

**Synthesis and properties of novel π -SnS particles and
their potential in photocatalytic H₂ evolution
performance**

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Thesis submitted for the degree of Doctor of Philosophy in Engineering



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Chapter 1 General Introduction

1.1 Introduction

The rapid advancement of modern economies has been heavily reliant on the overexploitation of fossil fuels, resulting in two critical global challenges: energy security crises and environmental degradation^[1]. First, the inherent limitations of non-renewable resources, their finite nature and uneven geographical distribution, have led to severe socioeconomic consequences, including corporate bankruptcies and economic stagnation in energy-dependent nations. Second, fossil fuel combustion has become the primary driver of climate change, manifesting in rising global temperatures, increased frequency of extreme weather events, and cascading ecological disasters. Notable examples include accelerated glacial melting in critical regions like the Alps and Greenland, which not only threatens marine ecosystems but also contributes to alarming sea-level rise^[2]. Furthermore, climate change has been linked to the expanded prevalence of infectious diseases such as dengue fever, posing significant public health risks^[3]. In response, the global energy landscape is undergoing a transformative shift toward sustainable alternatives. Solar, wind, nuclear, tidal, and geothermal energy systems are being deployed at unprecedented scales. As illustrated in Figure 1-1, renewable electricity generation is projected to surge by nearly 90% from 2023 levels, exceeding 17,000 TWh by 2030^[4], marking a decisive transition toward a cleaner energy future.

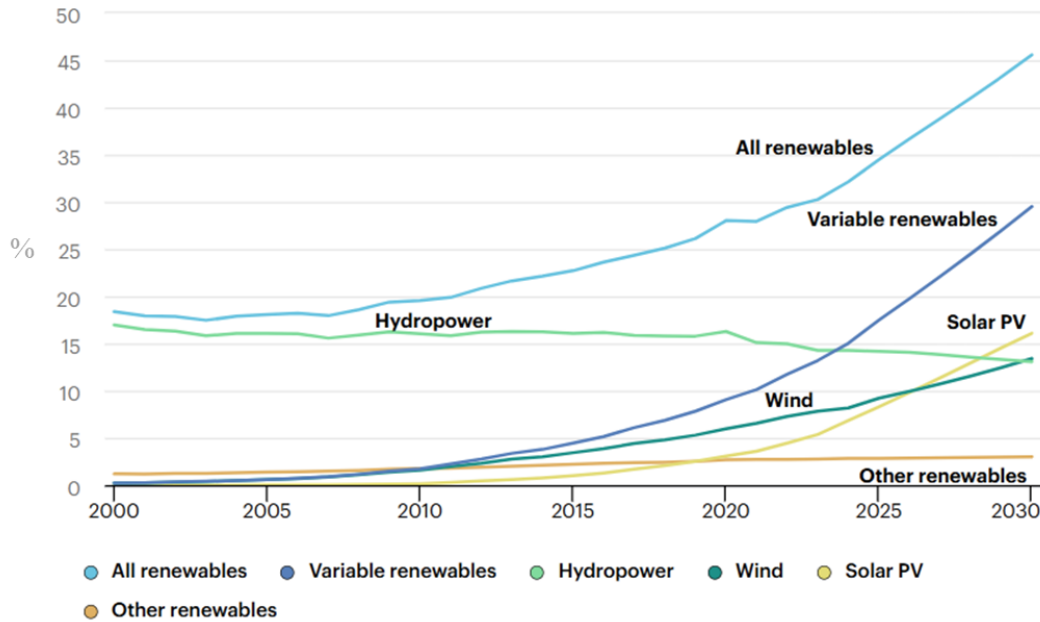


Figure 1-1. Share of renewable electricity generation by technology, 2000-2030.^[4]

Solar energy has emerged as the most promising renewable alternative to fossil fuels due to its abundance, inexhaustibility, and global availability. Beyond conventional photovoltaics, artificial photosynthesis inspired by natural photosynthetic systems provides an innovative approach to solar energy utilization that can effectively address the inherent challenges of solar intermittency and low energy density. As illustrated in Figure 1-2(a), natural photosynthesis converts H_2O and CO_2 into carbohydrates and O_2 using solar photons.^[5] This process can be artificially replicated (Figure 1-2(b)) through photocatalytic systems that transform solar energy into storable chemical fuels, including CH_4 , CH_3OH , CO , H_2 , and O_2 . Among these solar fuels, hydrogen stands out as particularly attractive owing to its exceptional energy density (142 MJ/kg) and clean combustion^[6,7]. Current industrial hydrogen production remains predominantly dependent on fossil fuel reforming (accounting for ~95% of global H_2 production), which not only perpetuates carbon emissions but also exacerbates environmental degradation^[8]. In this context, photocatalytic water splitting for "green" hydrogen generation represents a transformative solution for sustainable energy development, offering a carbon-neutral pathway to renewable fuel production^[9,10].

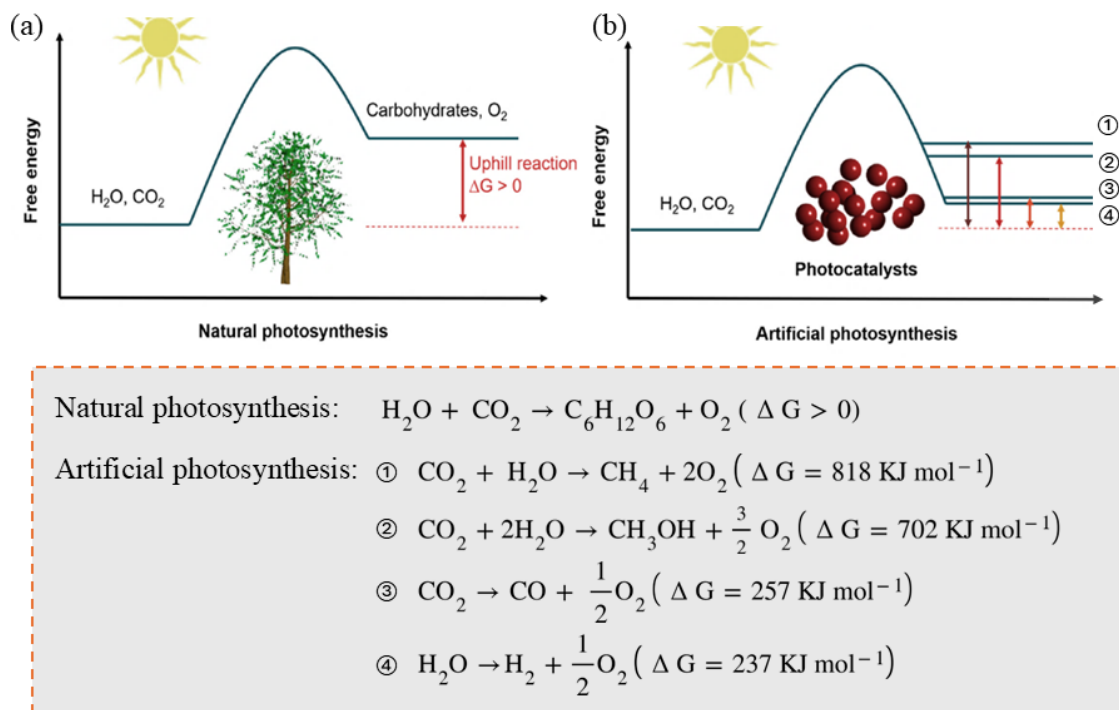


Figure 1-2. Schematic illustration of (a) natural and (b) artificial photosynthetic systems.^[5]

Current technologies for solar-driven hydrogen production primarily fall into three categories: photovoltaic-electrolysis (PV-EC), photoelectrochemical (PEC), and particulate photocatalysis systems (Figure 1-3).^[11]

1. PV-EC systems integrate three key components: a solar photovoltaic cell (light absorber), an oxygen evolution catalyst (OEC), and a hydrogen evolution catalyst (HEC). While effective, these systems face challenges including high costs and material stability issues, particularly concerning PV cell corrosion in aqueous electrolytes.
2. PEC systems employ a photoelectrode-electrode configuration that typically requires external bias to overcome overpotential and other energy losses, adding complexity to system design and operation.
3. Particulate photocatalysis offers distinct advantages through its simple powder suspension format, which significantly reduces costs and system complexity.

compared to PV-EC and PEC approaches. Recent advances in photocatalyst "sheet" configurations have further enhanced the scalability potential of this technology ^[12].

Despite these advantages, particulate photocatalysis currently faces limitations in solar-to-hydrogen (STH) conversion efficiency, which remains below the 10% threshold considered commercially viable ^[13]. Nevertheless, significant progress has been made in recent years, and with continued research efforts, this approach shows strong promise for practical large-scale implementation ^[11,14].

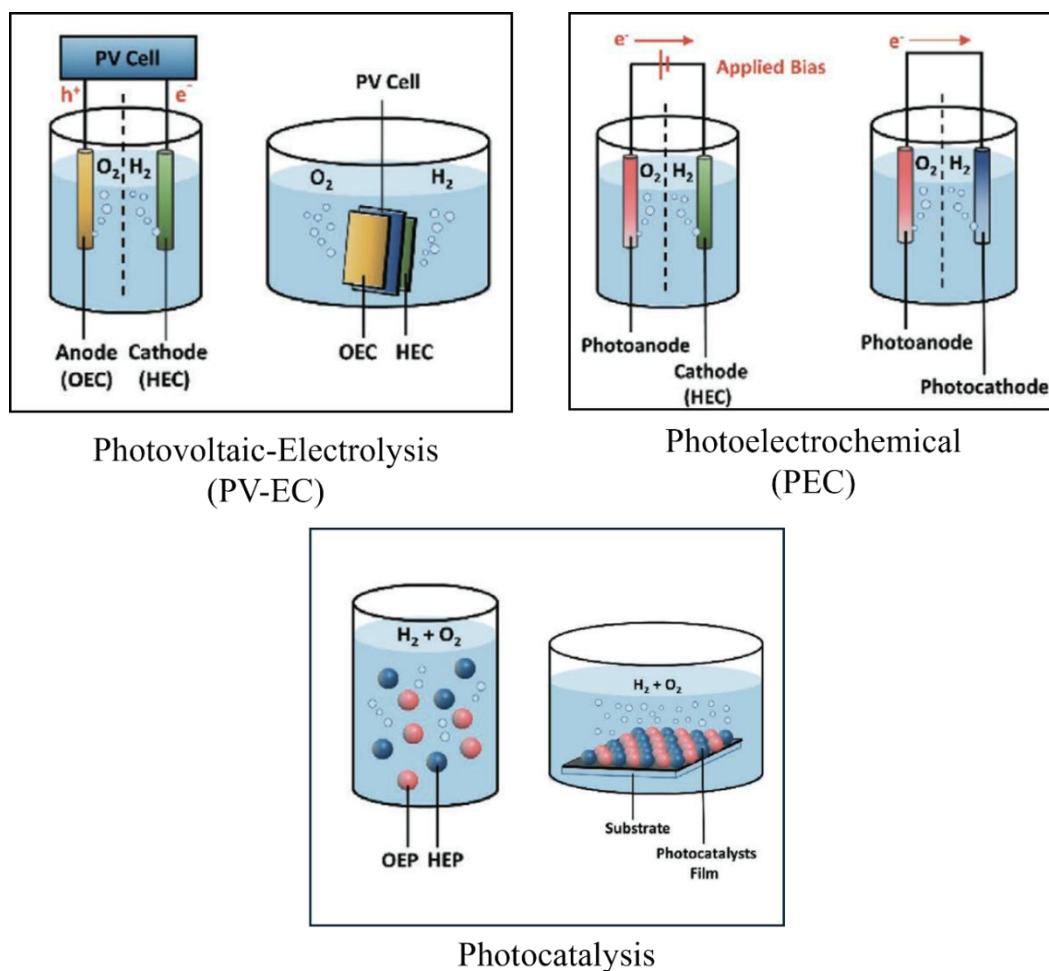


Figure 1-3. Schematic illustration of solar water splitting technologies: PV-EC, PEC, and particulate photocatalysis. ^[11]

1.2 Particulate photocatalysts

1.2.1 Thermodynamics and kinetics of photocatalysis

1.2.1.1 Basics of overall water splitting

Like natural photosynthesis, photocatalytic overall water-splitting is an uphill chemical reaction with an increased Gibbs free energy of 237 KJ mol^{-1} as shown in equation (1)



According to equation (2), it requires two electrons H_2 evolution reaction (HER), and correspondingly four holes for O_2 evolution reaction (OER) as seen in equation (3). Ideally, the photocatalyst will first be excited by absorbing photons with energy equal to or greater than its bandgap (E_g). As a result, it will generate pairs of photoexcited electrons (e^-) in a higher energy state conduction band (CB) and empty holes (h^+) left in a lower energy state valence band (VB), as step 1 shows in Figure 1-4 (a). In step 2, the photoinduced electrons and holes will migrate to the surface of photocatalysts separately. However, the separated electrons and holes may recombine in this process, leading to a reduced electron-hole separation efficiency. In step 3, the carriers that successfully migrate to the surface will eventually participate in oxidation or reduction reaction with the absorbed reactants. For efficient H_2 and O_2 evolution, the CB potential of the photocatalyst is required to be more negative than the H_2 production level, H^+/H_2 (-0.41 V) while the VB potential must be more positive than the water oxidation level, $\text{O}_2/\text{H}_2\text{O}$ ($+0.82 \text{ V}$). ^[11]

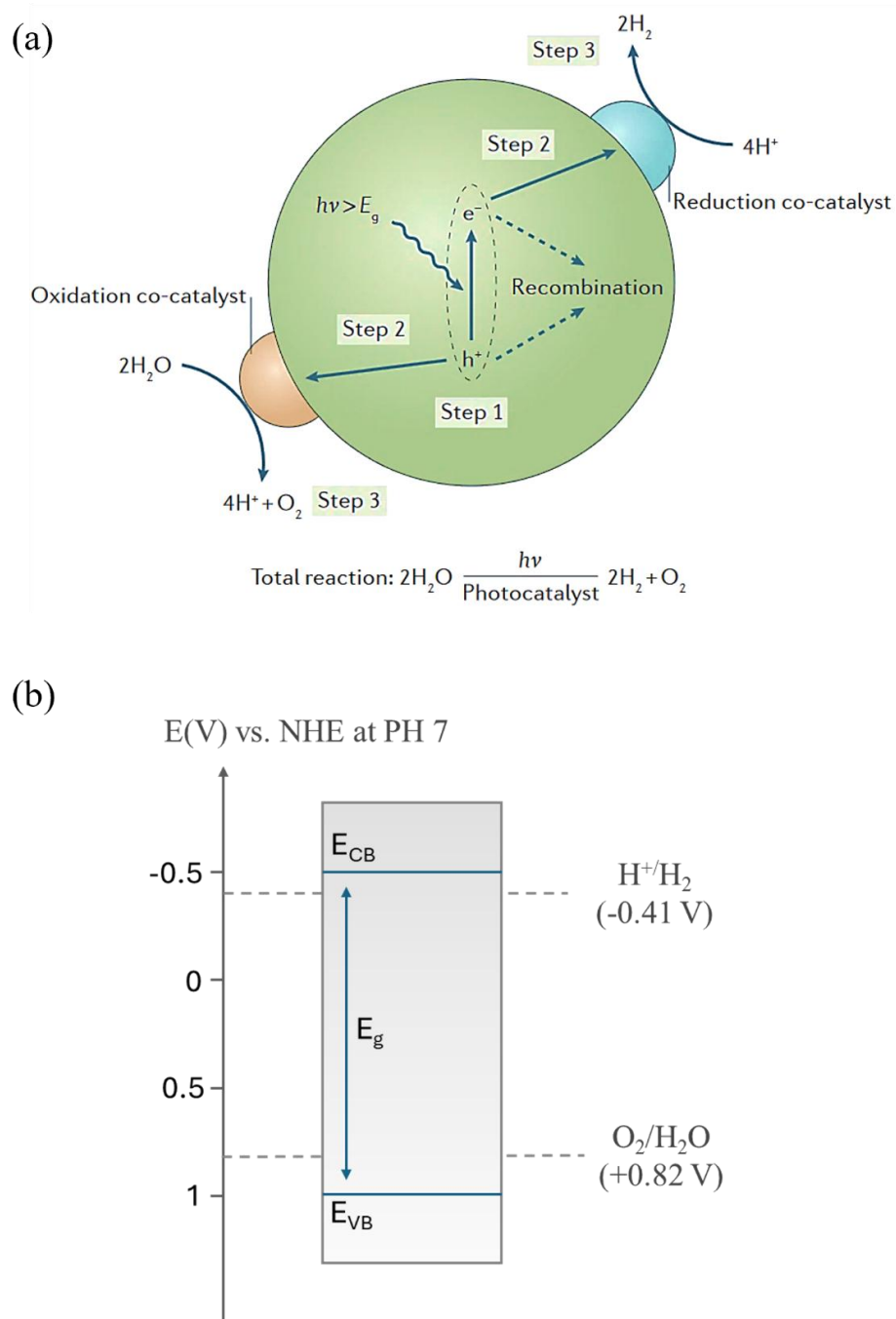


Figure 1-4. Schematic illustration of (a) the main processes within the photocatalytic overall water-splitting reaction. (b) the electronic structure requirement for efficient water-splitting. E_g : semiconductor bandgap ^[11,13]

1.2.1.2 Charge transfer between semiconductor and cocatalyst

Cocatalyst is an important component for most semiconductors to achieve high photocatalytic activity. The main function of the cocatalyst is to promote the effective separation of charge carriers and provide reactive sites for $\text{H}_2/\text{H}_2\text{O}$ evolution.^[15] Metals, especially noble metals, are often used as reduction cocatalysts (HECs).^[16,17] The efficiency of HER is determined by the cocatalyst's ability to capture photoexcited electrons from the semiconductor, its catalytic activity to reduce H^+ , and its ability to bind surface $\text{H}\cdot$ to release H_2 . The metals with large functions (or lower Fermi levels) are inclined to form a Schottky junction with photocatalysts, resulting in the formation of a built-in electric field and thus improving the separation efficiency of charge carriers from photocatalysts to cocatalysts, as shown in Figure 1-5(a).^[18,19] Pt is usually seen as the most efficient cocatalyst due to its largest work function. Besides, the M-H bond between the metal and the absorbed $\text{H}\cdot$ is critical to generate $\text{H}\cdot$ and H_2 .^[20,21] The metal Pt's adsorption and desorption free energy for $\text{H}\cdot$ is close to zero, making it easier to combine and release $\text{H}\cdot$ thermodynamically. In addition, some semiconductors including metal oxides and hydroxides can also form a similar built-in electric field with photocatalysts by aligning the band structure effectively. As shown in Figures 1-5(b) and (c), the formed band alignment is like type I or type II heterojunctions, which facilitates the transfer of photoexcited electrons from photocatalysts to cocatalysts.^[22]

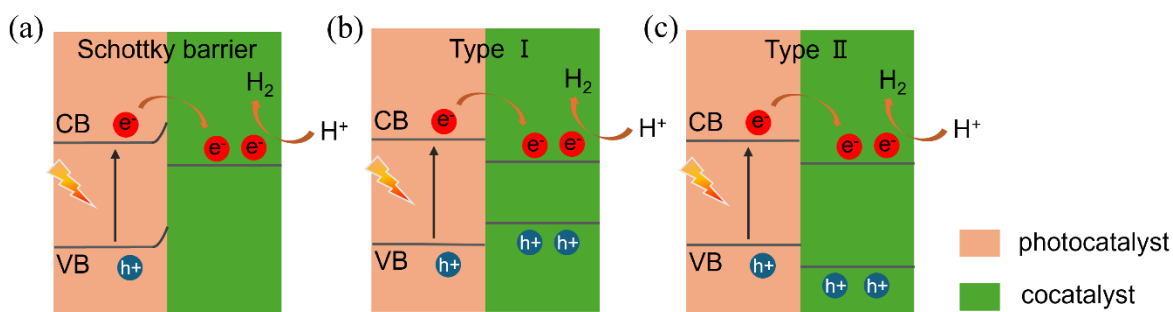


Figure 1-5. Schematic diagram of charge transfer through: (a) Schottky barriers, (b,c) heterojunctions for photocatalytic H_2 evolution in the semiconductor/transition-metal-based cocatalyst system.^[22]

1.2.2 Conditions for high efficiency of solar energy conversion

Consistent with the photocatalytic process, the efficiency of energy conversion is mainly determined by light absorption, carrier separation and migration, and chemical reactions on the surface of photocatalysts.

1) Light absorption: At present, most of the efficient photocatalysts for H₂ production are wide bandgap semiconductors due to the strong redox potential of the CB/VB level. For example, the commercialized photocatalyst TiO₂ has a bandgap of 3.0-3.2 eV. Contrastingly, the strong redox potential of CB/VB level narrowed the range of solar light utilization. In other words, TiO₂ can effectively absorb and utilize ultraviolet light, which accounts for 5% of sunlight but cannot absorb visible light and infrared light which account for 45% and 50% of sunlight, respectively. As a result, the efficiency of using sunlight is very low.^[23] Similarly, most traditional oxide semiconductor photocatalysts like ZnO are limited in further applications due to the wide band gap.^[24] Therefore, besides the appropriate CB and VB potentials, the semiconductors used for photocatalytic water splitting reactions should have as narrow a bandgap as possible to absorb and utilize more visible and near-infrared light.

2) Carrier separation and migration: The photoexcited electrons and holes have a lifetime of nanoseconds to migrate to the surface of photocatalysts and participate in redox reactions with the adsorbed reactants. However, electron-hole pairs recombination due to the Coulomb force is in competition with the charge transfer process which impedes the supply of photogenerated electrons and holes.^[25] The flash recombination is in the order of 10⁻⁹ s, which is much faster than the chemical reaction on the surface (10⁻⁸ to 10⁻³ s), making the recombination of charge inevitable.^[26] On the other hand, the catalyst itself has crystal defects including internal defects and surface defects, disordered interface and boundaries, which act as recombination centers for the carriers and cause the catalyst to lose its photocatalytic activity.^[27, 28] Therefore, improving crystal quality and reducing crystal defects play a crucial and fundamental role in effective carrier separation and the corresponding photocatalytic reaction.

3) Surface chemical reaction: When the photoelectrons migrate to the surface successfully, they will react with the H^+ that adsorbed on the photocatalyst surface and H^+ is therefore reduced to H_2 . In this process, the absorption and activity of surface H^+ and the desorption of generated H_2 jointly determine the efficiency of the surface chemical reaction. As a result, the surface properties are of great importance for surface chemical reactions. Usually, the adsorption and reaction are concentrated in the active sites exposed on the catalyst surface.^[29] Controlling the ratio of active sites and their activation potential is the key to tuning the capacity of H_2 generation. For example, catalysts with a larger specific surface area such as ultrathin two-dimensional catalysts or mesoporous catalysts are believed to supply more active sites for reaction, thus getting a better photocatalytic performance.^[30] The catalyst with different crystal planes can build an electric field due to the surface potential difference, which can improve carrier separation and transfer efficiency. In addition, some specific crystal planes of Bi_2VO_4 and $SrTiO_3$ show higher adsorption of H^+ and redox activity, which also improves photocatalytic efficiency.^[31,32] Generally, unsaturated coordination sites have higher site activity, making them more receptive to reactants during catalytic reactions, because such sites have more suspended chemical bonds.

1.2.3 Semiconductor materials for H_2 generation

A diverse range of semiconductor photocatalysts has been extensively investigated for hydrogen generation, primarily encompassing metal oxides, metal (oxy)nitrides, metal sulfides, and organic semiconductor materials. Among these, metal oxides represent one of the most widely studied categories in photocatalytic water splitting research.

