

# Isomorphous Substitution Synthesis and Photoelectric Properties of Spinel AgInSnS<sub>4</sub> Nanosheets

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absorption in the visible-light region and have a direct band gap of about 1.54 eV. The band structure analysis indicates that the AgInSnS<sub>4</sub> product should display p-type conduction. Photocurrent measurements reveal that the spin-coated thin film of AgInSnS<sub>4</sub> nanosheets can exhibit a broad, sensitive, fast, and stable photoelectric response. The favorable optical and photocurrent properties suggest a significant potential of the prepared spinel AgInSnS<sub>4</sub> nanocrystals for applications in photovoltaics and other optoelectronic devices.

# INTRODUCTION

Multinary metal chalcogenides, as the term suggests, refer to the chalcogenide compounds containing two or more kinds of metal elements. This material system possesses tremendous numbers, types, and complexity due to its rich structural diversity and high compositional flexibility. As a result, multinary metal chalcogenides have been the research hotspots for exploring advanced multifunctional materials.<sup>1</sup> Among them, a fairly large number of metal chalcogenides have tetrahedrally bonded structures (adamantine-like or diamondlike structures), namely, tetrahedral chalcogenides. Normally, each metal atom is tetrahedrally coordinated by four chalcogen atoms and vice versa. Besides, there are also some defect tetrahedral chalcogenides with vacancy substitutions. In this case, tetrahedral coordinated multinary metal chalcogenides with various structures, such as (defect) chalcopyrite, (defect) stannite, kesterite, famatinite, spinel, etc., have been extensively developed. It is significant that these tetrahedral chalcogenides are invariably semiconductors with band gaps below 3 eV, making them promising for vast applications.<sup>2</sup>

The quaternary  $I-III-IV-VI_4$  (I = Cu, Ag; III = Al, Ga, In; IV = Si, Ge, Sn; VI = S, Se, Te) family compounds, as a group of adamantine phases, mostly crystallize in a tetragonal defect chalcopyrite structure or a cubic spinel structure. In the former unit cell, compared to the normal chalcopyrite  $I-III-VI_2$ , one

of the two I-III pairs are replaced by the vacancy-IV pair, generating a formula of I<sub>0.5</sub>D<sub>0.5</sub>-III<sub>0.5</sub>IV<sub>0.5</sub>-VI<sub>2</sub>, viz., I-III-IV-VI4. In the spinel unit cell, I atoms are on the tetrahedral sites, while III and IV atoms share the octahedral sites and have a random distribution with 50% occupation probability each, giving rise to a disordered phase.<sup>4-6</sup> Copper/silver indium tetrathiostannates (CuInSnS<sub>4</sub> and AgInSnS<sub>4</sub>) are the most typical representatives among the I-III-IV-VI<sub>4</sub> chalcogenide spinels. However, very limited research has been dedicated to their preparation and properties.<sup>7-10</sup> Especially, to the best of our knowledge, the nanocrystals of spinel CuInSnS<sub>4</sub> and AgInSnS<sub>4</sub> have not been reported. Recently, however, Gupta's group has synthesized  $CuInSnS_4$  nanocrystals with wurtzite and defect chalcopyrite structures.<sup>11</sup> As for spinel AgInSnS<sub>4</sub>, it was first synthesized by Strick et al. from the elements at 700 °C.<sup>7</sup> Then, a solid–vapor reaction method was employed by Ohachi and Pamplin to prepare AgInSnS<sub>4</sub> spinel phase by annealing AgInS<sub>2</sub> powder and SnS<sub>2</sub> vapor at 680  $^{\circ}$ C.<sup>8</sup>

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Figure 1. Schematic illustration of the structural transformation from spinel  $In_{3-x}S_4$  to spinel AgInSnS<sub>4</sub> phase based on an isomorphous substitution process.

Additionally, spinel AgInSnS<sub>4</sub> thin films were also prepared by a spray pyrolysis method.<sup>12,13</sup> In this context, it should be highly desirable to develop a convenient method for the fabrication of spinel AgInSnS<sub>4</sub> nanocrystals.

