameters of non-hydrogen atoms for ASS	106
Table A6. Atomic coordinates and displacement parameters of non-hydrogen atoms for CTS	107
Table A7. Atomic coordinates and displacement parameters of non-hydrogen atoms for IAS	107

Abbreviations

LIBs	Lithium Ion Batteries
SIBs	Sodium Ion Batteries
UV-Vis	Ultraviolet-Visible
IR	Infrared
ILs	Ionic Liquids
MOFs	Metal-Organic Frameworks
0D	Zero Dimensional
1D	One Dimensional
2D	Two Dimensional
3D	Three Dimensional
TM	Transition Metal
SBUs	Secondary Building Units
CV	Crystal Violet
RhB	Rhodamine B
MO	Methyl Orange
MB	Methylene Blue
MG	Malachite Green
Rh6G	Rhodamine 6G
CR	Congo Red
PVP	Polyvinylpyrrolidone

PEG-400	Polyethylene Glycol-400
[HMIM]Cl	1-Hexadecyl-3-Methylimidazolium Chloride
[HTBP]Br	Hexadecyltributylphosphonium Bromide
SDS	Sodium Dodecyl Sulfate
NA	Nonanoic Acid
OA	Octanoic Acid
EA	Elemental Analysis
SCXRD	Single Crystal X-ray Diffraction
PXRD	Powder X-ray Diffraction
EDS	Energy Dispersive X-ray Spectroscopy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
AFM	Atomic Force Microscopy
TGA	Thermogravimetric Analysis
SAED	Selected-Area Electron Diffraction

Chapter 1

Introduction

1.1 Background

1.1.1 Charming Properties of Crystalline Metal Chalcogenides

Crystalline metal chalcogenides possess fascinating structures and versatile physical and chemical properties, which enable potential applications in the fields of photocatalysis,¹⁻⁹ ion-exchange,¹⁰⁻²¹ nonlinear optics,²²⁻²⁴ and lithium/sodium-ion batteries (LIBs/SIBs),^{25, 26} etc. Compared with traditional metal oxides, metal chalcogenides have narrower optical band gaps and show different semiconductor properties. The crystalline metal chalcogenides with noncentrosymmetric structures can show second harmonic generation nonlinear optical response in infrared (IR) region, such as AgGaS₂ and AgGaSe₂. While nonlinear oxides, e.g. LiB₃O₅ (LBO), KTiOPO₄ (KTP), and β -BaB₂O₄ (BBO), are more suitable to UV-Vis and near-IR regions of the spectrum.²⁷ Crystalline metal chalcogenides could be used as efficient photocatalysts for toxic and colored wastewater treatment.²⁸ For example, nanorod Sb₂S₃ was used as a photocatalyst for methyl orange (MO) decomposition under visible light illumination and the photodegradation ratio was up to 97% after irradiated for 50 min.²⁹ The microporous metal chalcogenides not only can work as molecular sieves for catalysis, ion-exchange and adsorption, but also possess the semiconductor properties used as LIBs/SIBs anode materials.³⁰ For instance, microporous metal chalcogenides show high ion-exchange

ability and selectivity for heavy metal ions and alkali or alkaline-earth metal ions, which can be applied to the disposal of nuclear waste, separation of heavy metal ions and purification of drinking water. A series of crystalline germanium- or tin-rich zeolite like chalcogenides with greatly improved thermal and chemical stability have been investigated for multiple applications. Among them, highly stable CPM-120-ZnGeS can function as a robust photocatalyst for water splitting to generate H_2 under UV-Vis light irradiation. In the presence of Na_2S - Na_2SO_3 as sacrificial agents, the overall activity of H_2 production is as high as $2\text{ mmol h}^{-1}\text{ g}^{-1}$ and the catalytic activity keeps undiminished under illumination as long as 200 h. Furthermore, CPM-120-ZnGeS is also utilized for ion-exchange with diverse metal or complex cations, fast ion conductivity, and photoelectric response.⁷ Recently, crystalline metal chalcogenides are explored as anode materials for LIBs, which presents outstanding electrochemical performance and good cycling properties.²⁵ Crystalline metal chalcogenides also contribute to clean energy system, with the prospect of exploring the adaptability of such materials to industrial applications. Therefore, there is a compelling need to prepare more new metal chalcogenides with highly chemical stability and explore their potential applications.

The coordination modes between metal ions and chalcogen Q^{2-} ($Q = S, Se, Te$) or polychalcogen ions Q_n^{2-} are multifarious, which will be affected by the species and valences of metal ions. Therefore, the crystalline metal chalcogenides possess versatile architectures and interesting physicochemical properties. In addition, multiple ways to develop new synthetic methods provide favorable conditions to obtain metal

chalcogenides with novel structures and good performance. There are a variety of methods to synthesize metal chalcogenides, such as high temperature solid-state process,³¹ hydro(solvo)thermal synthesis,³² ionothermal method and surfactant-thermal strategy.³³ The high temperature solid-state method is suitable to prepare inorganic chalcogenides with alkali metals or alkaline-earth metals as cations. This method demands high thermal activation and usually the reaction temperature is higher than 800 °C. Hydro(solvo)thermal synthesis is a much milder and softer synthetic method by employing polar solvents as reaction media at a relatively low temperature ($T < 200\text{ }^{\circ}\text{C}$)^{34, 35} while ionothermal synthesis uses ionic liquids (ILs) as reaction media, where ILs are one kind of molten salts with melting points below 100 °C. However, ionothermal method is limited by the categories and expensive prices of ILs. Different from hydro(solvo)thermal and ionothermal synthesis, surfactant-thermal method employs surfactants as reaction media. Surfactants possess some unique characteristics, such as cheaper price and multifunctional properties (e.g., cationic, anionic, neutral, acidic or basic). In 2013, Zhang QC et al. firstly used the surfactant-thermal method and successfully synthesized a series of new thioarsenates ranging from zero dimensional (0D) cluster to three dimensional (3D) framework.³⁶ Since then, more and more novel metal chalcogenides possessing diverse structures and interesting properties have been obtained through the surfactant-thermal method. In addition, this method has also been successfully applied to synthesize novel metal-organic frameworks (MOFs).³⁷ Recent studies demonstrate that surfactants can not only serve as promising reaction media to

improve the crystal quality and quantity but also act as templates in the formation of chalcogenide frameworks.³⁸ This dissertation will utilize the surfactant-thermal strategy to conduct the syntheses of new crystalline metal chalcogenides.

1.1.2 Applications of Crystalline Metal Chalcogenides

Owing to their fascinating architectures, multiple compositions and abundant physicochemical properties, crystalline metal chalcogenides have shown potential applications, especially in aqueous organic pollutants degradation and lithium/sodium storage. Among the causes of water pollution, the emitting of organic pollutants and radioactive substances not only breaks the ecological balance, but also affects people's normal life to a large extent. Therefore, access to fast and feasible method to eliminate the pollutants is of inevitable significance. One economical and efficient way for the elimination of organic pollutants is photocatalytic degradation, which has attracted extensive research interests in recent decades. Crystalline metal chalcogenides with narrower optical band gaps, adapting to visible light adsorption, are good candidates for photocatalytic degradation of aqueous organic pollutants.

For the applications in LIBs and SIBs, although nanomaterials can provide unique properties as effective electrode materials, tedious synthesis and modification procedures are required to produce such nanostructures.³⁹ Besides, the storage stability of Sb/Sn-based materials often becomes worse with dozens of cycles, which is similar to those high energy-density anode alloy materials (e.g. silicon and germanium).⁴⁰⁻⁴⁴

This common phenomenon, frequently observed in conventional inorganic materials, is believed to be resulted from the large volume expansion and pulverization due to mechanical degradation of these electrode materials, especially at high current densities.⁴² In view of these limitations, it is essentially important to develop novel and easy-preparing negative electrode materials with good electrochemical performance. Crystalline metal chalcogenides with various structures and compositions provide great choice as superior electrode materials for high-performance lithium/sodium storage. This dissertation will focus on the syntheses of novel crystalline metal chalcogenides and the investigation of their applications in dye degradation, LIBs and SIBs.

1.1.2.1 Applications in Dye Degradation

Photocatalysis is defined as a process in which the catalysts absorb photons, whose energy is equal or large than the band gap of catalysts, to create energetic electrons and holes, which can initiate redox reactions. In 1972, the photocatalytic water splitting on TiO₂ electrodes was firstly discovered.⁴⁵ And then, photocatalytic processes, including water splitting and aqueous pollutants degradation, have been studied for decades and developed into a multidisciplinary research topic in the domain of semiconductors. As we all know, the optical band gaps of most metal oxides are wide and only correspond to ultraviolet (UV) light adsorption. Fig. 1.1 shows the wavelengths of solar energy transmitted and absorbed by the atmosphere, of which the UV light only occupies 5% while the visible light accounts for as high as 43%. Therefore, it is essentially indispensable to develop semiconductor photocatalysts according to visible light

adsorption.

Figure 1.1. Wavelengths of solar energy transmitted and absorbed by the atmosphere.

Compared with traditional oxides, sulfides possess narrower optical band gaps for visible light adsorption. Different from sulfide nanomaterials, crystalline metal chalcogenides show various architectures that range from 0D clusters to 3D open frameworks. Moreover, the integration of transition metal (TM) ions into the crystalline metal chalcogenides will construct more secondary building units (SBUs) that will enrich both of the structural diversities and physicochemical properties of crystalline metal chalcogenides. Thus, crystalline metal chalcogenides have great potential to be used as efficient photocatalysts for organic pollutants degradation.

1.1.2.2 Application in Lithium/Sodium Storage

Lithium/sodium-ion battery (LIB/SIB) is a type of rechargeable battery, in which lithium/sodium ions move from the positive electrode to the negative electrode during charge and back when discharging.

Figure 1.2. A schematic illustration of the working principles of a $C_6/LiCoO_2$ lithium-ion cell. During charge process, lithium ions diffuse from $LiCoO_2$ structure (the cathode) into graphite (C_6) structure (the anode) with concomitant redox of the two electrodes, respectively. The reverse process occurs during discharge.

Compared with metallic lithium used in a non-rechargeable lithium battery, LIBs use an intercalated lithium compound as one electrode material. The electrolyte that allows for ionic movement, and the two electrodes are the constituent components of a lithium-ion cell. During charge and discharge processes, lithium ions shuttle reversibly between two electrodes, as shown in Fig. 1.2. In SIBs, sodium ions act as charge carriers.

However, the application of LIBs and SIBs has been mostly confined by the poor cycling life and severe pulverization due to high volume expansion/contraction as well as the large irreversible capacity during the repeated lithiation and delithiation process. Hence, it is urgent to explore novel anode materials with high reversibility, good rate capability and long cycling stability. Tin and antimony-based materials have been regarded as the most attractive candidates of anode materials for LIBs with a higher capacity compared with that of the commercially-available graphite electrode.⁴⁶⁻⁴⁸ Among them, thiostannates and thioantimonates have attracted great attention owing to their high theoretical capacity, natural abundance and low toxicity.⁴⁹⁻⁵¹ Especially, crystalline metal thiostannates and thioantimonates with small molecules as structure-directing agents are potential candidates to be developed as superior anode materials for LIBs and SIBs.

1.2 Objectives

- The first objective of this dissertation is to synthesize a series of novel crystalline metal chalcogenides through surfactant-thermal method.

Crystalline metal chalcogenides are always closely investigated attributing to their fascinating structures and abundant properties. Generally, the physical properties of metal chalcogenides are mainly dependent on their structures and compositions. Due to the presence of stereochemically active lone electron pairs, Sb(III) ions prefer to adopt asymmetric coordination geometries $\text{Sb}^{\text{III}}\text{S}_n$ ($n=3-5$). These asymmetric geometries

usually undergo self-condensation by vertex or/and edge sharing S atoms to form condensed polyanions, so the binary thioantimonates present various architectures. Moreover, the incorporation of TM ions into the binary thioantimonates moieties will construct more SBUs that not only enrich the structural diversities but also integrate the physicochemical properties of TM ions. A series of novel crystalline thioantimonates will be synthesized and fully characterized with common physical and chemical strategies.

- The second objective is to test the photocatalytic degradation properties with as-prepared novel thioantimonates as efficient photocatalysts.

Crystal violet (CV) and rhodamine B (RhB), which are found to be highly cytotoxic and refractory fluorescein dyes for humans, were chosen as model pollutants to evaluate the photocatalytic activities of the as-prepared thioantimonates. Compared with metal oxides, metal thioantimonates possess narrower optical band gaps suitable for visible light absorption. The pure phase of each compound will be carefully prepared and then used as efficient photocatalysts to investigate their photodegradation performance.

- The third objective is to explore lithium/sodium storage properties with as-prepared novel crystalline metal chalcogenides as anode materials.

Crystalline metal chalcogenides with small molecules acting as structure-directing agents are great candidate for highly-performed lithium/sodium storage. The small molecules are usually located in the channels or interlayer space, which could

accommodate the possible volume expansion during cycling. Additionally, the heterocyclic organic molecules can act as both channels and reservoirs for reversible lithiation and delithiation.

1.3 Scope

In this dissertation, novel crystalline metal chalcogenides will be synthesized through surfactant-thermal strategy and different TM ions will be integrated to enrich structural diversities and physicochemical properties. All the syntheses will start from commercially available reagents and crystalline metal chalcogenides will be prepared using autoclaves.

Physical and chemical characterizations will be carried out after the syntheses of crystalline chalcogenides. SCXRD will be used to analyze the crystal structure. PXRD will be used for phase analysis. SEM equipped with EDS will be applied to observe the crystal morphologies and confirm the contents of sulfur and metallic elements. TEM is utilized to observe sample crystallinity. EA will be used to confirm the contents of C, N and H. The solid-state UV-Vis diffuse-reflectance spectrum will be utilized to analyze the optical band gap. TGA will be used to study the thermal stability and verify the contents of C, N and H.

All the photocatalytic experiments will be investigated in Pyrex glass cell containing a quartz window and the light source is a 300 W Xe lamp (Newport) with a long-pass cut-off filter ($\lambda > 420$ nm). The photocatalyst will be dispersed in an aqueous solution of

organic dye. The degradation efficiency is defined as C/C_0 , where C is the remnant absorption of organic dye at each irradiated time interval and C_0 is the initial absorption when the adsorption/desorption equilibrium is achieved. The organic dye absorption will be analyzed on a UV-Vis spectrometer and the standard curve will be established before the test.

The as-prepared crystalline samples will be grinded for several minutes before used. Working electrode will be prepared by mixing grinded sample with carbon black/carbon nanotubes (CNTs) and polyvinylidene fluoride (PVDF) as the binder in a weight ratio of 7:2:1 in N-methyl-2-pyrrolidinone (NMP) solvent. The electrochemical measurements are carried out using two-electrode coin cells with pure lithium foil/sodium metals as both the counter and the reference electrodes at room temperature. The coin cells will be assembled in an Ar-filled glove box with concentrations of moisture and oxygen below 0.1 ppm. The charge-discharge tests will be performed with a NEWARE battery tester.

1.4 Organization

This dissertation is organized in the following structure:

Chapter 2 provides literature review on the preparation methods of crystalline metal chalcogenides, and the comparison of advantages and disadvantages among different synthetic methods;

Chapter 3 presents the syntheses, crystal structures and characterizations of four novel

crystalline metal chalcogenides that are used as photocatalysts for dye degradation under visible light irradiation;

Chapter 4 presents the syntheses, crystal structures and characterizations of three novel crystalline metal chalcogenides that are explored as anode materials for rechargeable LIBs and SIBs.

Chapter 5 gives the conclusions and outlook.

Chapter 2

Synthetic Methods of Crystalline Metal Chalcogenides

In the preparation of metal chalcogenides, different synthetic methods have demonstrated to affect their structures and properties. The high temperature solid-state method is adopted to prepare metal chalcogenides with high-density.³¹ In 1989, R.L. Bedard et al. firstly utilized the hydro(solvo)thermal method and successfully synthesized a series of microporous germanium(IV) and tin(IV) sulfides with organic amines as structure-directing agents.³² After that, hydro(solvo)thermal method has been widely used to prepare metal chalcogenides and lots of new compounds with novel structures and potential applications are obtained. In the past years, the ionothermal method has been used to prepare binary metal chalcogenide nanocrystals, crystalline open-framework selenidostannates and discrete supertetrahedral clusters. Recently, another new method, the surfactant-thermal method has been applied to synthesize metal chalcogenides and a series of chalcogenides with novel architectures and interesting properties have been prepared. However, the surfactant-thermal method is still in its infancy and will no doubt go further.