Metal oxides are one of the most common semiconductor materials in the current research of photocatalytic water splitting. They usually have positive VB potential (about +3V vs. HNE, PH = 0), so it is difficult to find an oxide with a narrow bandgap to absorb visible light and a sufficiently negative CB potential to satisfy the reduction of H^+ . Considering the advantages of the rich variety and good stability, many researchers have explored various modification methods to improve their light absorption and charge separation efficiency. Plasmonic metal-semiconductor composites based on the surface plasmon resonance (SPR) effect provide an

effective approach to overcome the limitation from the wide bandgap of oxides. Various plasmonic metals such as Au, Ag and Cu have been widely introduced to the surfaces of semiconductors including PbTiO_3 ^[33], SrTiO_3 ^[34], and TiO_2 ^[35] to enhance light absorption ability. Doping with metal elements is another effective way to narrow the bandgap of oxide semiconductors. The research by Kudo et al. showed that Mn, Ru, Rh or Ir-doped SrTiO_3 can produce obvious optical responses in the visible light region, which is attributed to the excitation of the impurity energy level introduced in the forbidden band of SrTiO_3 .^[36] Besides, Domen et al. proposed the concept of “defect engineering” by doping low-valent cations to enhance photocatalytic activity. The Al-doped SrTiO_3 with specific structure design had achieved nearly 100 % photocatalytic total water splitting external quantum efficiency.^[37]

The family of metal sulfide photocatalysts encompasses diverse materials, with over thirty reported variants incorporating transition metals (Zn, Cd, In, Sn, Cu, etc.).^[38,39] Usually, metal sulfides have narrow bandgaps and conduction band minimums (CBM) that are conducive to H^+/H_2 reduction^[40], making them very attractive in H_2 production using visible light. However, the practical applications are not satisfactory. This is mainly because the narrow bandgap leads to a higher carrier recombination.^[41] Besides, the S^{2-} contained in the crystals is easily oxidized by photogenerated holes, resulting in photocorrosion and thereby reducing their catalytic activity.^[42] For example, CdS is one of the most widely studied materials responding to visible light. Since there are still great challenges in regulating CdS itself, the deposition of cocatalyst is often required to enhance its photocatalytic H_2 production activity. Xu et al. prepared Pt/CdS photocatalyst by the photodeposition method, getting a H_2 evolution activity of $1300 \mu\text{mol}\cdot\text{h}^{-1}$.^[43] Yan et al. proposed the use of redox dual cocatalysts to optimize CdS photocatalytic activity. The Pt-PbS/CdS composite showed excellent photocatalytic H_2 production with a high apparent quantum efficiency (AQE) of 93 % at 420 nm. As an oxidation co-catalyst, PbS effectively promotes the transfer of photogenerated holes, thereby significantly inhibiting the carrier recombination and the occurrence of photocorrosion.^[44]

1.3 π -SnS: An emerging candidate for efficient photocatalysis

1.3.1 Properties of SnS

SnS naturally crystallizes in an orthorhombic structure (space group: *Pnma*), exhibiting anisotropic vibrational characteristics due to its layered structure.^[45] The individual layers are interconnected through weak van der Waals forces, which result in chemically inert surfaces devoid of dangling bonds and surface states.^[46] This structural feature prevents Fermi-level pinning, endowing SnS with exceptional chemical and environmental stability.^[47] The compound further demonstrates notable chemical robustness in acidic media^[48] and outstanding thermal stability, with characteristic melting and boiling points of 880°C and 1230°C, respectively. At room temperature, SnS possesses a work function of ~4.2 eV and dissociation energies of ~4.5 eV^[49].

The orthorhombic phase of SnS remains compositionally stable across a range of stoichiometries ($\text{Sn:S} = 1:1 + x$). In this system, excess chalcogen atoms stoichiometrically generate tin vacancies, where each additional sulfur atom introduces two holes into the crystal lattice, leading to intrinsic p-type semiconductor behavior.^[50] Under normal temperature and pressure (NTP) conditions, SnS exhibits dual optical transitions, featuring both indirect (1.07-1.25 eV) and direct (1.30-1.39 eV) bandgaps, with the specific values being highly dependent on synthesis methodology and exact stoichiometry. Notably, SnS possesses a high absorption coefficient larger than 10^4 cm^{-1} , a value that substantially outperforms conventional photovoltaic absorbers, including CdTe, CIS, and CIGS^[49].

In addition to its thermodynamically stable orthorhombic phase (*Pnma*; Figure 1-6(a)), SnS exhibits rich polymorphism with several metastable phases that have attracted considerable scientific attention. The principle metastable polymorphs include: These include: 1) The rocksalt phase (*Fm-3m*; Figure 1-6(b)), stabilized through epitaxial strain in thin-film configurations^[51]; 2) A high-temperature orthorhombic modification (*Cmcm*; Figure 1-6(c)) that becomes thermodynamically accessible above 600°C^[52]; and 3) The zincblende structure (*F-43m*; Figure 1-6(d)), initially identified in 1962 through vapor deposition of SnS on rocksalt substrates^[53]. Each polymorph exhibits distinct electronic and optical properties,

offering tunable characteristics for optoelectronic applications. The rocksalt phase, for instance, shows metallic conductivity, while the zincblende structure exhibits a significantly narrower bandgap compared to the ambient orthorhombic phase. This phase diversity enables SnS potential for materials engineering through controlled polymorph stabilization, offering a versatile platform for property-by-design approaches in semiconductor technology.

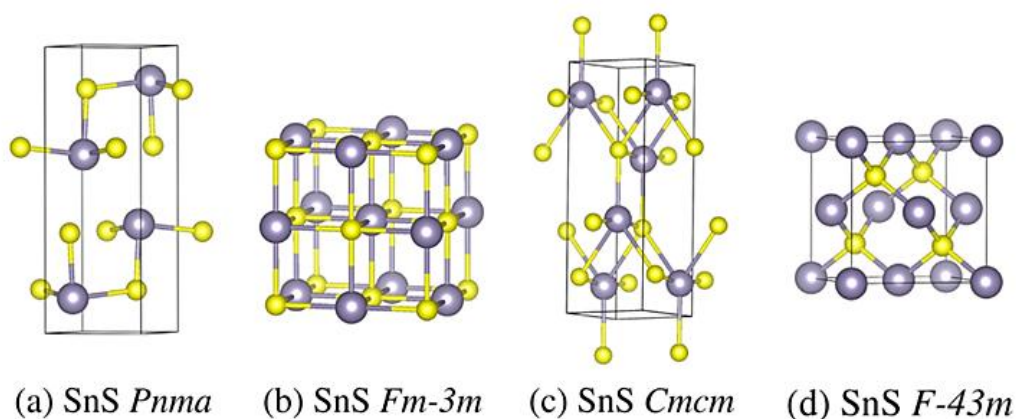


Figure 1-6. Crystal structure of SnS. (a) orthorhombic ground state phase, (b) rocksalt phase, (c) orthorhombic high temperature phase, (d) zincblende phase. (gray purple: tin atoms, yellow: sulfur atoms)

1.3.2 Research progress on SnS photocatalyst

With the advantageous properties mentioned above, SnS has emerged as a highly promising photocatalyst material. Various SnS nanostructures, including nanocubes, spherical polyhedrons and nanosheets, have demonstrated exceptional photocatalytic activity in methylene blue (MB) degradation. ^[54] Systematic studies reveal a strong morphology-dependent photocatalytic performance, with nanocubes exhibiting superior activity attributed to their predominant (011) facets. Comparative analysis indicates these (011) surfaces display significantly enhanced photodegradation efficiency compared to the (010) and (001) facets characteristic of spherical polyhedrons. Despite these advances, research on the photocatalytic H₂ evolution performance of such SnS nanostructures remains scarce in the literature. Several studies have investigated photoelectrochemical H₂ generation using SnS thin films through precise control of surface microstructures and exposed facets, achieving a

remarkable photocurrent density of up to 23 mA cm^{-1} and demonstrating SnS's potential for solar fuel production. [55-58]

In most cases, SnS has been employed in the construction of hybrid photocatalysts through strategic combination with various functional materials, such as $\text{C}_3\text{N}_4/\text{SnS}$ heterostructures [59], $\text{SnS}/\text{ZnIn}_2\text{S}_4$ heterostructures [60], CdS/SnS composites [61], MoSe_2/SnS heterostructures [62], $\text{SnS}/\text{aminated-C}$ composites [63], etc. These heterostructures leverage interface engineering principles, where the formation of built-in electric fields at the interfaces significantly enhances charge carrier separation and facilitates efficient charge transfer processes. Furthermore, $\text{TiO}_2\text{-SnS}/\text{SnS}_2$ core-shell heterostructures have been developed. [64] In this system, the mixed-phase SnS/SnS_2 introduces oxygen-related defect states that effectively narrow the bandgap of TiO_2 , thereby extending its photoresponse into the visible light region. This innovative approach substantially improves the solar energy utilization efficiency of wide-bandgap oxide semiconductors. Despite these advances, current SnS-based photocatalytic systems have yet to fully exploit its potential capacity considering the suitable bandgap and high charge carrier mobility. Further optimization of microstructure control in SnS particles, films, or heterostructures remains crucial for achieving their theoretical performance.

1.3.3 π -SnS: An emerging candidate for efficient photocatalysis

In 2015, a novel phase in the binary SnS system was reported. It was obtained as a highly symmetric nano tetrahedra with ultralow synthesis yield. [65] Structural characterization through zonal precession electron diffraction (PED) pattern analysis identified the phase as cubic (space group P2_13 , lattice parameter $a = 11.7 \text{ \AA}$), featuring a 64-atom unit cell configuration. Subsequent studies successfully fabricated π -SnS thin films, yielding a refined lattice constant of $a = 11.587 \text{ \AA}$ through X-ray diffraction analysis [66]. The cubic symmetry of this phase demonstrates exceptional structural compatibility with conventional semiconductor substrates (e.g., Si, GaAs), suggesting promising applications in heterojunction device engineering for microelectronics. Optical measurements revealed that the bandgap values of π -SnS is $1.5\text{--}1.8 \text{ eV}$ [65-67], indicating a more effective optical

absorption, which makes it a promising candidate for efficient solar energy conversion. For instance, a solar cell with an absorber layer of π -SnS has achieved a conversion efficiency of 1.28%.^[68] Besides, π -SnS particles demonstrated favorable photocatalytic activity.^[54, 69]

At the same time, π -SnS is a metastable phase as its formation energy is computed to be 2.19 kJ/mol higher than its orthorhombic ground state (α -SnS), and the thermodynamic stabilization mechanism remains enigmatic.^[70] The metastable nature of π -SnS presents both scientific challenges and technological opportunities. While preliminary progress has been made in characterizing this novel phase, yet there are still many unknowns, and some hurdles have to be resolved. 1) For synthesis challenges, the current predominant synthesis method—hot injection—relies on organic surface ligands to control nucleation and growth kinetics. However, the fundamental relationships between surface chemistry, morphological control, and resultant physical properties remain poorly understood. Moreover, scalable production of phase-pure, well-defined π -SnS particles faces substantial obstacles, despite being crucial for practical implementation in nanodevice technologies. 2) In the field of catalysis, the mechanism of π -SnS particles and SnS-based nanostructures is still unclear due to the insufficiently precise nanostructures and absence of in situ characterization. Besides the band structure, the effects of surface chemical states and defect engineering on catalytic performance require systematic investigation to elucidate the underlying reaction mechanisms. 3) As a metastable phase, the practical utility of π -SnS hinges on its kinetic stability against transformation to α -SnS. Atomic-level understanding of phase transition pathways—including lattice reorganization dynamics and microstructural evolution—is essential for rational material design. Furthermore, its response to external stimuli (thermal, mechanical, and electrical) demands comprehensive evaluation, particularly given its potential in emerging thermoelectric applications.

1.4 The aim of this study

To address the challenges mentioned above, this study proposes a facile one-pot solvothermal synthesis of novel π -SnS particles, coupled with a systematic investigation of their structural and functional properties. To be specific,

- (i) To prepare pure π -SnS particles with a simplified preparation process and minimized organic reagents and investigate the nucleation/growth kinetics of this metastable phase by tuning the surfactants and sulfur sources. (Chapter 2)
- (ii) To apply the synthesized π -SnS particles in photocatalytic H_2 evolution, with systematic investigations into the particle size and surface ligands on their performance. (Chapter 3)
- (iii) To evaluate the thermal stability and phase transition characteristics of the surfactant-stabilized metastable π -SnS particles, and their influence on the performance of photocatalytic H_2 evolution. (Chapter 4)

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Chapter 2 Synthetic understanding of π -SnS particles

2.1 Introduction

The discovery of π -SnS has attracted the attention of many scientists to the synthesis of this new phase and its properties. To date, π -SnS films have been obtained by a variety of techniques including chemical bath deposition ^[1], thermal evaporation ^[2], atomic layer deposition ^[3], and spray pyrolysis ^[4]. Until now, a few reports on the synthesis of π -SnS nanocrystals have been published, mainly using “hot injection” method that relies on the rapid and homogeneous mixing of reagents at high temperatures. Miranti et al. prepared π -SnS colloidal nanocrystals with diameters of 4-10 nm, which exhibit a quantum confinement effect with strong variations in energy band gaps.^[5] Thiourea, tetrathiourea tin (II) chloride complexes, were typically used as a single molecular precursor for the synthesis of high-quality tin sulfide nanoparticles with various morphologies.^[6] Although the “hot injection” method has persisted as the most useful for producing homogeneous nanocrystals, it suffers from limited scalability and inconsistent reproducibility ^[7], hindering practical production and applications.

Herein, we report a simple and facile solvothermal method to synthesize π -SnS nanoparticles with tunable size, size distribution and morphology by adjusting the precursor, surfactant and temperatures. Simple tin chloride (SnCl_2) and thiourea/elemental sulfur were dissolved or dispersed in oleylamine (OLA) as the precursor, and hexamethyldisilazane (HMDS) was used as an additional surfactant. Although these reagents have been widely employed as precursors in the “hot injection” synthesis of tin sulfide (SnS) particles, various critical issues remain to be optimized and elucidated. Firstly, the “hot injection” method usually involves intricate preparation procedures and diverse surfactant systems, introducing substantial randomness that compromises experimental reproducibility. Secondly, HMDS is commonly employed to get monodisperse SnS particles, but its underlying mechanistic role remains poorly understood. Lastly, existing precursor studies have predominantly focused on tin-surfactant ligand complexes, while largely overlooking the critical role of sulfur sources in particle synthesis. To address these issues, we used a one-pot precursor containing the above-

mentioned reagents and obtained pure π -SnS monodisperse aggregates and tetrahedra through systematic optimization of HMDS dosage and sulfur source selection. UV-Vis spectra function as a molecular fingerprint with characteristic peak shifts and intensity changes reflecting ligand exchange and intermediate species formation in the various precursors; it serves as a useful tool for monitoring the dynamic structural evolution of molecular species and metal-ligand complexes during precursor preparation. Simultaneous X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis were employed to monitor phase evolution and morphological development. The role of HMDS in stabilizing the generation of π -SnS and sulfur source reactivity (thiourea vs. S_8) in dictating nucleation kinetics was highlighted.

2.2 Experimental procedure

Materials. Tin(II) chloride ($SnCl_2$, 97 %, Wako Pure Chemical Industries, Ltd), elemental sulfur powder (S_8 , 99.99 %, Kojundo chemical laboratory Co., Ltd), oleylamine (OLA, FUJIFILM Wako Pure Chemical Corporation), hexamethyldisilazane (HMDS, Apolloscientific.co.uk) and thiourea (H_2NCSNH_2 , Nacalai Tesque, Inc.) were purchased as raw materials. Sodium Sulfite (Na_2SO_3 , 97 %), sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 96 %) and hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) were purchased from Nacalai Tesque, Inc. Purified water ($18.2\text{ M}\Omega \cdot \text{cm}$) was obtained from a filtration system purchased from Merck & Co., Inc.

α -SnS nanoplates synthesis. 0.3640 g $SnCl_2$ and 0.1766 g thiourea are mixed in a beaker with 32 mL oleylamine under an N_2 atmosphere. The mixture is stirred magnetically at room temperature for 30 min to remove moisture and air. Subsequently, heat it at 70 °C using a hot plate and maintain for 20 min. Next, the precursor is transferred to a Teflon-lined stainless-steel autoclave and subjected to solvothermal treatment at 200 °C for 5- 15 h before naturally cooling down. The synthesized precipitate is purified by washing and centrifugation (3500 rpm, 10 min, 4-5 times) and finally dried naturally for subsequent characterization.

π -SnS nanocluster synthesis. 0.3640 g $SnCl_2$ and 0.1766 g thiourea are mixed in a beaker with 32 mL oleylamine under an N_2 atmosphere. The mixture is stirred magnetically at room

temperature for 30 min, during which HMDS (0.3- 0.8 mL) is added to the mixture. The mixture is subsequently heated at 70 °C using a hot plate and maintained at this temperature for 20 min. A color change from yellow to translucent colorless takes place upon HMDS addition. Next, the precursor is transferred to a Teflon-lined stainless-steel autoclave and subjected to solvothermal treatment at 200 °C for 15 h. After cooling down, the synthesized precipitate is purified by washing and centrifugation (3500 rpm, 10 min, 4-5 times). Finally, the purified precipitate was dried naturally for subsequent characterization.

π -SnS tetrahedrons synthesis. 0.3640 g SnCl₂ and 0.0744 g elemental sulfur are mixed in a beaker with 32 mL oleylamine under an N₂ atmosphere. The mixture is stirred magnetically at room temperature for 30 min, during which 0.6 mL HMDS is added to the mixture. The mixture is subsequently heated at 70 °C using a hot plate and maintained at this temperature for 30 min. Further increase the temperature to 150 °C and keep it for another 30 min. The mixture gradually becomes a homogeneous orange precursor. Next, the precursor is transferred to a Teflon-lined stainless-steel autoclave and subjected to solvothermal treatment at 200 °C for a certain period of time before naturally cooling down. The synthesized SnS nanoclusters are purified by washing with ethanol and centrifugation treatment (1500-3000 rpm, 10 min, 4-5 times) and finally dried naturally for subsequent characterization.

Characterization methods. Field emission scanning electron microscopy (FE-SEM, JEOL JSM-6500) was required to observe the morphology of SnS particles. Powder X-ray diffraction with Cu K α irradiation at 45 KV and 40 mA has been carried out to determine the particles' crystal structure. Transmittance spectra were measured by UV-Vis spectrophotometer (Shimazu UV-2600) to characterize the optical properties of precursors and synthesized particles and further to discuss the nucleation mechanism and evaluate the bandgap of SnS particles.

2.3 Results and discussion

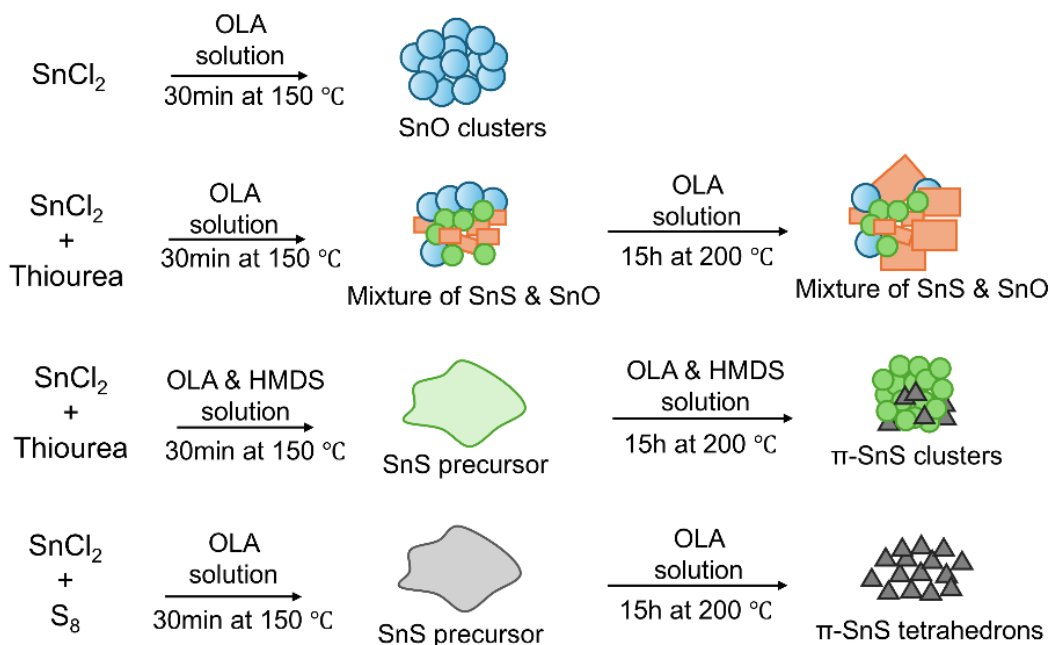


Figure 2-1. Schematic illustration of the formation of SnS plates, clusters and tetrahedra.

Figure 2-1. summarizes the synthesis procedure via a solvothermal method using the one-pot precursor consisting of SnCl_2 and sulfur sources. When preparing precursors, it was found that SnCl_2 rapidly forms a brown precipitate upon heating within 30 min. The precipitate was identified as tin oxide. The use of thiourea successfully generates SnS platelets as the dominant product, but complete elimination of SnO byproducts was not accessible. Notably, adding trace amounts of HMDS led to the exclusive formation of pure π -SnS clusters and several tetrahedra. Further replacing thiourea with elemental sulfur as the sulfur source, pure π -SnS tetrahedra were obtained.

2.3.1 SnS nanoparticles prepared with thiourea

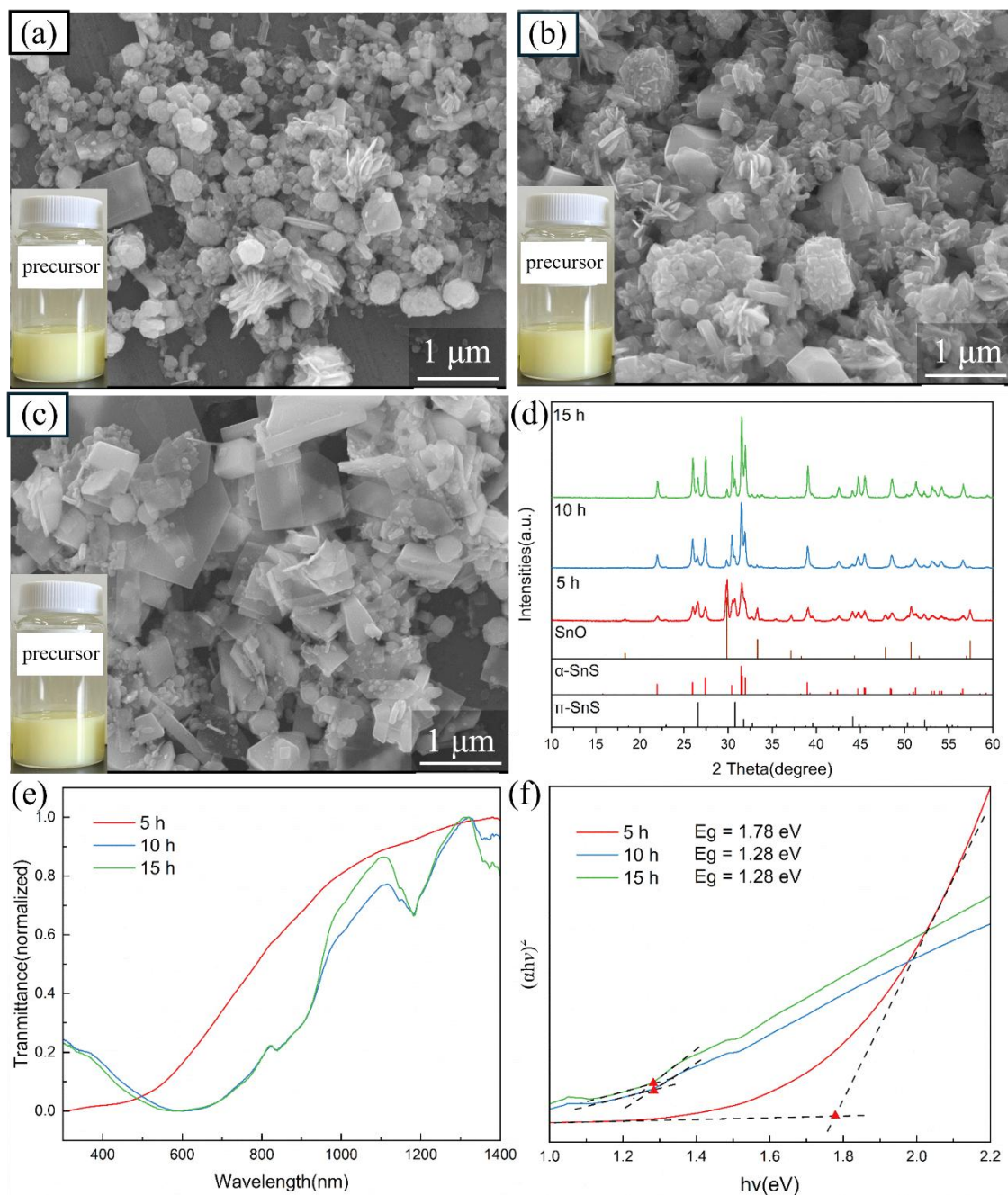


Figure 2-2. SEM images of particles prepared without HMDS under various preparation times: (a) 5 h, (b) 10 h, (c) 15 h. (d) Corresponding powder XRD patterns of the samples. (e) UV-Vis transmittance spectra and (b) corresponding Tauc's plots indicating the bandgap of the particles. Inset: precursor formed at 70 $^{\circ}\text{C}$.

