

Supporting Information

Facile Synthesis of Ternary Homogeneous $\text{ZnS}_{1-x}\text{Se}_x$ Nanosheets with Tunable Bandgaps

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Experimental Section

Materials

All chemicals were used without further purification. Hydrazine hydrate 85% ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, AR), ethylenediamine (AR), zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR], thioacetamide (AR), ethanol (AR) were obtained from Sino-Pharm Chemical Reagent Co., Ltd. Selenium powder (99.99%) were purchased from Sigma Aldrich. The water used in all experiments was ultra-pure water (Millipore, 18M Ω cm).

Synthesis of the lamellar precursor, $\text{ZnS}_{1-x}\text{Se}_x \cdot 0.5\text{en}$

In a typical synthesis of lamellar precursor $\text{ZnS}_{0.4}\text{Se}_{0.6} \cdot 0.5\text{en}$ (en stands for ethylenediamine), 1 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.4 mmol thioacetamide (TAA) were added in 10 mL of ethylenediamine. Then, 0.6 mmol Se powder was dissolved in 2 mL of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. All solutions was transferred to a 25 mL Telfon-lined stainless steel vessel and sealed. The vessel was heated to 413 K and kept for 12 h, and then cooled down to room temperature. The precipitation was centrifuged, washed extensively with water and absolute ethanol, and then dried in a vacuum at 333 K to obtain the lamellar precursor.

The synthesis procedure of the $\text{ZnS}_{1-x}\text{Se}_x \cdot 0.5\text{en}$ is similar to $\text{ZnS}_{0.4}\text{Se}_{0.6} \cdot 0.5\text{en}$ except that the Se/S molar ratio was modulated by a 1 mmol mixture of TAA and Se powder.

Caution! Hydrazine hydrate is highly toxic and unstable! Extreme care should be exercised.

Synthesis of alloyed ZnS_{1-x}Se_x (0≤x≤1) nanosheets

Ternary phase-pure ZnS_{1-x}Se_x (0≤x≤1) nanosheets were obtained by calcining the corresponding lamellar precursor (ZnS_{1-x}Se_x·0.5en) at 723 K for 0.5 h in N₂ atmosphere.

According to thermogravimetric (TG) analysis (Figure S8), nearly all organic ligand (en) was removed from the precursors at 723 K, and higher temperature (such as 1373K) will lead to further decomposition of ZnS_{1-x}Se_x nanosheets. Thus, the calcination temperature was selected as 723 K.

Characterization

Scanning electron microscopy (SEM, JSM-6700F) was used to characterize the morphologies of the synthesized materials. The microstructure and chemical compositions of the as-prepared samples was determined by a field-emission TECNAI F20 transmission electron microscope (TEM) integrated with an energy-dispersive X-ray analyzer (EDX) operating at 200 kV. The crystal structure of as-synthesized materials was characterized by X-ray powder diffraction (XRD) (Rigaku MiniFlex II diffractometer) using Cu-K α radiation. Thermogravimetric (TG) experiments were carried out on NETZSCH STA 449C Jupiter thermogravimetric analyzer in N₂ with the sample heated in an Al₂O₃ crucible at a heating rate of 10 K min⁻¹. The XPS studies were performed with a ThermoFisher ESCALAB250 X-ray photoelectron spectrometer (powered at 150 W) using Al K α radiation ($\lambda = 8.357 \text{ \AA}$). The optical properties were investigated at room temperature using UV-vis diffuse reflectance spectroscopy (DRS), which was carried out on a Perkin-Elmer Lambda 950 UV/vis/near-IR spectrophotometer equipped with an integrating sphere attachment and barium sulfate as the reflectance standard.

The effect of sintering temperature on the optical properties

It is necessary to point out, when the precursors was calcinated at 723 K, the little residual organic matter on the nanosheets could cause broadening of diffuse reflectance spectra (Figure S9). While at the higher calcination temperature (1173 K), the diffuse reflectance spectra turns to be much sharper (Figure S10). Importantly, the band gap value is

negligibly changed. Thus high calcination temperature was selected to obtain sharp diffuse reflectance spectra. Meanwhile, in order to avoid phase change, the calcination temperature was optimized independently according to different Se content. Finally, the sharp diffuse reflectance spectra was obtained via high temperature calcination (for $x \leq 0.8$, 1173 K, for $x=1$, 973 K) and displayed in Figure 4(a).