2.1 High Temperature Solid-State Method

The diffusion coefficients in solids are very low (in the order of $10^{-12} \text{ cm}^2 \text{ s}^{-1}$), so the traditional solid-state synthesis requires high thermal activation to meet the solid-state diffusion. In this method, the reactants will be measured out in a specific ratio according

to the target product and heated to high temperatures. In solid-state synthesis, the chemical reaction will proceed on the phase interface of reactants to form product layer by thermal conduction, and the reactants need to get through the product layer for interdiffusion to conduct the further reaction. Therefore, to overcome the diffusion resistance, the reaction temperature is usually required to be higher than 600 °C and then reaction can be continued. The crystalline metal chalcogenides prepared through this method are thermodynamically stable with high density and high symmetry.^{31, 52, 53}

2.2 Hydro(solvo)thermal Method

The hydro(solvo)thermal method is usually conducted in polar solvents, such as water, ethanol and organic amines, and the reaction temperature is normally lower than 200 °C that represents a softer and milder synthetic strategy.³⁴ Under the hydro(solvo)thermal condition, water or organic solvents are in critical or supercritical state and the activation of reactants will be increased, which will lead to some intermediate state and metastable state products. The mild reaction environment of hydro(solvo)thermal synthesis makes it possible to prepare open-framework metal chalcogenides with organic solvents as templates or structure-directing agents. Firstly, H. Schafer and W.S. Sheldrick et al. synthesized a series of group 14 and 15 metal chalcogenides with alkali metals as cations using the hydro(solvo)thermal method.⁵⁴⁻⁵⁷ And then M.G. Kanatzidis et al. started the preparation of transition metal chalcogenides.^{58, 59} Subsequently, hydro(solvo)thermal method has been widely used to prepare metal chalcogenides and a large amount of compounds with various structures were obtained.⁶⁰ For example, P.Y. Feng et al.

successfully synthesized open-framework metal chalcogenides constructed with tetrahedral clusters as secondary building units under hydro(solvo)thermal condition.⁶¹ Additionally, the extended inorganic-organic hybrid chalcogenides constructed by linking organic ligands to tetrahedral chalcogenide clusters can also be synthesized under hydro(solvo)thermal conditions.⁶³ J. Dai et al. have discussed the effects of organic chelating amines on the synthesis of metal chalcogenides based on group 13-15 metals.⁶⁴

2.3 Ionothermal Method

Due to the high solubility of ionic liquids, in recent years, ionothermal method has been regarded as a popular way to synthesize crystalline materials. The ionic liquids have many unique properties, such as low vapor pressure, less volatile, excellent thermal stability, wide liquid regions and favorable solvating properties for a range of polar and non-polar compounds, which have received wide attention and are accepted as “green solvents”. Especially, the ionothermal method has been successfully applied to the preparation of metal-organic frameworks and molecular sieves, and a lot of compounds with novel structures and excellent performance were obtained. For the preparation of metal chalcogenides, ionothermal method is mainly used to synthesize binary metal sulfide nanomaterials while the preparation of new metal chalcogenides with ionic liquids as cations is less reported. In 2005, Y.J. Zhu et al. firstly obtained the rod-like nanomaterials of Sb_2S_3 and Bi_2S_3 with $[\text{BMIM}][\text{BF}_4]$ as a solvent.⁶⁵ Using the same ionic liquid as reaction medium, S.H. Yu et al. synthesized various morphologies of

Bi₂S₃ nanophase by changing the reaction time, temperature and pH value.⁶⁶ In 2009, M.G. Kanatzidis et al. obtained the first cationic chalcogenide [Sb₇S₈Br₂](AlCl₄)₃ (Fig. 2.1) through ionothermal method, of which the cation consists of double-cubane cluster.⁶⁷ Thereafter, his group got 2D layered metal chalcogenides halide [Sb₂Te₂Br](AlCl₄) and [Bi₂Te₂Br](AlCl₄).⁶⁸ Subsequently, other groups also started the research on ionothermal method and obtained a series of novel crystalline metal chalcogenides.^{69, 70} X.Y. Huang et al. successfully synthesized a series of crystalline microporous selenidostannates and four largest discrete supertetrahedral (T5) cluster compounds based on Cu-Ga/In-S.⁷¹⁻⁷⁸

Figure 2.1. Structure of the compound [Sb₇S₈Br₂](AlCl₄)₃.⁶⁷

2.4 Surfactant-thermal Method

Apart from traditional methods for the synthesis of crystalline metal chalcogenides, the surfactant-thermal method, one novel synthetic method, has been applied to prepare novel crystalline metal chalcogenides in recent years. Surfactants, consisting of both hydrophilic and hydrophobic groups, can lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. Surfactants have been extensively adopted in the preparation of nanocrystals or mesoporous materials. It is known that surfactants are recognized as soft templates in tailoring the shapes, sizes, and surface properties of nanoparticles. Additionally, surfactants can also be used to control the pore sizes and phases of mesoporous compounds.⁷⁹⁻⁸¹ Actually, in addition to the same characteristics as ionic liquids, surfactants also possess some unique properties, such as the low price and multifunctional properties (e.g. neutral, cationic, anionic, basic and acidic). Therefore, surfactants can act as promising reaction media to grow novel crystalline materials with multifarious architectures and interesting properties (Fig. 2.2). In 2013, our group firstly used surfactants as reaction media in the preparation of crystalline chalcogenidoarsenates with structures ranging from 0D cluster to 3D open framework.³⁶ In constant study and trial, we found that surfactant-thermal method can also be used to prepare metal-organic frameworks, crystalline oxochalcogenide and metal halides.^{37, 82-85}

Figure 2.2. Surfactants used in the surfactant-thermal method for chalcogenides preparation.

In our preliminary study, two nonionic surfactants (PVP, PEG-400) and one ionic surfactant ([HMIM]Cl) were used to synthesize a train of thioarsenates ranging from 0D cluster to 3D open framework (Fig. 2.3).³⁶ The controlled tests indicated that there are no crystal (for 0D, 1D and 3D compounds) or only a bit of (less than 3% yield) crystals (for 2D compound) obtained when surfactant was removed from reaction system.

Figure 2.3. (a) The discrete clusters (0D); (b) Anionic chains (1D); (c) Anionic layer (2D) and (d) Open framework (3D) of thioarsenates firstly obtained through surfactant-thermal method.³⁶

Following this synthetic strategy, two novel crystalline selenidostannates, 1D-[DBUH]₂[Hg₂Sn₂Se₆(Se₂)] (**1**) and 1D-[DBUH]₂[Hg₂Sn₂Se₇] (**2**), were synthesized by employing PEG-400 as reaction medium (Fig. 2.4).⁸⁶ Interestingly, under the same reaction condition, compound **1** could transform into compound **2** with a longer heating time, which indicates that compound **1** is kinetically stable while **2** is thermodynamically stable. However, only compound **2** was obtained when PEG-400 was removed or substituted by other conventional organic solvents, which demonstrates the kinetic regulating effect of PEG-400 in the growth of compound **1**.

Figure 2.4. (a) The anionic $[\text{Hg}_2\text{Sn}_2\text{Se}_6(\text{Se}_2)]^{2-}$ ribbon of **1**; (b) The anionic $[\text{Hg}_2\text{Sn}_2\text{Se}_7]^{2-}$ ribbon of **2**.⁸⁶

Constant efforts have been put into the exploration of novel crystalline materials through surfactant-thermal method, and some crystalline chalcogenides, oxochalcogenide, metal-organic frameworks and halides were obtained. Among them, $(\text{N}_2\text{H}_4)_2\text{Mn}_3\text{Sb}_4\text{S}_8(\mu_3\text{-OH})_2$,⁸⁴ $[\text{MnSb}_2\text{S}_4(\text{N}_2\text{H}_4)_2]$ and $[\text{Mn}(\text{tepa})\text{Sb}_6\text{S}_{10}]$,⁶ show active visible-light-driven property of hydrogen production. Two ammonium-directed Ag–Sb–S compounds, $(\text{NH}_4)\text{AgSb}_4\text{S}_7\cdot\text{H}_2\text{O}$ and $(\text{NH}_4)\text{AgSb}_2\text{S}_4$, display the ability to degrade crystal violet and rhodamine B under visible light irradiation.⁸ Moreover, two novel metal chalcogenides have been explored as anode materials for lithium ion

batteries and showed high capacities.^{25, 26} Intriguingly, one polymer-chalcogenide single crystal, $[\text{DBNH}]_2[\text{Sn}_3\text{Se}_7] \cdot \text{PEG}$, was successfully synthesized through trapping polyethyleneglycol (PEG) within a selenidostannate matrix with PEG-400 as reaction medium (Fig. 2.5).³⁸ Moreover, table 2.1 lists the crystalline metal chalcogenides prepared under surfactant-thermal media. Table 2.2 summarizes the metal-organic frameworks and metal bromides synthesized by surfactant-thermal strategy.

Figure 2.5. (a) The nanochannels of inorganic layers are threaded by extended PEG chains; (b) The single PEG chain in $[\text{DBNH}]_2[\text{Sn}_3\text{Se}_7] \cdot \text{PEG}$.³⁸

Table 2.1. Summary of crystalline metal chalcogenides prepared through surfactant-thermal method

No.	Compounds	Surfactants	Ref.
1	$[\text{NH}_4]_8[\text{Mn}_2\text{As}_4\text{S}_{16}]$	Polyvinylpyrrolidone (PVP)	36
2	$[\text{Mn}(\text{NH}_3)_6][\text{Mn}_2\text{As}_2\text{S}_8(\text{N}_2\text{H}_4)_2]$	Polyethylene Glycol-400 (PEG-400)	
3	$[\text{enH}][\text{Cu}_3\text{As}_2\text{S}_5]$	PEG-400	
4	$[\text{NH}_4][\text{MnAs}_3\text{S}_6]$	1-Hexadecyl-3-Methylimidazolium Chloride ([HMIM]Cl)	
5	$[\text{DBUH}]_2[\text{Hg}_2\text{Sn}_2\text{Se}_6(\text{Se}_2)]$	PEG-400	86
6	$[\text{DBUH}]_2[\text{Hg}_2\text{Sn}_2\text{Se}_7]$	PEG-400	
7	$(\text{N}_2\text{H}_4)_2\text{Mn}_3\text{Sb}_4\text{S}_8(\mu_3\text{-OH})_2$	Hexadecyltributylphosphonium Bromide ([HTBP]Br)	84
8	$[\text{MnSb}_2\text{S}_4(\text{N}_2\text{H}_4)_2]$	PEG-400	6
9	$[\text{Mn}(\text{tepa})\text{Sb}_6\text{S}_{10}]$	Sodium Dodecyl Sulfate (SDS)	
10	$[\text{DBNH}]_2[\text{Sn}_3\text{Se}_7] \cdot \text{PEG}$	PEG-400	38
11	$[\text{DBNH}]_3[\text{Sn}_4\text{Se}_8(\text{Se}_6)(\text{Se}_2)_{1/2}]$	PEG-400	
12	$\text{Mn}_3\text{Ge}_2\text{S}_7(\text{NH}_3)_4$	PEG-400	87
13	$[\text{Mn}(\text{en})_2(\text{H}_2\text{O})][\text{Mn}(\text{en})_2\text{MnGe}_3\text{Se}_9]$	PEG-400	
14	$(1,2\text{-dapH})_2[\text{Mn}(1,2\text{-dap})_2]\text{Ge}_2\text{Se}_7$	PEG-400	
15	$(1,3\text{-dapH})(\text{puH})\text{MnGeSe}_4$	PEG-400	25
16	$(\text{H}_3\text{O})_2(\text{enH}_2)\text{Cu}_8\text{Sn}_3\text{S}_{12}$	Octylamine	
17	$[\text{NH}(\text{CH}_3)_2][\text{Sb}_4\text{S}_5(\text{S}_3)]$	Octylamine	26
18	$(\text{NH}_4)\text{AgSb}_4\text{S}_7 \cdot \text{H}_2\text{O}$	PEG-400	8
19	$(\text{NH}_4)\text{AgSb}_2\text{S}_4$	PEG-400	
20	ACu_2SbS_3 (A = K, Rb, Cs)	PEG-400	88
21	ACuSb_2S_4 (A = Rb, Cs)	PEG-400	89
22	$[\text{enH}][\text{Cu}_2\text{AgSnS}_4]$	Octylamine	90
23	$\text{NaAg}_2\text{AsS}_3 \cdot \text{H}_2\text{O}$	PEG-400	91
24	KAg_2AsS_3	PEG-400	

Table 2.2. Summary of metal-organic frameworks and metal bromides prepared through surfactant-thermal method

No.	Compounds	Surfactants	Ref.
1	$[\text{Co}_3(\mu_3\text{-OH})(\text{HBTC})(\text{BTC})_2\text{Co}(\text{HBTC})] \cdot (\text{HTEA})_3 \cdot \text{H}_2\text{O}$	Nonanoic Acid (NA)	37
2	$[\text{Co}(\text{BTC})] \cdot \text{HTEA} \cdot \text{H}_2\text{O}$	NA	
3	$[\text{Co}_3(\text{BTC})_4] \cdot (\text{HTEA})_4$	NA	
4	$\text{M}(\text{BTC})\text{Cu}(\text{py})_2$ (M = Co, Mn, Ni, Zn)	PEG-400	83
5	$(\text{HTEA})_2[\text{M}_3(\text{BDC})_3\text{Cl}_2]$ (M = Zn, Co, Fe)	PEG-200	82
6	$(\text{HTEA})[\text{Zn}(\text{IPA})\text{Cl}]$	PEG-200	
7	$(\text{HTEA})_2[\text{M}_3(\text{IPA})_4]$ (M = Cd, Fe, Zn, Co)	PEG-200	
8	$(\text{HTEA})_3[\text{Co}_3(\text{BTC})_3]$	PEG-400	92
9	$(\text{HTEA})[\text{Co}_3(\text{HBTC})_2(\text{BTC})]$	NA	
10	$[\text{Ni}_2(\text{H}_2\text{L}_2)(\text{bpy})_2] \cdot 2\text{H}_2\text{O}$	PEG-400	93
11	$\text{Ni}_2\text{L}(\text{bpy})_{1.5}$	PEG-400	
12	$(\text{HTEA})_4[(\text{Zn}_4\text{O})_2\text{Zn}(\text{BTC})_6]$	PEG-400	94
13	$(\text{HTEA})_4[\text{Zn}_5(\text{BTC})_2(\text{HBTC})_4]$	Octanoic Acid (OA)	
14	$[\text{Zn}_9(\mu_3\text{-O})_2(\text{BTC})_6(\text{H}_3\text{O})_4]$	PEG-400	
15	$[\text{Zn}_3(\mu_3\text{-O})(\text{BTC})_2(\text{H}_3\text{O})_2]$	PEG-400	
16	$[\text{Zn}(\text{HBTC})(\text{H}_2\text{BTC})\text{Py}(\text{H}_3\text{O})]$	OA	
17	$[\text{Zn}(\text{HBTC})(\text{Py})_2]$	[HTBP]Br	
18	$\text{C}_6\text{NH}_7\text{PbBr}_3$	PVP	85
19	$(\text{C}_{12}\text{N}_2\text{H}_{14})_2\text{Pb}_7\text{Br}_{18}$	SDS	
20	$(\text{C}_{12}\text{N}_2\text{H}_{14})_2\text{Pb}_3\text{Br}_{10}$	PEG-400	
21	$[\text{BV}]_6[\text{Pb}_9\text{Br}_{30}]$	[HMIM]Cl	95

All of new crystalline materials synthesized under surfactant-thermal conditions

demonstrate that surfactants play an important role in controlling crystal growth. Especially, the study on metal chalcogenides indicates that the syntheses with surfactants as additives provide high opportunity to obtain novel metal chalcogenides with diverse structures and interesting properties. Nonetheless, employing surfactants as reaction media to prepare metal chalcogenides is still in its infancy, and more efforts are needed to study the reaction mechanism of surfactant-thermal method. Table 2.3 lists the advantages and disadvantages of different synthetic methods.

Table 2.3. The advantages and disadvantages of different synthetic methods to prepare metal chalcogenides

Method	Advantage	Disadvantage
High temperature solid-state method	Crystals are prepared according to stoichiometric ratio reactions.	Reaction temperature and energy consumption are very high.
Hydro(solvo)thermal method	Intermediate and metastable state crystals are easily synthesized. Reactions proceed in mild conditions and crystals are in good quality.	By-products are formed. It is difficult to separate the crystals and by-products.
Ionothermal method	Ionic liquids possess many unique properties and the reactions proceed in mild and soft conditions.	Products are difficult to crystallize.
Surfactant-thermal method	Surfactants act as reaction additives to control crystal growth. Surfactants also serve as templates and counterions. Reactions proceed in mild and soft conditions.	By-products are formed. It is difficult to separate the crystals and by-products.

In view of the above-mentioned advantages and disadvantages of four synthetic methods and the successful application of surfactants as reaction media to prepare crystalline

materials, in this dissertation, the preparation of novel crystalline metal chalcogenides will employ surfactant-thermal method. Meanwhile, different TMs will be integrated into the chalcogenides to enrich structural diversities and physicochemical properties. Attributing to the narrower optical band gaps and small molecules directed structures, the as-prepared crystalline metal chalcogenides will be tested as photocatalysts for organic pollutants degradation and anode materials for LIBs/SIBs.

Chapter 3

Crystalline Metal Chalcogenides for Photocatalytic Degradation

3.1 Literature Review

It should be noted that inorganic metal chalcogenide nanocrystals as photocatalysts for aqueous organic pollutants degradation has been explored in recent years. Among the degradation experiments, different dyes are chosen as model pollutants to examine the photocatalytic activities of metal chalcogenide nanocrystals. Different morphologies of Sb_2S_3 nanocrystals, including nanotubes, nanorods and nanowires, show a high-performance on methyl orange (MO) degradation under visible-light irradiation.^{29, 96, 97} Furthermore, Bi_2S_3 nanorods, the same main group metal sulfide, have demonstrated the ability to photodegrade Rhodamine B (RhB) under the visible light irradiation.⁹⁸ The nanocrystal In_2S_3 has shown visible-light-driven photocatalytic activity on MO degradation, which exhibits higher degradation ability than $\text{TiO}_{2-x}\text{N}_x$.⁹⁹ Some binary transition metal sulfides, such as ZnS nanospheres,¹⁰⁰ Cu_2S microrings,¹⁰¹ mesoporous FeS_2 , CoS_2 , and NiS_2 ,¹⁰² also have been evaluated as photocatalysts to degrade organic pollutants. The mesoporous selenide, MoSe_2 , shows a remarkable photocatalytic activity on RhB degradation under the visible light illumination.¹⁰³ Moreover, ternary and quaternary hybrid metal chalcogenides nanocrystals as efficient visible-light-driven photocatalysts have also been investigated.¹⁰⁴⁻¹¹⁰ Table 3.1 gives a summary of these metal chalcogenide nanocrystals as photocatalysts for aqueous organic pollutants

degradation.