Isomorphous substitution is the replacement of framework atoms in crystalline compounds with atoms of other elements without changing the overall crystal structure. Apparently, such a method can create an isostructural series of compounds and then offer a powerful strategy for material design and optimization.<sup>14–18</sup> Actually, it has been widely applied in tailoring the physicochemical properties of zeolites,<sup>19–22</sup> metal–organic frameworks (MOFs),<sup>23–26</sup> and other inorganic materials.  $2^{7-30}$  In this work, for the first time, the isomorphous substitution method is developed for the preparation of spinel AgInSnS<sub>4</sub> nanocrystals using spinel indium sulfide  $(In_{3-r}S_4)$  as the precursor. According to the normalization of the spinel formula  $(A)_t(B_2)_{o}C_4$ ,  $In_{3-x}S_4$  can be described as  $(In_{1-x}\prod_{x})_{t}(In_{2})_{o}S_{4}$ , in which In atoms occupy part of tetrahedral (t) sites and all of the octahedral (o) sites. In the same way, spinel AgInSnS<sub>4</sub> can be expressed as  $(Ag)_t(InSn)_0S_4$ . In other words, Ag atoms substitute all of the In atoms and vacancies  $(\Box)$  in tetrahedral sites, and Sn atoms replace half of the In atoms in octahedral sites. Figure 1 schematically illustrates the transformation from spinel indium sulfide to spinel AgInSnS<sub>4</sub> phase through an isomorphous substitution process. As a semiconductor, the optical absorption properties, band structure, and photoelectric behaviors of the prepared spinel AgInSnS<sub>4</sub> nanocrystals have been systematically investigated.

## EXPERIMENTAL SECTION

**Materials.** All chemicals and reagents were used as received without any additional purification. Anhydrous indium trichloride  $(InCl_3, 99.9\%)$ , anhydrous tin tetrachloride  $(SnCl_4, analytical grade, 2.226 g mL<sup>-1</sup>)$ , oleic acid  $[CH_3(CH_2)_7CH=CH(CH_2)_7COOH, analytical grade]$ , oleylamine  $[CH_3(CH_2)_7CH=CH(CH_2)_7CH_2NH_2, 80-90\%]$ , and 1-octadecene  $[CH_3(CH_2)_{15}CH=CH_{22} > 90.0\%]$  were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Anhydrous silver nitrate (AgNO<sub>3</sub>, primary reagent grade, purity  $\geq$  99.95%), sodium diethyldithiocarbamate trihydrate (NaS<sub>2</sub>CN-(CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>·3H<sub>2</sub>O, analytical grade), and thiourea (NH<sub>2</sub>CSNH<sub>2</sub>),  $\geq$  99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Hexane  $[CH_3(CH_2)_4CH_3, \geq 97.0\%]$ , benzene  $(C_6H_6, \geq 99.5\%)$ , and absolute ethanol (CH<sub>3</sub>CH<sub>2</sub>OH,  $\geq 99.7\%)$  were obtained from Tianjin Damao Chemical Reagent Factory. Deionized water was produced from a Milli-Q system from Millipore (Bedford).

**Synthesis of Spinel Indium Sulfide Parent Precursor.** For isomorphous substitution, the spinel indium sulfide precursor was first prepared by a solvothermal method as described in our previous work with minor modifications.<sup>31</sup> Briefly, 0.442 g of InCl<sub>3</sub> (2 mmol) and

0.25 g of thiourea (slightly excessive) were dissolved in 2 mL of deionized water to get a clear solution. After being transferred into a stainless steel autoclave with a Teflon liner and filled with benzene to 80% of its capacity, the autoclave was sealed and heated in an oven at 160 °C for 12 h. After being naturally cooled to room temperature, the supernatant liquid was decanted the precipitates were dispersed into absolute ethanol. Afterward, the precipitates were filtered off, washed with deionized water and absolute ethanol several times, and dried at 50 °C in air for several hours. Finally, the obtained orange powder was fully ground in an agate mortar and collected for further use.