Figure 2-2 presents SnS samples synthesized from OLA precursors containing SnCl_2 and thiourea. OLA coordinates with SnCl_2 to form a soluble $\text{SnCl}_x(\text{OLA})_n^{(2-x)}$ complex [8], typically yielding a yellow translucent solution at elevated temperatures. However, in our system heated under 70°C , we observe a yellow suspension (inset) that is attributed to the relatively low temperature, leading to SnCl_2 's incomplete dissolution and aggregated $[\text{xSnCl}_2\text{-OLA}]$ complexes. Thiourea was selected as the sulfur source based on its demonstrated effectiveness in producing high-quality metal sulfides, particularly in the synthesis of PbS colloidal quantum dots (CQDs).^[9] Figures 2-2(a-c) exhibit the morphology evolution of SnS particles with reaction time. After 5 hours of reaction, the product predominantly forms spherical nanoclusters with a size ranging from tens to hundreds of nanometers, nanoflowers composed of self-assembled nanosheets and several nanoplates. With extended reaction times, the sample shows increased population density of nanoflowers (10 h) and a progressive emergence of bigger-sized platelets (15 h).

Figure 2-2(d) shows the phase evolution through the corresponding XRD patterns. At the initial 5-hour reaction stage, the diffraction pattern reveals three coexisting phases: (1) prominent SnO peaks (PDF #04-005-4541), (2) metastable π -SnS (cubic, PDF #04-004-4273), and (3) ground state α -SnS (orthorhombic, PDF #03-065-3812). Extending the reaction duration to 10 and 15 h resulted in the dominant layered-structure α -SnS, which is consistent with its typical morphology of platelets observed from SEM images.^[10-12] The formation of SnO in this system is probably attributed to residual water present in the oleylamine solvent. Yang et al. got tin oxide hydroxide by dissolving SnCl_2 in water and heating at 60°C .^[13] The substantial increase in orthorhombic α -SnS originates from its thermodynamically favored growth kinetics compared with the cubic π -SnS crystallites. (This content will be discussed later) The UV-Vis transmittance spectrum (Figure 2-2(e)) of the samples prepared with 5 h exhibits a broad range of absorption from UV to 1000 nm, with an onset at around 580 nm and slight shoulders at ~ 830 nm and ~ 930 nm, demonstrating the coexistence of multiple phases. Its corresponding optical bandgap (Figure 2-2(f)) is 1.78 eV. For the samples prepared with 10 and 15 h, the absorption in the UV range decreased and showed a maximum at around 600 nm in the visible region. They show the onsets at ~ 930

nm and an obvious shoulder at ~ 830 nm, corresponding to the bandgap of 1.28 eV, which is consistent with previously reported values for α -SnS (1.07-1.20 eV).^[14-16] The reduction in transmittance around 1100-1300 nm suggests near UV-Vis-near IR absorption of the particles.

By introducing an appropriate amount of HMDS, a significant modification in morphology was observed. As shown in Figure 2-3, the precursor decolorized to a semi-transparent and colorless state, while thiourea remained undissolved, indicating that SnCl_2 preferentially coordinates with HMDS and form $[\text{Sn-HMDS}]$ complexes. When adding 0.3-0.4 mL HMDS, the platelets shown in Figure 2-3(c) gradually disappeared and were replaced by spherical nanoparticle aggregates (~ 200 -800 nm) and self-organized nanoflowers (~ 1 μm) composed of nanosheets. (Figures 2-3(a) and 2-3(b)) Increasing HMDS to 0.6 mL yielded monodisperse aggregates (200- 300 nm in size) composed of primary nanoparticles ≤ 100 nm and several tetrahedra. (Figure 2-3(c)) The XRD pattern (Figure 2-3(d)) revealed the corresponding crystal structures. Surprisingly, SnO was eliminated upon HMDS addition. Previous studies have reported that amorphous products that are highly susceptible to oxidation would appear if HMDS were absent.^[17-19] As is well known that HMDS is often used as a surface passivator to convert hydrophilic -OH terminated surfaces to hydrophobic $-\text{OSi}(\text{CH}_3)_3$ groups through silylation reactions. In this way, HMDS may form stable complexes with Sn^{2+} ions (e.g., $[\text{Sn}(\text{N}(\text{SiMe}_3)_2)_2]$ ^[8, 20-21] through $\text{N} \rightarrow \text{Sn}$ coordination bonds, creating a hydrophobic barrier that sterically blocks $\text{H}_2\text{O}/\text{O}_2$ access to the metal center and thereby preventing the formation of SnO. Notably, the relative percentage of orthorhombic α -SnS exhibited an inverse correlation with HMDS concentration. At the threshold of 0.6 mL HMDS, complete phase purity of cubic π -SnS was achieved, evidenced by the disappearance of characteristic α -SnS diffraction peaks. We believe this phase selectivity also arises from HMDS reprogramming the Sn^{2+} solvation shell, which will be discussed in detail in the following. The phase evolution was also reflected in transmittance spectra (Figures 2-3(e) and 2-3(f)). The sample prepared with 0.3 mL maintains characteristics similar to HMDS-free samples, exhibiting a bandgap of 1.29 eV. Upon increasing HMDS to 0.4 mL, the spectrum develops distinct dual absorption thresholds at 1.30 eV and 1.64 eV, corresponding to the coexistence of α -SnS and

π -SnS. Further with 0.6 mL HMDS, it showed an onset of ~ 650 nm with a bandgap of 1.74 eV, corresponding to the wider bandgap of cubic π -SnS (1.5-1.8 eV).^[22]

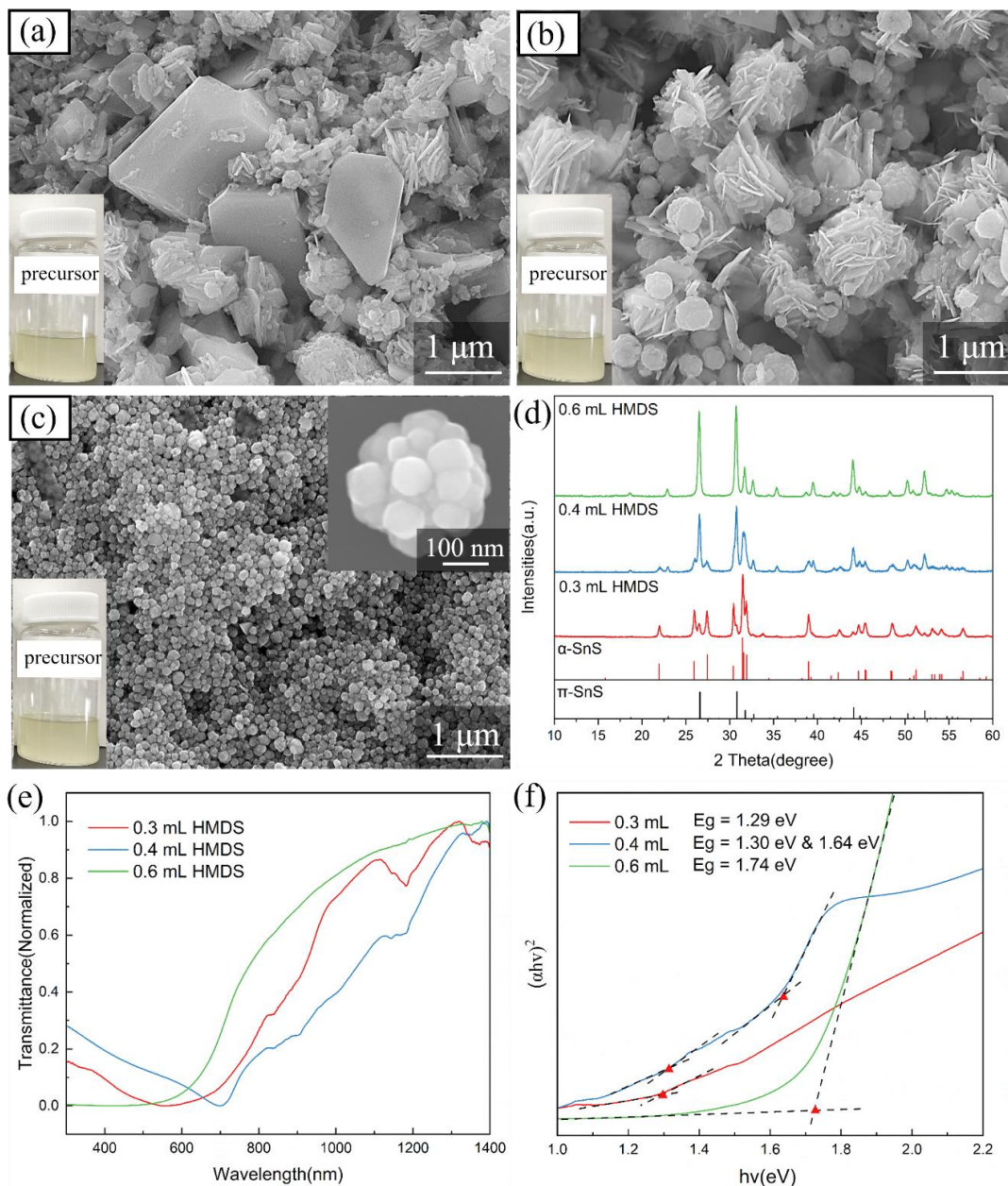


Figure 2-3. SEM images of particles prepared under 15 with various volumes of HMDS: (a) 0.3 mL, (b) 0.4 mL, (c) 0.6 mL. (d) Corresponding powder XRD patterns of the samples. (e) UV-Vis transmittance spectra and (f) corresponding Tauc's plots indicating the bandgap of the particles. Inset: precursor formed at 70 $^{\circ}\text{C}$.

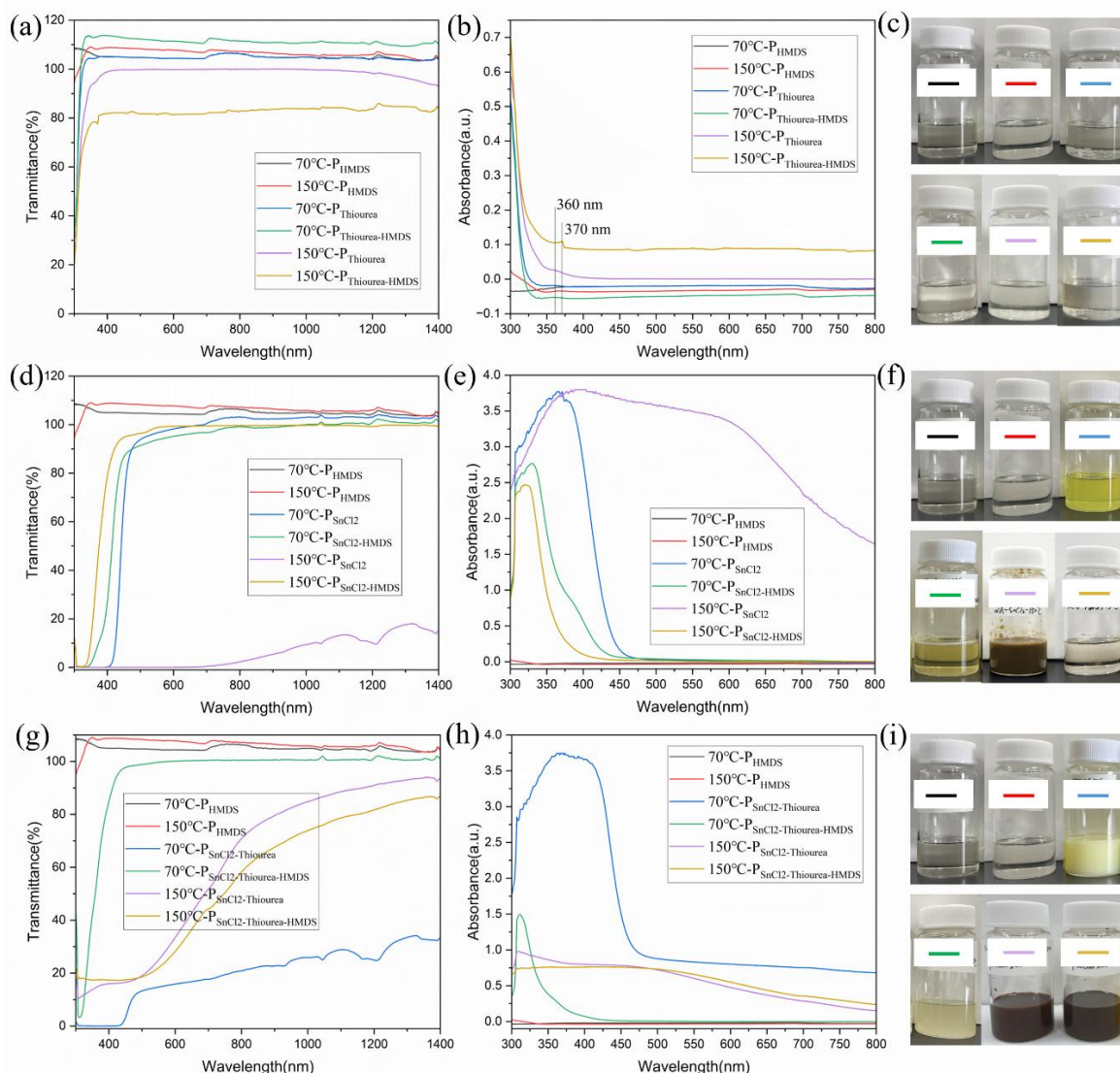


Figure 2-4. (a) UV-Vis transmittance spectra, (b) absorbance spectra, and (c) photographs of the precursors based on thiourea. (d) UV-Vis transmittance spectra, (e) absorbance spectra, and (f) photographs of the precursors based on SnCl₂. (g) UV-Vis transmittance spectra, (h) absorbance spectra, and (i) photographs of the precursors based on thiourea and SnCl₂. The absorbance spectra are transformed from transmittance spectra using the formula: $A = -\log(T)$.

To validate the occurrence of ligand exchange and identify potential intermediate species, we conducted systematic UV-Vis spectroscopic characterization of the various precursor solutions. (Figure 2-4) HMDS exhibited negligible optical absorption across 300-1400 nm with oleylamine. Dispersing thiourea in OLA/HMDS resulted in an apparent absorption peak at approximately 300 nm (Figures 2-4 (a) and 2-4(b)), which is attributable to the undissolved

thiourea particles (Figure 2-4(c)).^[23] Thiourea remained solid at 70 °C and began to dissolve at 150 °C due to the strong intermolecular hydrogen bonding in the crystalline state. However, rapid re-solidification occurred once the solutions were removed from the heat, resulting in minor variations in the overall spectral transmittance. The weak peak at 360-370 nm might originate from the transient solvation of thiourea. In contrast, when SnCl₂ was dispersed in OLA/HMDS, distinct optical absorption signals were observed. At 70 °C, the OLA system exhibited a broad absorption band centered at 378 nm (300-450 nm), while the HMDS-contained solution showed a blue-shifted feature at 340 nm, indicating ligand-dependent electronic transitions in the tin complexes. (Figures 2-4(d) and 2-4(e))^[24] SnCl₂ was dissolved in OLA and formed a homogenous yellow solution. Upon HMDS addition, the solution turned pale yellow, providing further evidence of ligand exchange. (Figure 2-4(f)) At 150 °C, the OLA system developed a broad absorption across 300-800 nm, and the precursor became brown, yielding some powders; at the same time, the HMDS-contained solution became completely transparent, with the absorption peak further blue-shifting to 322 nm. These consecutive blue shifts (378 to 340 to 322 nm) and decolorization of the solutions indicate progressive changes in the coordination environment of Sn species. The ligand exchange from [Sn-OLA] to [Sn-HMDS] resulted in increased steric hindrance, requiring higher absorption energy. To figure out whether thiourea and SnCl₂ undergo independent coordination with OLA/HMDS or form coupled complexes that modify the precursor reactivity, thiourea and SnCl₂ were mixed in OLA/HMDS. As shown in Figures 2-4(g) and 2-4(h), at 70 °C, the OLA system shows an absorption enhancement around 378-450 nm with opaque yellow turbidity in the precursor compared to the precursor that contains only SnCl₂; meanwhile, the HMDS-contained mixed solution further shifted the absorption peak to 311 nm and exhibited similar decolorization of the precursor. These spectroscopic changes demonstrated that thiourea and Sn species do not behave independently in the precursor but rather form unstable $[\text{Sn}(\text{thiourea})_x(\text{OLA})_y]^{2+}$ and stable $[\text{Sn}(\text{thiourea})_x(\text{HMDS})_y]^{2+}$ complexes.^[23, 25] At 150 °C, however, the mix precursors produced a brown turbid suspension that is similar to SnCl₂ precursor regardless of HMDS presence. They showed a slight broad

absorption across 300-800 nm. And the HMDS-containing system exhibited a stronger absorption peak at 310 nm compared to the HMDS-free counterpart.

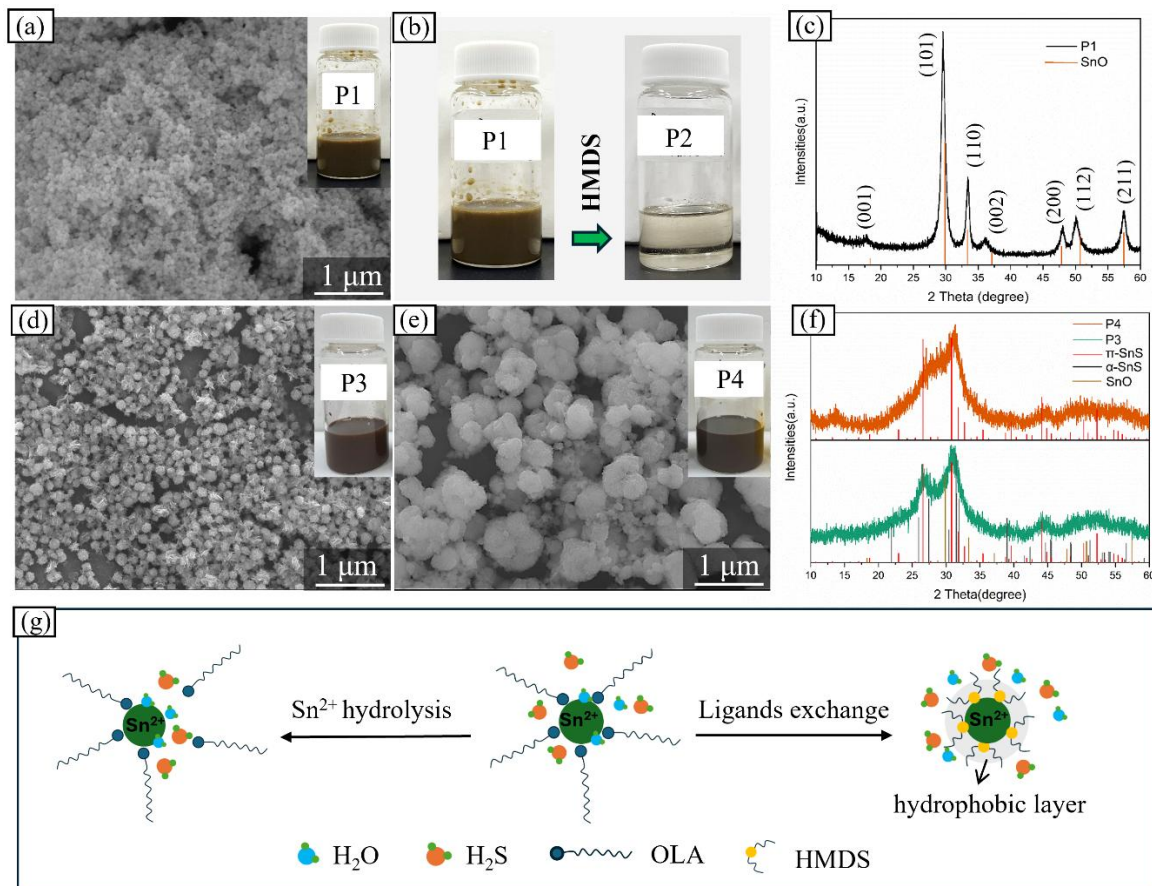
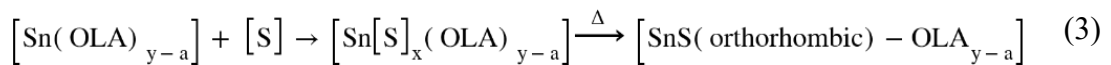
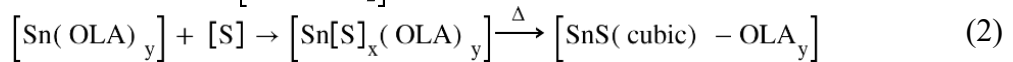


Figure 2-5. (a) SEM image of the particles from P1. (b) Pictures of precursor P1 and P2 (c) Powder XRD pattern of the particles from P1. SEM images of the particles from (d) P3, and (e) P4. (f) Powder XRD pattern of the particles from P3 and P4. (g) Schematic diagram of Sn complex in precursor. P1: Sn precursor, P2: Sn precursor with 0.6 mL HMDS, P3: mix precursor, P4: mix precursor with 0.6 mL HMDS, formed at 150 °C.

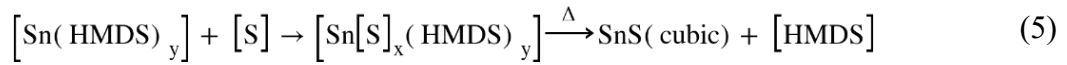
To gain detailed information on the powder obtained from the precursors, SEM observation and XRD analysis were further employed. As shown in Figure 2-5(a), the SEM image shows that the particles are spherical and the size is below 100 nm. XRD analysis confirms the phase as SnO (PDF # 04-005-4541), though with noticeable peak shifts relative to the reference pattern. (Figure 2-5(c)). This deviation, we believe, is attributed to crystallographic imperfections (induced defects) such as oxygen vacancies, considering the oxygen deficiency

under N_2 atmosphere. The shift to lower peaks: $\Delta 2\theta = 0.46^\circ$ for (001) and 0.97° for (002) suggested the expansion of the c-axis, which may favor the existence of oxygen vacancies. [26, 27] P2 precursor yielded no powder and turned into a more transparent and colorless solution. (Figure 2-5(b)) This phenomenon provides direct evidence that the introduction of HMDS would protect the $SnCl_2$ in OLA from oxidation. Instead, the thiourea-mediated synthesis yielded monodisperse spherical aggregates (100-200 nm) with different morphological features from P1. As shown in Figure 2-5(d), the spherical aggregates exhibited dual fundamental structural configurations: amorphous nanoparticles and amorphous nanosheets. The reaction of P4 with HMDS also yielded some powder, exhibiting larger amorphous aggregations up to $\sim 1 \mu m$. (Figure 2-5(e)) The XRD patterns of P3 and P4 powders in Figure 2-5(f) exhibit similar broad diffraction features characteristic of poorly crystalline materials. P3 demonstrates partially resolved peaks at $2\theta = 26.6^\circ$, 30.8° and a weak peak at $2\theta = 13.7^\circ$, which indicates the coexistence of α -SnS, π -SnS and SnO. P4 shows a complete peak overlap forming a broad hump ($2\theta = 25^\circ$ - 35°), suggesting much lower crystallinity. This phenomenon is consistent with their optical absorption characteristic at 310 nm. The stronger peak at $2\theta = 13.7^\circ$ may indicate the formation of pure π -SnS crystals.