Table 3.1. Summary of metal chalcogenide nanocrystals as photocatalysts for organic pollutants degradation

No.	Catalyst	Pollutant	Light Source	Ref.
1	Sb ₂ S ₃ nanotubes	Methyl Orange (MO)	Visible light	96
2	Sb ₂ S ₃ nanorods	MO	Visible light	29
3	Sb ₂ S ₃ nanowires	MO	Visible light	97
4	Bi ₂ S ₃ nanorods	Rhodamine B (RhB)	Visible light	98
5	ZnS nanospheres	<i>p</i> -nitrophenol	UV-light	100
6	Cu ₂ S microrings	Methylene Blue (MB)	Daylight	101
7	In ₂ S ₃ nanocrystals	MO	Visible light	99
8	Mesoporous FeS ₂ , CoS ₂ , and NiS ₂	MB	Visible light	102
9	MoSe ₂	RhB	Visible light	103
10	Ag ₃ SbS ₃	MB, MO Malachite Green (MG) Rhodamine 6G (Rh6G)	Visible light	104
11	AgInS ₂ nanoparticles	MO	Visible light	105
12	AgIn ₅ S ₈ nanoparticles	MO	Visible light	106
13	ZnIn ₂ S ₄ microspheres	MO	Visible light	107
14	ZnIn ₂ S ₄ microspheres	MO, RhB Congo Red (CR)	Visible light	108
15	Zn _x Cd _{1-x} S nanocrystals	MO, CR, RhB <i>p</i> -hydroxyazobenzene	Visible light	109
16	Cu ₂ ZnGeS ₄ colloidal nanocrystals	RhB	Visible light	110

Up to now, more than twenty crystalline chalcogenides with the property of photocatalytic degrading organic pollutants have been successfully synthesized. Most

of these crystalline chalcogenides displayed the ability to degrade RhB under visible light illumination. One crystalline thioantimonate, $[\text{AEPH}_2][\text{GeSb}_2\text{S}_6] \cdot \text{CH}_3\text{OH}$ (AEP = N-(2-aminoethyl)piperazine), possesses the ability to degrade RhB.¹¹¹ Its optical band gap was about 2.47 eV, and the photodegradation ratio reached 85.1% after being exposed to visible light for 8 h. The photocatalytic process did not change the composition and structure of catalyst, demonstrating its chemical stability. Another crystalline thioantimonate $[\text{Mn}(\text{tren})]\text{HgSb}_2\text{Se}_5$ (tren=tris(2-aminoethyl)amine), possessing a narrower band gap (~ 1.89 eV), could degrade RhB more efficiently under visible irradiation.¹¹² The photodegradation result indicated that RhB degradation ratio reached 97% when exposed to visible light for 4 h and almost completely degraded after 5 h. Furthermore, XRD characterization indicated that $[\text{Mn}(\text{tren})]\text{HgSb}_2\text{Se}_5$ is a stable photocatalyst. However, the isomorphic compounds, $[\text{TM}(\text{tren})]\text{HgSb}_2\text{Se}_5$ (TM = Fe, Co), did not show any activity on RhB degradation. Among a series of transition metal complexes directed mercury thioantimonates, only $[\text{Ni}(1,2\text{-dap})_3]\text{HgSb}_2\text{S}_5$, $[\text{Mn}(\text{dien})_2]\text{HgSb}_2\text{S}_5$ and $[\text{Ni}(\text{dien})_2]\text{Hg}_3\text{Sb}_4\text{S}_{10}$ were able to degrade RhB under visible light irradiation.¹¹³

An open-framework mixed-valent chalcogenidostannate, $[\text{CH}_3\text{NH}_3]_2\text{Ag}_4\text{Sn}^{\text{IV}}_2\text{Sn}^{\text{II}}\text{S}_8$, displayed visible-light-driven photocatalytic degradation of CV.¹¹⁴ After 200 min illumination, the degradation ratio of CV reached 92%. Remarkably, a small organic amine directed chalcogenidostannate, $[\text{CH}_3\text{NH}_3]_2[\text{H}_3\text{O}]\text{Ag}_5\text{Sn}_4\text{Se}_{12} \cdot \text{C}_2\text{H}_5\text{OH}$, could degrade CV up to 96% when exposed to visible light for only 10 min.¹¹⁵ Unsaturated

Mn complex decorated thioarsenates, $(\text{NH}_4)[\text{Mn}(2,2'\text{-bipy})_2]\text{AsS}_4$, was able to degrade CV under visible light irradiation and the degradation ratio reached 90% exposed to visible light for 30 min.¹¹⁶ The parallel experiment with N-doped P25 as a photocatalyst was conducted under the completely same condition, however, the degradation ratio of CV was less than 18% after 60 min irradiation. Two Ag-Sb-S complexes, $(\text{NH}_4)\text{AgSb}_4\text{S}_7\cdot\text{H}_2\text{O}$ and $(\text{NH}_4)\text{AgSb}_2\text{S}_4$, were able to degrade crystal violet (CV) and RhB under visible light irradiation. Moreover, both compounds displayed selective photocatalytic abilities on CV degradation.⁸ Similarly, photocatalytic results demonstrated that $\text{Mn}_2\text{Ga}_4\text{Sn}_4\text{S}_{20}[\text{Mn}_2(\text{en})_5]_2\cdot 4\text{H}_2\text{O}$ displayed higher catalytic activity on CV degradation than RhB under visible light irradiation.¹¹⁷ With as-prepared 1D telluridoindate as a catalyst, photocatalytic experiments of MO and RhB degradation have shown that $[\text{In}_3\text{Te}_5(\text{dien})]\cdot\text{H}_3\text{O}\cdot\text{H}_2\text{O}$ has selective degradation ability on MO.¹¹⁸

A series of layered indium chalcogenidoantimonates $[\text{Me}_2\text{NH}_2]_2\text{In}_2\text{Sb}_2\text{S}_{7-x}\text{Se}_x$ ($x = 0$ (**1**), 2.20(**2**), 4.20(**3**), 7(**4**)) are able to degrade MO in the presence of UV and visible light.⁹ With the proportion of Se increasing, the optical absorption edges of compounds **1-4** have a red-shift, being tested to be about 2.31, 1.93, 1.78 and 1.61 eV, respectively. Parallel tests of MO degradation were carried out in the presence of UV and visible light, respectively. The experimental results indicated that the MO degradation ratio over compound **1** reached 96.8% after 3 h UV-light irradiation, which is much higher than that of other compounds. However, under visible light irradiation, the compound contains more Se shows higher photocatalytic degradation efficiency. After 10 h visible

light irradiation, the MO degradation ratio over compound **4** reached 91.5% while compounds **1** and **2** only reached 18.3% and 11.5%, respectively. The MO degradation tests over these layered chalcogenidoantimonates demonstrate that photocatalytic activity could be extended from UV to visible light region as the Se content increased, which is consistent with their tunable absorption edges. However, $[\text{Me}_2\text{NH}_2]_2\text{In}_2\text{Sb}_2\text{S}_{7-x}\text{Se}_x$ failed to degrade colorless substrates of salicylic acid and 4-chlorophenol in the presence of visible light.

Additionally, the photocatalytic activities of tellurides as catalysts were also explored under UV light irradiation.¹¹⁸⁻¹²⁰ Table 3.2 lists the crystalline metal chalcogenides as photocatalysts for dye degradation.

Table 3.2. Summary of crystalline metal chalcogenides as photocatalysts for organic pollutants degradation

No.	Catalyst	Pollutant	Light Source	Ref.
1	[AEPH ₂][GeSb ₂ S ₆]·CH ₃ OH	RhB	Visible light	111
2	[CH ₃ NH ₃] ₂₀ Ge ₁₀ Sb ₂₈ S ₇₂ ·7H ₂ O	RhB	Visible light	121
3	[Ni(1,2-dap) ₃]HgSb ₂ S ₅ [Mn(dien) ₂]HgSb ₂ S ₅ [Ni(dien) ₂]Hg ₃ Sb ₄ S ₁₀	RhB	Visible light	113
4	[CH ₃ NH ₃] ₂ Ag ₄ Sn ^{IV} ₂ Sn ^{II} S ₈	CV	Visible light	114
5	(NH ₄)AgSb ₄ S ₇ ·H ₂ O (NH ₄)AgSb ₂ S ₄	RhB, CV	Visible light	8
6	(NH ₄)[Mn(2,2-bipy) ₂]AsS ₄	CV	Visible light	116
7	Mn ₂ Ga ₄ Sn ₄ S ₂₀ [Mn ₂ (en) ₅] ₂ ·4H ₂ O	RhB, CV	Visible light	117
8	[CH ₃ NH ₃] ₂ [H ₃ O]Ag ₅ Sn ₄ Se ₁₂ ·C ₂ H ₅ OH	CV	Visible light	115
9	Cd ₈ S(SPh) ₁₄ (DMF) ₃ [Cd ₈ S(SPh) ₁₄ (DMF)(bpy)] _n	RhB, MB	Visible light	122
10	α-EuZrS ₃	MB	Visible light Sunlight	120
11	Sn ₂ SiS ₄	RhB	Visible light	123
12	[Me ₂ NH ₂] ₂ In ₂ Sb ₂ S _{7-x} Se _x (x= 0(1), 2.20(2), 4.20(3), 7(4))	MO	UV-light Visible light	9
13	[Mn(tren)]HgSb ₂ Se ₅	RhB	Visible light	112
14	(Bmmim) ₈ In ₈ Sn ₈ Se ₃₀ (Se ₄) ₂	MO	Visible light	77
15	Ba ₂ AsGaSe ₅	RhB	Visible light	124
16	Ba ₂ ZnSe ₃	RhB	Visible light	125
17	Dy ₄ S ₄ Te ₃	RhB	UV-light	126
18	[In(en) ₃][In ₅ Te ₉ (en) ₂]	MO	UV-light	119
19	[In ₃ Te ₅ (dien)]·H ₃ O·H ₂ O	MO, RhB	UV-light Visible light	118

3.2 Experimental Section

All starting materials employed in this dissertation were analytic grade and directly used without further purification. The contents of Mn, Ag, Sb and S were analyzed using JEOL/JSM-6360 SEM equipped with EDS. Powder X-ray diffraction (PXRD) tests were conducted on Bruker D8 Advance diffractometer with a graphite-monochromatized Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$). The data collections were conducted with 2θ ranging from 5° to 65° . Elemental analyses were recorded on a PerkinElmer 2400 Series II CHNS/O instrument. A Model UV-2501 PC has been employed to measure the solid-state UV-Vis diffuse-reflectance spectra of powder samples with the BaSO $_4$ plate as a standard (100% reflection). The absorption spectra were converted from the reflectance spectra through Kubelka–Munk function: $\alpha/S = (1-R)^2/2R$,¹²⁷ in which R is the reflectance, α represents the absorption coefficient, and S means the scattering coefficient that is independent of wavelength when the particle size of samples is bigger than $5 \text{ }\mu\text{m}$. The studies of thermal stability were conducted on TGA TA Instruments Q500 under flowing pure N $_2$ with the temperature rate of $10 \text{ }^\circ\text{C}/\text{min}$ up to $900 \text{ }^\circ\text{C}$.

3.2.1 Syntheses

Synthesis of [MnSb $_2$ S $_4$ (N $_2$ H $_4$) $_2$] (MAS-1)

A mixture of Mn powder (1.00 mmol, 55 mg), Sb $_2$ S $_3$ (0.40 mmol, 136 mg), S (1.00 mmol, 32 mg), hydrazine monohydrate (98%, 2.0 ml), and polyethylene glycol-400

(PEG-400, 2.0 ml) was sealed into an autoclave equipped with a Teflon liner (20 ml) and heated at 120 °C for 7 days. (*Note: Extra attention should be paid due to the toxicity and strongly reducing ability of hydrazine monohydrate.*) After cooling to room temperature, the mixture was washed with ethanol and red plate crystals of **MAS-1** were obtained by filtration and selected by hand (yield: 45% based on Sb).

*Synthesis of [Mn(tepa)Sb₆S₁₀] (**MAS-2**)*

A mixture of Mn powder (1.00 mmol, 55 mg), Sb₂S₅ (0.80 mmol, 320 mg), S (1.00 mmol, 32 mg), tetraethylenepentamine (technical grade, 3.0 ml), distilled water (1 ml), and sodium dodecyl sulfate (SDS, 1.0 g) was sealed into an autoclave equipped with a Teflon liner (20 ml) and heated at 160 °C for 7 days. After cooling to room temperature, the mixture was washed with ethanol and orange block crystals of **MAS-2** were obtained by filtration and selected by hand (yield: 77% based on Sb).

*Synthesis of (NH₄)AgSb₄S₇·H₂O (**SAS-1**)*

Ag powder (0.50 mmol, 54mg), Ga₂O₃ (0.25 mmol, 47 mg), Sb powder (0.50 mmol, 61 mg), S powder (2.50 mmol, 80 mg), hydrazine monohydrate (reagent grade, 2.0 ml), and poly(ethylene glycol) (average M_n 400, 2.0 ml) were mixed in a Teflon cup (20 ml). Then, the autoclave was sealed and kept at 160 °C for 6 days. After naturally cooling to room temperature, the resulted crystals were washed with alcohol (ethanol) for several times. The pure black block crystals of **SAS-1** were selected by hand (yield: 52 % based on Sb). Elemental analyses for **SAS-1**, Calcd, N: 1.64, H: 0.70; Found, N: 1.78, H: 0.13.

*Synthesis of $(\text{NH}_4)\text{AgSb}_2\text{S}_4$ (**SAS-2**)*

The preparation procedure of compound **SAS-2** was similar to **SAS-1** except that Ga_2O_3 powder was removed from reaction system. After naturally cooling to room temperature, red plate crystals of compound **SAS-2** (yield: 46 % based on Sb) and some amorphous byproducts were obtained. The pure phase single crystals of **SAS-2** were selected manually. EA for compound **2**, Calcd, N: 2.82, H: 0.81; Found, N: 2.13, H: 0.15.

Note: The presence of surfactants are important for the preparation of **MAS-1** and **MAS-2**. As a partial solvent, PEG-400 provides an advantageous environment to promote the synthesis of **MAS-1**. Furthermore, when the concentration of this surfactant was decreased or even removed, no crystal was produced. Compound **MAS-2** was prepared in an anionic surfactant (SDS) medium. When this surfactant was removed, only a small amount (less than 5% yield) of crystals was obtained. Our research demonstrates the potentiality and essentiality of surfactants as reaction media for the preparation novel crystalline chalcogenides.

During the synthesis of compound **SAS-1**, Ga_2O_3 powder, acting as mineralizer, was indispensable. When Ga_2O_3 was removed from reaction system, only red lamellate crystals of **SAS-2** were obtained. If Ga_2O_3 was replaced by In_2S_3 or 1,10-phenanthroline, no single crystal or only compound **SAS-2** was obtained, respectively. It was also reported that GeO_2 played a critical role in the preparation of 3D homochiral phosphor even though GeO_2 did not enter the crystal structure.¹²⁸

3.2.2 Single Crystal X-ray Crystallography

SCXRD data collection were conducted on a Bruker APEX Smart with a graphite-monochromatized and 0.5 mm mono cap-collimated Mo-K α radiation source (λ = 0.71073 Å). The cell refinement and data reduction were performed using SAINT program of APEX3 software. The structures were analyzed through direct method and refined by full-matrix least-squares on F^2 using SHELX-97.¹²⁹ CCDC numbers are 1063498 for compound **MAS-1**, 1063497 for compound **MAS-2**, 1536159 for compound **SAS-1** and 1536160 for compound **SAS-2**. Relevant crystallographic data and structure refinement details of four compounds are listed in Table 3.3 and Table 3.4.

Table 3.3. Crystallographic data and structure refinements for compounds MAS-1 and MAS-2

	MAS-1	MAS-2
Chemical formula	N ₄ H ₈ MnSb ₂ S ₄	C ₈ H ₂₃ N ₅ MnSb ₆ S ₁₀
Formula mass	490.78	1295.75
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> (Å)	19.5086(12)	19.5792(9)
<i>b</i> (Å)	4.3906(3)	15.3226(5)
<i>c</i> (Å)	11.8646(6)	10.7599(4)
α (deg)	90.00	90.00
β (deg)	92.972(5)	110.455(4)
γ (deg)	90.00	90.00
<i>V</i> (Å ³)	1014.89(11)	3024.5(2)
<i>T</i> /K	293(2)	100.1(5)
<i>Z</i>	4	4
<i>D</i> _{cal} (g/cm ³)	3.159	3.107
Theta (deg)	3.44-24.99	3.34-29.71
<i>R</i> (int)	0.0313	0.0315
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0277	0.0611
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0521	0.1743
GOF on <i>F</i> ²	0.924	1.038

Table 3.4. Crystallographic data and structure refinements for compounds ASS-1 and SAS-2

	SAS-1	SAS-2
Chemical formula	NH ₆ AgSb ₄ S ₇ O	NH ₄ AgSb ₂ S ₄
Formula mass	855.35	497.65
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	6.874(2)	11.548(9)
<i>b</i> (Å)	9.281(3)	7.395(6)
<i>c</i> (Å)	11.747(4)	11.083(8)
α (deg)	75.989(3)	90
β (deg)	85.686(3)	116.731(8)
γ (deg)	80.955(3)	90
<i>V</i> (Å ³)	717.5(4)	845.3(11)
<i>T</i> /K	296(2)	296(2)
<i>Z</i>	2	4
<i>D</i> _{cal} (g/cm ³)	3.959	3.910
Theta (deg)	1.788 - 27.289	1.975 - 27.231
<i>R</i> (int)	0.0212	0.0446
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0185	0.0812
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0521	0.2625
GOF on <i>F</i> ²	1.161	1.221

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right]^{1/2}.$$

3.2.3 Photocatalysis

The photocatalytic activities over as-prepared crystalline metal chalcogenides for the degradation of CV and RhB have been investigated in Pyrex glass cell containing a

quartz window, which can allow vertical illumination going through. The light source was a 300 W Xe lamp (Newport) with a long-pass cut-off filter ($\lambda > 420$ nm). The above-mentioned Pyrex glass cell was maintained at 20 degrees centigrade with a jacketed circulation of cooling system. In all reactions, prior to irradiation, the photocatalysts (50 mg for both compounds) were suspended in CV or RhB (40 mL, 10 ppm) aqueous solution, respectively. The reaction mixture was then magnetically stirred for 1 h in the dark to reach adsorption/desorption equilibrium. Around 1.5 mL suspension was taken from the reaction cell continually at specific intervals. All suspensions were centrifugalized at a speed of 10000 rpm/min for 10 min, and the resulting solutions were analyzed on a UV-Vis spectrometer (UV2450, Shimadzu). Meanwhile, controlled experiments (without photocatalyst) were also performed under identical conditions. The degradation efficiency is defined as C/C_0 , where C is the remnant absorption of organic dye at each irradiated time interval and C_0 is the initial absorption when the adsorption/desorption equilibrium was achieved.