Synthesis of Metal Diethyldithiocarbamate Precursors. In this study, silver and tin diethyldithiocarbamates (abbreviated as dedc) were used as reactants. For the synthesis of silver diethyldithiocarbamate [Ag(dedc)], 10 mmol Na(dedc) (2.253 g) and 10 mmol AgNO<sub>3</sub> (1.699 g) were, respectively, dissolved in 50 and 20 mL of deionized water to obtain two clear aqueous solutions. Subsequently, the AgNO<sub>3</sub> solution was slowly introduced into the Na(dedc) solution dropwise under magnetic stirring. During the mixing of two solutions, the yellow precipitates could be immediately observed. After complete addition, the mixture was stirred for an additional 30 min for sufficient reaction, and the precipitates were filtered by suction, washed with absolute ethanol and deionized water, and dried at 50 °C in an oven. After grinding, the resulting Ag(dedc) powder could be obtained for further use. As for the preparation of Sn(dedc)<sub>4</sub> precursor, 20 mmol Na(dedc) (4.506 g) and 5 mmol SnCl<sub>4</sub> (0.585 mL) were used as the starting materials keeping other reaction conditions constant. Accordingly, the orange-red Sn(dedc)<sub>4</sub> powder also can be synthesized.

Synthesis of Spinel AgInSnS<sub>4</sub> Nanocrystals. In a typical preparation, 1 mmol Ag(dedc) (0.256 g) precursor, 0.5 mmol spinel indium sulfide (0.163 g, based on the formula  $In_2S_3$ ) precursor, and 1 mmol Sn(dedc)<sub>4</sub> (0.712 g) precursor were loaded into a 100 mL fourneck round-bottom flask with a mixture of 5 mL of oleic acid (OA), 5 mL of oleylamine (OLA), and 10 mL of 1-octadecene (ODE). After the solution was magnetically stirred to be uniformly dispersed, the flask was attached to a standard Schlenk line. Under continuous magnetic stirring, the reaction system was then degassed by alternately evacuating and backfilling with high-purity Ar three times. The reaction mixture was then heated to 120 °C with a heating mantle and further degassed by vacuum pumping and Ar purging alternately three times. Thereafter, the solution was further heated up to 280 °C and maintained at this temperature for 1 h in an Ar atmosphere. After the reaction was complete, the heating mantle was allowed to be removed, and the reaction system was naturally cooled down to ambient temperature with the protection of Ar gas. For facilitating precipitation, 30 mL of absolute ethanol was poured into the flask. In this case, the precipitates could be centrifuged off at 8000 rpm for 2 min and washed with abundant benzene and absolute ethanol alternately several times by redispersion and centrifugation. Ultimately, the products were able to be redispersed in hexane easily, and then the dark brown powder also could be successfully obtained after centrifugation and drying at 50 °C for several hours under vacuum.

Sample Characterizations. X-ray powder diffraction (XRD) tests were implemented on an Empyrean diffractometer operating at 40 kV and 40 mA and using Cu K $\alpha_1$  radiation ( $\lambda = 1.5406$  Å) (PANalytical, The Netherlands). Transmission electron microscopy (TEM) photos, high-resolution TEM (HRTEM) images, selected area electron diffraction (SAED) patterns, and energy-dispersive X-ray spectroscopy (EDS) spectrum together with EDS elemental mapping photographs were obtained from a JEM-2100F (field emission) scanning transmission electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) photos were taken from a Quanta 200F environmental scanning electron microscope (FEI, Netherlands). X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) tests were performed on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher Scientific) using a monochromatic Al  $K\alpha$  radiation ( $h\nu$  = 1486.6 eV) and a monochromatic He I radiation  $(h\nu = 21.22 \text{ eV})$ , respectively. The room-temperature ultravioletvisible-near-infrared (UV-vis-NIR) absorption spectrum was collected on a Lambda 750 UV-vis-NIR spectrophotometer (Perkin-Elmer).