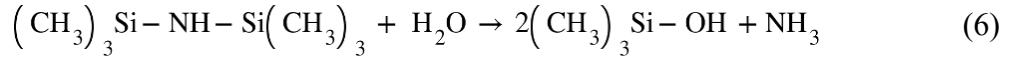
Based on these observations, we propose to explain the reactions as follows. $SnCl_2$ gradually dissolve in OLA by interaction with OLA molecules, forming $[Sn(OLA)_x]^{2+}$ complexes dispersed in the precursor and forming a yellow precursor at $70^\circ C$. However, elevated temperature induces partial detachment of OLA ligands from Sn^{2+} . This ligand destabilization [28] creates unprotected Sn sites vulnerable to hydrolysis or oxidation, thus facilitating the formation of SnO. Under thiourea-mediated conditions, coupled complexes such as $[Sn(thiourea)_x(OLA)_y]^{2+}$ are formed and nucleate to SnS due to the efficient sulfur release from thiourea ([S]) through a thermally activated decomposition. [25]



The crystallization way of SnS exhibits strong ligand-dependent phase selection, governed by surface coordination dynamics. Partially OLA-depleted Sn sites favored the formation of orthorhombic α -SnS or tetragonal SnO with layered structures. (chemical formula (2)) While the fully OLA-passivated Sn sites enable isotropic growth to form the cubic π -SnS. (chemical formula (3)) With HMDS addition, Sn^{2+} preferentially coordinates with HMDS molecules, altering nucleation kinetics in the following ways:



HMDS displaces OLA via stronger Sn-N(SiMe₃)₂ bonds (chemical formula (4)), forming sterically shielded [Sn(N(SiMe₃)₂)₂] complexes and constructing a hydrophobic shell around Sn^{2+} . [29-31] The hydrophobic layer acts as a physical barrier to protect Sn^{2+} from O₂/ H₂O, effectively suppressing the formation of SnO. (Figure 4(g)) In addition, HMDS is known to be hygroscopic and to react with moisture to form ammonia and other reaction products [32], as the formula (6) shows:



Here, HMDS acts as a chemical scavenger to remove the moisture. Correspondingly, the stronger bonding of [Sn(N(SiMe₃)₂)₂] complexes raises the kinetic barrier for cubic π -SnS nucleation, resulting in smaller amorphous intermediates (Figure 2-5(e)) and broadened XRD peaks around $2\theta = 25\text{-}35^\circ$ (Figure 2-5(f)).

2.3.2 SnS particles prepared with elemental sulfur

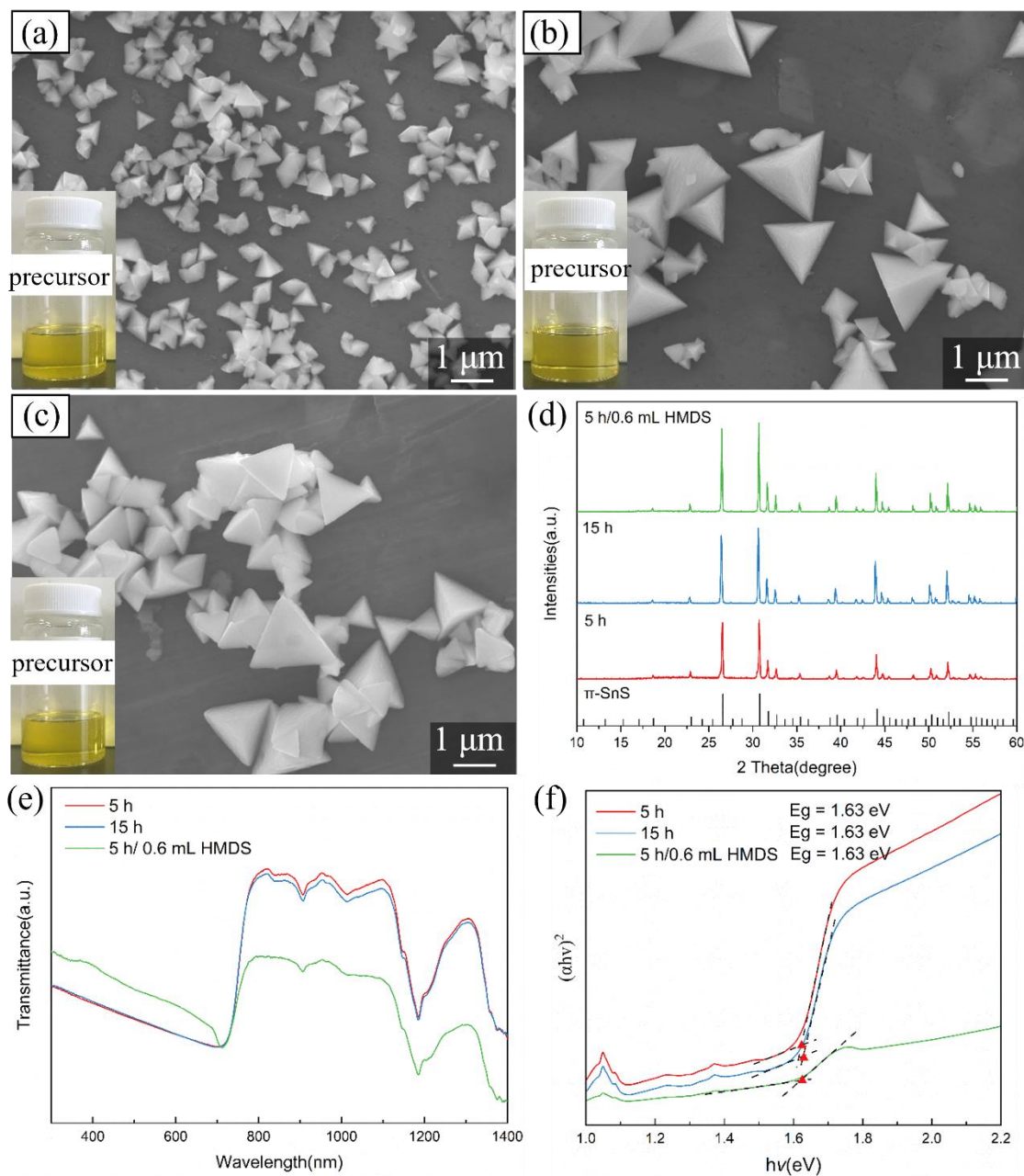


Figure 2-6. SEM images of particles prepared from elemental sulfur: (a) under 5 h, (b) under 15h, (c) under 5 h with 0.6 mL HMDS. (d) Corresponding powder XRD patterns of the samples. (e) UV-Vis transmittance spectra and (f) corresponding Tauc's plots indicating the bandgap of the particles. Inset: precursor formed at 150 $^{\circ}\text{C}$.

To investigate the influence of sulfur sources on the synthesis of SnS particles, we replaced thiourea with elemental sulfur (S_8). Remarkably, the introduction of elemental sulfur not only

served as an effective sulfur precursor but also suppressed the oxidation of Sn^{2+} ions in the solution, stabilizing a homogeneous and transparent yellow solution, as the inset shows. Upon reacting at 200 °C for 5 h, some well-defined regular tetrahedra with the edge lengths ranging from 100 nm to 1 μm were obtained. (Figure 2-6(a)) Extended reaction time (15 h) led to broader size dispersion (up to 2 μm edge length), indicative of progressive particle growth. (Figure 2-6(b)) With 0.6 mL HMDS additive, the 5-hour reaction produced tetrahedral particles showing a 50% size increase (maximum edge length: 1.5 μm) compared to the control sample (maximum: 1 μm). (Figure 2-6(c)) Consistent with the phenomenon in the thiourea-based system, this size enhancement suggests that HMDS elevates the nucleation barrier and redirects the reaction thermodynamics toward the growth of pre-existing nuclei, ultimately yielding larger tetrahedral crystals. XRD analysis (Figure 2-6(d)) unambiguously identifies the tetrahedral particles as pure cubic π -SnS, with no observable peaks corresponding to α -SnS or other impurities. Figure 2-6(e) reveals a consistent absorption onset at approximately 700 nm and pronounced infrared absorption in the 1100-1300 nm region. The sharp absorption threshold indicates minimal band tailing- a signature of low defect concentrations and high crystallinity. As quantitatively determined from Tauc's plots (Figure 2-6(f)), all three samples demonstrate a consistent optical bandgap of 1.63 eV, in excellent agreement with theoretical predictions for cubic SnS (1.5-1.7 eV).

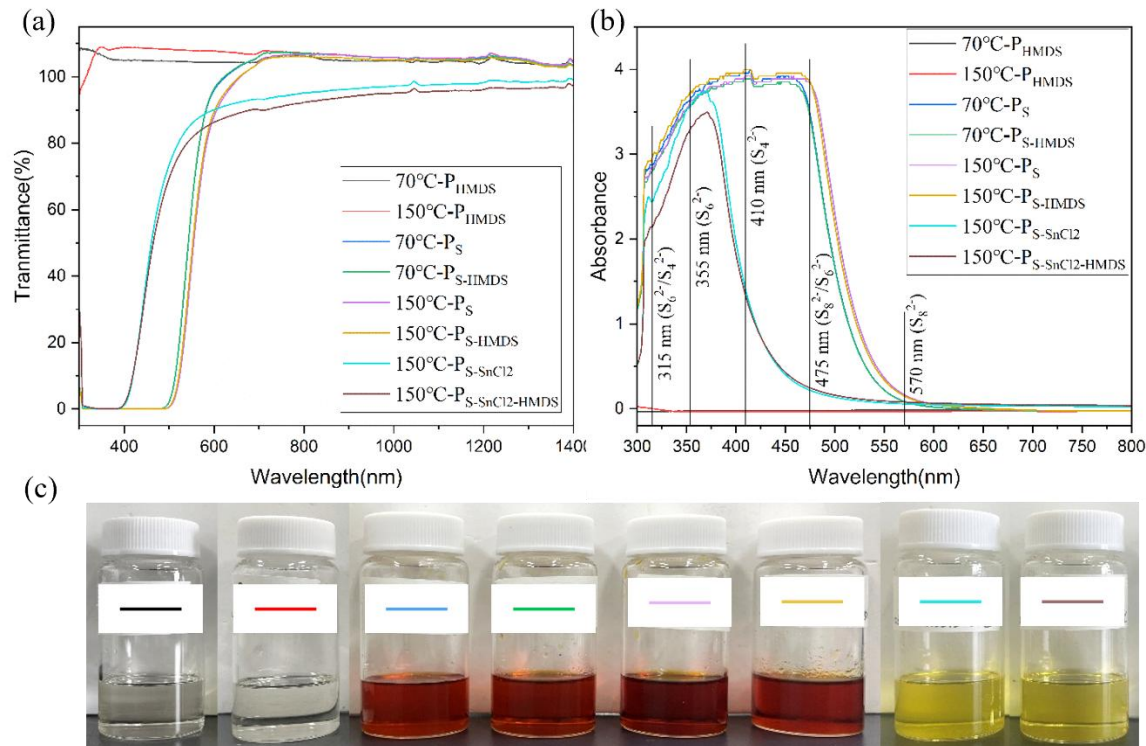
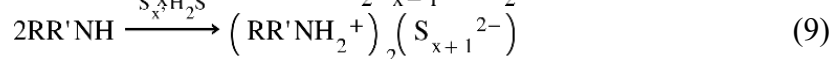
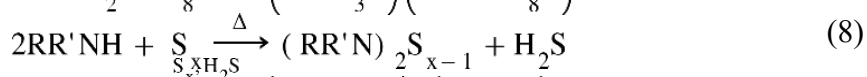
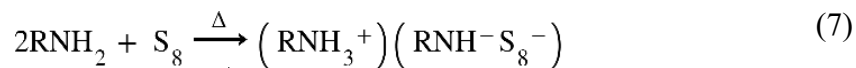


Figure 2-7. (a) UV-Vis transmittance spectra of the precursor using elemental sulfur. (b) Corresponding absorbance spectra transformed from transmittance spectra using the formula: $A = -\log(T)$ and (c) photograph of the corresponding precursors.

Conventional wisdom holds that employing elemental sulfur as the sulfur source in precursor systems presents significant challenges due to the complex reaction pathways that involve multi-step reduction from S_8 to reactive S^{2-} via polysulfide intermediates (S_x^{2-}).^[33] The reactions^[34] are presented as follows:



S_8 ring is opened by the nucleophilic attack of amine groups, yielding alkylammonium polysulfides. (Formula (7)) Secondary amines will react with sulfur to form two N-S bonds, resulting in the liberation of H_2S . (Formula (8)) Furthermore, the generated H_2S participates in a redox equilibrium with residual S_x , where amino groups act as electron donors to facilitate the formation of polysulfide anions (S_x^{2-} , $x \geq 2$). (formula (9)) In the presence of

SnCl₂, we believe that tin centers undergo cooperative coordination with polysulfide anions (S_x²⁻) and OLA ligands to form metastable intermediates ^[35], as illustrated below:



The formation of this intermediate effectively suppresses the hydrolysis or oxidation of Sn²⁺ ions in OLA, resulting in a homogeneous and transparent yellow precursor at elevated temperatures. To validate this hypothesis, the optical properties of the precursor solution were measured under controlled conditions. As shown in Figures 2-7(a) and 2-7(b), the addition of S₈ to OLA/HMDS at 150 °C generates a broad absorption band (310-600 nm), corresponding to the transitions of polysulfide species (S_x²⁻, x = 2-8) ^[36]. While the introduction of SnCl₂ narrows the band to 310-500 nm, demonstrating the consumption of free polysulfides at 370-600 nm and the selective formation of [SnS_x(OLA)₂]²⁺ complexes. Figure 2-7(c) visually documents the progressive color evolution of the transparent precursors, providing direct evidence of the stepwise chemical transformations occurring with the addition of S₈ (colorless to red) and SnCl₂ (red to yellow). Given the minimal spectral changes directly attributable to HMDS, HMDS's potential secondary roles are not discussed here.

2.3.3 Proposed nucleation and growth mechanism

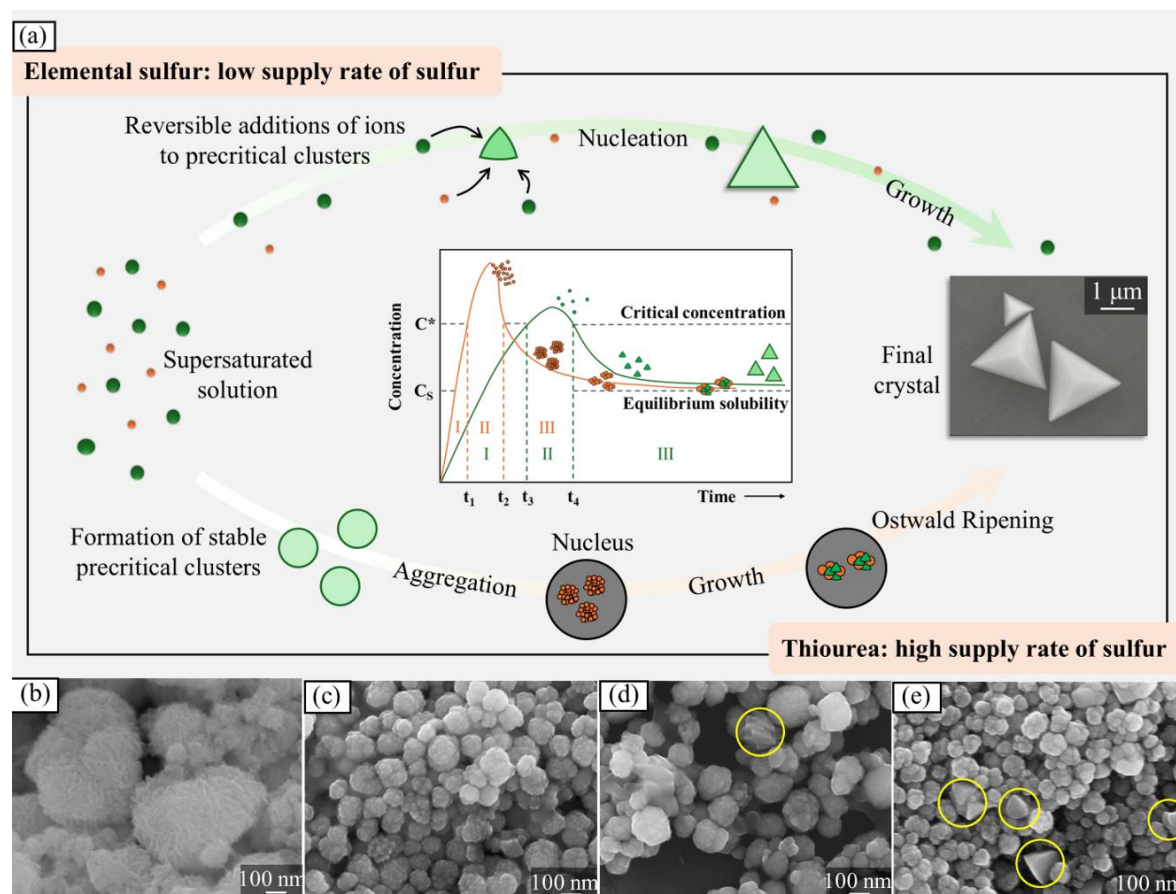


Figure 2-8. (a) Schematic diagram of nucleation and growth of π -SnS particles with different sulfur sources. Inset: Lamer diagram- pre-nucleation stage (I), nucleation (II) and growth (III) as a function of reaction time in S_8 system (green curve) and thiourea system (orange curve). (b) SnS precritical clusters formed at 75 °C for 30 min. SnS aggregations formed at (c) 90 °C for 15 h, (d) 120 °C for 15 h, (e) 200 °C for 15 h.

It has been reported that the morphology of SnS particles is critically governed by the surface-binding ligands, which modulate crystal growth kinetics through selective facet stabilization and colloidal stability control. [37, 38] Here, we emphasize the sulfur release kinetics as the dominant factor in SnS particles' morphology control. Our experimental observations of the S_8 -based system, characterized by low particulate yield and persistent yellow coloration of the post-synthesis supernatant, indicate incomplete reaction of the precursor solution. On the one hand, thermodynamic stabilization of the $[SnS_x(OLA)_2]^{2+}$ intermediate shows a high nucleation energy barrier, delaying crystalline SnS formation. [33,39] As shown in Figure 2-

8(a), the S_8 system undergoes a slow conversion to precritical clusters in stage I [40-42], yielding a small amount of SnS nucleus. (green curve) The residual intermediates maintain a sustained supersaturation level, in which the low supply of active sulfur prefers the continued growth into larger tetrahedral SnS particles. As a result, non-uniform-sized tetrahedral particles with high crystallinity were obtained using elemental sulfur as the sulfur source. In contrast, thiourea is well-known for the burst nucleation in the synthesis of sulfides. [43-45] The high supply rate of active sulfur results in a fast conversion to precritical clusters and yielding a large number of monodisperse crystal aggregates (orange curve) at a short time. [46,47] At the same time, the abrupt decrease in supersaturation also suppressed further particle growth, resulting in stabilized nanocrystals with uniform size. Notably, a minority fraction of tetrahedral particles was observed in the SnS aggregates, indicating the possibility of evolution from spherical aggregates to regular tetrahedra. However, prolonged reaction time to 48 h induced little observable morphological transformation in the nanoparticle aggregations. By tuning reaction temperatures (from 90 °C to 200 °C), the morphology evolution from primary clusters to well-defined tetrahedral particles was observed, as shown in Figures 2-8(b-e). Due to the limited concentration after burst nucleation in the thiourea system, this process follows Ostwald ripening kinetics but requires additional thermodynamic driving forces to overcome the strong stabilization effects imposed by surface ligands.

2.4 Summary of this chapter

In summary, this part supplies a simple and facile “one-pot” solvothermal method for synthesizing the emerging cubic π -SnS particles with tunable phases and morphologies. Particularly, how to understand the nucleation and growth of SnS was investigated by tuning precursor reactivity, including the behavior of surfactant ligands and sulfur sources, and thermal kinetics. We found the critical interplay between sulfur precursor reactivity and metal-ligand coordination in determining the polymorph selection of SnS nanocrystals. With high reactive sulfur sources (e.g., thiourea), weak Sn^{2+} -OLA coordination permits rapid sulfur or oxygen incorporation, kinetically favoring orthorhombic α -SnS and tetragonal SnO nucleation; while strong Sn^{2+} -HMDS binding stabilizes the $[Sn[S]_x(N(SiMe_3)_2)_y]$

intermediates, thermodynamically driving cubic π -SnS formation. With less reactive sulfur (e.g., elemental sulfur), a higher activation energy is required to release the active sulfur, enabling thermodynamic stabilization of π -SnS crystals. In addition, the reactivity of sulfur sources (thiourea vs S_8) directly modulates nucleation rates, consistent with the Lamer diagram, leading to different growth trajectories to the final tetrahedral morphology: thiourea-Ostwald ripening vs S_8 - classic growth. By decoupling the effects of sulfur precursor chemistry from metal-ligand coordination, this work establishes fundamental principles for targeted synthesis of metastable phases, with implications extending to other IV-VI semiconductor systems.

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Chapter 3 π -SnS tetrahedrons with enhanced photoactivity

3.1 Introduction

Following the successful synthesis of cubic π -SnS nanoparticles described in Chapter 1, the tetrahedrons demonstrate significantly enhanced photocatalytic H_2 evolution activity compared with the aggregates. Though the application for photocatalytic dye degradation has already proved that π -SnS nanoparticles are favorable for dye adsorption and catalyzing the degradation.^[1-3] However, the application for photocatalytic H_2 evolution in suspension form has not been realized as far as we know. Therefore, in this chapter, we continue to use the one-pot solvothermal method to prepare pure π -SnS 3D cubic crystals. During the synthesis process, we systematically optimized both the solvothermal reaction duration and the concentration of HMDS ligands to investigate their impacts on nanoparticle size distribution, crystallographic quality, and photocatalytic efficiency. The critical influence of surface ligands on modulating the crystals' crystallinity and enhancing the tetrahedra's photocatalytic efficiency was demonstrated.

3.2 Experimental Procedure

Materials. For the synthesis of SnS particles, tin(II) chloride ($SnCl_2$, 97%, Wako Pure Chemical Industries, Ltd), elemental sulfur powder (S, 99.99%, Kojundo Chemical Laboratory Co., Ltd), oylamine (OLA, FUJIFILM Wako Pure Chemical Corporation), and hexamethyldisilazane (HMDS, Apollo Scientific. Co. Uk) were used as raw materials. Sodium sulfite (Na_2SO_3 , 97%), sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 96%) and hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) were purchased from Nacalai Tesque, Inc as sacrificial agents and co-catalyst source separately for the experiment on H_2 evolution. All of the ingredients were used without further purification. Purified water ($18.2\text{ M}\Omega \cdot \text{cm}$) was obtained from a filtration system that was purchased from Merck & Co., Inc. α -SnS platelets, for comparison, were provided by Nihon Seiko Co., Ltd and were further centrifuged at 600 rpm to obtain the particles with sizes of less than $1.5\text{ }\mu\text{m}$.