3.3 Fundamental Principles of Semiconductor Photocatalyst

From the standpoint of semiconductor photochemistry, the role of photocatalysis is to initiate or accelerate specific redox reactions in the presence of an irradiated photocatalyst. When illuminated with photons, the photocatalyst absorbs the photons whose energy are larger or equal to its band gap. The excited electron (e_{cb}^-) promotes into the conduction band (CB) from the valence band (VB) while a hole (h_{vb}^+) remains in the VB (Fig. 3.1I). Then both of the excited electron (e_{cb}^-) and hole (h_{vb}^+) migrate to

the semiconductor surface. The excited electrons (e_{cb}^-) in the CB exhibit a strong reductive capacity and could react with the electron acceptors (A) (Fig. 3.1III), such as O_2 absorbed on the semiconductor surface or dissolved in the water, to yield superoxide radicals $O_2^{\cdot-}$ (Eq. 3.1). The holes (h_{vb}^+) in the VB exhibit a strong oxidative potential and can react with surface adsorbed electron donors (D) (Fig. 3.1IV), including H_2O and organic pollutants, to produce $\cdot OH$ radicals (Eq. 3.2) and organic pollutants radicals (Eq. 3.3). Up to now, both of O_2 and organic pollutants are in activated state and the subsequent radical reactions (Eq. 3.4 - 3.6, Fig. 3.1V) will complete the facile oxidative degradation of organic pollutants. Additionally, the excited electrons and holes may get trapped in the metastable surface states (Fig. 3.1VI and VII). Note that the excited CB electrons and VB holes can recombine (Fig. 3.1II) due to scavenger or crystalline defects.^{28, 130, 131}

Figure 3.1. Schematic illustration of the fundamental principles of photocatalysis: (I) the generation of exciton by a photon; (II) the exciton recombination to liberate heat or light; (III) the reductive reaction conducted by a CB electron; (IV) the oxidative reaction conducted by a VB hole; (V) the further pollutants degradation to produce mineralization products; (VI) the trapping of a CB electron and (VII) a VB hole at the semiconductor surface.¹³⁰

3.4 Results and Discussion

3.4.1 Crystal Structure Analyses

[MnSb₂S₄(N₂H₄)₂] (**MAS-1**)

SCXRD analysis revealed that compound **MAS-1** crystallizes in the monoclinic space group $C2/c$. In the asymmetric unit of **MAS-1**, Sb1 is coordinated by three S atoms (two S1 and one S2) to form a $[Sb^{III}S_3]^{3-}$ pyramid with the Sb-S bond lengths ranging from

2.3989(16) to 2.5101(16) Å. Mn1 lies within an octahedral environment (Fig. 3.2a), coordinating to four hydrazine ligands through four N atoms (two N1 and two N2) and two $[\text{Sb}^{\text{III}}\text{S}_3]^{3-}$ via two S atoms (S2). The Mn-S2 bond length is 2.6662(15) Å and the bond length of Mn-N lies in the range of 2.263(5) - 2.283(5) Å, which are consistent with the values reported in the literature.^{2, 4, 84, 112, 132-134} In the stretched octahedral cluster $[\text{MnS}_2\text{N}_4]^{2-}$, all the axial *trans* bond angles are the ideal value of 180°. These stretched octahedral clusters form a 1D $[\text{MnS}_2\text{N}_4]_n^{2n-}$ chain along the *b*-axis, which connects the $[\text{SbS}_2]_n^{n-}$ chain (Fig. 3.2b) via vertex-sharing S atoms to give the formation of the neutral layer $[\text{MnSb}_2\text{S}_4(\text{N}_2\text{H}_4)_2]$ (Fig. 3.2c).

It is worth mentioning that compounds **MAS-1** and 3D- $[\text{Mn}_2\text{Sb}_4\text{S}_8(\text{N}_2\text{H}_4)_2]$ (**MAS-3**)¹³³ have the same stoichiometric ratio of elemental Mn, Sb and S, both of whose reaction solvent include hydrazine monohydrate. However, their structural characteristics are totally different: a) **MAS-1** is a layered structure, while compound **MAS-3** is a 3D framework; b) Mn centers in **MAS-1** coordinate with two S atoms and four N atoms while in **MAS-3** Mn atom adopts MnS_4N_2 coordination; c) all Sb atoms in **MAS-1** adopt trigonal pyramids SbS_3 while in **MAS-3** all Sb sites have either four-fold coordinated SbS_4 configurations or square pyramidal SbS_5 geometries. Furthermore, compound **MAS-1** was prepared in surfactant medium while compound **MAS-3** was solvothermally synthesized by using hydrazine monohydrate as reaction medium.

Figure 3.2. (a) Coordination environment of Mn²⁺ ion in compound MAS-1; (b) The [SbS₂]_nⁿ⁻ chain formed by [Sb^{III}S₃]³⁻ clusters; (c) The 2D layered structure of compound MAS-1 viewed along the *c*-axis. H atoms are omitted for clarity.

[Mn(tepa)Sb₆S₁₀] (**MAS-2**)

SCXRD analysis indicates that compound **MAS-2** crystallizes in the monoclinic space group *C2/c*. In the asymmetric unit of **MAS-2**, three crystallographically independent Sb atoms (Sb1, Sb2 and Sb3) are present, all of which form [Sb^{III}S₃]³⁻ trigonal pyramids by coordinating with three S atoms. The Sb-S distances range from 2.411(4) to 2.619(4) Å, which are similar to previously reported values in thioantimonate compounds.^{10, 135-137} The Mn atom is in a heavily distorted octahedral environment and coordinated by five N atoms from one tepa molecule and one S atom (S2) from [Sb^{III}S₃]³⁻ cluster. The

bond length of Mn-S2 is 2.581(8) Å, indicating strong covalent interactions. Furthermore, the disordered Mn is split into two equivalent positions (Mn-S2 (min) 2.586(9) Å, Mn-S2 (max) 3.686(8) Å), as shown Fig. 3.3.¹³⁸

Figure 3.3. The layered structure of compound MAS-2 further stacks into a 3D structure through weak Mn–S interaction. The weak interaction between Mn-S2 [3.686(8) Å] is indicated as blue dashed lines. The disordered tepa molecules are not shown for clarity.

In *bc* plane, two Sb1 and two Sb2 give the formation of the 8-membered window [Sb₄S₈]⁴⁻, the size of which is approximately 6.35×3.25 Å (Fig. 3.4b). The 24-membered window [Sb₁₂S₂₄]¹²⁻ is formed by four of Sb1, Sb2 and Sb3, whose dimension is nearly 15.59×3.70 Å (Fig. 3.4c). Moreover, two different windows and elemental Mn form the neutral layered structure [MnSb₆S₁₀] (Fig. 3.4a). In compound **MAS-2**, the tepa molecule is heavily distorted. Nonetheless, it was still failed to determine the positions of tepa molecules even though the diffraction data of the as-prepared sample was collected at low temperature (100K).

Figure 3.4. (a) The neutral layered structure $[\text{MnSb}_6\text{S}_{10}]$ in compound MAS-2 viewed along the a -axis; (b) the sizes of the 8-membered window and (c) the 24-membered window in MAS-2. H atoms are omitted for clarity.

$(\text{NH}_4)\text{AgSb}_4\text{S}_7 \cdot \text{H}_2\text{O}$ (SAS-1)

SCXRD data bespeak that compound **SAS-1** crystallizes in the triclinic space group $P-1$ and possesses 3D open-framework $[\text{AgSb}_4\text{S}_7]_n^{n-}$ with NH_4^+ ions and water molecules situated in the channels as structure-directing agents or templates.

The asymmetric unit of **SAS-1** (Fig. 3.5a) consists of one crystallographically independent Ag^+ ion, four Sb^{3+} ions, seven S^{2-} ions, one NH_4^+ cation and one water

molecule, respectively. The disordered Ag is split into two equivalent positions Ag1 and Ag2, which adopt a distorted tetrahedral coordination geometry with four S atoms and the bond lengths range from 2.559(4) to 2.798(4) Å (Ag1 and Ag2-based average bond length) similar to those reported in the literature.¹³⁹ Both Sb1 and Sb2 have trigonal pyramidal geometries by coordinating to three S atoms, while Sb3 and Sb4 are coordinated with four S atoms to form trigonal bipyramid geometries. The bond lengths of Sb-S ranging from 2.4040(12) to 2.8792(12) Å are similar to the previously-reported values in thioantimonates compounds.¹²¹ Vertex-sharing of two [AgS₄]-[Sb1S₃]-[Sb4S₄]-[Sb4S₄]-[Sb2S₃]-[Sb3S₃] units produces a 24-membered ring [Ag₂Sb₁₀S₁₂] and the longest two-atom distance is 16.38 Å (Fig. 3.5b). Such rings are interconnected via Ag atoms to constitute 1D-channels along *a* direction, which are further stacked in *bc* plane to present the 3D open-framework [AgSb₄S₇]_{*n*}⁻ with NH₄⁺ ions and molecular waters located in the channels (Fig. 3.5c).

Compounds **SAS-1** and 2D-CsAgSb₄S₇ (**CSAS**)¹⁴⁰ have the same stoichiometric ratio of elemental Ag, Sb and S, but their structures are totally different: a) compound **SAS-1** has open-framework structure while **CSAS** is layered structure; b) in **SAS-1**, two Sb atoms have trigonal pyramidal geometries and the other two form trigonal bipyramid geometries. Each Sb atom is coordinated by three S atoms in compound **CSAS**; c) compound **SAS-1** is prepared through the surfactant-thermal method while **CSAS** is synthesized by high temperature solid-state process.

Figure 3.5. (a) Asymmetric unit of compound SAS-1; (b) 24-membered ring labelled with the longest two-atom distance; (c) view of the open-framework architecture of SAS-1 along *a* axis with one 24-membered ring circled. H atoms are omitted for clarity.

(NH₄)AgSb₂S₄ (SAS-2)

SCXRD analysis reveals compound SAS-2 crystallizes in monoclinic space group $P2_1/c$ and has 2D anionic layers $[\text{AgSb}_2\text{S}_4]_n^{n-}$ separated by NH_4^+ cations produced from the decomposition of hydrazine (Fig. 3.6a). The asymmetric unit of SAS-2 consists of one unique Ag^+ ion, two Sb^{3+} ions, four S^{2-} ions and one NH_4^+ cation. The Ag atom adopts slightly distorted tetrahedral geometry coordinating with four S atoms with Ag-S

distances falling in the range of 2.542(6)~2.674(6) Å, which are comparable with those in BaAgSbS₃ and BaAgSbS₃·H₂O,¹⁴¹ [C₄N₂H₁₄][Ag₃Sb₃S₇] and [C₂N₂H₉]₂[Ag₅Sb₃S₈],¹³⁹ [C₂H₉N₂][Ag₂SbS₃],¹⁴² CsAgSb₄S₇,¹⁴⁰ Cs₃Ag₂Sb₃S₈, α-/β-Cs₂AgSbS₄, and Cs₂AgAsS₄.¹⁴³ As for two crystallographic Sb(1) and Sb(2) atoms, both of which adopt trigonal pyramidal geometries to coordinate with three sulfur atoms. The distance between S and Sb ranges from 2.417(6) to 2.529(6) Å. Vertex-sharing of two trigonal-pyramid Sb(1)S₃ primary building units, one Sb(2)S₃ and one distorted-tetrahedral Ag(1)S₄ unit produce an 8-membered ring; such rings are interconnected via corner-sharing S(1) and Sb(1) atoms to constitute a 1D [AgSb₂S₅]_n³ⁿ⁻ ribbon extending along the *c* axis (Fig. 3.6b). The [AgSb₂S₅]_n³ⁿ⁻ ribbons are condensed by sharing the S(4) and Ag(1) atoms to give rise to the anionic layer [AgSb₂S₄]_nⁿ⁻ (Fig. 3.6c).

Figure 3.6. (a) A packing view of compound SAS-2 along the b axis displaying the interlayer space where ammonium ions are located; (b) the $[\text{AgSb}_2\text{S}_5]_n^{3n-}$ ribbons and (c) 2D anionic layers $[\text{AgSb}_2\text{S}_4]_n^{n-}$. H atoms are omitted for clarity.

3.4.2 Characterization

All of the as-prepared crystalline metal chalcogenides have been characterized by EDS PXRD, solid-state UV-Vis diffuse-reflectance spectra and TGA.

3.4.2.1 EDS Analyses

The energy dispersive X-ray spectroscopy (EDS) was conducted on JEOL/JSM-6360 SEM. The EDS data of **MAS-1** and **MAS-2** confirm the presence of elemental Mn, Sb and S, respectively (Fig. 3.7a and b). The EDS data of **SAS-1** and **SAS-2** demonstrate the presence of Ag, Sb and S elements, respectively (Fig. 3.7c and d).

Figure 3.7. The energy dispersive X-ray spectroscopy of (a) MAS-1; (b) MAS-2; (c) SAS-1 and (d) SAS-2.

3.4.2.2 PXRD Analyses

The simulated PXRD patterns of the as-prepared samples are derived from their single-crystal X-ray diffraction data. The experimental PXRD patterns of bulk phases of **MAS-1**, **MAS-2**, **SAS-1** and **SAS-2** are well matched with their simulated ones, respectively (Fig. 3.8a - d), demonstrating the phase purity of each as-prepared sample.

Figure 3.8. PXRD patterns of compound (a) MAS-1; (b) MAS-2; (c) SAS-1 and (d) SAS-2.

3.4.2.3 Optical Properties

All of the solid-state UV-Vis diffuse-reflectance spectra were tested at room temperature, which are used to verify that all as-prepared metal chalcogenides are semiconductors. The solid-state UV-Vis diffuse-reflectance spectra of compounds **MAS-1** and **MAS-2** were converted into optical absorption data by using the Kubelka-Munk function.¹²⁷ The optical band gaps of compounds **MAS-1** and **MAS-2** are estimated to be 1.97 eV and 2.12 eV, respectively, which are consistent with their crystal colors (Fig. 3.9a and b). The band gaps of **MAS-1** and **MAS-2** show a blue shift compared with the binary chalcogenides, such as In_2S_3 (1.9 eV),⁹⁹ Sb_2S_3 (1.66 eV),²⁹ and MoSe_2 (1.37 eV).¹⁰³ Intriguingly, even though the compounds have the same chemical compositions, their

band gaps may vary widely. The optical band gap of **MAS-1** is narrower than 3D- $[\text{Mn}_2\text{Sb}_2\text{S}_5(\text{N}_2\text{H}_4)_3]$ (2.09 eV),² but it is wider than that of 3D- $\text{Mn}_2\text{Sb}_4\text{S}_8(\text{N}_2\text{H}_4)_2$ (1.59 eV).¹³³ As shown in Fig.3.9c and d, the optical band gaps could be calculated from the steep adsorption edges as 1.70 eV for **SAS-1** and 1.85 eV for **SAS-2**, which may be due to the charge transfer from sulfur-based valence band to silver/antimony-based conduction band.¹⁴¹ The absorption edges are narrower than those of the known Ag-Sb-S compounds, such as BaAgSbS_3 (2.2 eV),¹⁴¹ $[\text{C}_4\text{N}_2\text{H}_{14}][\text{Ag}_3\text{Sb}_3\text{S}_7]$ (1.9 eV) and $[\text{C}_2\text{N}_2\text{H}_9]_2[\text{Ag}_5\text{Sb}_3\text{S}_8]$ (1.9 eV),¹³⁹ KAg_2SbS_3 (2.1 eV) and $\text{K}_2\text{Ag}_3\text{Sb}_3\text{S}_7$ (2.2 eV),¹⁴⁴ and $\text{CsAgSb}_4\text{S}_7$ (2.04 eV).¹⁴⁰

Figure 3.9. Solid-state optical absorption spectra of compounds (a) **MAS-1**; (b) **MAS-2**; (c) **SAS-1** and (d) **SAS-2**. Insets in (a) to (d) are the photographs of crystals of **MAS-1**, **MAS-2**, **SAS-1** and (d) **SAS-2**, respectively.

3.4.2.4 Thermal Analyses

All of thermogravimetric analyses (TGA) were performed from room temperature (RT) to 900 °C under a N₂ atmosphere, which are used to examine the purities and thermal stabilities of the as-prepared crystalline metal chalcogenides. The TGA curve of compound **MAS-1** shows that there is one distinct stage with weight loss of 12.78% from 207 °C to 310 °C (Fig. 3.10a), corresponding to the loss of two hydrazine molecules per formula unit (calcd: 13.06%). Compound **MAS-2** is stable up to 285 °C and then a sharp drop of 16.18% was observed up to 348 °C (Fig. 3.10b), which is attributed to the loss of one tepa molecule per formula unit (calcd: 14.61%). For compound **SAS-1**, as shown in Fig. 3.10c, the weight loss (~6.12%) between 100 and 300 °C is close to the removal of one H₂O, one NH₃ and half H₂S per formula unit (6.08%). The weight loss (~6.69%) between 200 and 300 °C is close to the loss of one NH₃ and half H₂S per formula unit (6.85%) of compound **SAS-2** (Fig. 3.10d).

Figure 3.10. TGA curves for compounds (a) MAS-1; (b) MAS-2; (c) SAS-1 and (d) SAS-2.