Photoelectric Tests. A silicon wafer coated with a 100 nm thick silicon dioxide dielectric layer (SiO<sub>2</sub>/Si) was used as the substrate for photoelectric tests. A piece of silicon wafer  $(1 \text{ cm} \times 1 \text{ cm})$  was ultrasonically cleaned with acetone, absolute ethanol, and deionized water in sequence for 10 min. The synthesized AgInSnS<sub>4</sub> nanocrystals were redispersed into hexane to prepare a homogeneous solution with a concentration of 10 mg mL<sup>-1</sup>. A thin film of AgInSnS<sub>4</sub> nanocrystals was then fabricated on the as-cleaned silicon wafer by spin-coating, followed by annealing at 300 °C for 5 min to remove the solvents and ligands. The spin-coating/annealing process was handled in a N2purged glovebox and repeated three times. Finally, two Ag electrodes were deposited onto the obtained AgInSnS<sub>4</sub> nanocrystals thin film via vacuum evaporation, thereby completing the fabrication of photoelectric response device. The electrical measurements were carried out using an SR570 low-noise current preamplifier (Stanford Research System), a DS345 synthesized function generator (Stanford Research System), and a Keithley 2400 source meter (Keithley). A 300 W Xenon lamp (HSX-F/UV300, Beijing NBeT Technology Co., Ltd.) was used as the light source. Additionally, for the spectral photoresponse tests, the continuous and monochromatic wavelength light source was supplied by an F4600 fluorescence spectrophotometer (Hitachi, Japan) with a 150 W Xe lamp.

#### RESULTS AND DISCUSSION

**Phase Analysis.** The phase structure of the prepared sample and parent precursor was examined by XRD analysis. As displayed in Figure 2, the typical XRD patterns of the synthesized sample show fairly strong and sharp diffraction peaks, suggesting a good crystallinity. All of these diffraction peaks can be strictly indexed to the face-centered cubic spinel



Figure 2. Observed XRD patterns of the as-synthesized spinel AgInSnS<sub>4</sub> sample together with the simulated XRD patterns of the spinel AgInSnS<sub>4</sub> phase (JCPDS card no. 29-1140).

structure (space group  $Fd\overline{3}m$ ) of AgInSnS<sub>4</sub> phase with a calculated lattice constant of a = 10.777 Å, which is highly consistent with the standard data (JCPDS card file no. 29-1140, a = 10.769 Å). No diffraction peaks arising from some other possible phase contaminants, such as binary or ternary sulfides and metal oxides, can be perceived, implying that the synthesized AgInSnS<sub>4</sub> sample should have a satisfactory purity level. Inevitably, to confirm the isomorphous substitution in this study, the XRD patterns of the parent precursor should also be measured. As shown in Figure S1 in the Supporting Information, the XRD patterns of the indium sulfide precursor are extremely similar to those of the AgInSnS<sub>4</sub> product. They can be readily indexed to a cubic spinel phase with a calculated lattice parameter of a = 10.727 Å, which is in good agreement with the reported results of spinel indium sulfide, including JCPDS card file no. 88-2495 (spinel  $In_{2.77}S_4$ , a = 10.728 Å), no. 84-1385 (spinel  $In_{21.333}S_{32}$ , a = 10.774 Å), and no. 65-0459 (spinel  $In_2S_3$ , a = 10.774 Å). Owing to the similarity of the XRD patterns between spinel AgInSnS<sub>4</sub> and spinel indium sulfide, Rietveld refinements of XRD data for the AgInSnS<sub>4</sub> sample and indium sulfide precursor were performed. The corresponding refinement results are presented in Figures S2 and S3, respectively. A good fitting can be obtained between the observed pattern and the calculated one. In this case, it should be reasonable to believe that the formation of the isostructural AgInSnS<sub>4</sub> phase may be the result of the isomorphous substitution of the spinel indium sulfide parent phase. Undoubtedly, all three indium sulfide phases can be collectively described as the general formula of spinel structure  $(In_{1-x}\square_x)_t(In_2)_oS_4$ , namely,  $In_{3-x}S_4$ . In this context, for the formation of spinel  $(Ag)_t(InSn)_oS_4$  by isomorphous substitution, as illustrated in Figure 1, Ag atoms occupy all of the tetrahedral sites, while In and Sn atoms share all of the octahedral sites. It should be noted that it is scarcely possible to distinguish between spinel  $In_{3-x}S_4$  and spinel AgInSnS<sub>4</sub> phases only on the basis of the XRD results. Therefore, more material characterizations are necessary for confirming the formation of the spinel AgInSnS<sub>4</sub> phase.