Synthesis method. 0.3640 g $SnCl_2$ and 0.0744 g elemental sulfur were dispersed in 32 mL OLA. Under a nitrogen atmosphere, the mixture was stirred magnetically at room

temperature for 30 minutes to remove air and moisture. After that, a predetermined amount of HMDS was added to the mixture in some cases. The mixture was then heated on a hot plate with the temperature set to 70 °C. After 30 minutes, the temperature was increased to 150 °C and the mixture was left for another 30 minutes. Finally, the mixture became a homogeneously yellow solution. The solution was transferred to a 50 mL Teflon-lined stainless steel reaction kettle and reacted at 200°C for several hours. The obtained precipitates were centrifuged for 10 minutes at 1500-3000 rpm and washed using ethanol, the process of which was repeated 4 times. After being dried in air, grey black SnS powder was obtained. The two series of SnS samples were named T- and H- to investigate the effects of solvothermal reaction time and the amount of HMDS, respectively, where each number represents time (hours) and amount (mL). Heat treatment was carried out at 300 or 400°C for some samples to remove the ligands that possibly absorbed on the surface of SnS particles.

Characterization methods. The crystal structure of the samples was detected by an X-ray diffractometer (XRD, Malvern Panalytical Empyrean) using Cu K α irradiation at 45 KV and 40 mA. The full width at half maximum (FWHM) of the (400) peak was evaluated from the software Highscore (Malvern Panalytical). The morphologies were characterized by using field emission scanning electron microscopes (FE-SEM, JEOL JSM-6500) and transmission electron microscopy (TEM, JEOL JEM-2010). Selected area electron diffraction (SAED) was also obtained by TEM equipment. The size distribution of the particles was determined by measuring the length of the particle edge in SEM images using the software Nano Measurer. Transmittance spectra were measured by using UV-Vis spectrophotometer (Shimadzu UV-2600) to characterize the light absorption and evaluate the bandgap of SnS particles. Room-temperature photoluminescence was obtained by a fluorescence lifetime analysis system (Hamamatsu Photonics C7990-01) using an excitation laser with a wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed using an X-ray photoelectron spectrometer (ESCA, SHIMADZU) with an Mg K α (1.253 KeV) X-ray source (operating voltage and current: 10 kV and 20 mA, respectively)

Measurement of photocatalytic activity. The photocatalytic activities of SnS particles were evaluated using SnS powder dispersed in an aqueous solution consisting of 4 ml 0.1 mol/L Na₂S and 4 ml 0.1 mol/L Na₂SO₃ in a glass tube. The amount of SnS particles was 4 mg. After that, H₂PtCl₆·6H₂O was added as a source of a Pt cocatalyst to be loaded on the surface of π -SnS particles by the photoreduction method. The amount of Pt was 1 wt.%. Argon gas was passed through the solution with magnetic stirring for 15 minutes to remove air and the tube was sealed with a rubber plug. One glass tube acted as a reactor and was irradiated from the side using a 300 W Xenon lamp with a wavelength of more than 300 nm through a quartz window for which light transmittance was around 93%. The evolved H₂ was collected using a syringe and its volume was analyzed by a gas chromatograph (J-Science Lab CGC-001T) equipped with a thermal conductivity detector using Ar as a carrier gas.

3.3 Results and discussion

3.3.1 Morphology

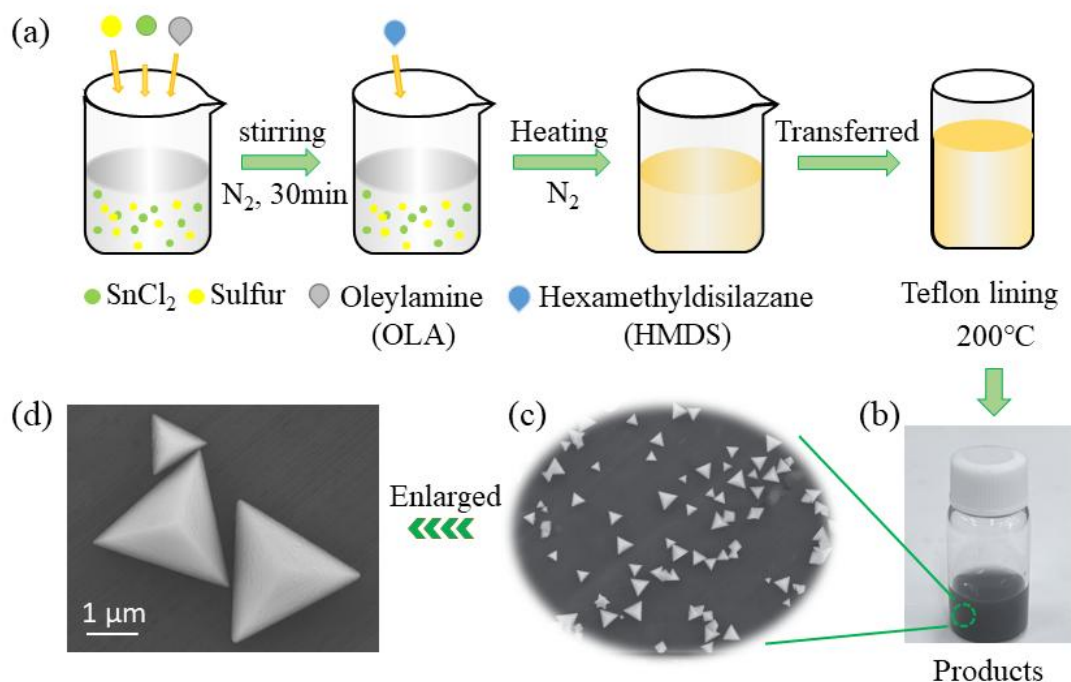


Figure 3-1. (a) Process for preparation of π -SnS particles, (b) π -SnS particles dispersed in ethanol, (c) SEM image and (d) enlarged SEM image of π -SnS particles.

As Figure 3-1(a) shows, all the raw materials were dispersed in oleylamine simultaneously under an N_2 atmosphere. With continuous magnetic stirring, the mixture became a translucent yellow solution by adjusting the heating temperature. In this way, the preparation process was simplified and all the materials were dissolved, forming a homogeneous precursor solution. Figure 3-1(b) shows the obtained π -SnS particles dispersed in ethanol, exhibiting a black color. An SEM image of the powder is shown in Figure 3-1(c). All of the particles present an ideal tetrahedral shape. They were dispersed evenly and no agglomeration occurred. The clear edges and flat surfaces of the regular tetrahedrons can be seen in Figure 3-1(d).

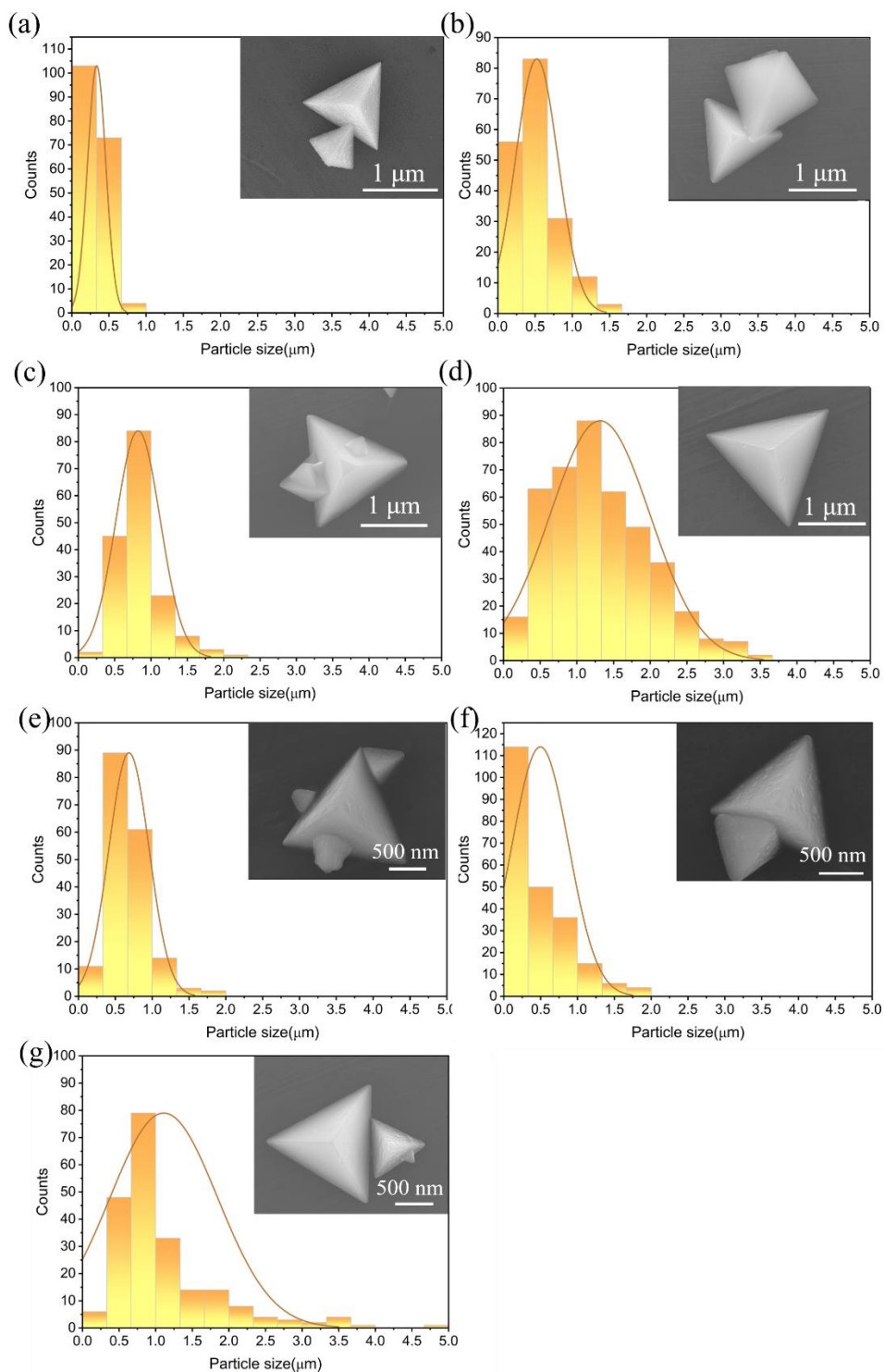


Figure 3-2. Particle size distributions of samples (a) T05, (b) T10, (c) T15, (d) T20, (e) H06, (f) H08 and (g) H09.

Figure 3-2 shows the particle size distribution in terms of the edge length of tetrahedra by counting about 200 particles. Figures 3-2(a-d) indicate that the particle size distribution becomes wider as the solvothermal reaction time increases from 5 h to 20 h. At the initial stage (5 h), all particles maintain sub-micron dimensions ($<1\ \mu\text{m}$). Upon reaching 20 h, the system develops a broad size distribution (up to $3.5\ \mu\text{m}$), as evidenced by Figure 3-2(d). This phenomenon indicates that prolonged reaction time induces concurrent particle growth and ongoing nucleation, which is consistent with the classical nucleation-growth kinetics described in Chapter 2 and is attributed to the ultralow supply of active sulfur from elemental sulfur. Specifically, the thermodynamic drive to minimize surface energy results in progressive broadening of the particle size distribution over time. ^[4] The particle size distributions were analyzed using Gaussian fitting, with mean diameters summarized in Table 3-1. A clear positive correlation was observed between the particle size and solvothermal duration.

Table 3-1. Average particle size, FWHM of 400 diffraction, and bandgap of the samples with different solvothermal reaction times.

Sample	Average particle size / μm	FWHM / degree	Bandgap / eV
T05	0.3167	0.1092	1.629
T10	0.5140	0.1151	1.637
T15	0.8377	0.0640	1.628
T20	1.3174	0.0468	1.631

A comparison between Figures 3-2(e) and 3-2(a) for H- series samples indicates that HMDS seems to be a promoter in the growth of particles. When the amount of HMDS increased from 0.6 to 0.8 mL, there was no obvious difference in particle size or morphology as can be seen in Figure 3-2(f). On the other hand, Figure 3-2(g) for sample H09 shows that a higher concentration of HMDS leads to a broadened size distribution. Several reports ^[5-8] have indicated that HMDS may play an important role in promoting nucleation. Contrary to

previous assumptions, our findings in Chapter 1 suggest that HMDS suppresses nucleation events. This inhibition redirects the reactive sulfur species (released from elemental sulfur) toward preferential deposition onto existing crystal nuclei, thereby promoting particle growth. The corresponding average particle sizes are shown in Table 3-2.

Table 3-2. Average particle size, FWHM of 400 diffraction and bandgap of the samples with different volumes of HMDS.

Sample	Average particle size / μm	FWHM / degree	Bandgap / eV
T05	0.3167	0.1092	1.629
H06	0.6748	0.0468	1.625
H08	0.3315	0.0624	1.616
H09	1.1088	0.0384	1.619

3.3.2 Crystalline properties

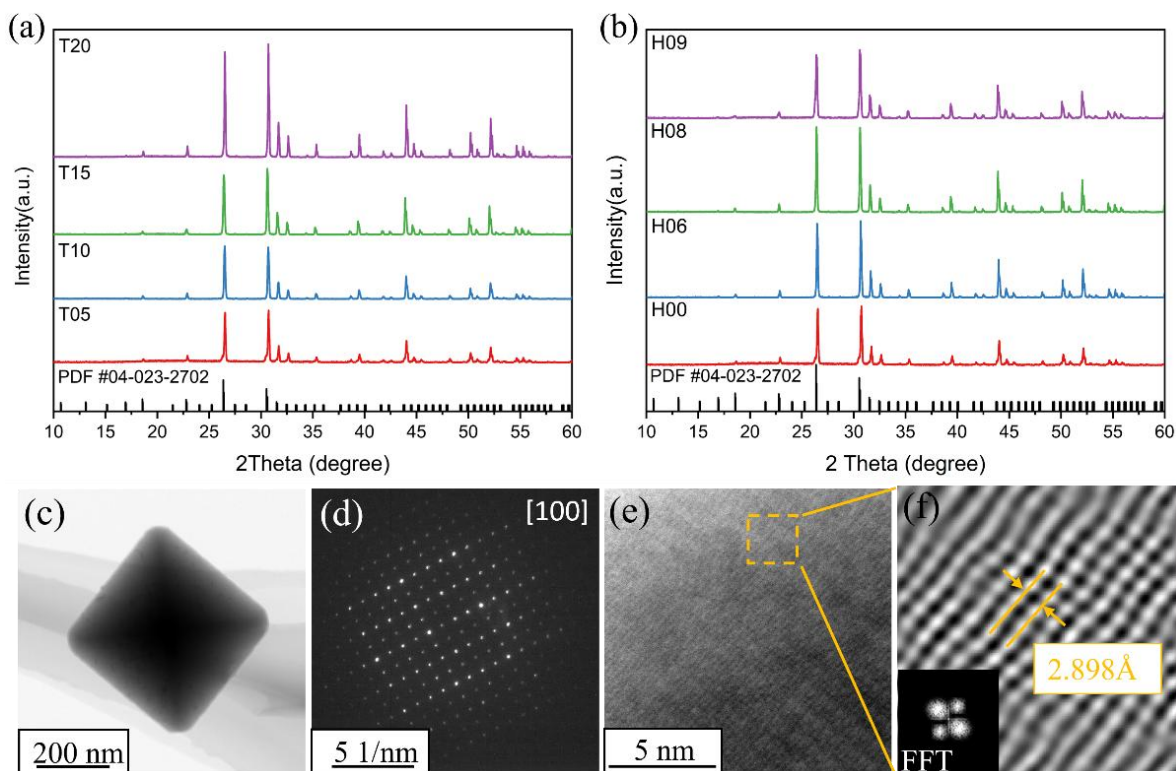


Figure 3-3. XRD profiles for SnS particles (a) with various time, (b) various amount of HMDs (c) TEM image of a particle indicating the shape of a tetrahedron (sample T05), (d) SAED of a single tetrahedron indicating on the [100] zone axis, (e) HRTEM image of an edge of the tetrahedron and (f) enlarged HRTEM image simulated from the FFT pattern.

The phase purity and crystallographic structure of the synthesized SnS particles were confirmed by XRD analysis (Figure 3-3(a, b)). All diffraction peaks exhibit perfect correspondence with the cubic π -SnS reference pattern (PDF #04-023-2702), with no detectable impurities (e.g., elemental sulfur or SnS₂). According to Bragg's Law, the lattice constants calculated from this work are $a = b = c = 11.68$ Å, which is near the value of 11.70 Å in a previous study on π -SnS.^[9] FWHM values of 400 diffractions for each sample are shown in Table 1. For sample T05, the value was 0.1092°, and it was reduced to 0.0468° when the solvothermal reaction time was increased to 20 h (sample T20). This progressive sharpening of diffraction peaks with extended solvothermal duration (5 to 20 h) confirms

enhanced crystallinity and grain growth, corroborating the SEM-observed morphological development.

3.3.3 Optical properties

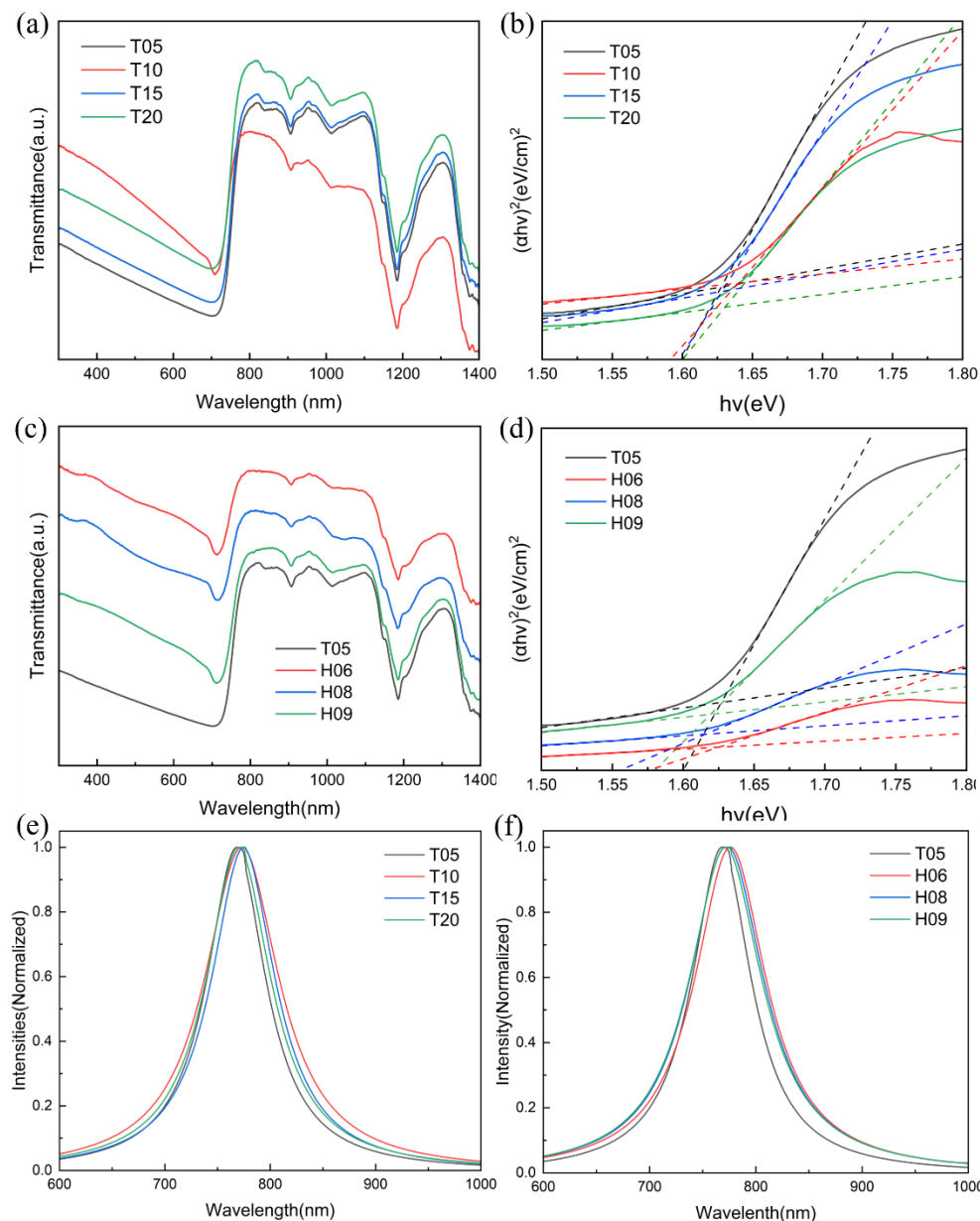


Figure 3-4. (a) UV-Vis transmittance spectra of T- series samples, (b) corresponding Tauc's plots, (c) UV-Vis transmittance spectra of H- series samples, (d) corresponding Tauc's plots, and photoluminescence (PL) spectra for (e) T- and (f) H- samples at room temperature.

Optical absorption characteristics were investigated through UV-Vis transmittance spectroscopy. All samples exhibited strong visible light absorption, as evidenced by low transmittance across the 400-700 nm range (Figure 3-4a). The minimum transmittance observed in the red light region (~ 650 nm) corresponds to direct interband transitions between the valence and conduction bands. Notably, significant sub-bandgap absorption occurred in the near-infrared region (~ 1200 nm), suggesting potential utility for NIR photodetection applications. The band gap was estimated from Tauc's plot, which is the relationship between $(\alpha h\nu)^2$ ($\alpha = 2.303$) and photon energy ($h\nu$), according to absorbance spectra that are converted from transmittance spectra ^[10-12]. Linear extrapolation of the absorption edges (Figure 3-4b) yielded a consistent direct bandgap of 1.63 eV for T-series samples, independent of reaction time (Table 1). In addition, HMDS modification (H-series samples) induced negligible variations in both transmission spectra (Figures 3-4(c-d)) and bandgap values (1.62 eV, Table 2), indicating the ligand's minimal influence on the electronic structure of π -SnS. Photoluminescence (PL) characterization of T-series samples (Figure 3-4e) revealed broad emission peaks centered at 765 nm (1.62 eV), matching the optical bandgap determined by UV-Vis spectroscopy. While previous studies ^[13-15] have correlated PL intensity with charge recombination rates, quantitative analysis in our system is complicated by particle sedimentation effects during measurement. Larger particles preferentially settled in the cuvette, creating a non-representative size distribution in the laser-excited volume. Consequently, we refrain from quantitative recombination rate comparisons and reserve detailed carrier lifetime analysis for future studies. For HMDS-modified samples (Figure 3-4f), the emission peak redshifted to 770 nm (1.61 eV), maintaining consistency with corresponding UV-Vis absorption edges.

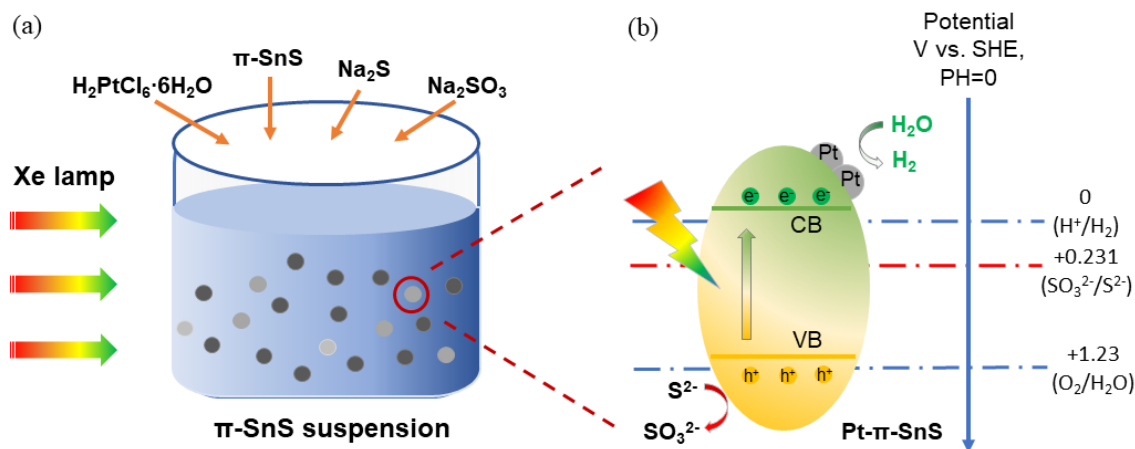
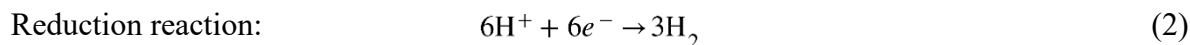


Figure 3-5. Schematic diagram for (a) the photocatalytic system and (b) photoexcitation mechanism of a π -SnS photocatalyst.