3.5 Photocatalytic Activities

CV and RhB, which are found to be highly cytotoxic and refractory fluorescein dyes for humans, were chosen as model pollutants to assess the photocatalytic activities of compounds **MAS-1**, **MAS-2**, **SAS-1** and **SAS-2**. The control studies in the absence of photocatalysts under visible light irradiation showed that there were no significant changes in CV or RhB concentration, demonstrating relative stabilities of CV and RhB. Before light illumination, the adsorption/desorption equilibrium was achieved in the dark. When illuminated for 1.5 h, the degradation ratio of CV over compound **MAS-1** reached 95% (Fig. 3.11a). However, the CV degradation over **MAS-2** was inefficient compared with **MAS-1** and 93% of CV was degraded when exposed to visible light for

4h (Fig. 3.11b). The low degradation efficiency over **MAS-2** may be due to its wider optical band gap. Degradation ratio of CV reached 96% exposed to visible light for 1 h when compound **SAS-1** was used as the photocatalyst (Fig. 3.11c), while nearly 94% of CV was degraded within only 5 min over **SAS-2** (Fig. 3.11d), illustrating a satisfyingly photocatalytic activity on CV of compound **SAS-2** compared with other metal chalcogenides.^{114, 116} Furthermore, the stabilities of compounds **MAS-1**, **MAS-2**, **SAS-1** and **SAS-2** were examined by PXRD and there are no crystallographic changes before and after the photocatalytic activities (Fig. 3.12a - Fig. 3.12d).

Figure 3.11. Photocatalytic degradation of CV over compounds (a) MAS-1; (b) MAS-2; (c) SAS-1 and (d) SAS-2 monitored as the normalized change in concentration as a function of illumination time. The insets in (a) to (d) showed the temporal changes of CV solutions.

Figure 3.12. PXRD patterns of compounds (a) MAS-1; (b) MAS-2; (c) SAS-1 and (d) SAS-2 before and after the CV photodegradation.

The RhB degradation experiments over compounds **MAS-1**, **MAS-2**, **SAS-1** and **SAS-2** were illuminated for 10 h. Degradation ratio of RhB over **MAS-1** reached 81% (Fig. 3.13a) while only 59% of RhB was decolorized over **MAS-2** (Fig. 3.13b). About 91% of target contaminant was decolorized after exposure to visible light for 10 h over compound **SAS-1** (Fig. 3.13c), however, the degradation ratio was only 54% over **SAS-2** under same illumination time (Fig. 3.13d). The degradation efficiencies on RhB indicated that compounds **MAS-1**, **MAS-2**, **SAS-1** and **SAS-2** had lower photocatalytic activities than other reported metal chalcogenides.^{121, 124, 145} The results demonstrated that all as-prepared samples display selectively photocatalytic abilities of CV under

visible light irradiation. In addition, PXRD characterizations indicated that there were no crystallographic changes in **MAS-1**, **MAS-2**, **SAS-1** and **SAS-2** before and after the photocatalytic processes, indicating the high stabilities of as-prepared samples as the photocatalysts (Fig. 3.14a - d).

For the CV degradation, **SAS-2** displays highest efficiency and **SAS-1** shows the highest activity for RhB degradation. We attribute the highly photocatalytic efficiencies and stabilities to suitable energy band gaps corresponding to the absorption of visible light coupled with high stabilities of the skeleton structure of silver thioantimonates.

Figure 3.13. Photocatalytic degradation of RhB over compounds (a) MAS-1; (b) MAS-2; (c) SAS-1 and (d) SAS-2 monitored as the normalized change in concentration as a function of illumination time. The insets in (a) to (d) showed the temporal changes of RhB solutions.

Figure 3.14. PXRD patterns of compounds (a) MAS-1; (b) MAS-2; (c) SAS-1 and (d) SAS-2 before and after the RhB photodegradation.

3.6 Summary

In summary, two novel manganese thioantimonates $[\text{MnSb}_2\text{S}_4(\text{N}_2\text{H}_4)_2]$ (**MAS-1**) and $[\text{Mn}(\text{tepa})\text{Sb}_6\text{S}_{10}]$ (**MAS-2**) as well as two new silver thioantimonates $(\text{NH}_4)\text{AgSb}_4\text{S}_7 \cdot \text{H}_2\text{O}$ (**SAS-1**) and $(\text{NH}_4)\text{AgSb}_2\text{S}_4$ (**SAS-2**) have been successfully prepared through the surfactant-thermal strategy and fully characterized. Both **MAS-1** and **MAS-2** possess neutral 2D layer structure and compound **MAS 1** is the fourth example in the Mn/Sb/S-hydrazine family. The great attractive feature of compounds **SAS-1** and **SAS-2** is that ammonium ions not only act as counterions but also play as structure-directing agents or templates. The optical band gaps are estimated to be ~ 1.97

eV for **MAS-1**, ~ 2.12 eV for **MAS-2**, ~ 1.70 eV for **SAS-1** and ~ 1.85 eV for **SAS-2**, respectively, indicating that all of the as-prepared compounds exhibiting semiconductor properties. The photocatalytic experiments showed that all as-prepared samples were able to degrade CV and RhB under visible light irradiation. Moreover, all compounds displayed selectively photocatalytic abilities on CV degradation. Compound **SAS-2** displays highest efficiency on CV degradation and **SAS-1** shows the highest activity for RhB degradation. We attribute the highly photocatalytic efficiencies of two silver thioantimonates to their suitable energy band gaps corresponding to the visible light absorption coupled with high stabilities of the skeleton structure. The presence of surfactants are important for the preparation of **MAS-1** and **MAS-2**. As a partial solvent, PEG-400 provides an advantageous environment to promote the crystallization of **MAS-1**. And no crystal was obtained if the concentration of PEG-400 was decreased or even removed. Compound **MAS-2** was prepared in an anionic surfactant (SDS) medium. When this surfactant was removed, only a small amount (less than 5% yield) of crystals was obtained. It is noteworthy that compounds **SAS-1** and **SAS-2** were prepared in the same procedure except that Ga_2O_3 was added in the preparation of **SAS-1**, which indicated that Ga_2O_3 powder, acting as mineralizer, could regulate structure diversities. Our research bespeaks the potentiality and essentiality of surfactants as reaction media for the preparation of novel crystalline metal chalcogenides. We believe that the surfactant-thermal method is a promising strategy for preparing novel crystalline inorganic materials with diverse structures and interesting properties. Furthermore, the

combination of surfactant-thermal method and metal oxides as mineralizer could be a promising way to prepare other novel crystalline metal chalcogenides.

Chapter 4

Crystalline Metal Chalcogenides for Lithium/Sodium-ion Batteries

4.1 Literature Review

Normally, the commercial LIBs compose of a lithium compound cathode (for example, LiCoO_2 or LiFePO_4), a graphitic anode and an organic carbonate electrolyte with achieved energy densities of $\sim 120\text{-}150 \text{ Wh kg}^{-1}$.¹⁴⁶ However, a critical bottleneck of LIBs is the low theoretical specific capacity (up to 372 mA h g^{-1}) of conventional graphite anodes, which is unable to meet increasing demands for efficient energy.^{146, 147} In addition, environmental-friendly components are also very important to be considered as the rising awareness of environmental issues. Therefore, many current researches focus on alternative anode materials such as Si (4200 mA h g^{-1}),¹⁴⁸⁻¹⁵⁰ Sn (994 mA h g^{-1}),¹⁵¹⁻¹⁵³ P (1552 mA h g^{-1})¹⁵⁴⁻¹⁵⁶ and Sb (660 mA h g^{-1})^{157, 158}. Unfortunately, their application has been mostly confined by their poor cycling life and severe pulverization due to high volume expansion/contraction of nearly 400% as well as the large irreversible capacity during the repeated lithiation and delithiation process.

Going beyond the limitation of current LIBs requires exploring new electrode materials with optimized structures. The control over the morphology, composition and pore structures of the active materials has been proven to be a promising strategy for their applications in LIBs. In particular, porous materials are attractive because of their accommodation of the volume expansion during the repeated lithiation and delithiation

process, large surface-to-volume ratio with the improved contact area between electrode materials and electrolyte, as well as short diffusion length for lithium ions. For example, FePO_4 nanoflakes with ordered channels,¹⁵⁹ mesoporous $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$,¹⁶⁰ and Co_3O_4 nanowall arrays,¹⁶¹ have been used as electrode materials for LIBs and exhibited superior electrochemical properties. Besides, materials with ultrathin 2D morphology are of great interest for lithium ion batteries applications,¹⁶²⁻¹⁶⁴ since their ultrathin thickness provides much shorter paths for fast lithium ion diffusion and its large surface areas offers the increased active sites.

Tin-based materials have been regarded as the most attractive candidates of anode materials for LIBs with a higher capacity ($> 600 \text{ mA h g}^{-1}$) compared with that of the commercial graphite electrode.⁴⁶⁻⁴⁸ Among them, tin sulfides have attracted great attention owing to their high theoretical capacity, natural abundance and low toxicity.⁴⁹⁻⁵¹ However, their long-term cycling properties are still far from satisfactory. I–III–VI and I–IV–VI series of tin-based ternary sulfides semiconducting materials, including Ag-Sn-S ,¹⁶⁵ Cu_3SnS_4 ,¹⁶⁶ and Cu_2SnS_3 ¹⁶⁷ have drawn much attention due to their wide applications in photocatalytic activity for hydrogen evolution, photovoltaic devices and so on. Unlike those extensively studied transition metal oxides,¹⁶⁸⁻¹⁷⁰ or sulfides,¹⁷¹⁻¹⁷³ the investigation of ternary thiostannates as anode materials for lithium ion batteries have not been paid much attention. Table 4.1 gives a summary of reported tin-based anode materials for LIBs.

Table 4.1. A survey of electrochemical properties of Tin-based materials for LIBs

Active Anode	Cycling Capability	Cycling Stability	Ref.
SnS ₂ nanoparticles	293 mAh g ⁻¹ after 50 cycles at 50 mA g ⁻¹ (a capacity fade of 4.7 mAh g ⁻¹ per cycle)	55.6% of an initial capacity of 527 mAh g ⁻¹	174
SnS ₂ powder	400 mAh g ⁻¹ after 25 cycles at 50 mA g ⁻¹	66.6% of an initial capacity of 600 mAh g ⁻¹	175
SnO ₂ nanowires	300 mAh g ⁻¹ up to the 50th cycle	60% of the fifth-cycle capacity	176
SnO ₂ hollow structures	About 500 mAh g ⁻¹ at 100 mA g ⁻¹ after 40 cycles	43.8 % of an initial capacity of 1140 mAh g ⁻¹	177
2D-SnS ₂ nanoplates	583 mAhg 100 mA g ⁻¹ after 30 cycles	85% of the 2rd-cycle capacity	178
SnS ₂ nanotablets	168 mAh g ⁻¹ at 0.5 C after 200 cycles	60% of the initial capacity of 1250 mAh g ⁻¹	179

To achieve more stable and higher energy-density rechargeable batteries, new negative electrode materials have to be designed and developed. Strong investigations on transitional metal-based redox-active materials have been conducted for a few decades.¹⁸⁰ For examples, copper oxide (CuO) possesses a theoretical capacity of 674 mAh g⁻¹,¹⁸⁰ while α -Fe₂O₃¹⁸¹ and Co₃O₄⁴² can even achieve a high practical specific capacity of 911 mAh g⁻¹ and 927 mAh g⁻¹, respectively. Alternately, metal sulfides have also raised much attention as anode materials for LIBs due to their metallic character, rich redox chemistry and good thermal stability.¹⁸²⁻¹⁸⁴ Among such materials, alloy-based SbS_x have been studied as promising anode materials for LIBs,¹⁸⁵⁻¹⁸⁸ because they can undergo both the conversion reaction between Li and SbS_x and the alloying reaction between Sb and Li, which can result in high charge and discharge capacities. Furthermore, through conversion and alloying reactions, antimony (Sb) and indium (In)

- containing materials, particularly their chalcogenide and composite materials, have demonstrated much improved performance as compared with the commercialized graphite anode.^{40, 41, 189-192} Table 4.2 lists a summary of the electrochemical properties of superior chalcogenide anode materials for LIBs.

Table 4.2. A survey of electrochemical properties of sulfides for LIBs

Active Anode ^{Ref.}	Cycling Capability	Current Density	Potential Window (voltage versus Li/Li⁺)
(NH ₄)InSb ₂ S ₅ ·phen (IAS) ¹⁹³	1138 mAh g ⁻¹ after 80 cycles & 634 mAh g ⁻¹ after 1000 cycles	143 mA g ⁻¹ & 2.85 A g ⁻¹	3.0-0.005 V
(H ₃ O) ₂ (enH ₂)Cu ₈ Sn ₃ S ₁₂ (CTS) ¹⁹⁴	563 mAh g ⁻¹ after 100 cycles	100 mA g ⁻¹	3.0-0.01 V
[NH(CH ₃) ₂][Sb ₄ S ₅ (S ₃)] (ASS) ¹⁹⁵	568 mAh g ⁻¹ after 50 cycles	100 mA g ⁻¹	3.0-0.01 V
SnS ₂ nanoplates ¹⁹⁶	935 mAh g ⁻¹ after 30 cycles	200 mA g ⁻¹	3.0-0.0 V
MoS ₂ nanosheets ¹⁹⁷	585 mAh g ⁻¹ after 70 cycles	100 mA g ⁻¹	3.0-0.005 V
MoS ₂ 3D architectures ¹⁹⁸	1009 mAh g ⁻¹ after 80 cycles	100 mA g ⁻¹	3.0-0.01 V
Mesoporous WS ₂ ¹⁹⁹	805 mAh g ⁻¹ after 100 cycles	100 mA g ⁻¹	3.0-0.01 V
ZrS ₂ nanodiscs ²⁰⁰	~550 mAh g ⁻¹ after 50 cycles	69 mA g ⁻¹	1.2-0.02 V
VS ₄ /GO ²⁰¹	954 mAh g ⁻¹ after 100 cycles	100 mA g ⁻¹	3.0-0.01 V
Sb ₂ S ₃ 3D bundles ²⁰²	548 mAh g ⁻¹ after 100 cycles	100 mA g ⁻¹	3.0-0.01 V
Sb ₂ S ₃ /rGo ¹⁸⁹	720 mAh g ⁻¹ after 50 cycles	250 mA g ⁻¹	2.5-0.01 V
In ₂ S ₃ nanoplates ²⁰³	837 mAh g ⁻¹ after 30 cycles	50 mA g ⁻¹	3.0-0.001 V

4.2 Experimental Section

All chemicals were commercially available and used without further purification. The scanning electron microscope (SEM) image and elemental analyses of Cu, In, Sb, Sn and S were performed on an EDS-equipped JEOL/JSM-6360A SEM. Transmission electron microscopy (TEM) images were taken with JEOL 2100F at 200 kV. Atomic force microscopy (AFM) (Digital Instruments) was used to determine the thickness of the nanosheets. Elemental analyses (N, C, H) were performed on an Elementary Vario El III instrument. Sample weight is typically 5 mg and accuracy up to 5%. Powder X-ray diffraction data were recorded on a Bruker D8 Advance diffractometer with a graphite-monochromatized Cu K_{α} radiation. The data were collected with 2θ in a range of 5° - 65° . The FT-IR spectra (KBr pellets) were recorded on a PerkinElmer FTIR spectrophotometer in the range 500 - 4000 cm^{-1} . Thermal stability study was carried out on a TGA Q500 instrument under flowing N_2 with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ up to $900\text{ }^{\circ}\text{C}$.

The precursor $\text{Na}_4\text{SnS}_4 \cdot 14\text{H}_2\text{O}$ was synthesized through a solution reaction. Firstly, 60 mmol $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was dissolved in 50 mL of H_2O with stirring. Then 15 mmol of SnCl_4 was added into 25 mL H_2O dropwise with continuous stirring. The immediately formed yellow precipitates would be dissolved with stirring and the mixture became greenish liquid. It was stirred at $45\text{ }^{\circ}\text{C}$ for 15 h and then added to 200 mL methanol and stored in refrigerator for 24 h.

4.2.1 Syntheses

Synthesis of $[NH(CH_3)_2][Sb_4S_5(S_3)]$ (ASS)

A mixture of Sb_2S_3 powder (0.40 mmol, 136 mg), S (3.00 mmol, 96 mg), N, N-Dimethylformamide (DMF, HPLC grade, 2.0 ml), hydrazine monohydrate (98%, 0.5 ml) and octylamine (99 %, 1.5 ml) was sealed into an autoclave equipped with a Teflon liner (20 ml) and heated at 160 °C for 6 days. After cooling to room temperature, the mixture was washed with ethanol and red plate crystals of **ASS** were obtained by the filtration and the pure phase was selected by hand (yield: 72 % based on Sb).

Synthesis of $(H_3O)_2(enH_2)Cu_8Sn_3S_{12}$ (CTS)

A mixture of Cu_2S powder (0.25 mmol, 40 mg), $Na_4SnS_4 \cdot 14H_2O$ (0.25 mmol, 147 mg), S (1.00 mmol, 32 mg), ethylenediamine (99.5 %, 2.0 ml), and octylamine (99 %, 2.0 ml) was sealed into an autoclave equipped with a Teflon liner (20 ml) and heated at 160 °C for 6 days. After cooling to room temperature, the mixture was washed with ethanol and black polyhedron crystals of **CTS** were obtained by filtration and selected by hand (yield: 49 % based on Cu). Elemental analysis (EA) for compounds **CTS**, Calcd, N: 2.101, C: 1.801, H: 1.21; Found, N: 2.126, C: 2.332, H: 1.238.

Synthesis of $(NH_4)InSb_2S_5 \cdot phen$ (IAS)

In_2O_3 powder (0.25 mmol, 69.4 mg), Sb powder (1.00 mmol, 121.8 mg), S powder (4.00 mmol, 128 mg), 1,10-phenanthroline (0.5 mmol, 90.1mg), hydrazine monohydrate

(reagent grade, 1.0 ml), and poly(ethylene glycol)-400 (PEG-400, 2.0 ml) were sealed into an autoclave equipped with a Teflon liner (20 ml). Then, the autoclave was heated to 160 °C and kept for 6 days. After naturally cooling to room temperature, the mixture was washed with ethanol for several times and red rod crystals of **IAS** were obtained by filtration and selected manually (yield: 67 % based on Sb). Elemental analyses (EA) for compound **IAS**: Calcd, N: 5.86, C: 20.1, H: 1.69; Found, N: 5.88, C: 19.53, H: 1.42.