Morphology Analysis. TEM and HRTEM observations were conducted to investigate the morphology and microstructure of the prepared spinel AgInSnS<sub>4</sub> sample. As presented in Figure 3a, the overview TEM image reveals that the product is composed of a large number of sheetlike nanocrystals with an average lateral size of around 100 nm. From the highmagnification TEM image in Figure 3b, the thickness of these nanosheets can be evaluated to be about 10 nm according to the upstanding nanosheets. Moreover, the HRTEM image of the spinel AgInSnS<sub>4</sub> nanosheets is shown in Figure 3c. The well-resolved two-dimensional (2D) lattice fringes can be clearly observed, indicating a good crystallinity of the fabricated nanosheets. The characteristic interplanar spacings can be measured to be 0.31 and 0.24 nm, perfectly matching with the d-spacings of (222) and  $(\overline{240})$  crystal planes of the spinel AgInSnS<sub>4</sub> phase, respectively. The inset of Figure 3b gives the corresponding polycrystalline SAED patterns of the sample. As expected, all of the diffraction rings also can be well-indexed to the cubic spinel structure of the AgInSnS<sub>4</sub> phase. To further demonstrate the production of AgInSnS<sub>4</sub> other than In3-xS4, EDS spot analysis and the elemental mapping of the sample were also carried out. As shown in Figure S4, the EDS spectrum distinctly demonstrates the presence of silver, indium, tin, and sulfur elements, besides the signals of carbon and copper resulted from the amorphous



Figure 3. (a) Low-magnification TEM image, (b) high-magnification TEM image, and (c) HRTEM image (inset: SAED pattern) as well as (d) high-angle annular dark-field imaging (HAADF) image and the corresponding EDS elemental mapping images of (e) Ag, (f) In, (g) Sn and (h) S of the as-synthesized spinel  $AgInSnS_4$  sample.



Figure 4. XPS spectra of the as-fabricated spinel  $AgInSnS_4$  nanosheets including (a) the survey spectrum together with the corresponding highresolution XPS spectra for (b) Ag 3d, (c) In 3d, (d) Sn 3d, and (e) S 2p core levels.

carbon film supported copper grid in TEM tests. Based on the EDS spectrum data, the molar ratio of Ag/In/Sn/S can be estimated to be 1:0.97:1.05:4.36, which is very close to the stoichiometry of the AgInSnS<sub>4</sub> phase. The excessive S probably

originated from the adsorbed sulfur species due to the large excess of dedc. Moreover, in Figure 3d-h, the EDS elemental mapping images visualize the homogeneous distribution of Ag, In, Sn, and S throughout each nanocrystal. Accordingly, the

EDS results can confirm the successful formation of the AgInSnS<sub>4</sub> phase. The morphology of the spinel  $In_{3-r}S_4$ precursor was also examined by SEM and TEM observations. Figure S5a,b shows the SEM images of the prepared  $In_{3-x}S_4$ precursor before grinding, revealing that it consists of marigold-like microspheres. The hierarchical architecture is built from the interconnected nanosheets on the surface of microspheres. The TEM images in Figure S6a,b further reveal a flowerlike morphology and the component nanosheets. After violent grinding, as can be seen from the SEM images in Figure S5c,d, the flat particles can be obtained with a broad size distribution from tens to hundreds of nanometers owing to the destruction of those marigold-like microspheres. However, as displayed in Figure S6c,d, the corresponding TEM images reveals that the as-grinded spinel In<sub>3-x</sub>S<sub>4</sub> precursor is actually composed of nanosheets with the size of no more than about 100 nm and thickness of about 10 nm, which are very similar to those of the final spinel AgInSnS<sub>4</sub> product, providing additional evidence in support of the isomorphous substitution mechanism.