Figure 3-5(a) presents a schematic illustration of the photocatalytic hydrogen production system. In this configuration, proton reduction to molecular hydrogen (H_2) is driven by photoexcited electrons through the following reactions:



From a thermodynamic perspective, effective photocatalytic hydrogen evolution requires the conduction band minimum (CBM) of semiconductors to possess a more negative potential than the H^+/H_2 redox couple (0 V vs. SHE). As illustrated in Figure 3-5(b), this energetic alignment enables photoexcited electrons to reduce protons ($2\text{H}^+ + 2e^- \rightarrow \text{H}_2$) [16]. Concurrently, sulfide ions (S^{2-}) serve as sacrificial electron donors, undergoing oxidation by photogenerated holes to complete the redox cycle.

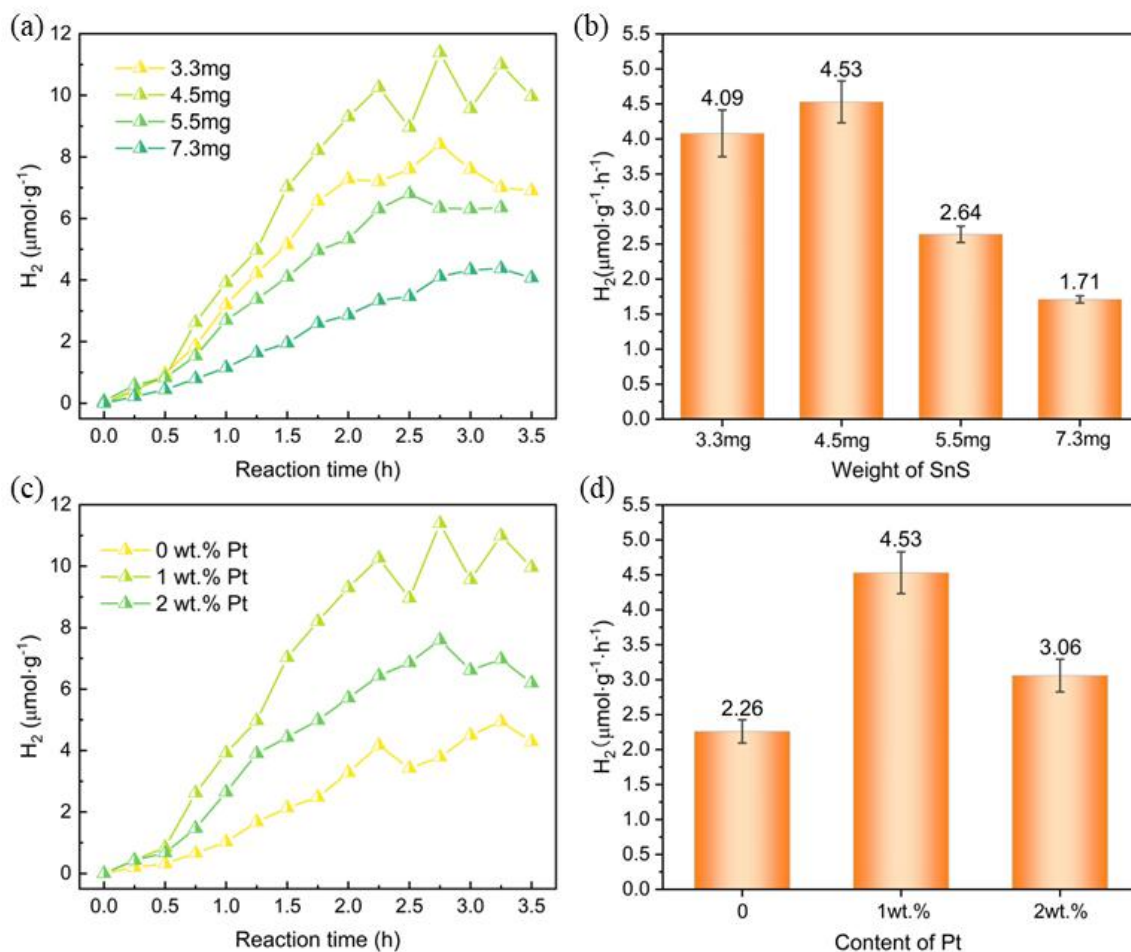


Figure 3-6. (a) Dependence of the amount of H₂ production on photocatalyst concentration for T10, (b) photocatalytic H₂ production efficiency for different weight of powder SnS T10, (c) dependence of the amount of H₂ production on Pt concentration for T10, (d) photocatalytic H₂ production efficiency for different concentrations of Pt for T10.

Sample T10 was employed to systematically investigate the effects of photocatalyst loading and Pt cocatalyst content on H₂ production performance. As shown in Figure 3-6(a), the amount of H₂ increased with reaction time. However, the H₂ production rate before 0.5 h is lower compared with that after 0.5 h, which may be caused by the fact that the time less than 0.5 h is not enough for complete photodeposition of Pt nanoparticles from Pt⁴⁺ precursors onto the π -SnS surface. Therefore, H₂ production efficiency was evaluated after 0.5 h. Optimal hydrogen production (4.53 μmol·g⁻¹·h⁻¹) was achieved at a photocatalyst loading of 4.5 mg, representing an ideal balance between light absorption and mass transport. Higher

loadings (>4.5 mg) resulted in decreased efficiency due to light penetration limitations and particle aggregation effects ^[17]. Similarly, Pt loading studies (Figure 3-6(c,d)) revealed maximal activity at 1 wt.% cocatalyst concentration. This optimum represents a compromise between sufficient active sites and avoidance of light shielding/excessive charge recombination ^[18]. Based on these findings, subsequent experiments employed 4.5 mg of π -SnS with 1 wt.% Pt loading.

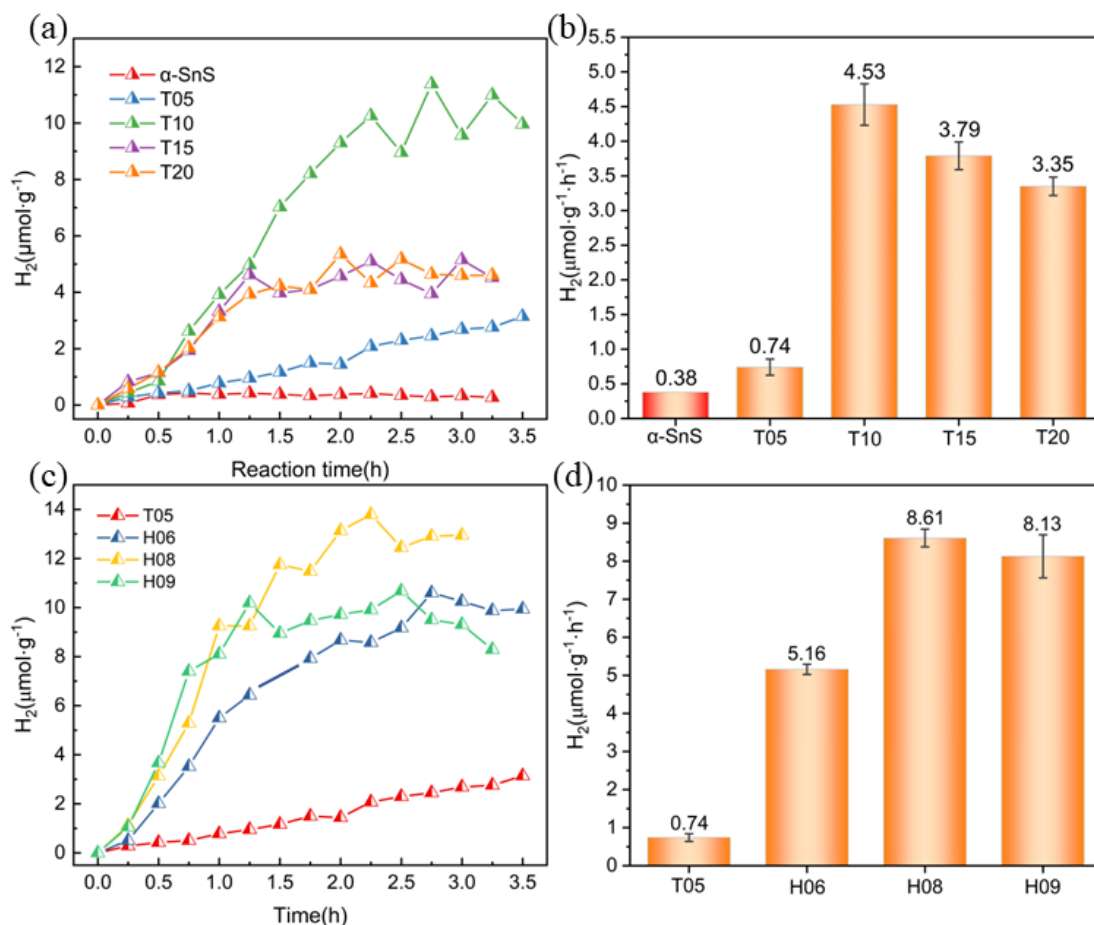


Figure 3-7. (a) Photocatalytic H₂ production with light radiation time, (b) H₂ generation efficiency for T-series samples, (c) photocatalytic H₂ production and (d) H₂ generation efficiency for H-series samples.

The results of photoactivity are shown in Figure 3-7. Figures 3-7(a) and 3-7(b) show the amount of H₂ produced with time and H₂ production efficiency, respectively, for T-series samples together with α -SnS. For sample α -SnS, the amount of H₂ increases slowly until 0.5

h. After that, the amount seems to be saturated and even slightly decreased possibly due to the sealing of the container for H_2 production being insufficient. The efficiency is $0.38 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which was evaluated from the slope of the curve within 0.5 h in Figure 3-7(a). The poor photoactivity of α -SnS particles was attributed to the edge of the conduction band not being sufficiently negative to generate H_2 .^[19] On the other hand, for π -SnS of sample T05, which has a particle size similar to that of α -SnS, the amount of H_2 produced shows a slowly increasing trend with an increase in irradiation time. The efficiency is $0.74 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, two times higher than that of α -SnS particles. When the solvothermal reaction time was 10 h (sample T10), the efficiency of H_2 production was greatly improved to $4.53 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. However, the amount of H_2 fluctuated after 2.25 h and tended to remain constant. Similar situations were also observed in samples T15 and T20 after 1.25 h. This phenomenon may originate from the agglomeration of catalyst particles observed in photocatalytic experiments, which was seen even under stirring by a magnetic stirrer. The agglomeration reduced the surface area that supplied active sites for H_2 evolution and the particles sometimes settled at the bottom of the container, thereby inhibiting continued production of H_2 .^[20] Surprisingly, by adding HMDS to the precursor solution, the obtained particles prepared even with a solvothermal reaction time of 5 h exhibited greatly enhanced photocatalytic H_2 evolution capacity. As shown in Figures 3-7(c) and 3-7(d), the H_2 evolution capacity is enhanced with an increase in the amount of HMDS. When the amount of HMDS is 0.8 ml (sample H08), the highest efficiency of $8.61 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ was obtained. The efficiency is about 12-fold greater than that for sample T05 ($0.74 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$). Beyond its established role in modulating precursor chemistry and controlling nucleation-growth kinetics in Chapter 2, HMDS has been demonstrated to significantly enhance the photocatalytic activity of the resulting particles in this chapter.

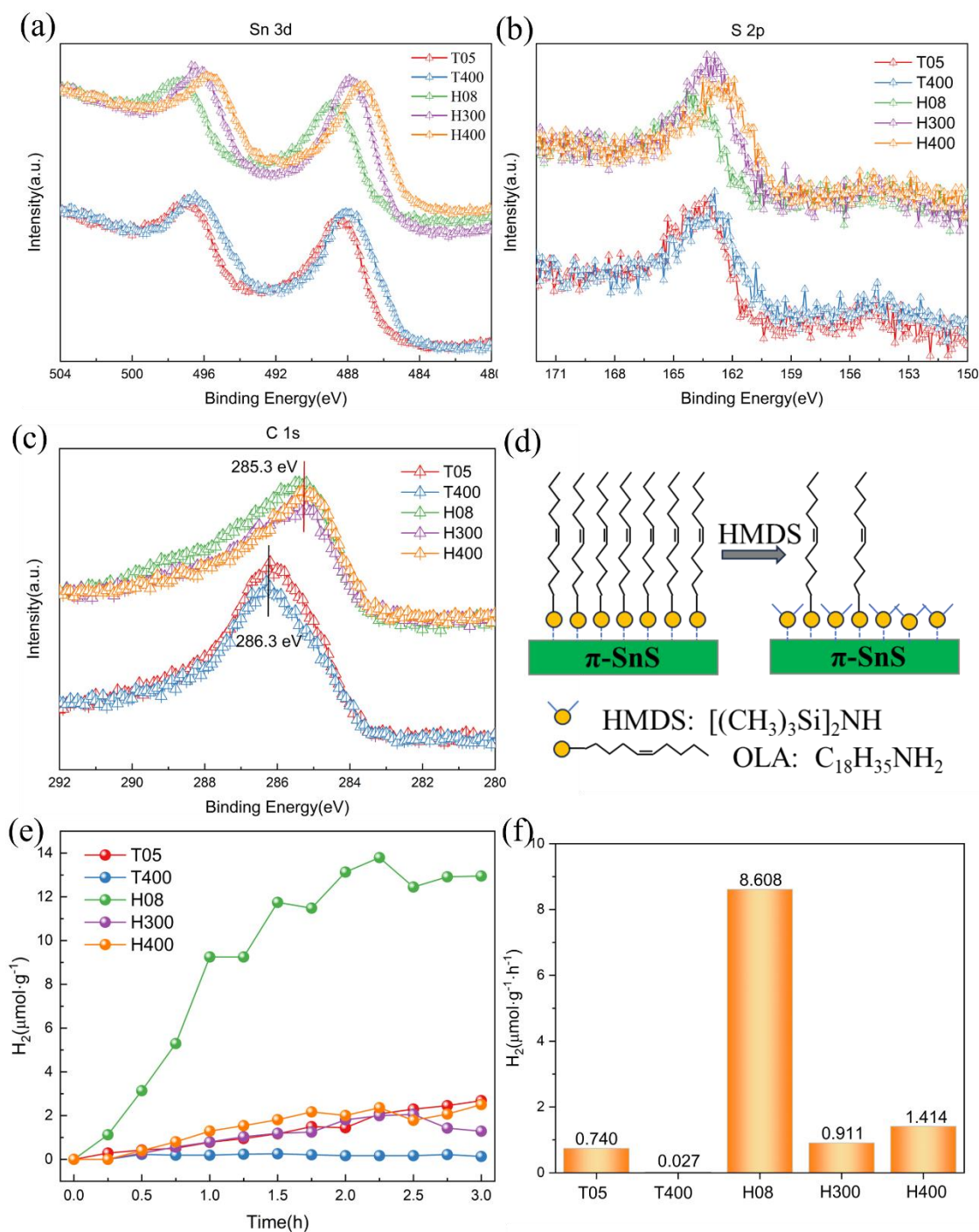


Figure 3-8. XPS spectra of (a) Sn 3d, (b) S 2p, and (c) C 1s for π -SnS particles. (d) Schematics illustrating the binding structure of surfactant molecules on the surface of π -SnS particles. (e) H_2 production and (f) H_2 production efficiency of the samples before and after annealing.

To confirm the effect of HMDS, a post-annealing treatment under an N_2 atmosphere was performed in samples T05 and H08 to remove organic molecules that may be present on the surface of π -SnS particles. The annealing temperature was set according to the boiling point of OLA and HMDS molecules. XPS measurements were performed on π -SnS particles before and after annealing. As shown in Figure 3-8(a), after annealing, the intensity of Sn 3d peaks of both samples T05 and H08 increases, indicating that organic molecules were effectively removed from the π -SnS surface. In addition, a chemical shift to a lower energy was observed in both samples. The reason is worth exploring and will be discussed in the next Chapter. The S 2p peak shown in Figure 3-8(b) shows a trend similar to that for Sn 3d. Accordingly, the intensity of C 1s peaks was reduced, as can be seen in Figure 3-8(c). What is interesting is that the peak for H08 is located at 285.3 eV, while the peak for T05 is located at 286.3 eV. For sample T05, the main C originates from OLA and the corresponding XPS peak shows stronger intensity due to the long carbon chain structure of OLA molecules. By adding HMDS, most or part of the OLA molecules attached to the π -SnS surface are replaced by HMDS molecules with a short chain structure, as shown in Figure 3-8(d). It was also reported that the molecules of HMDS interact with Tin ions to form Tin-HMDS complexes during the preparation of a precursor solution to assist the formation of crystal particles.^[21-23] Figures 3-8(e) and 3-8(f) show the performance of the H_2 evolution ability of π -SnS particles before and after annealing. The H_2 generation ability declined sharply after annealing. Sample T05-400, which is sample T05 after annealing at 400°C, nearly lost its hydrogen production capacity. The H_2 generation efficiency of H08 decreased from 8.608 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ to 0.911 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ and 1.141 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ after annealing at 300 and 400 °C, respectively (H300 and H400 in the figure). The observed performance degradation unequivocally demonstrates the critical function of surface-bound organic ligands in maintaining the hydrogen evolution capacity of π -SnS particles. HMDS may effectively mitigate the surface charge recombination, thereby substantially enhancing the photocatalytic activity of π -SnS tetrahedrons.^[24]

3.4 Summary of this chapter

In this Chapter, by a simple one-pot solvothermal method, the emerging pure π -SnS 3D tetrahedrons prepared with various time and volumes of HMDS are investigated. UV-Vis transmittance spectra and PL analysis revealed the bandgap of ~ 1.62 eV for π -SnS tetrahedrons. It was proved that the addition of HMDS during the preparation process plays an important role for the photocatalytic activity of π -SnS tetrahedrons. π -SnS particles prepared with 0.8 ml HMDS showed the highest H_2 evolution efficiency of $8.61 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ under visible light irradiation, about 12-fold higher than the efficiency of π -SnS particles prepared without HMDS ($0.74 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) and 23-fold higher than that of α -SnS particles with a similar size ($0.38 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) for H_2 generation from water. XRD revealed that an appropriate amount of HMDS facilitates the formation of π -SnS tetrahedrons with excellent crystallinity, which improves charge transfer and separation efficiency of the photogenerated electron-hole pairs during photocatalysis. XPS measurements and post-annealing treatment confirmed the existence of organic ligands on the surface of π -SnS tetrahedrons and the better passivation effect of HMDS ligands compared to OLA ligands.

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Chapter 4 Martensite-like phase transition of π -SnS tetrahedrons

4.1 Introduction

Chapter 3 demonstrated the potential photocatalytic performance of tetrahedral SnS particles. Equally crucial is their stability, which ensures sustained catalytic activity during prolonged photoreactions. As is known that π -SnS is a metastable phase as its formation energy is computed to be 2.19 kJ/mol higher than that of the orthorhombic ground state (α -SnS).^[1] Understanding the thermodynamic stability and solid-solid phase transition is crucial to control phase-dependent properties and applications. Experimentally, π -SnS has been observed to be kinetically stable at room temperature. To date, π -SnS films have been obtained by a variety of techniques including chemical bath deposition^[2], thermal evaporation^[3], atomic layer deposition^[4] and spray pyrolysis^[5]. Under an inert gas atmosphere, the thin films are thermally stable up to 300-400 °C, while over 400 °C secondary phases like SnS₂ and metallic Sn were observed.^[6-8] The particles of π -SnS with various shapes, typically tetrahedrons and spheres, are synthesized using colloidal (surfactant-assisted) methods.^[9-11] Greyson *et al.* reported that these microcrystals remain stable at 300 °C for 3 h under Ar atmosphere but transform into α -SnS at 250 °C in oleylamine.^[12]

The phase stability of particles is often affected by the relative contribution of surface energies to the total Gibbs free energy. High surface energy allows surface atoms to rearrange to achieve the ground state. Such situations can typically be alleviated by impurity incorporation or particle agglomeration, thereby maintaining the stability of metastable phases. Density-functional theory (DFT) calculations demonstrated that the metastable π -SnS particles may be effectively stabilized by surface ligands.^[13] Several interesting reports are also available on the meta-stability of ligand-capped π -SnS with annealing temperature. The triethanolamine-capped nanoparticles were stable up to 400°C and transformed to orthorhombic phase partly at 450 °C under vacuum for 1 h.^[11] Fridman *et al.*^[14] reported the high phase stability at 400°C of polyvinylpyrrolidone-capped π -SnS nano-cubes. Little difference in the impact of different surface ligands on the stability of π -SnS nanoparticles

was seen. However, the intrinsic properties of surface ligands were proved to be crucial to H_2 evolution performance of π -SnS in our previous work ^[15] and, logically, to its physicochemical properties. In the present work, we report on the isothermal annealing study for oleylamine (OLA)-capped π -SnS particles and hexamethyldisilazane(HMDS) & OLA-capped π -SnS particles, respectively. The temperature- and time-dependent phase transition behavior and its effect on particles' morphology are investigated. The mechanism involved in the ligand-affected phase stability and transformations, as well as the associated structure evolution, is detailed using X-ray diffraction, X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy and High-resolution transmission electron microscopy. Notably, a Martensite-like phase transformation in SnS is proposed for the first time.

4.2 Experimental procedure

Materials. Tin(II) chloride ($SnCl_2$, 97 %, Wako Pure Chemical Industries, Ltd) and elemental sulfur powder (S_8 , 99.99 %, Kojundo chemical laboratory Co., Ltd) were used as raw materials without further purification. Oleylamine (OLA, FUJIFILM Wako Pure Chemical Corporation) and hexamethyldisilazane (HMDS, Apolloscientific.co.uk) were used as the solvent and ligands. Sodium Sulfite (Na_2SO_3 , 97 %), sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 96 %) and hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) were purchased from Nacalai Tesque, Inc. and used for hydrogen evolution experiments. Purified water ($18.2 M\Omega \cdot cm$) was obtained from a filtration system. (Direct-Q UV3, Merck & Co., Inc.)

Synthesis of π -SnS particles. π -SnS particles were synthesized via a solvothermal method adapted from our previous work. In a typical procedure, 0.3640 g of $SnCl_2$ and 0.0744 g of elemental sulfur were dissolved in 32 mL of oleylamine (OLA) under magnetic stirring and heating. After 15 min, 0.8 mL of hexamethyldisilazane (HMDS) was introduced into the solution. Upon formation of a transparent and homogeneous precursor, the mixture was transferred to a 50 mL Teflon-lined stainless-steel autoclave and heated at 200 °C for 5 h. Throughout the synthesis, a continuous N_2 flow was maintained to prevent oxidation and moisture absorption. The resulting precipitate was washed four times with ethanol and air-

dried. The obtained samples were labeled as OSNS (OLA-capped π -SnS) and HSNS (HMDS & OLA-capped π -SnS), respectively.

Post-Annealing treatment. The as-prepared π -SnS particles were subjected to post-annealing in a quartz boat under an N_2 atmosphere at temperatures of 400, 500, 600, and 650 °C (see Figure S1 for the temperature profile). After annealing, the furnace was turned off, and the powder was allowed to cool naturally to room temperature.