4.2.2 Single Crystal X-ray Crystallography

SCXRD data collection were conducted on a Bruker APEX Smart with a graphite-monochromatized and 0.5 mm mono cap-collimated Mo-K α radiation source ($\lambda = 0.71073$ Å). The cell refinement and data reduction were performed using SAINT program of APEX3 software. The structures were analyzed through direct method and refined by full-matrix least-squares on F^2 using SHELX-97.¹²⁹ CCDC numbers are 1430117 for compound **ASS**, 1408735 for compound **CTS** and 1505742 for compound **IAS**. Relevant crystallographic data and structure refinement details of three compounds are listed in Table 4.2.

Table 4.3. Crystallographic data and structure refinements for compounds ASS, CTS and IAS

	ASS	CTS	IAS
Chemical formula	C ₂ NH ₇ Sb ₄ S ₈	C ₂ N ₂ H ₁₆ OCu ₈ Sn ₃ S ₁₂	C ₁₂ N ₃ H ₁₂ InSb ₂ S ₅
Formula mass	788.57	1333.39	716.87
Crystal system	Orthorhombic	Cubic	Monoclinic
Space group	<i>Ama2</i>	<i>F-43c</i>	<i>P2₁/m</i>
<i>a</i> (Å)	10.0371(4)	18.040(2)	3.8688(12)
<i>b</i> (Å)	26.6752(13)	18.040(2)	18.756(6)
<i>c</i> (Å)	5.9349(3)	18.040(2)	12.443(4)
α (deg)	90.00	90.00	90.00
β (deg)	90.00	90.00	90.819(4)
γ (deg)	90.00	90.00	90.00
V (Å ³)	1589.02(13)	5871.0(12)	902.8(5)
<i>T</i> /K	293(2)	293(2)	100(2)
<i>Z</i>	4	4	2
D _{cal} (g/cm ³)	3.296	3.116	2.637
Theta (deg)	2.54-25.00	3.19-27.00	1.964 - 26.996
R (int)	0.0268	0.0653	0.0419
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0505	0.0374	0.0451
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.1554	0.1058	0.1189
GOF on F ²	1.096	1.118	1.092

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right]^{1/2}.$$

4.3 ASS for Lithium Storage

4.3.1 Electrochemical Measurements

The as-prepared products [NH(CH₃)₂][Sb₄S₅(S₃)] were ground for about 10 min before

used. The working electrode was prepared by mixing **ASS** with carbon black and PVDF as the binder in a weight ratio of 7:2:1 in NMP solvent. The slurry was coated on a copper foil and dried in a vacuum oven at 60 °C overnight. The electrochemical measurements were carried out using two-electrode coin cells (X2 Labwares, Singapore) with pure lithium foil as both the counter and the reference electrodes at room temperature. Celgard 2400 membrane was used as the separator, and the electrolyte was 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 in volume). Cell assembly was carried out in an Ar-filled glovebox with the concentrations of both moisture and oxygen below 1.0 ppm. The mass loading for each battery is about 0.8mg/cm².

4.3.2 Crystal Structure Analysis

SCXRD analysis reveals that compound **ASS** belongs to the orthorhombic space group *Ama2*. Structural analysis indicates that compound **ASS** is constructed by 1D neutral ribbons [Sb₄S₅(S₃)] and dimethylamine molecules. The asymmetric unit (Fig. 4.1a) consists of one and two halves Sb³⁺ ions, two and four halves S²⁻ ions and half dimethylamine molecule, respectively. In the inorganic [Sb₄S₅(S₃)] chain of **ASS**, all crystallographically independent Sb atoms (Sb1, Sb2 and Sb3) are coordinated to three S atoms to form [Sb^{III}S₃]³⁻ trigonal-pyramidal geometries with Sb-S distances ranging from 2.391(7) to 2.487(5) Å, which is similar to the previously reported values in thioantimonate compounds.^{6, 10, 84, 135, 137} Two Sb1 and one Sb2 connect to each other via corner-sharing S1 and S2 atoms to construct a six-membered [Sb₃S₃] ring while Sb3

and S₃ that is composed of two S5 and one S4 form a four-membered [Sb(S₃)] ring. The bond length of S4-S5 is 2.418(7) Å, which is a little longer than the reported values.^{204,}
²⁰⁵ Both kinds of rings [Sb₃S₃] and [Sb(S₃)], as shown in Fig. 4.1b, are alternatingly arranged through the connecting of Sb1-S5 to form an infinite [Sb₄S₅(S₃)]_n chain along the *a*-axis (Fig. 4.1c). The dimethylamine molecules are located in the inter-chain spaces and form N-H⋯S and C-H⋯S hydrogen bonds with the S atoms to result in a pseudo-2D network (Fig. 4.2 and 4.3).

Figure 4.1. (a) Asymmetric unit of compound ASS; (b) alternatingly arranged two rings, [Sb₃S₃] and [Sb(S₃)]; (c) view of the infinite [Sb₄S₅(S₃)]_n chains and dimethylamine molecule along the *a*-axis.

Figure 4.2. The pseudo-2D network of ASS viewed along the b direction. H-bonding interactions are shown in dotted lines.

Figure 4.3. Packing diagram of ASS viewed along the c direction. H-bonding interactions are shown in dotted lines.

4.3.3 Characterization

It is noteworthy that no crystal was observed if octylamine was replaced by SDS or NA. Only small crystallites with poor quality were obtained when octylamine was removed or replaced with PEG-400 and suberic acid. The purity and thermal stability of **ASS** have been examined by PXRD (Fig. 4.4a) and TGA. As shown in Fig. 4.5, the weight loss of compound **ASS** from 220 °C to 260 °C is 9.45%, corresponding to the loss of one dimethylamine molecule and one S per formula unit (calcd: 9.77%).

The morphologies of grinding **ASS** were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. The SEM image (Fig. 4.4b) of **ASS** shows the original morphology of the as-obtained crystalline product. After grinded the as-obtained samples for about 10 minutes, the products mainly present in 2D morphology, as shown in Fig. 4.4c. The TEM image (the inset of Fig. 4.4c) shows a typical piece of nanosheets obtained after grinding. The selected-area electron diffraction (SAED) pattern (Fig. 4.4d) reveals the high degree of crystallinity of **ASS**. The marked pattern can be attributed to the planes of (200), (01-1) and (21-1), respectively. To further confirm the thickness of the nanosheets, atomic force microscopy (AFM) measurement was also conducted, as shown in Fig. 4.6a. Cross-sectional profiling (Fig. 4.6b) shows that the thickness of one typical nanosheet is about 20nm, which indicates the ultrathin property of compound **ASS**.

Figure 4.4. Characterization of compound ASS. (a) XRD pattern; (b) SEM image of the as-obtained crystalline product; (c) SEM image of grinding product (the inset is a typical TEM image); (d) SAED pattern.

Figure 4.5. TGA curve for compound ASS.

Figure 4.6. (a) AFM scans of $[\text{NH}(\text{CH}_3)_2][\text{Sb}_4\text{S}_5(\text{S}_3)]$ nanosheets; (b) the corresponding cross-sectional thickness.

4.3.4 Electrochemical Lithium Storage

The electrochemical performance of compound **ASS** was evaluated with 20% carbon black and 10% PVDF as the binder in EC/DEC electrolyte. To investigate the redox behavior of **ASS**, the cyclic voltammetry (CV) measurement was carried out in the voltage window of 0.01–3.0 V at a scan rate of 0.1 mV s^{-1} at room temperature. As shown in Fig. 4.7a, during the first cathodic scan, three main peaks centered at 1.7 V, 1.3 V and 0.75 V appear. The two peaks around at 1.7 V and 1.3 V are related to the conversion reaction of $[\text{NH}(\text{CH}_3)_2][\text{Sb}_4\text{S}_5(\text{S}_3)]$ to Sb and Li_2S . The lower peak at 0.75 V is due to the alloying between Sb and Li. For the first anodic scan, two peaks at 1.1 V and 1.8 V are observed, which correspond to the delithiation process of Li_xSb and the continuous oxidation of Sb, respectively. It is similar to the previously reported results, indicating the mechanism for the redox reaction process of **ASS** is similar to the reported ones.^{185, 186, 206} During subsequent cycles, the shape of CV curves can almost be retained, indicating the good stability of the electrochemical process. The constant current charge-

discharge profiles of 1st, 2nd and 3rd cycles are shown in Fig. 4.7b. As can be seen, the initial discharge capacity of 1385 mAh g⁻¹ and a charge capacity of 813 mAh g⁻¹ can be obtained, indicating the large reversible capacity. Furthermore, the potential plateaus are in good agreement with the redox peaks in the CV curves. For the following 2nd and 3rd charge and discharge curves, they are almost overlapped, which also demonstrates the good stability of compound **ASS** as the anode materials of LIBs.

The rate performance of the [NH(CH₃)₂][Sb₄S₅(S₃)] electrode at room temperature was further investigated by cycling the half-cell at different current densities (0.1-5 A g⁻¹). Fig. 4.7c shows galvanostatic profiles (5th cycle of each current density) of compound **ASS** in half-cell. It is found that the observed curves show the similar sloped behavior. The charge-discharge specific capacities at different current densities are shown in Fig. 4.7d. Reversible capacities of about 720 mAh g⁻¹ at a current density of 0.1 A g⁻¹, 620 mAh g⁻¹ at 0.2 A g⁻¹, 585 mAh g⁻¹ at 0.5 A g⁻¹, 521 mAh g⁻¹ at 1 A g⁻¹, 405 mAh g⁻¹ at 2 A g⁻¹, and 310 mAh g⁻¹ at 5 A g⁻¹ are achieved, respectively. It should be noted that a specific capacity of 678 mAh g⁻¹ can still be obtained after intensive cycles.

Good cycling performance is a critical factor in practical application of next-generation LIBs. Therefore, the long-term cycling properties of compound **ASS** are performed at a current density of 0.1 A g⁻¹, as shown in Fig. 4.7e. During 2nd to 50th cycles, it is found that 78.2% of capacity can be retained. In addition, coulombic efficiency during cycles can almost keep at 100 %, which indicates the good cycling properties of compound **ASS** as an anode material of LIBs.

Figure 4.7. Electrochemical characterization of ASS anode. (a) Cyclic voltammograms between 0.01 and 3.0 V measured at a scan rate of 0.1 mV s⁻¹; (b) the charge and discharge curves at a current density of 0.1 A g⁻¹; (c) the charge-discharge curves at different current densities; (d) rate performance at different rates; (e) capacity as a function of cycle numbers at a current density of 0.1 A g⁻¹

4.3.5 Summary

In summary, crystalline thioantimonate [NH(CH₃)₂][Sb₄S₅(S₃)] (ASS) has been

successfully synthesized via the surfactant-thermal strategy. After grinding, the resulted compound ASS presented as ultrathin nanosheets that can offer fast ion diffusion and increased active sites as well as good accommodation ability for volume expansion, which are favourable properties for LIBs. Employed as an anode material of LIBs, grinding ASS exhibits high reversible specific capacity of 568 mAh g⁻¹ over 50 cycles at a current density of 0.1 A g⁻¹ and excellent rate capability of 301 mAh g⁻¹ at a current density of 5 A g⁻¹. Our research indicates that crystalline chalcogenides could be a promising candidate as an anode material for next-generation LIBs.

4.4 CTS for Lithium Storage

4.4.1 Electrochemical Measurements

The as-prepared samples were first grinded for about 10 minutes. For the electrode preparation, 70 wt% of the as-prepared active materials, 20 wt% active carbons, and 10 wt% PVDF binder were mixed with NMP. The slurry was coated onto Cu foil used as working electrodes. Then they were dried in a vacuum oven at 50 °C for 12h. Electrochemical measurements were carried out on CR2032 coin-type cells with lithium metal as the counter/reference electrode, a Celgard 2400 membrane as the separator, and 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 1:1, v/v). The coin cells were assembled in an Ar-filled glove box with concentrations of moisture and oxygen below 0.1 ppm. The charge-discharge tests were performed with a NEWARE battery tester at a voltage window of 0.01-3.0 V.

Cyclic voltammetry (0.01-3V, 0.1 mV s⁻¹) was carried out on Solartron analytical equipment (Model 1470E).

4.4.2 Crystal Structure Analysis

SCXRD analysis revealed that **CTS** crystallizes in the cubic space group $F\bar{4}3c$ and contains a 3D anionic open-framework $[\text{Cu}_8\text{Sn}_3\text{S}_{12}]^{4-}$ with disordered H_2en^{2+} and H_3O^+ located in the channels as charge-balanced species. In the asymmetric unit of **CTS**, Cu1 and Cu2 adopt $[\text{CuS}_3]$ planar trigonal geometries by coordinating to three $\mu_3\text{-S}^{2-}$ ions. The Cu-S bond lengths range from 2.253(7) to 2.257(7) Å that are consistent with the values in the similar structures.^{4, 207, 208} Sn1 is tetrahedrally coordinated by four $\mu_3\text{-S}^{2-}$ ions with the Sn-S bond length of 2.4012(18) Å. Each $\mu_3\text{-S}^{2-}$ ion bridges two Cu (Cu1 and Cu2) sites and one Sn (Sn1) center. The crucial building block of 3D **CTS** is icosahedral $[\text{Cu}_8\text{S}_{12}]^{16-}$ cluster (Fig. 4.8a and b), which consists of a cubic array of eight Cu^+ ions bridged by $\mu_3\text{-S}^{2-}$ ions, and the icosahedral shape is defined by twelve bridging $\mu_3\text{-S}^{2-}$ ions. The adjacent $[\text{Cu}_8\text{S}_{12}]^{16-}$ clusters are linked by discrete Sn^{4+} ions, which makes them behave like superoctahedral units, to give rise to a Cu-Sn-S framework with 3D channels (Fig. 4.9).

Interestingly, 3D anionic open frameworks $[\text{Cu}_8\text{Ge}_5\text{S}_{16}]^{4-}$ (**CGS-1**),⁴ $[\text{Cu}_8\text{Ge}_4\text{S}_{14}]^{4-}$ (**CGS-2**)²⁰⁸ and $[\text{Cu}_8\text{Ge}_3\text{S}_{12}]^{4-}$ (**CGS-3**)²⁰⁷ are also constructed with the icosahedral $[\text{Cu}_8\text{S}_{12}]^{16-}$ clusters as building blocks. In compound **CGS-1**, the icosahedral $[\text{Cu}_8\text{S}_{12}]^{16-}$ clusters are linked by the dimeric $[\text{Ge}_2\text{S}_2]^{4+}$ units in *a* and *b* directions, and Ge^{4+} ions in

c direction, with disordered protonated amines located in the 3D channels. While in **CGS-2**, the icosahedra are linked by $[\text{Ge}_2\text{S}_2]^{4+}$ units in *a* direction and Ge^{4+} sites in *b* and *c* directions. In compound **CGS-3**, the icosahedral $[\text{Cu}_8\text{S}_{12}]^{16-}$ clusters are linked by discrete Ge^{4+} sites in three directions, while in CTS the linkers are Sn^{4+} ions.

It is worth mentioning that although CTS and $3\text{D}-(\text{H}_2\text{en})_2\text{Cu}_8\text{Sn}_3\text{S}_{12}$ (**CTS-1**)²¹ have the same formula of the anionic open-framework $[\text{Cu}_8\text{Sn}_3\text{S}_{12}]^{4-}$ with protonated ethyleneamines as charge balance agents, their structural characteristics are obviously different: a) in CTS, the icosahedral $[\text{Cu}_8\text{S}_{12}]^{16-}$ clusters are linked by Sn^{4+} ions. In compound **CTS-1**, the icosahedra are cross-linked through $[\text{Cu}_8\text{S}_{16}]^{24-}$ clusters, which the Sn^{4+} ions are incorporated into; b) in CTS, there is only a single channel system, while **CTS-1** possesses two interpenetrating channel systems along $\langle 100 \rangle$ directions and two interpenetrating channel systems along $\langle 110 \rangle$ directions.

Figure 4.8. Icosahedral $[\text{Cu}_8\text{S}_{12}]^{16-}$ cluster and its connectivity with six Sn^{4+} ions: (a) Ball and stick mode and (b) polyhedral mode.

Figure 4.9. View of the 3D Cu–Sn–S framework along *bc* direction

4.4.3 Characterization

The purity and stability of **CTS** have been examined by PXRD and TGA. The amounts of protonated water and ethylenediamine were confirmed by EA and TGA analysis. Fig. 4.10a shows the SEM image of as-prepared sample **CTS**. As demonstrated in Fig. 4.10c, a d-spacing of 0.285 nm in high-resolution transmission electron microscopy (HRTEM) image can be obtained, corresponding to the (026) plane. This plane can be indexed to the powder XRD (Fig. 4.10b) peak centered at 31.34°. The SAED pattern (Fig. 4.10d) reveals the high degree of crystallinity of **CTS**. Clearly, it bespeaks the product belongs to the cubic system. The thermal stability of **CTS** was examined by TGA. As shown in Fig. 4.11, the weight loss of compound **CTS** from room temperature to 300 °C is 10.81%,

corresponding to the loss of one ethylenediamine, two H₂O and one and a half H₂S molecules per formula unit (calcd: 11.04%).

Figure 4.10. Characterization of CTS. (a) SEM image; (b) XRD pattern; (c) High-resolution TEM image; (d) SAED pattern.

Figure 4.11. TGA curve for compound CTS.