Composition Analysis. The chemical composition and states of the synthesized AgInSnS<sub>4</sub> sample were further analyzed by XPS measurements using C 1s photoelectron (284.6 eV) as a reference. As depicted in the XPS survey spectrum (Figure 4a), the obvious photoelectron peaks of only five elements containing silver, indium, tin, sulfur, and carbon can be observed. Therein, the carbon signal should originate from the carbon reference for calibration. To quantitate the atomic ratio and inspect the valence states of these elemental species, the high-resolution XPS spectra were also tested in the Ag 3d, In 3d, Sn 3d, and S 2p binding energy regions, respectively. For the former three 3d core-level spectra, all of them comprise the conspicuously strong doublet peaks. In Figure 4b, two binding peaks at 367.6 and 373.6 eV with a separation of 6.0 eV can be ascribed to the spin orbits of Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$ , respectively, which are indicative of a monovalent silver (Ag<sup>+</sup>). The core-level spectrum of In 3d is presented in Figure 4c, and two characteristic peaks at 444.4 and 452.0 eV can be observed giving a peak splitting of 7.6 eV, corresponding to the binding energies of In  $3d_{5/2}$  and In  $3d_{3/2}$ for trivalent indium (In<sup>3+</sup>) state, respectively. Figure 4d shows the core spectrum of Sn 3d, in which the two peaks are located at 486.3 and 494.7 eV and can be assigned to Sn  $3d_{5/2}$  and Sn 3d<sub>3/2</sub> with a spin-orbit splitting of 8.4 eV, indicating the presence of Sn(IV) state, respectively. The high-resolution XPS spectrum of S 2p core, as exhibited in Figure 4e, can be resolved into a set of doublet peaks at 161.4 and 162.6 eV with a doublet splitting of 1.2 eV, which can be attributed to the S  $2p_{3/2}$  and  $\hat{S} 2p_{1/2}$  orbits of  $\hat{S}^{2-}$  ions, respectively. All these XPS results are well consistent with the literature data.<sup>32</sup> Furthermore, the quantitative analysis of the core level XPS results can demonstrate an atomic ratio of Ag/In/Sn/S = 1:0.94:1.08:4.45, which is very close to the EDS results, further corroborating the AgInSnS<sub>4</sub> composition.

**Optical Absorption Analysis.** As the representative multifunctional semiconductors, multinary metal chalcogenides hold great potential in photoelectric and optoelectronic applications. Therefore, the room-temperature optical absorption property of the as-synthesized spinel AgInSnS<sub>4</sub> nanosheets was explored by UV–vis–NIR absorption spectroscopy and further used to examine the band gap energy of the sample. From the absorption spectrum displayed in Figure 5a, it can be found that the AgInSnS<sub>4</sub> sample exhibits a strong absorption



**Figure 5.** (a) UV-vis-NIR absorption spectrum and (b) the corresponding Tauc plot of  $(\alpha hv)^2$  versus (hv) of the as-synthesized spinel AgInSnS<sub>4</sub> nanosheets.

over the entire visible-light spectral region. A clear absorption edge with a long absorption tail can be observed. To determine the optical band gap of a semiconductor, a Tauc plot is normally used in accordance with the equation of  $\alpha hv = A(hv)$  $(-E_{\sigma})^{n/2}$ , in which  $E_{\sigma}$  is the band gap energy, hv is the photon energy,  $\alpha$  is the absorption coefficient, A is a proportionality constant, and the exponential n is a pure constant associated with the transition characteristics of semiconductors, equal to 1 for direct semiconductors and 4 for indirect ones. Then, the Tauc plot of  $(\alpha hv)^2$  versus (hv) of the obtained AgInSnS<sub>4</sub> sample is presented in Figure 5b. Accordingly, a direct band gap energy of 1.54 eV can be evaluated by extrapolating the linear portion of the Tauc plot curve in the band edge region to intercept (hv) axis at  $(\alpha hv)^2 = 0$ . It is worth mentioning that this band energy value has a relatively large difference from that of the AgInSnS<sub>4</sub> thin film (1.89 eV) reported by Ortega-López's group.<sup>12,13</sup> Since the prepared spinel AgInSnS<sub>4</sub> nanocrystals have a strong and broadband visible-light absorption as well as an optimal direct band gap energy, it would be expected to be a new promising candidate for applications in thin-film solar cells.

**Band Structure Analysis.** So far, the electronic structure of the spinel AgInSnS<sub>4</sub> phase has not yet been reported in either the theoretical or experimental literature as far as we are aware. To this end, UPS test was performed to assess the energy bands of the fabricated spinel AgInSnS<sub>4</sub> sample using a monochromatic He I excitation (21.22 eV) as the ultraviolet source with a constant pass energy of 2 eV. The binding energies were first calibrated by setting the Fermi level  $(E_{\rm F})$  at 0 eV based on a clean Au reference. Figure 6a presents the collected UPS spectrum of the prepared spinel AgInSnS<sub>4</sub> sample. In the low kinetic energy region, a prominent cutoff at 16.23 eV can be determined. Then, the location of the vacuum level  $(E_{vac})$  can be fixed at 21.22 eV above the cutoff energy. In other words, the Fermi level  $(E_F)$  of the sample thus should be -4.99 eV versus the vacuum level. Moreover, the valence band energy  $(E_{\rm V})$  can be identified by linearly extrapolating the leading edge of the valence band spectrum