Characterization and H_2 evolution measurement. Field Emission Scanning Electron Microscopy (FE-SEM, JSM-6500, JEOL) was used to characterize the morphology of SnS particles. X-ray diffraction was conducted using the X-ray diffractometer (Empyrean, Malvern Panalytical) with Cu $K\alpha$ at 45 KV and 40 mA to identify the phases and crystal structure. The surface chemistry of SnS particles was characterized through X-ray photoelectron spectroscopy (XPS, ESCA-3400, Shimadzu) using Mg $K\alpha$ (1.253 KeV) with an operating voltage of 10 kV and a current of 20 mA. Fourier-transform infrared spectroscopy (INVENIO, BRUKER) was further measured to confirm the existence of surface ligands. The transmittance spectrum was measured by a UV-Vis spectrophotometer (UV-2600, Shimadzu) to evaluate the optical properties. High-resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL) and selected area electron diffraction (SAED) were measured to analyze the precise morphology of particles and the corresponding crystal phase. H_2 evolution performance of SnS particles was evaluated by a gas chromatograph (CGC-001T, J-Science Lab) under irradiation from a 300 W Xenon lamp.

4.3 Results and discussion

4.3.1 Morphology

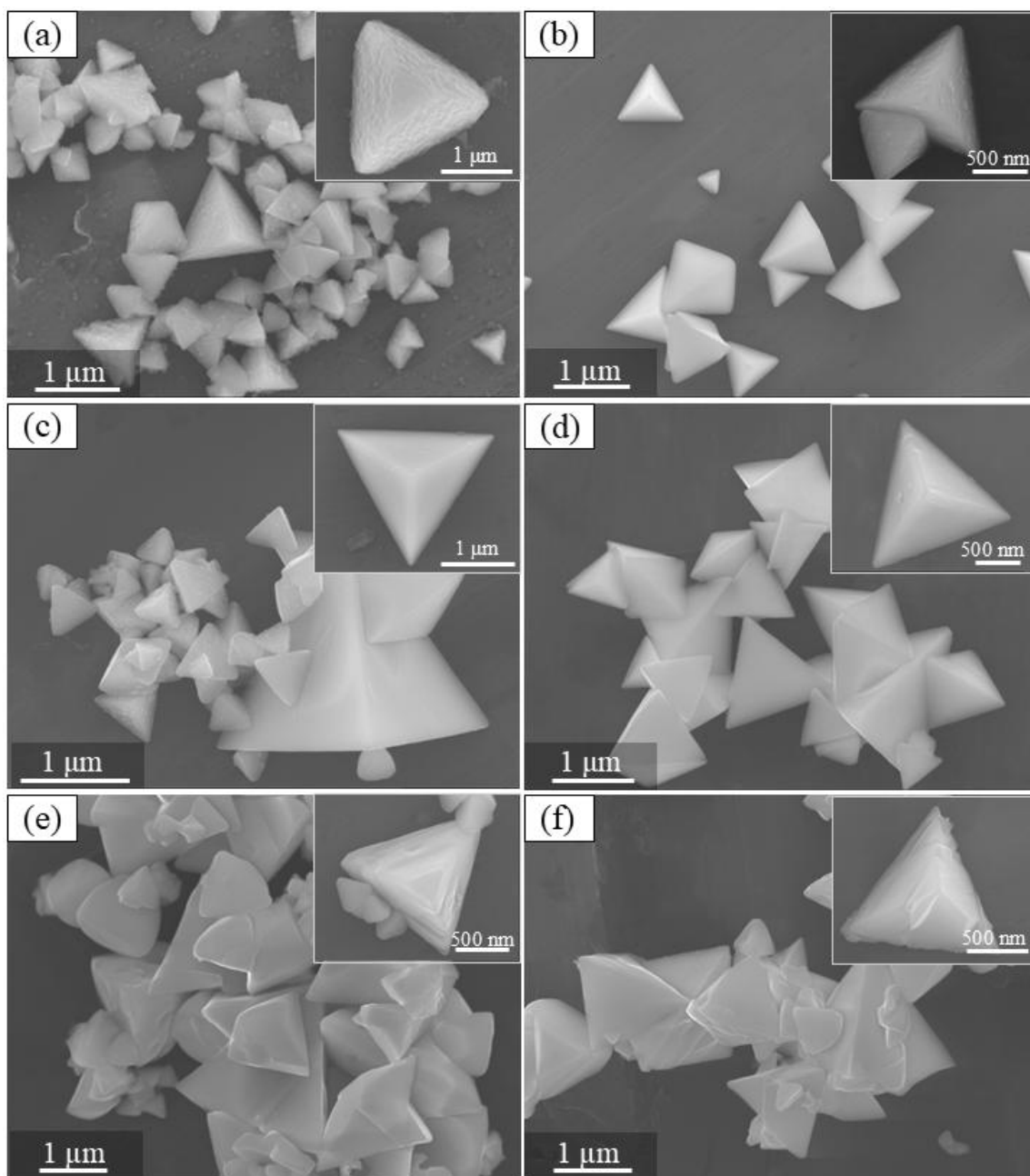


Figure 4-1. SEM images of OLA/HMDS-capped SnS particles before and after annealing. (a) OSNS, (b) HSNS, (c) OSNS-400, (d) HSNS-400, (e) OSNS-650 and (f) HSNS-650. The numbers of labels represent the annealing temperatures.

The typical morphologies of SnS particles before and after annealing are shown in Figure 4-1. As revealed in Figure 4-1(a), OSNS exhibited regular nano- and micro-tetrahedrons with clear edges and several truncated tetrahedrons, which were also reported by Deng *et al.* [16] A high degree of roughness was observed on the surfaces (inset Figure). HSNS (Figure 4-1(b)) also exhibits a tetrahedral shape but with reduced roughness, suggesting that HMDS may change the surface state of the tetrahedrons. After annealing at 400 °C, the surfaces became smoother (Figures 4-1(c) and 4-1(d)), with the formation of several concave pits. For OSNS-400, the surface roughness was still observed on the small-sized tetrahedrons. Increasing the temperature to 650 °C, the tetrahedral structure became deformed and fragmented. As shown in Figures 4-1(e) and 4-1(f), the edges of the tetrahedrons became indistinct, while severe concave pits, cracks and chips developed. The number of such defective particles gradually increased with temperature.

4.3.2 Crystalline properties

Figure 4-2 shows XRD profiles of SnS particles under various annealing conditions. In Figure 4-2(a), the peaks detected in OSNS conform well to the cubic π -SnS with a space group of $P213$ (PDF #04-023-2702, $a = b = c = 11.60 \text{ \AA}$). After annealing at 400 °C for 10 minutes, the cubic phase was maintained in OSNS-400. While in OSNS-500, several diffractions attributed to the orthorhombic α -SnS (PDF #03-065-3812, $Pnma$, $a = 4.34 \text{ \AA}$, $b = 11.20 \text{ \AA}$, $c = 3.99 \text{ \AA}$) were observed, indicating that some π -SnS particles had transformed into α -SnS at 500 °C. The diffractions are significantly enhanced in OSNS-600 and dominated in OSNS-650, indicating that cubic π -SnS gradually transformed into orthorhombic α -SnS with increased temperatures. Meanwhile, a small diffraction peak was observed around 22°-24° in OSNS-600 and OSNS-650. This diffraction comes from the elemental tin which crystallized during the cooling process owing to the escape of sulfur atoms at high annealing temperatures. Such sulfur loss is a common phenomenon in SnS when annealed in an inert atmosphere due to its high vapor pressure of sulfur. [17-19]

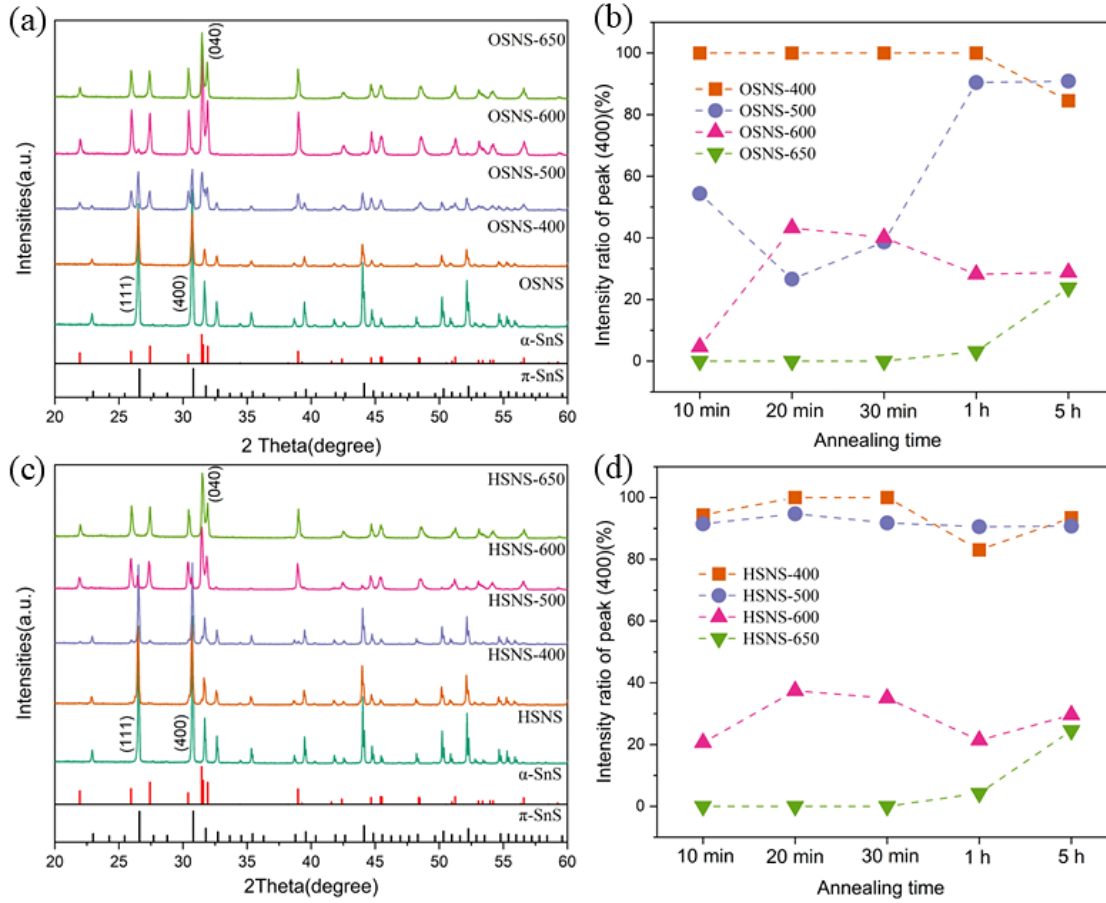


Figure 4-2. Crystal structure of OLA/HMDS-capped SnS particles before and after annealing. (a) XRD pattern of OSNS samples annealed for 10 min. (b) Intensity ratio of the (400) peak from XRD analysis over time. (c) XRD pattern of HSNS samples annealed for 10 min. (d) Corresponding intensity ratio of (400) peak over time.

Figure 4-2(b) shows the effect of annealing time on OSNS samples. Since no impurity phases are present, the fraction of π -SnS was evaluated using the relative intensity of diffractions expressed by the following equation:

$$R_{400} = \frac{I_{\pi 400}}{I_{\pi 400} + I_{\alpha 040}},$$

where R_{400} represents the intensity ratio of 400 diffraction from π -SnS. $I_{\pi 400}$ and $I_{\alpha 040}$ are the peak intensities of 400 and 040 diffractions of π -SnS and α -SnS, respectively. As shown in Figure 4-2(b), R_{400} of OSNS-400 remained 100% from 10 min to 1 h, but decreased to 84.51%

after 5 h of annealing, indicating a slight phase transition to α -SnS. In OSNS-500, nearly half of the SnS particles transformed to α phase with 54.39% π phase left. However, it exhibited non-linear behavior with the annealing time from 10 min to 5 h. A similar trend was observed in OSNS-600 and OSNS-650. Within 30 min, R_{400} dropped to 0% in OSNS-650, suggesting a rapid and complete phase transition from π phase to α phase. Interestingly, the π phase reappeared with prolonged annealing: the R_{400} values of 3.11% and 23.80% at 1 and 5 h, respectively.

As reported in our previous work, HMDS promotes the formation of highly crystalline π -SnS tetrahedrons. The thermal stability of such tetrahedrons was also evaluated. Figure 4-2(c) shows the XRD profiles of HSNS samples before and after annealing for 10 min. Unlike OSNS, weak diffractions from α -SnS were detected at 400 °C and 500 °C in HSNS, which stems from the participation of the ligands: HMDS. Surprisingly, the fraction of π -SnS remains higher with R_{400} staying above 90% as annealing time increases (Figure 4-2(d)), indicating that the adding of HMDS may promote the stability of the particles. HSNS-600 and HSNS-650 show a similar phase behavior to OSNS samples. Gautam et al. reported a “reversible” transformation phenomenon in titanium dioxide between rutile and anatase phases.^[20] Similar behavior was observed in our SnS particles OSNS-650 and HSNS-650. This may originate from a slight difference in the formation energies of α -SnS and π -SnS.

4.3.3 Surface chemistry

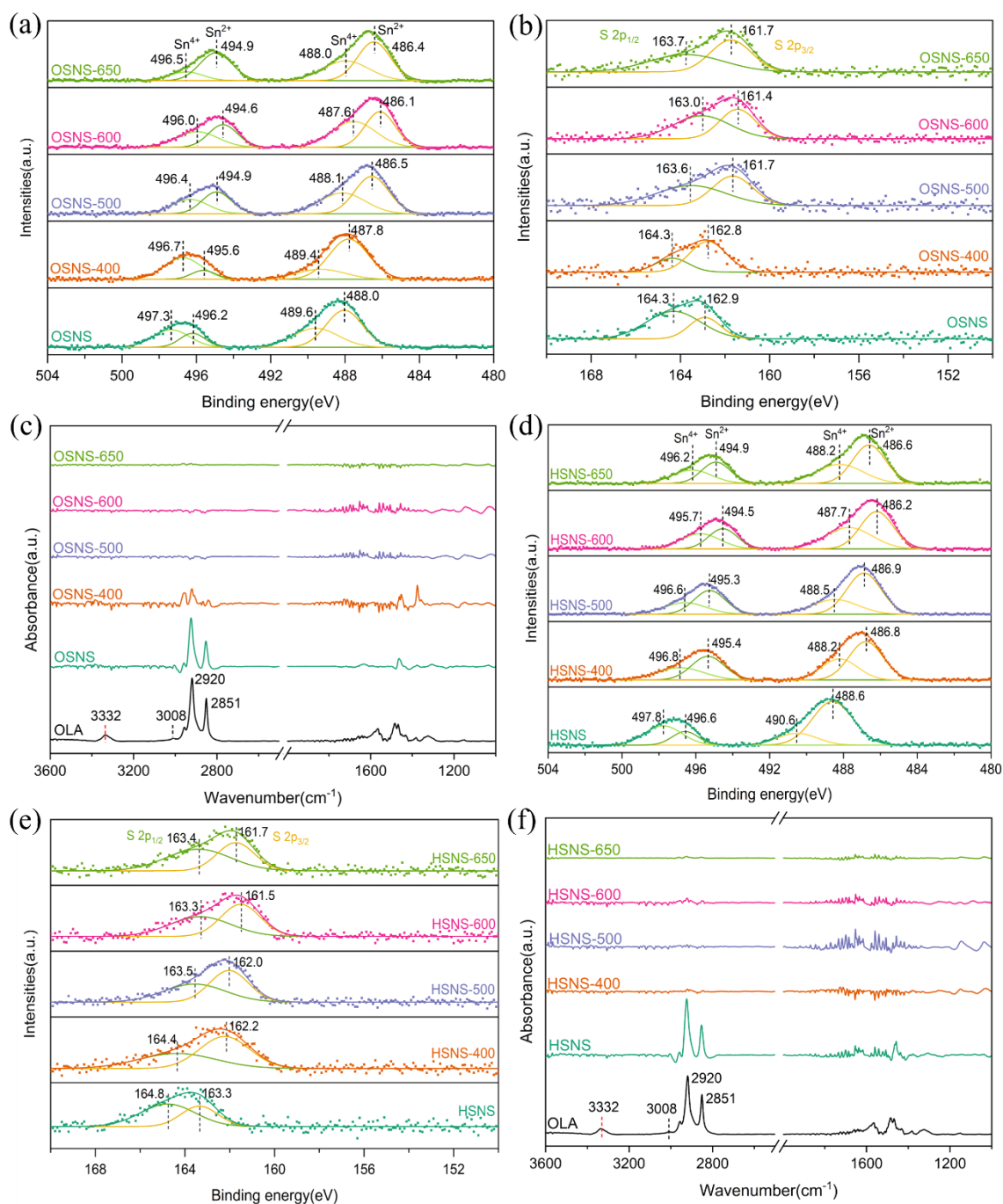


Figure 4-3. (a) Sn 3d, (b) S 2p XPS spectra, and (c) FT-IR spectra of OSNS samples. (d) Sn 3d, (e) S 2p XPS spectra, and (f) FT-IR spectra of HSNS samples.

XPS and FT-IR measurements were conducted to confirm the presence of surface ligands and the related surface behavior of SnS before and after annealing for 10 min. The XPS spectra of Sn 3d (Figure 4-3(a)) reveal the coexistence of Sn^{4+} and Sn^{2+} in all samples. The peaks at 488.0 and 496.5 eV in OSNS correspond to $3d_{5/2}$ and $3d_{3/2}$ states of Sn^{4+} , respectively, and the peaks at 486.4 and 494.9 eV are attributed to the states of Sn^{2+} .^[21-23] A similar spectrum is observed in OSNS-400, while the peaks shift to lower energy in samples OSNS-500, OSNS-600 and OSNS-650. The presence of Sn^{4+} is attributed to the oxidation of surface Sn^{2+} during high-temperature annealing or the sample preparation process for XPS. The S 2p spectra in Figure 4-3(b) are mainly deconvoluted into two peaks corresponding to S $2p_{3/2}$ and S $2p_{1/2}$ orbitals. As observed in the case of Sn, the S 2p spectrum of OSNS-400 is similar to that of OSNS, while a slight energy shift of peak positions is exhibited in the samples annealed at higher temperatures. The energy shift of Sn 3d and S 2p is well consistent with the surface ligand behavior shown in Figure 4-3(c). The symmetric and asymmetric stretching vibrations of the methylene group ($-\text{CH}_2$) at 2851 and 2920 cm^{-1} from pure OLA were also observed in OSNS, indicating that OLA molecules were successfully capped on the surface of the synthesized SnS particles. The marked peak at 3332 cm^{-1} originates from the symmetric stretching vibration of the amine group ($-\text{NH}_2$), which was absent in the spectra of OSNS. It was reported that this signal is suppressed by the oriented interaction between the amine group and the Sn atoms on the SnS surface.^[24] In OSNS-400, the signals from $-\text{CH}_2$ were much weakened, meaning that large amounts of OLA ligands desorbed from the surfaces after annealing at 400 °C for 10 min. No signal from OLA was observed at higher temperatures, suggesting that the interacting OLA ligands desorbed completely. In other words, the energy shift in the XPS spectra was caused by the absence of surface OLA ligands. Choi et al. reported a similar energy shift in XPS peaks due to indium-oleate complexes.^[25] Generally, OLA and oleic acid are well known as Lewis base molecules due to the presence of an amine or carboxy group. In the case of OLA, the lone pair of the amine group interacts with Sn atoms of SnS, theoretically leading to a lower energy shift in the Sn valence states. However, the XPS spectra exhibit an opposite trend that shows a higher energy shift with OLA ligands. This suggests that OLA may behave in a Lewis acidic manner, but further

investigation is necessary to clarify its role. Figures 4-3(d) and 4-3(e) show the XPS spectrum of HSNS samples, where a peak shift is observed in the sample annealed at a lower temperature of 400 °C (HSNS-400). Correspondingly, the FT-IR signals (Figure 4-3(f)) from OLA disappeared in HSNS-400, which further confirmed the role of OLA in causing a shift to higher binding energy in XPS spectra. On the other hand, the absence of FT-IR signals of OLA in HSNS-400 may also provide evidence for the partial ligand exchange of OLA by HMDS. Unfortunately, we could not detect the signals from HMDS due to insufficient molecules capping on the SnS surfaces. [26,27]

4.3.4 Proposed Martensite-like phase transition

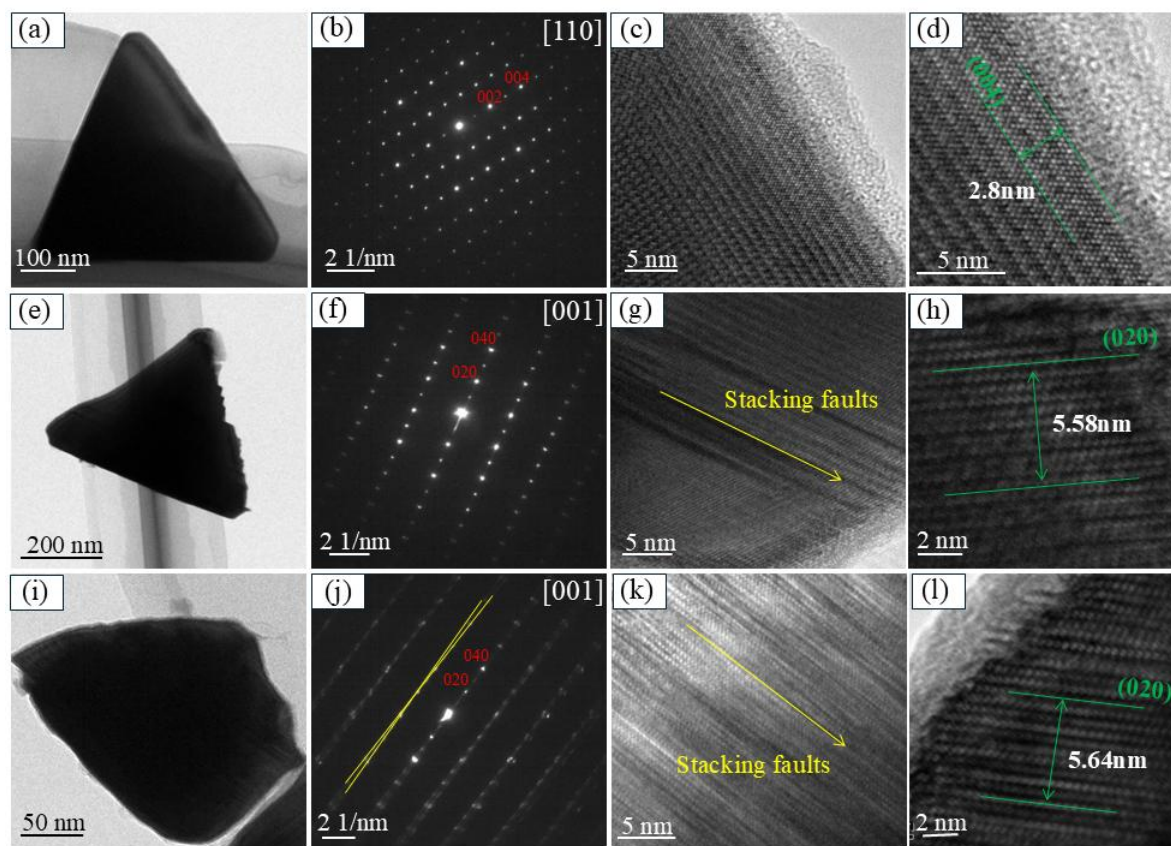


Figure 4-4. TEM observations of SnS particles after annealing. (a) Bright field image, (b) SAED pattern with [110] zone axis, and (c, d) HRTEM images of the same particle from OSNS-500. (e, i) Bright-field images, (f, j) SAED pattern with [001] zone axis, and (g, h) (k, l) HRTEM images of OSNS-650.