4.4.4 Electrochemical Lithium Storage

With the aim of exploring the potential application of **CTS** for lithium ion batteries, we evaluated the electrochemical performance with various electrochemical measurements. Fig. 4.12a shows the typical CV curves at room temperature during first 3 cycles (0.01-3V, 0.1 mV s⁻¹). For the first cathodic scan, one sharp peak located at 1.54 V, the second broad one at 1.05 V and a small peak at 0.35 V are observed. These peaks can be related to the phase transformation, the decomposition of **CTS** into Cu and Sn embedded in a Li₂S matrix, and the formation of Li_xSn alloy, respectively.²⁰⁹ For the first anodic scan, two broad peaks at 0.56 V and 1.25 V and a sharp one at 1.9 V accompanied by one at 2.1V are found. The oxidation peak at 0.56 V is known to represent the delithiation process of Li_xSn alloy.²¹⁰⁻²¹² The other three anodic peaks can be attributed to the

continuous oxidation of Cu and Sn. During the subsequent cycles, two new cathodic peaks at 1.56 V and 1.64 V appear because of some irreversible reactions. The shape of CV curves can almost retain indicating the good stability of the electrochemical process. As the galvanostatic charge-discharge curves also provide detailed information on electrochemical activity, we illustrated the discharge/charge curves for 1st, 2nd, 3rd, 5th and 100th cycles in a voltage range of 0.01-3.0 V (Fig. 4.12b). As can be seen, discharge capacity (1385 mAh g⁻¹) and subsequent charge capacity (870.3 mAh g⁻¹) show a large initial reversible capacity. In addition, the potential plateaus observed are in good agreement with the redox peaks in the CV curves.

Rate performance of the **CTS** electrode at both room temperature and 50 °C was further examined by first cycling the cell at 0.1 A g⁻¹ for five cycles with a gradual increase of the discharge/charge rates to as high as 10 A g⁻¹, as shown in Fig. 4.12c. The outstanding reversibility of the electrode can be deduced from the almost 100 % coulombic efficiency of each cycle at both room temperature and 50 °C, respectively. Reversible capacities at room temperature of about 800 mAh g⁻¹ at a discharge/charge rate of 0.1 A g⁻¹, 650 mAh g⁻¹ at 0.2 A g⁻¹, 520 mAh g⁻¹ at 0.5 A g⁻¹, 430 mAh g⁻¹ at 1 A g⁻¹, 215 mAh g⁻¹ at 5 A g⁻¹, 108 mAh g⁻¹ at 10 A g⁻¹ are achieved, respectively. It should be noted that a capacity of 623 mAh g⁻¹ at 0.1 A g⁻¹ can still be achieved after intensive cycles. In addition, notable capacities at evaluated temperature (50 °C) can also be obtained--about 500 mAh g⁻¹ at 0.1 A g⁻¹, 410 mAh g⁻¹ at 0.2 A g⁻¹, 350 mAh g⁻¹ at 0.5 A g⁻¹, 283 mAh g⁻¹ at 1 A g⁻¹, 181 mAh g⁻¹ at 5 A g⁻¹, 88 mAh g⁻¹ at 10 A g⁻¹. After intensive cycles,

453 mAh g⁻¹ at 0.1 A g⁻¹ can also be got. The high reversible capacities at both room temperature and 50 °C indicates the excellent rate performance of the **CTS**. Hence, we can reasonably infer that the excellent rate performance of the **CTS** proves both the large lithium ion storage and good kinetics, arising from not only the enhanced contact areas between the active materials and electrolyte but also the short lithium ions pathways due to the overall 3D nano-channels distribution in the **CTS** structures.

The long-term cycling properties of the **CTS** at both room temperature and 50 °C were also characterized with a current density of 0.1 A g⁻¹ as shown in Fig. 4.12e. One can see that **CTS** undergoes a capacity drop during the initial cycles (1st to 5th cycle) at both temperatures. The capacity drop is commonly observed in previous studies of transition metal oxides or sulfides as anode materials for LIBs,²¹³ which could be due to some irreversible reactions at the beginning. During the following cycles, good stability at room temperature can be observed with only 7.2% capacity drop after even 100 cycles. Remarkably, although relatively low capacities compared with those at room temperature are obtained at evaluated temperature (50 °C), **CTS** still shows good stability with 91.8% retention from 6th to 100th cycle. The good performance at both room temperature and evaluated temperature demonstrates its promising application of lithium ion batteries with long cycling life. The good cycling performance is comparable to or even better than those reported in previous literatures. This is possibly due to the unique structure of 3D open framework, which is able to accommodate large volume change along with the redox reactions. Thus the possibility of structure collapse can be

reduced significantly.

To gain insight into the reason that single crystals **CTS** with unique 3D open framework possessed such good cycling performance as electrode materials for LIBs, electrochemical impedance spectroscopy (EIS) was further performed at equilibrium open circuit potential (≈ 0 V). Fig. 4.12d shows the Nyquist spectra of the electrode materials before and after cycling in the frequency range of 100 kHz to 100 mHz, respectively. In impedance spectroscopy, high frequency activity was attributed to charge transfer phenomenon, whereas the low frequency region is ascribed to the mass transfer process. In order to quantify these respective values, a theoretical equivalent circuit of $R_s(Q(R_{ct}Z_w))$ is used to fit the experimental data, where R_s is the ohmic resistance; R_{ct} is the charge transfer resistance; Q is the double layer capacitance and Z_w is the Warburg impedance. With fitting method, R_{ct} of before (203Ω) and after (272Ω) cycling can be obtained. A slight increase of R_{ct} indicates negligible decay of charge transfer kinetics, further revealing the good cycling properties of **CTS** as potential anode materials for LIBs.

Figure 4.12. Electrochemical characterization of CTS anode. (a) Cyclic voltammograms between 0.01 and 3.0 V measured at a scan rate of 0.1 mV s⁻¹; (b) the charge and discharge curves of CTS at a current density of 0.1 A g⁻¹; (c) rate performance at different rates; (d) Nyquist plots of CTS electrode before and after cycles, respectively. The inset is the equivalent circuit; (e) capacity as a function of cycle numbers at a current density of 0.1 A g⁻¹

4.4.5 Summary

In summary, single crystal 3D-(H₃O)₂(enH₂)Cu₈Sn₃S₁₂ has been successfully prepared, in which the interconnected micro-channels (diameter of 1 nm) overall distributed and

both of H_2en^{2+} and H_3O^+ cations located in the micro-channels. This structure is very favorable for good electrolyte penetration and fast de/lithiation process as well as good accommodation ability for volume expansion. In addition, H_2en^{2+} and H_3O^+ can serve as useful stabilizers to avoid structure collapse. Therefore, when explored as electrode materials for lithium ion batteries, it exhibits outstanding electrochemical performance with a high capacity of 563 mA h g^{-1} at a current density of 0.1 A g^{-1} after 100 cycles as well as good cycling properties with only 7.2 % capacity loss from 5th to 100th cycle. This exploration can open up a new future of ternary thiostannate single crystal for lithium ion batteries.

4.5 IAS for Lithium/Sodium Storage

4.5.1 Electrochemical Measurements

To get a homogeneous slurry of the electrode material, **IAS** was first ground for 5 mins to obtain its powder form. A viscous mixture was made by adding **IAS** powders, carbon nanotubes (CNTs) and PVDF (with a weight ratio of 7:2:1) into NMP solvent. The mixture was stirred with a magnetic stirrer for two days and later transferred onto a battery grade copper foil current collector. The electrode material was dried under vacuum at 60° for 12 hours to thoroughly evaporate the NMP solvent. The obtained electrode was cut into smaller-sized circular disks to be used as the anodes. For half-cell lithium battery fabrication, lithium metals were used as the counter electrodes and 1M LiPF_6 in EC/DMC (1:1 in volume) was applied as the electrolyte solution. Celgard 2400

membrane was used as the separator. For half-cell sodium battery fabrication, sodium metals were used as the counter electrodes and 1M NaClO₄ in EC/DEC (1:1 in volume) with 10 wt% fluoroethylene carbonate (FEC) was applied as the electrolyte solution. Glass fiber was used as the separator. The cell assembly process was conducted in an argon-filled glovebox with less than 1 ppm of oxygen and moisture content, respectively. Before testing, the assembled cells (both lithium and sodium cells) were placed for 10 hours to ensure the electrodes were thoroughly rinsed by their electrolyte solutions. Electrochemical cell performance of **IAS** was obtained under room temperature on a NEWARE multichannel battery tester in the voltage range between 0.005 and 3.0 V. CV was conducted on an electrochemical analyzer (CH Instrument CHI604e) with a scan rate of 0.2 mV/s. EIS was performed on CHI604 in the ranges of 1Hz-100kHz (the 1st cycle) and 0.1Hz-100kHz (the 5th & 10th cycles).

4.5.2 Crystal Structure Analysis

SCXRD data indicate that **IAS** crystallizes in the monoclinic space group $P2_1/m$ and contains 2D anionic layers $[\text{InSb}_2\text{S}_5]_n^{n-}$ with *phen* molecules and NH_4^+ ions located in interlayers. The asymmetric unit of **IAS** (Fig. 4.13a) consists of half In^{3+} ion, one Sb^{3+} ion, two and one half S^{2-} ions, half NH_4^+ ion and half *phen* molecule, respectively. In1 adopts a distorted octahedral configuration and coordinates with six S atoms (Fig. 4.13b) with bond lengths ranging from 2.554(1) to 2.692(1) Å. The disordered Sb, which is

split into Sb1 and Sb1a, is coordinated with five S atoms (Fig. 4.13c). The Sb-S bond lengths range from 2.402(1) to 2.895(1) Å (the bond length is calculated from Sb1 and Sb1a), which is similar to the previously reported values in thioantimonate compounds.^{121, 214-217} The octahedral units $[\text{InS}_6]^{9-}$ connect with each other through S1 atoms to form 1D ribbon $[\text{InS}_4]_n^{5n-}$ (Fig. 4.14a). The rectangular pyramids $[\text{SbS}_5]^{7-}$ connect to each other via corner-sharing atoms of S2 and disordered S3 to construct 1D chain $[\text{SbS}_3]_n^{3n-}$. Two $[\text{SbS}_3]_n^{3n-}$ chains further connect with each other by S3 atoms to generate the double-chain $[\text{Sb}_2\text{S}_5]_n^{4n-}$ (Fig. 4.14c). The ribbons of $[\text{InS}_4]_n^{5n-}$ and $[\text{Sb}_2\text{S}_5]_n^{4n-}$ arrange through the connecting of S1 and S2 atoms to form an infinite layer $[\text{InSb}_2\text{S}_5]_n^{n-}$ (Fig. 4.14b). The *phen* molecules and NH_4^+ ions are located in the interlayer space (Fig. 4.15).

Figure 4.13. (a) Asymmetric unit of IAS with labelled bond lengths of Sb-S and In-S; (b) the coordination of In atom and (c) Sb atom.

Figure 4.14. View of the (a) 1D ribbon $[\text{InS}_4]_n^{5n-}$; (b) 2D layer $[\text{InSb}_2\text{S}_5]_n^{n-}$ and (c) double-layer $[\text{Sb}_2\text{S}_5]_n^{4n-}$ of IAS.

Figure 4.15. Stacking diagram of IAS viewed along *a* direction.

4.5.3 Characterization

The phase purity and thermal stability of **IAS** were confirmed by PXRD and TGA, respectively. The contents of ammonium and *phen* were verified by EA and TGA test. The simulated PXRD pattern of **IAS** is derived from its single-crystal X-ray diffraction data. The experimental PXRD pattern of bulk phase of **IAS** is well matched with its simulated one (Fig. 4.16a), indicating the phase purity of **IAS**. As shown in Fig. 4.16b, compound **IAS** is stable up to 280 °C and then follows the weight loss of NH₃, H₂S, *phen* molecule and the sublimation of S.

Figure 4.16. (a) PXRD patterns of compound **IAS**; (b) TGA curve of **IAS**.

4.5.4 Electrochemical Lithium Storage

To investigate the electrochemical properties of **IAS**, half-cells were fabricated by using lithium metals as the counter electrodes. The redox reactions of **IAS** were investigated by CV analysis. Fig. 4.17a presents the CV profiles of the first three scans between 3.0 and 0.0 V. The main difference between the 1st cycle and the following cycles (2nd and

3rd) was the existence of an additional cathodic peak at 1.08 V, which could be attributed to the formation of a solid electrolyte interface (SEI).²¹⁸ This peak disappeared in the following cycles, confirming the irreversible lithiation caused by SEI. For the 2nd and 3rd cycles, there were two distinct pairs of reduction/oxidation peaks, revealing the high reversibility of **IAS** during the redox reactions. In detail, the first pair of peaks at 1.57 V and 1.96 V was attributed to the conversion reaction of Sb³⁺ and In³⁺ to form metallic Sb and In, and vice versa (Eq. 4.1).^{41, 189} The peaks at a lower potential of 0.43 and 1.25 V might be due to the metal alloying reactions,^{41, 190} accompanying with the absorption of lithium-ions into the organic structure (Eq. 4.2 – 4.4).²¹⁹ Importantly, the shape and area of the CV curves kept almost the same during the 2nd and 3rd cycles, revealing a good reversibility of **IAS**.

Lithium-ion storage of **IAS** was investigated within the cutoff potential window of 3.0-0.005 V. The voltage profiles of the initial three cycles were displayed in Fig. 4.17b. The current density applied consistently for both the discharge and charge was 143 mA g⁻¹. At this rate, **IAS** delivered an initial discharge specific capacity of 1884 mAh g⁻¹ with a high and reversible value of 1107 mAh g⁻¹ in the following charge process. This capacity storage corresponds to the delithiation of approximately 29.6 lithium-ions. The capacity is nearly three times the value over the commercially available graphite anode (372 mAh g⁻¹). Regarding the reversibility, the initial CE of **IAS** was 58.77%. The large capacity loss was mainly due to the formation of a SEI on the electrode surface,²¹⁸ which was confirmed by the CV profiles. Nevertheless, the CE quickly increased to 93.53% in the

second cycle and could be maintained at a high level of > 98% in the following cycles.

The redox plateaus of **IAS** during the discharging and charging were in well accordance with the redox peaks in the CV profiles. Therefore, referring to the redox reaction study from the CV profiles as well as the previous investigations on Sb and In based sulfides,^{41, 189, 190, 220} the possible reactions between **IAS** and lithium are proposed as below:

where $n_1 + n_2 + n_3 + n_4 \approx 29.6$

With about 29.6 lithium-ions involved into the reactions, the capacity originated from the above reactions is consistent with the specific capacity of 1107 mAh g⁻¹ at 143 mA g⁻¹. It is worthy to highlight that the high lithium-ion storage of **IAS** could be maintained for 80 cycles without any capacity fading (Fig. 4.17c), indicating a stable structure of **IAS** as an anode material. The specific capacity of **IAS** after 80 cycles could still achieve at a high value of 1138 mAh g⁻¹, retaining a remarkable high retention of 97.6% of its capacity with respect to its second discharge (1166 mAh g⁻¹). Moreover, the CE of **IAS** after 80 cycles was as high as 99.04%. To the best of our knowledge, the reversible lithium-ion storage (1138 mAh g⁻¹ after 80 cycles) of **IAS** electrode is belonging to one

of the best performances among chalcogenide based electrode materials.^{182, 194-197, 199-201,}

²²¹ The unique In-Sb-S framework demonstrates a higher gravimetric capacity with an enhanced lithium-ion transportation. The outstanding performance is superior to the conventional In and Sb representatives, Sb₂S₃,¹⁸⁹ and In₂S₃,²⁰³ which delivers a capacity of only 720 mAh g⁻¹ (after 50 cycles) and 837 mAh g⁻¹ (after 30 cycles), respectively. Compared with the state-of-the-art superior chalcogenide anode materials (e.g. SnS₂, MoS₂, WS₂ etc.), **IAS** delivers much improved gravimetric capacity, cycling capability and rate performance. The performance is even better than many metal or metal oxide based anode materials.^{180, 222, 223} In addition to the electrochemical performance, considering the complex synthesis and tedious modification of nanostructured chalcogenide materials, our surfactant-thermal strategy offers an easy and bulk synthesis of novel chalcogenide anodes with higher lithium-ion storage and longer cycle lives in future. The excellent performance of **IAS** reveals its superiority to be deployed as an efficient anode for lithium-ion batteries. Rate performance of **IAS** was examined by applying different current densities. As shown in Fig. 4.17d, each current density consists of 10 cycles of charging and discharging. To begin with, a current density of 143 mA g⁻¹ was applied to the first 10 cycles. **IAS** exhibited an initial specific capacity of 1831 mAh g⁻¹ with a reversible capacity of 1092 mAh g⁻¹ in the following discharge. These capacity values were quite close to the values presented in the charge-discharge profiles (Fig. 4.17b), revealing a good repeatability of the assembled half-cells. In the following cycles, **IAS** could deliver a stable capacity of 885 mAh g⁻¹ at 428 mA g⁻¹ (the

11th-20th cycles), 817 mAh g⁻¹ at 1.14 A g⁻¹ (the 21st-30th cycles), 701 mAh g⁻¹ at 1.85 A g⁻¹ (the 31st-40th cycles) and 607 mAh g⁻¹ at 3.57 A g⁻¹ (the 41st-50th cycles). More importantly, the capacity of **IAS** could recover to a high value of 94.6% (1032 mAh g⁻¹) relative to its initial capacity when the current density was brought back to 143 mA g⁻¹. The results again showed that there was no capacity fading of **IAS** during each current density. This excellent rate performance is highly consistent with the good cycling performance, confirming the high reversibility and stability of **IAS** electrode under various current densities.