Figure 6. (a) UPS spectrum and (b) the schematic band structure diagram of the as-prepared spinel  $AgInSnS_4$  nanosheets. The inset of (a) gives an enlarged view in the valence band region.

to the baseline. As shown in the close-up view of the valence band (inset of Figure 6a), the valence band maximum (equivalent to the ionization potential) of the obtained spinel AgInSnS<sub>4</sub> sample should be at about 0.53 eV below the Fermi level, namely, -5.52 eV versus the vacuum level. Combined with the band gap energy (1.54 eV) determined from the Tauc plot, the conduction band energy  $(E_{\rm C})$  of the AgInSnS<sub>4</sub> sample thus can be calculated to be -3.98 eV versus the vacuum level. To visually display a band structure diagram of the synthesized AgInSnS<sub>4</sub> sample, Figure 6b schematically outlines the relationship between the different energy levels of  $E_{vac}$ ,  $E_{F'}$  $E_{\rm V}$  and  $E_{\rm C}$  based on the UPS and UV-vis-NIR results. According to the relative position of  $E_{\rm F2}$  it can be shown that the obtained AgInSnS<sub>4</sub> nanocrystals exhibit a p-type conduction, which is perfectly consistent with the results reported by Ortega-López's group.<sup>12,13</sup>

Photoelectric Properties. The photoelectric properties of the synthesized AgInSnS<sub>4</sub> sample were inspected using its thin film coated on a silicon substrate. The spectral response of the spinel AgInSnS<sub>4</sub> nanosheets thin film was measured in the range of 200-900 nm at a fixed direct current (dc) bias voltage of 1 V with two different illumination modes, using a continuous wavelength sweep and using different monochromatic wavelengths. The illumination intensity could be well controlled by the slit width (d) of the incident light. Figure 7a reveals the variation in photocurrent of the sample with a continuous spectrum under different illumination intensities. As can be distinctly seen, the sample exhibits a broadband photoresponse covering the whole energy range of the visible light, consistent with the optical absorption results. Importantly, two prominent response peaks centered at about 820 and 880 nm can be clearly detected. Considering the abruptly high photocurrent intensity of them, the two peaks should be originated from an instrumental response in spite of the fact that the photocurrent peak at 820 nm agrees well with the band gap energy of the synthesized AgInSnS<sub>4</sub> sample. Additionally, the spectral response of the sample is highly dependent on the illumination intensity. At low incident light intensities (4 and 10  $\mu$ W cm<sup>-2</sup>), the sample just shows very weak photoresponse, except its intrinsic band gap response. However, as the power density of the incident light is enhanced to 35 and 140  $\mu$ W cm<sup>-2</sup>, a continuous strong broadband photoresponse ranging from 300 to 900 nm can be achieved. For further verifying the broad photoresponse of the sample, the spectral response was also explored under different monochromatic wavelengths from 200 to 900 nm with an



**Figure 7.** (a) Spectral response of the as-obtained spinel AgInSnS<sub>4</sub> nanosheet thin film to the light with a continuous wavelength sweep at a fixed dc bias voltage of 1 V under different illumination intensities (i.e., different slit widths (*d*) of incident light). (b) Photoresponsivity of the AgInSnS<sub>4</sub> nanocrystal thin film to the light with different monochromatic wavelengths in the range of 200–900 nm at a 1 V bias under an illumination intensity of 140  $\mu$ W cm<sup>-2</sup> (i.e., *d* = 10 nm).

interval of 50 nm at an illumination intensity of 140  $\mu$ W cm<sup>-2</sup>. Similarly, as revealed in Figure 7b, the fabricated AgInSnS<sub>4</sub> sample displays an evident photoresponse within the wavelength range of 300–900 nm. Especially, the responsivity appears to be much stronger near the band edge. To exclude the potential photoresponse contribution from the silicon substrate, the spectral response and the time-dependent on– off photocurrent response of the bare silicon substrate were also investigated. As exhibited in Figures S7 and S8, the photoelectric results indicate that the photoresponse from bare silicon substrate is extremely weak in contrast with that of the as-prepared AgInSnS<sub>4</sub> sample and should be negligible.