To understand the phase transition process, the relationship between the morphology and crystal phase of an individual particle was investigated by TEM, Selected Area Electron Diffraction (SAED) and High-resolution TEM (HRTEM). Considering the similarity in morphology evolution and phase transition, OSNS-500 and OSNS-650 were selected for observation here. The TEM image (Figure 4-4(a)) of an OSNS-500 particle indicates a tetrahedral shape with slight edge rounding. The corresponding SAED pattern (Figure 4-4(b)) revealed the typical pattern of a single crystalline π -SnS with strong diffractions from 002 and 004. The forbidden reflections from 00 l ($l = 1, 3, 5, \dots$ odd numbers) derived from multiple diffractions due to the relatively large particle thickness (100 ~ 300 nm).^[28] The 002 systematic diffractions observed in the direction are consistent with the tetrahedrons consisting of (111) surfaces. HRTEM images shown in Figures 4-4(c) and 4-4(d) exhibit clear and regular lattice fringes. The length of 2.8 nm between 10 periods of the planes is well consistent with the lattice spacing of (400) planes for π -SnS (2.8 Å). OSNS-650 particles in Figures 4-4(e) and 4-4(i) show significant step edges and SAED patterns of α -SnS (Figures 4-4(f) and 4-4(j)) with [001] zone axis.^[29] In addition, the diffraction spots exhibit streaking along [010] direction, indicating the presence of stacking faults, which was further confirmed by the corresponding HRTEM images in Figures 4-4(g) and 4-4(k).^[30] Since the crystal structure of α -SnS consists of layered stacking along [010] direction, it is reasonable to assume that stacking faults form on the (010) planes. Figures 4-4(h) and 4-4(l) give the distances of 5.58 and 5.64 nm, respectively, for 10 periods of (020) planes, corresponding to the lattice parameter of the b -axis in α -SnS (11.2 Å). Notably, Figure 4-4(j) shows two sets of diffraction spots, meaning that there are two α -SnS crystal grains along the [001] zone axis and one rotated by a slight angle with the other. This indicates that the single-crystal π -SnS tetrahedrons transformed into polycrystalline α -SnS particles after annealing. The detailed mechanism of such solid-to-solid phase transition behavior will be clarified later. The heterostructure of α -phase and π -phase, as reported by Qin *et al.*^[31], was not observed in our TEM observations.

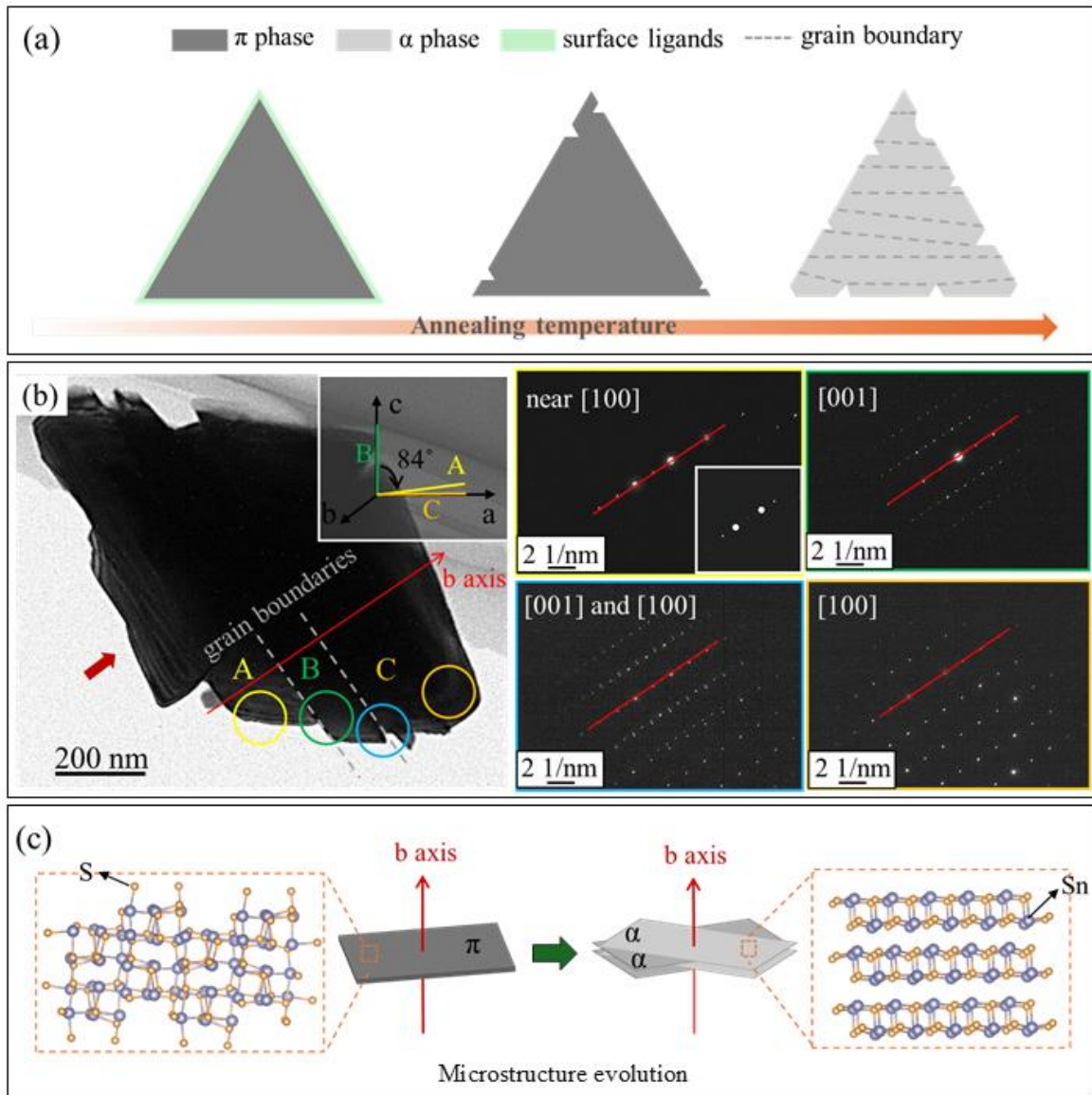


Figure 4-5. Schematic illustration of (a) structure evolution of SnS tetrahedrons with increased temperature. (b) TEM image of one SnS tetrahedron (OSNS-650) with various α -phase grains and their SAED patterns. inset: simulated SAED pattern corresponding to area A. (c) microstructure of π phase and α phase.

Based on the above characterizations, the microstructure evolution process through phase transition is discussed. As shown in Figure 4-5(a), the as-prepared tetrahedrons of the π -SnS single crystal were encapsulated with surface ligands, as confirmed by the FT-IR spectrum. At lower temperatures, most of the peripheral ligands desorbed, sometimes resulting in slight

morphological deformation, such as edge rounding and surface roughening. Upon higher temperatures, the inner layer of ligands begins to desorb and thus triggers the transformation from π phase to α phase ^[14]. Figure 4-5(b) shows a TEM image and the SAED pattern of adjacent grains A, B and C in α -SnS tetrahedrons. The blue region contains the interface between grains B and C. The red arrow indicates the b-axis of the original π -SnS tetrahedron. The SAED pattern of A is consistent with the simulated pattern (inset) that grain B rotates 84° clockwise around b-axis, indicating that A rotates 84° from B around b-axis. Similarly, the grain C rotates 90° from B around b-axis, confirmed by the SAED pattern from the blue area consisting of both B and C. As shown in Figure 4-5(c), we propose a diffusionless-like phase transition similar to martensitic transformations that do not involve random or diffusive atom movements and that result from only small relative displacements of neighboring atoms. Holding the cubic π -SnS tetrahedrons at high temperatures for 10 min resulted in the complete removal of surface ligands, leaving the surfaces in an unstable state. The relative rearrangement of surface atoms leads to phase transitions on the surface. Although there is a significant lattice mismatch between the π and α phases, the similarity in atomic bonding prevents the random formation of grains. In other words, the b-axis of the transformed α phase retains the direction of the b-axis of the original π phase, while the a-axis of the α phase undergoes alternating rotations of nearly 90° to form grains. This microstructure might relieve the lattice strain caused by the lattice mismatch between the disordered cubic structure and ordered layered orthorhombic structure ^[32]. This transition contributed to large amounts of grain boundaries and stacking faults, similar to those seen in martensitic alloys, resulting in the formation of stacked layered polycrystal α -SnS tetrahedrons. Such diffusionless-like transitions often occur via the formation of different microstructural features, many of which have not been observed in SnS previously but represent an important area of investigation for crystallization phenomena.^[33-35] Furthermore, the ability to introduce microstructure in SnS allows us to build more complex monochalcogenides that may facilitate better applications.

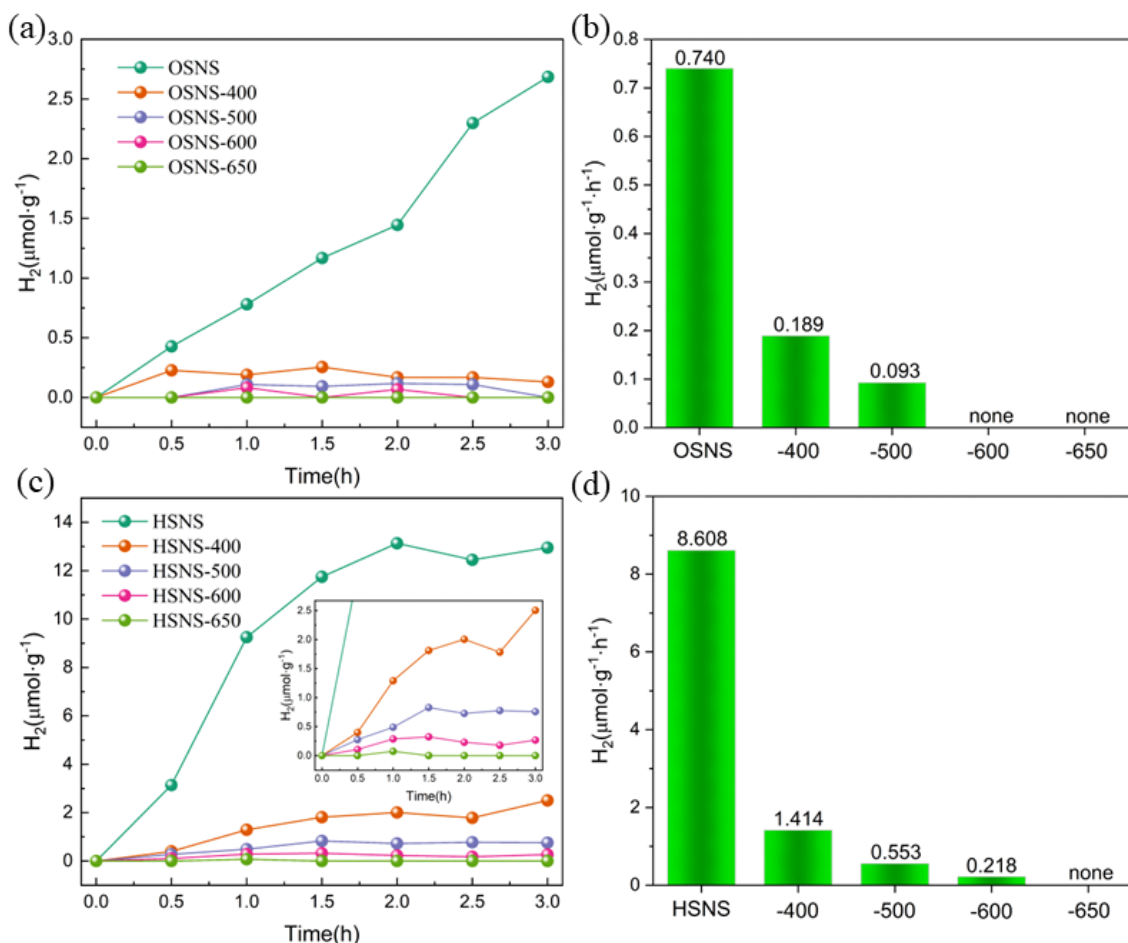
4.3.5 H₂ evolution performance

Figure 4-6. (a, c) Photocatalytic H₂ production with light radiation time and (b, d) H₂ generation efficiency for OSNS and HSNS before and after annealing.

The SnS particles were employed as photocatalysts for H₂ production using the particulate photocatalysis system [36]. As shown in Figure 4-6(a), hydrogen production increases with longer irradiation time for OSNS. Unfortunately, H₂ production in OSNS-400 was only maintained up to 1.5 h. Its efficiency (Figure 4-6(b)) significantly reduced to 0.189 μmol·g⁻¹·h⁻¹, approximately 3.9 times lower than 0.740 μmol·g⁻¹·h⁻¹(OSNS). The reduction is ascribed to the desorption of surface OLA ligands, as confirmed by FT-IR spectra, since no obvious changes in particle morphology and crystal phase were observed. An appropriate amount of surface ligands effectively suppress carrier recombination and maintain active

sites on the particle surface by passivating surface defects and preventing the formation of surface byproducts.^[37,38] The capacity of OSNS-500 further decreased to $0.093 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ and was absent in OSNS-600 and OSNS-650, which is attributed to the formation of the polycrystalline α phase. The lattice defects originate from π/α phase transition including stacking faults and grain boundaries provide numerous centers for carrier recombination, leading to poor photocatalytic activity. The photocatalytic properties of HSNS before and after annealing are shown in Figures 4-6(c) and 4-6(d). Consistent with our previous work, HSNS exhibits much better performance of H_2 generation, achieving the efficiency of $8.608 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$. After annealing at 400°C for 10 min (HSNS-400), the efficiency sharply dropped to $1.414 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$. This efficiency is still 7.48 times higher than that of OSNS-400. As speculated in FT-IR spectra, the ligand replacement of OLA by HMDS enables an increased absorption of free carriers, which facilitates the reduction of H^+ at the interface. As the temperature increased, the ligands desorbed or decomposed from the surface and the phase transition occurred, followed by a gradually weakened H_2 production capacity.

4.4 Summary of this chapter

In this chapter, the thermal stability and phase transition behavior of ligand-capped π -SnS particles were studied by comparing the OLA-capped tetrahedrons and HMDS-capped ones upon a post-annealing treatment. Through detailed XRD measurements, it was found the former showed stability up to 400°C , while the latter showed a higher temperature at 500°C . At higher temperatures, the transition from π phase to α phase occurred and was completed at 650°C within 10 min. In particular, a “reversible” phase transition with annealing time was observed for the first time. Through the analysis of TEM and SAED patterns, we proposed a Martensite-like phase transformation from π phase to α phase in ligand-capped SnS tetrahedrons. The phase transition is triggered by the desorption of surface ligands, which initiates the rearrangement of surface atoms and thus forms multiple nucleation sites for the ground state α phase on the surface. The subsequent transition excites the chain rearrangement of adjacent atoms to form α -SnS grains with large amounts of boundaries and stacking faults to balance the severe lattice mismatches. However, the boundaries and

stacking faults supply numerous sites for carrier recombination, leading to the poor photocatalytic H₂ evolution performance of the polycrystal α -SnS. This work reports a Martensite-like phase transformation phenomenon in SnS particles for the first time and provides a new strategy for controlling the stability of metastable particles by regulating surface ligands, which will significantly stimulate the interest of ligand-capped particles and their construction of microstructure in various applications.

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Chapter 5 General Conclusions

Synthetic understanding of π -SnS particles.

This part reports a simple and facile solvothermal method to synthesize π -SnS nanoparticles with tunable size, size distribution and morphology by adjusting the precursor, surfactant and temperature. Simple tin chloride (SnCl_2) and thiourea/elemental sulfur were dissolved or dispersed in oleylamine (OLA) as the precursor, and hexamethyldisilazane (HMDS) was used as an additional surfactant. When thiourea is employed as the sulfur source, it facilitates the concurrent nucleation of multiple crystalline phases, including orthorhombic SnS, cubic SnS, and tin oxide (SnO). Time-dependent studies reveal that orthorhombic SnS develops as the dominant product with prolonged reaction time, exhibiting characteristic plate-like morphology. Significantly, the introduction of hexamethyldisilazane (HMDS) as a phase-selective additive enables the preferential formation of monodispersed cubic SnS aggregates, effectively suppressing the growth of competing phases. UV-Vis spectroscopic analysis of the precursor solutions revealed a distinct blue shift in absorption spectra upon HMDS addition, indicative of ligand exchange where oleylamine (OLA) ligands coordinating to Sn ions were replaced by stronger-binding HMDS species. This modified coordination environment alters the nucleation pathway, favoring cubic SnS formation. In contrast, the weaker and less stable Sn-OLA complexes in HMDS-free solutions promote competitive nucleation of multiple crystalline phases (orthorhombic SnS, cubic SnS, and SnO), as evidenced by the broader absorption features.

Notably, when elemental sulfur (S8) replaced thiourea as the sulfur source, phase-pure cubic π -SnS particles with tetrahedral morphology were obtained even without HMDS. This remarkable phase selectivity originates from the in-situ formation of stable polysulfide-Sn complexes in the precursor solution. These structured intermediates effectively template cubic phase nucleation while suppressing competing formation of orthorhombic SnS and SnO byproducts. The morphological divergence stems from fundamentally distinct sulfur release kinetics: Thiourea undergoes rapid thermal decomposition, causing instantaneous supersaturation that triggers explosive nucleation followed by diffusion-limited growth.

Conversely, elemental sulfur's multi-step ring-opening and chain-scission processes ($S_8 \rightarrow S_n \rightarrow S_2$) (as evidenced by UV-Vis spectra) maintain low, steady-state sulfur activity, enabling sustained growth of tetrahedral crystals via layer-by-layer deposition - albeit with reduced yield due to incomplete sulfur utilization.

π -SnS tetrahedrons with enhanced photoactivity.

Photocatalytic hydrogen evolution testing revealed striking structure-activity relationships: While monodispersed π -SnS nanoaggregates exhibited negligible activity, the tetrahedral π -SnS crystals demonstrated significantly enhanced performance. Based on these, we conducted a systematic optimization of tetrahedral particle synthesis through: (i) time-dependent growth studies (5-20 h) to establish particle size-activity correlations, and (ii) controlled HMDS addition (6-8 at. %) to investigate surface modification effects on both phase purity and catalytic activity. Consistent with the proposed nucleation-growth mechanism, prolonged reaction time induced significant particle growth - the tetrahedral SnS crystals evolved from 316.7 nm to 1.32 μ m (mean size) while developing broader size distributions. Notably, HMDS modification (6-8 at.%) preserved the tetrahedral morphology but enhanced crystallinity, evidenced by XRD peak sharpening (FWHM decreasing from 0.1092° to 0.0624° in the (111) reflection). Optical characterization revealed bandgap stability ($E_g = 1.63 \pm 0.02$ eV by Tauc plot analysis) regardless of reaction time (5-20 h) or HMDS content, confirmed by consistent photoluminescence maxima at ~ 770 nm.

For the photocatalytic H_2 evolution performance, it was proved that the addition of HMDS during the preparation process plays an important role in the photocatalytic activity of π -SnS tetrahedrons. π -SnS particles prepared with 0.8 ml HMDS showed the highest H_2 evolution efficiency of $8.61 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ under visible light irradiation, about 12-fold higher than the efficiency of π -SnS particles prepared without HMDS ($0.74 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$) and 23-fold higher than that of α -SnS particles with a similar size ($0.38 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$) for H_2 generation from water. On the one hand, an appropriate amount of HMDS facilitates the formation of π -SnS tetrahedra with excellent crystallinity, which improves charge transfer and separation efficiency of the photogenerated electron-hole pairs in the bulk. More importantly, the

existence of surface ligands effectively passivates the surface defects that act as the centers for carrier recombination, thereby improving the photocatalytic H₂ generation performance. HMDS ligands show a better passivation effect than OLA ligands.

Thermal stability and phase transition behavior of π -SnS tetrahedrons.

The thermal stability and phase transition behavior of ligand-capped π -SnS particles were studied by comparing the OLA-capped tetrahedra and HMDS-capped ones upon a post-annealing treatment. Post-annealing morphological analysis revealed temperature-dependent structural degradation, with two characteristic failure modes emerging: (1) preferential corner rounding due to thermally activated surface atom migration, and (2) intra-particle cracking caused by anisotropic thermal stress accumulation during phase transformation. Through detailed XRD measurements, it was found that the former showed stability up to 400 °C, while the latter showed a higher temperature at 500 °C. At higher temperatures, the transition from π phase to α phase occurred and was completed at 650 °C within 10 min. In particular, a “reversible” phase transition with annealing time was observed for the first time. Through the analysis of TEM and SAED patterns, we proposed a Martensite-like phase transformation from π phase to α phase in ligand-capped SnS tetrahedra. The phase transition is triggered by the desorption of surface ligands, which initiates the rearrangement of surface atoms and thus forms multiple nucleation sites for the ground state α phase on the surface. The subsequent transition excites the chain rearrangement of adjacent atoms to form α -SnS grains with large amounts of boundaries and stacking faults to balance the severe lattice mismatches. However, the boundaries and stacking faults supply numerous sites for carrier recombination, leading to the poor photocatalytic H₂ evolution performance of the polycrystal α -SnS.

Suggestions for future studies

This study provides a comprehensive investigation into the synthesis-structure-property relationships of metastable cubic-phase tin sulfide (π -SnS) nanoparticles. Our findings establish that rational selection of sulfur precursors and surface ligands enables precise control over intermediate species in the precursor solution, which critically determines the phase purity and morphological evolution of the final product. The demonstrated strategy

highlights the fundamental importance of molecular-level understanding of precursor chemistry (coordination strength, decomposition kinetics). Further thermodynamic tailoring through ligand engineering (binding affinity, steric effects) will create new pathways for designing nanoparticles with controlled morphologies and sizes, which have broad implications for the reproducible synthesis of metastable nanomaterials and photocatalyst design through atomic-level surface control. For preliminary photocatalytic H₂ evolution assessment, we employed a basic suspension system, which demonstrated the material's fundamental activity while revealing several promising avenues for optimization. On the one hand, applications beyond the suspension system, such as thin-film configurations and hybrid systems (e.g., co-catalyst integration, Z-scheme architecture), are worth investigating. On the other hand, the carrier dynamics at the ligand-particle interface require detailed investigation to elucidate charge transfer barriers at ligand-SnS junctions, surface dipole effects on band bending and ligand-dependent recombination kinetics, which will enable rational ligand engineering in the catalytic research field.

List of research achievements

1. Journals relevant to this thesis

X. Du, I. Sumiyoshi, Y. Nose and S. Ikeda,

“Ligand-assisted synthesis of novel π -SnS tetrahedrons for enhanced photocatalytic H₂ evolution from water”

International Journal of Hydrogen Energy, vol. 95, pp. 309-316, 2024

X. Du, K. Kazumi, T. Utsunomiya, I. Sumiyoshi and Y. Nose,

“Martensite-like phase transformation of ligand-capped SnS tetrahedrons from π phase to α phase and its impact on H₂ evolution performance”

RSC advances, in peer review

X. Du and Y. Nose,

“Synthetic understanding of cubic π -SnS nanoparticles: decoupling the effects of precursor chemistry, surfactant and thermal kinetics”

In process

2. International conferences

X. Du, I. Sumiyoshi and Y. Nose,

"Annealing-induced phase transition of ligand-capped SnS tetrahedrons from π -phase to α -phase",

35th International Photovoltaic Science and Engineering Conference (PVSEC-35), November 12, 2024, Numazu, Japan

X. Du, I. Sumiyoshi and Y. Nose,

"Control of Size and Faceting of Emerging Tetrahedral π -SnS Particles",

34th International Photovoltaic Science and Engineering Conference (PVSEC-34), November 9, 2023, Shenzhen, China

X. Du, I. Sumiyoshi and Y. Nose,

"Tetrahedral π -SnS particles as photocatalyst for hydrogen production",

The 84th JSAP Autumn Meeting 2023(JSAP-84), September 20, 2023, Kumamoto, Japan

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