Figure 4.17. Electrochemical performance of IAS as anodes for LIBs. (a) CV profiles during the initial three cycles between 3.0 and 0.0 V at 0.2 mV/s. (b) Charge-discharge curves during the initial three cycles at 143 mAh g⁻¹. (c) Cycling performance and corresponding Coulombic efficiencies (CEs) at 143 mAh g⁻¹. (d) Rate performance and CE at various current densities from 143 mA g⁻¹ to 3.57 A g⁻¹

Long-term cycling is an effective method to assess the ultra-long stability of an electrode, especially the stability at a high current density. To further investigate the structural stability and to explore the maximum potential of **IAS** as a fast charge-discharge electrode material, 1000 cycles of charging and discharging was applied (Fig. 4.18a). The current density of the first 10 cycles was set at 143 mA g^{-1} . An initial capacity of 1723 mAh g^{-1} with a reversible capacity of 1022 mAh g^{-1} was achieved. Afterward, the current density was tuned to an ultra-high value of 2.85 A g^{-1} . It could be expected that the specific capacity of **IAS** dropped to 647 mAh g^{-1} from the 11th cycle. Amazingly, even after 1000 cycles, the cell could still work and deliver a reversible specific capacity of 634 mAh g^{-1} , approximating to a remarkable high retention of 98% of its initial capacity (the 11th cycle at 2.85 A g^{-1}). The CE of the cell was still as high as 99.62% at the 1000th cycle. To further confirm the long-term cycling capability of **IAS**, the voltage versus charge time profiles for the initial (the 11th cycle) and last cycle (the 1000th cycle) were shown (Fig. 4.18b and Fig. 4.18c). At the 11th cycle, the complete duration (step time) for one charge process was as fast as 13.60 mins (Fig. 4.18b). To be noted that, there was almost no change in the step time after the long-term cycling since a similar value of 13.25 mins was spent to charge the cell at the 1000th cycle (Fig. 4.18c). Such an outstanding cycling capability indicates the feasibility of **IAS** to be deployed as a suitable substitute for future rapid charge-discharge lithium-ion batteries. To study the kinetics of **IAS**, EIS was performed (Fig. 4.19). **IAS** shows normal features that each profile consists of a semi-circle (charge-transfer resistance) in the high frequency range

and a tail (Warburg resistance) in the low frequency range. IAS shows a semicircle of only $54\ \Omega$ at the 1st cycle (before charging and discharging) (inset of Fig. 4.19), indicating a low intrinsic charge-transfer resistance with a good kinetic reaction between the IAS electrode and the electrolyte. Although the charge-transfer resistance increased to $\sim 500\ \Omega$ at the initial cycles (5th cycle), the resistance did not further increase but decreased to $276\ \Omega$ in the following cycles (at the 10th cycle), revealing a stable performance during the charging and discharging.

Figure 4.18. Ultra-long cycling of IAS as anodes for LIBs. (a) Cycling and corresponding CEs of IAS at $2.5\ \text{A g}^{-1}$ for 1000 cycles. (b) Voltage vs. time profiles of IAS at the 11th. (c) Voltage vs. time profiles of IAS at the 1000th.

Figure 4.19. EIS profiles for IAS as an anode for LIBs.

4.5.5 Electrochemical Sodium Storage

Recently, sodium-ion batteries have become a promising alternative to LIBs due to the abundance and low cost of sodium metals.²²⁴ Tremendous studies have been conducted on alloy, oxide and sulfide based electrode materials.²²⁵ However, due to the poor insertion properties of Na-ions, existing anode materials for SIBs encounter low capacity and poor cyclability problems.²²⁶ In the present study, to evaluate the advantage of **IAS** as an anode material for SIBs, half-cells consisting of **IAS** electrodes and sodium metals were prepared. Fig. 4.20a shows the discharge-charge profiles of **IAS** at 50 mA g⁻¹. For the first cycle, **IAS** showed a high specific capacity of 1232 mAh g⁻¹ with a reversible capacity of 542 mAh g⁻¹ in the following charge. The reversible capacity slowly decayed to about 340 mAh g⁻¹ with a high CE of 96.35% at the 50th cycle (Fig. 4.20b). This good performance suggest that **IAS** could be a suitable material for the next-generation high performance SIBs. Furthermore, we investigated **IAS** at a higher

current density of 143 mAh g^{-1} as shown in Fig. 4.20c. **IAS** delivered an initial reversible capacity of 410 mAh g^{-1} with an average CE of 97.26% (excluding the first cycle) for 120 cycles. The results further reveal the potential of **IAS** to be adopted as a good sodium-storage material.

Figure 4.20. (a) Electrochemical performance of IAS as anodes for SIBs. (a) Charge-discharge curves during the initial three cycles at 50 mA h^{-1} . (b) Cycling performance and corresponding CEs at 50 mA h^{-1} . (c) Long-term cycling and corresponding CEs at 143 mA h^{-1} .

4.5.6 Summary

In summary, the novel crystalline metal chalcogenide $(\text{NH}_4)\text{InSb}_2\text{S}_5\text{:phen}$ (**IAS**) has been successfully synthesized via surfactant-thermal strategy and fully characterized.

One attractive feature of **IAS** is that NH_4^+ ions and *phen* molecules not only act as

counterions but as structure-directing agents or templates. The structure of **IAS** is very favorable for good electrolyte penetration. Molecular *phen* can act as both the channels and reservoirs for reversible lithiation and delithiation and accommodate the possible volume expansion during cycling. As a superior anode material, **IAS** has shown a significantly improved electrochemical performance (LIBs and SIBs) compared to the state-of-the-art chalcogenide based anode materials. The results may demonstrate the potential of **IAS** to be a stable and efficient anode material for next-generation high-performance rechargeable LIBs and SIBs.

Chapter 5

Conclusions and Future Work

5.1 Conclusions

A series of novel crystalline metal chalcogenides have been surfactant-thermally synthesized and fully characterized. Among them, two novel manganese thioantimonates $[\text{MnSb}_2\text{S}_4(\text{N}_2\text{H}_4)_2]$ (**MAS-1**) and $[\text{Mn}(\text{tepa})\text{Sb}_6\text{S}_{10}]$ (**MAS-2**) and two new silver thioantimonates $(\text{NH}_4)\text{AgSb}_4\text{S}_7 \cdot \text{H}_2\text{O}$ (**SAS-1**) and $(\text{NH}_4)\text{AgSb}_2\text{S}_4$ (**SAS-2**) have been used as efficient photocatalysts for aqueous organic pollutants degradation. Two manganese thioantimonates possess neutral layered structure while two silver thioantimonates are constructed with ammonium ions acting as counterions and structure-directing agents. The optical band gaps are estimated to be ~ 1.97 eV for **MAS-1**, ~ 2.12 eV for **MAS-2**, ~ 1.70 eV for **SAS-1** and ~ 1.85 eV for **SAS-2**, respectively, indicating these four compounds exhibiting semiconductor properties. The photocatalytic experiments indicate that four as-prepared samples are able to degrade CV and RhB under visible light irradiation. Moreover, all photocatalysts display selectively photocatalytic abilities on CV degradation. Compound **SAS-2** displays highest efficiency on CV degradation and **SAS-1** shows the highest activity for RhB degradation, which may be attributed to their suitable energy band gaps corresponding to the visible light absorption coupled with high stabilities of the skeleton structures.

Three novel crystalline metal chalcogenides have been explored as anode materials of

LIBs/SIBs. After grinding, compound $[\text{NH}(\text{CH}_3)_2][\text{Sb}_4\text{S}_5(\text{S}_3)]$ (**ASS**) presents as ultrathin nanosheets that can offer fast ion diffusion and increased active sites as well as good accommodation ability for volume expansion, which are favorable properties for LIBs. Employed as an anode material of LIBs, grinding **ASS** exhibits high reversible specific capacity of 568 mAh g^{-1} over 50 cycles at a current density of 0.1 A g^{-1} and excellent rate capability of 301 mAh g^{-1} at a current density of 5 A g^{-1} . Single crystal $(\text{H}_3\text{O})_2(\text{enH}_2)\text{Cu}_8\text{Sn}_3\text{S}_{12}$ (**CTS**) possesses open framework, in which the interconnected micro-channels (diameter of 1 nm) overall distributed and both of H_2en^{2+} and H_3O^+ cations located in the micro-channels. This structure is very favorable for good electrolyte penetration and fast de/lithiation process as well as good accommodation ability for volume expansion. In addition, H_2en^{2+} and H_3O^+ can serve as useful stabilizers to avoid structure collapse. Therefore, when explored as electrode materials for lithium ion batteries, **CTS** exhibits outstanding electrochemical performance with a high capacity of 563 mA h g^{-1} at a current density of 0.1 A g^{-1} after 100 cycles as well as good cycling properties with only 7.2 % capacity loss from 5th to 100th cycle. One attractive feature of $(\text{NH}_4)\text{InSb}_2\text{S}_5\cdot\text{phen}$ (**IAS**) is that NH_4^+ ions and *phen* molecules not only act as counterions but as structure-directing agents or templates. The structure of **IAS** is very favorable for good electrolyte penetration. Molecular *phen* can act as both the channels and reservoirs for reversible lithiation and delithiation and accommodate the possible volume expansion during cycling. **IAS** delivers a high capacity of 1107 mAh g^{-1} , good rate stability up to 3.57 A g^{-1} and ultra-long stability as a superior anode

for LIBs. The capacity retention could achieve a remarkable high value of 98% even after 1000 cycles of testing at 2.85 A g^{-1} . As anode material of SIBs, **IAS** provides a capacity of 542 mAh g^{-1} with a high CE of 96.35% at the 50th cycle. All of the results demonstrate that **ASS**, **CTS** and **IAS** exhibit significantly improved electrochemical performances compared to the state-of-the-art chalcogenide based anode materials. These results may bespeak the potential of crystalline metal chalcogenides as stable and efficient anode materials for next-generation high-performance rechargeable LIBs and SIBs.

5.2 Future Work

With the exploration of surfactant-thermal method recent years, dozens of novel crystalline metal chalcogenides, MOFs and metal bromides have been successfully synthesized. All of the as-obtained results impel us to continue our research on surfactant-thermal method and investigate the physicochemical properties and applications of crystalline compounds prepared through surfactant-thermal method. Therefore, the further research will contain three aspects:

- To continue the preparation of crystalline metal chalcogenides through surfactant-thermal method. In this dissertation, the as-obtained novel crystalline metal chalcogenides are mainly transition metal chalcogenides, including Mn/Ag/Cu-based chalcogenides. On one hand, the syntheses of Mn/Ag/Cu-based sulphides will be continued and different solvents and organic small

molecules as templates will be tried. On the other hand, other transition metals will be introduced into the synthesis system to prepare more ternary or even quaternary crystalline metal chalcogenides.

- To further study the photocatalytic properties of crystalline metal chalcogenides. Normally, the as-prepared single crystals are in millimetre-sized and ground samples mostly are micron-grade, ranging from several micrometres to several hundred micrometres. Hence, it is necessary to get the nanoscale samples that possess higher surface area and more active sites to improve the photocatalytic activities. In addition, the photocatalysts will be used for carbon dioxide reduction and water splitting to produce hydrogen and that related to urgent energy issue.
- To continue the exploration of crystalline metal chalcogenides as anode materials of LIBs and SIBs. Sn (994 mA h g^{-1}) and Sb (660 mA h g^{-1}) have high theoretical capacity, so the preparation of thiostannates and thioantimonates will be continued. Besides, open-framework crystalline thiostannates and thioantimonates with organic small molecules as templates or structure-directing agents will attract much attention, which may be benefit for the Na ions shuttling in the channels.

Appendixes

Atomic Coordinates of As-prepared Compounds

Table A1. Atomic coordinates and displacement parameters of non-hydrogen atoms for MAS-1

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Mn(1)	0	0	0	0.0167(3)
Sb(1)	-0.19738(2)	-0.12861(9)	-0.14176(3)	0.01627(16)
S(1)	-0.20648(8)	-0.2484(4)	-0.34391(13)	0.0179(4)
S(2)	-0.09543(8)	0.1713(4)	-0.15620(13)	0.0193(4)
N(1)	-0.0361(3)	0.3627(12)	0.1188(4)	0.0148(12)
N(2)	0.0687(3)	0.3644(12)	-0.0723(4)	0.0155(11)

Table A2. Atomic coordinates and displacement parameters of non-hydrogen atoms for MAS-2

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Mn(1)	0.0303(4)	0.2375(6)	0.2761(12)	0.112(5)
Sb(1)	0.2461(0)	0.1615(0)	0.1543(1)	0.0177(2)
Sb(2)	0.242(0)	0.4162(0)	0.1709(1)	0.0211(3)
Sb(3)	0.2326(1)	0.1255(1)	0.4768(1)	0.0269(3)
S(1)	0.3439(2)	0.5122(2)	0.1981(4)	0.0330(9)
S(2)	0.1704(2)	0.2468(2)	0.3422(4)	0.0309(8)
S(3)	0.3241(2)	0.0699(2)	0.0702(3)	0.0217(7)
S(4)	0.3208(2)	0.2919(2)	0.1603(3)	0.0197(7)
S(5)	0.3269(2)	0.1101(2)	0.3760(3)	0.0248(7)

Table A3. Atomic coordinates and displacement parameters of non-hydrogen atoms for SAS-1

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Ag(1)	-0.1687(6)	0.6583(3)	0.6272(4)	0.0364(6)
Ag(2)	-0.1869(6)	0.6642(4)	0.6135(4)	0.0443(8)
Sb(1)	0.39764(4)	0.44584(3)	0.65841(2)	0.01667(7)

Sb(2)	0.00780(3)	0.19011(3)	0.73260(2)	0.01602(7)
Sb(3)	0.25754(4)	0.88667(3)	0.52895(2)	0.01775(7)
Sb(4)	0.54944(4)	0.04201(3)	0.83936(2)	0.02007(7)
S(1)	0.25007(14)	0.01816(12)	0.95769(9)	0.0229(2)
S(2)	0.33622(14)	0.14036(11)	0.64183(8)	0.01938(19)
S(3)	0.03673(14)	1.09538(11)	0.34448(8)	0.01871(19)
S(4)	0.57730(14)	0.30638(11)	0.83682(8)	0.01806(19)
S(5)	-0.14282(15)	0.32471(11)	0.54117(8)	0.0206(2)
S(6)	0.06849(14)	0.44308(11)	0.76147(8)	0.01739(18)
S(7)	0.46444(14)	0.68613(11)	0.69888(9)	0.01986(19)
N(1)	0.2831(5)	0.3942(4)	1.0491(3)	0.0296(8)
O(1)	-0.1010(6)	0.3043(4)	1.0674(3)	0.0485(10)

Table A4. Atomic coordinates and displacement parameters of non-hydrogen atoms for SAS-2

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Ag(1)	0.33920(13)	0.50138(18)	0.66829(12)	0.0283(5)
Sb(1)	0.33781(9)	0.07570(13)	0.48760(8)	0.0147(4)
Sb(2)	0.36417(9)	0.53110(12)	0.33187(8)	0.0140(4)
S(1)	0.2239(3)	0.3771(4)	0.4217(3)	0.0154(7)
S(2)	0.2055(3)	-0.0945(5)	0.2866(3)	0.0168(8)
S(3)	0.1982(4)	-0.0069(5)	0.5967(3)	0.0174(8)
S(4)	0.4877(3)	0.2646(4)	0.3270(3)	0.0167(7)
N(1)	0.0041(11)	-0.2960(16)	0.3862(12)	0.028(3)

Table A5. Atomic coordinates and displacement parameters of non-hydrogen atoms for ASS

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Sb(1)	0.05226(9)	0.42968(4)	1.31284(17)	0.0248(3)
Sb(2)	0.2500	0.49087(7)	0.8582(3)	0.0350(5)
Sb(3)	-0.2500	0.37448(12)	1.5593(6)	0.0712(9)

S(1)	0.2500	0.3766(2)	1.3726(11)	0.0281(13)
S(2)	0.0632(5)	0.43027(18)	0.8982(9)	0.0319(11)
S(3)	-0.2500	0.2976(6)	1.794(2)	0.091(4)
S(4)	-0.2500	0.3755(2)	1.0683(11)	0.0248(13)
S(5)	-0.0707(4)	0.34889(17)	1.3126(12)	0.0390(11)
S(6)	0.2500	0.5162(3)	1.2447(12)	0.0331(15)
N(1)	0.2500	0.3175(11)	0.858(7)	0.066(9)
C(1)	0.126(2)	0.2912(9)	0.811(6)	0.065(7)

Table A6. Atomic coordinates and displacement parameters of non-hydrogen atoms for CTS

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Sn(1)	0.0000	0.2500	0.0000	0.0143(4)
Cu(1)	-0.08788(17)	0.08788(17)	0.08788(17)	0.0282(14)
Cu(2)	-0.08906(16)	0.08906(16)	-0.08906(16)	0.0233(12)
S(1)	-0.10943(11)	0.17423(9)	0.0003(6)	0.0188(5)
N(1)	-0.2500	0.2500	0.0000	0.26(2)
N(2)	-0.2500	0.2500	0.2500	0.27(2)
C(1)	-0.2500	0.2500	0.128(3)	0.27(2)

Table A7. Atomic coordinates and displacement parameters of non-hydrogen atoms for IAS

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
In (1)	0.5000	0.5000	0.5000	0.00927(18)
Sb(1)	-0.0001(10)	0.64631(11)	0.3543(2)	0.0193(5)
S(1)	0.0033(4)	0.59703(8)	0.53244(12)	0.0125(3)
S(2)	0.5112(6)	0.46168(10)	0.69699(14)	0.0265(4)
S(3)	0.4966(8)	0.73134(14)	0.4028(2)	0.0121(7)
N(1)	0.0215(19)	0.6778(3)	0.8207(5)	0.0251(14)
N(2)	0.526(3)	0.7500	0.6628(7)	0.029(2)
C(1)	0.022(3)	0.6072(5)	0.8214(7)	0.045(3)

C(2)	0.150(2)	0.7114(5)	0.9105(6)	0.0282(17)
C(3)	0.280(2)	0.6754(5)	1.0017(7)	0.037(2)
C(4)	0.424(3)	0.7143(6)	1.0926(7)	0.042(2)
C(5)	0.276(3)	0.5997(6)	0.9989(9)	0.058(3)
C(6)	0.134(4)	0.5667(6)	0.9084(9)	0.073(5)

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