The current–voltage (I-V) characteristics of the spinel AgInSnS<sub>4</sub> nanosheet thin film was also measured between -5 and 5 V under dark and light illumination to study its photoelectric properties. From the I-V curves presented in Figure 8a, it can be observed that the photocurrent is



**Figure 8.** (a) Current–voltage (I-V) curves of the as-obtained spinel AgInSnS<sub>4</sub> nanosheets thin film measured at an applied bias from -5 to 5 V under light illumination (red line) and in the dark (blue line). (b) Periodic on–off photocurrent response of the AgInSnS<sub>4</sub> nanosheets thin film as a function of the illumination time under the light irradiation at a fixed dc bias voltage of 5 V.

significantly enhanced under illumination in comparison with that in the dark, resulting in an  $I_{\text{light}}/I_{\text{dark}}$  ratio of 6.4. Then, the photoelectric response behavior of the AgInSnS<sub>4</sub> nanocrystal thin film was further characterized by testing the on/off switching photocurrent as a function of the illumination time (I-t curve) under periodic illumination. Figure 8b shows the I-t curve of the sample measured at a 5 V bias voltage for six on-off cycles. Apparently, the photocurrent response of the obtained AgInSnS<sub>4</sub> nanosheet thin film can be reversibly switched with alternate illumination and darkening periods. The reproducible response of the photocurrent virtually proves the outstanding photostability and photoreproducibility of the sample. In addition, it is well known that the response time and recovery time are also the key parameters for evaluating the photoresponse performance. In this regard, Figure S9 displays a corresponding close-up view on the rise time  $(t_r)$  and decay time  $(t_d)$  of the photocurrent. Accordingly, both  $t_r$  and  $t_d$  can be determined to be 0.15 s, manifesting the quick photoresponse of the prepared sample. For contrast, the periodic on-off photocurrent response of the sample at a bias voltage of 3 and 1 V was also measured, and the I-t curves along with the corresponding profile of  $t_r$  and  $t_d$  are presented in Figures S10 and S11, respectively. All these photoelectric response results reveal several favorable characteristics of the sample in terms of broad photoresponsivity, high photosensitivity, good photostability, and fast response speed, indicating that the synthesized spinel AgInSnS<sub>4</sub> nanosheets should be potential for applications in photovoltaic and photoconductive devices.

# CONCLUSIONS

We successfully synthesized the quaternary  $AgInSnS_4$  semiconductor nanocrystals with a cubic spinel structure for the first time based on a facile isomorphous substitution method adopting isostructural indium sulfide as the parent precursor. The product consists of nanosheets with an average lateral size of about 100 nm and a thickness of about 10 nm. The prepared spinel AgInSnS<sub>4</sub> nanosheets exhibit a strong absorption over the whole visible-light range with a direct band gap energy of 1.54 eV. Combined with the UPS results, the valence and conduction band energy of the AgInSnS<sub>4</sub> sample can be determined to be -5.52 and -3.98 eV versus the vacuum level, respectively, and it shows p-type conduction. More importantly, photoelectric measurements demonstrate that the newly developed spinel AgInSnS<sub>4</sub> nanosheets can display excellent photoresponse performance with broad responsivity, ideal sensitivity, high stability, good reproducibility, and fast response speed, rendering them potentially suitable for applications in photoelectric and optoelectronic devices.

### ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c03404.

XRD patterns, SEM, and TEM images of the spinel indium sulfide precursor; Rietveld refinement of the XRD patterns for the spinel AgInSnS<sub>4</sub> product and spinel indium sulfide precursor; EDS spectrum of the prepared AgInSnS<sub>4</sub> nanosheets; spectral response and switching photocurrent response of the bare silicon substrate; close-up view of the photocurrent rise and decay of the prepared AgInSnS<sub>4</sub> nanosheets thin film at a 5 V bias; and switching photocurrent response of the sample at a fixed bias voltage of 1 and 3 V (PDF)

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## Notes

The authors declare no competing financial interest.

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