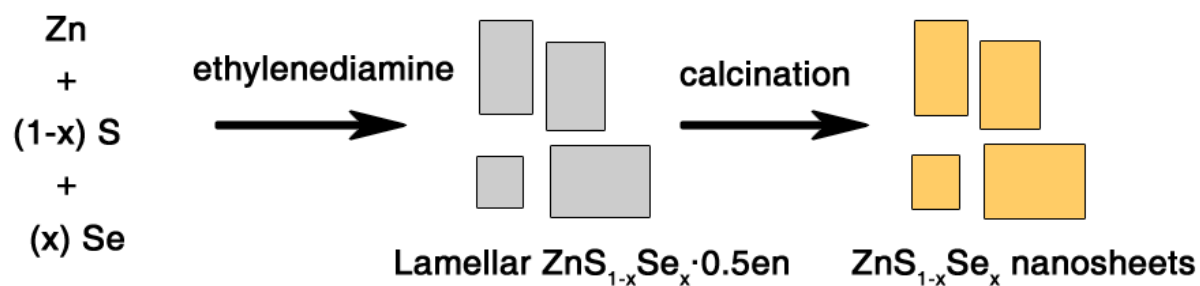


Figure S1. Scheme for the fabrication of $\text{ZnS}_{1-x}\text{Se}_x$ nanosheets. A lamellar inorganic-organic hybrid precursor ($\text{ZnS}_{1-x}\text{Se}_x \cdot 0.5\text{en}$) was initially prepared.

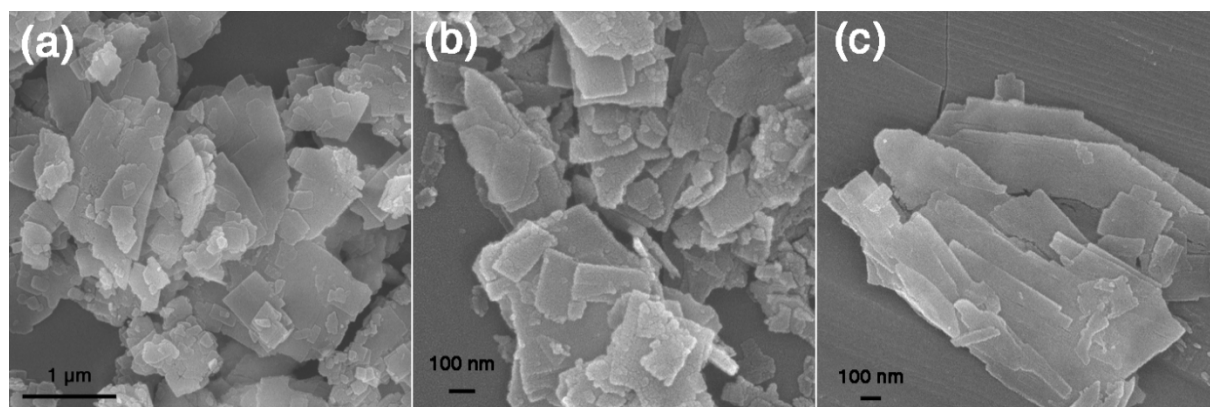


Figure S2. SEM images of as-synthesized $\text{ZnS}_{1-x}\text{Se}_x$ nanosheets. (a) $x = 0.2$, (b) $x = 0.4$, (c) $x = 0.8$.

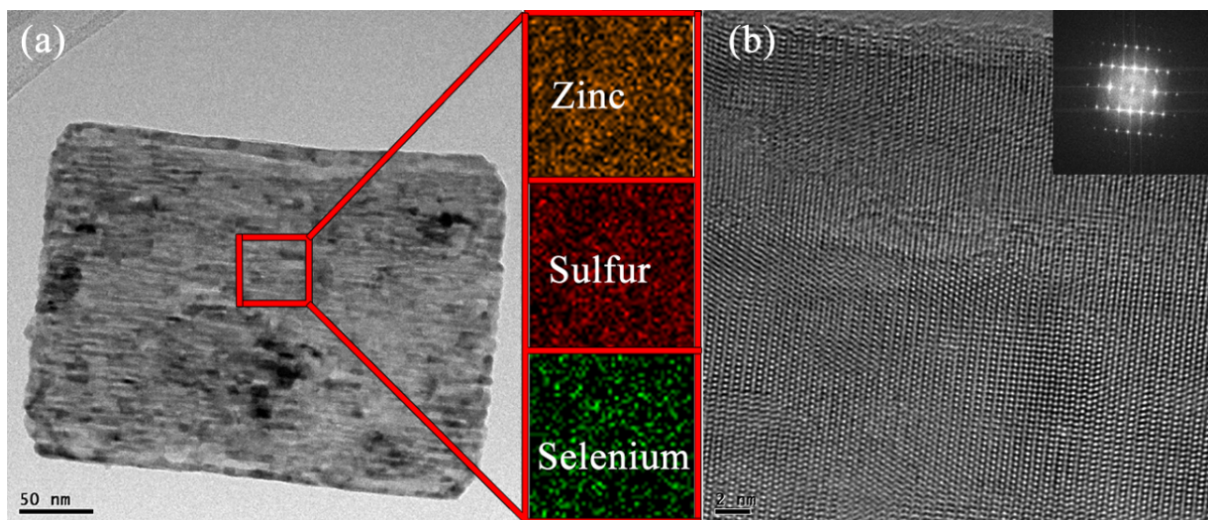


Figure S3. (a) TEM and EDS mapping images of an individual ternary ZnS_{0.8}Se_{0.2} nanosheet. (d) HRTEM image and corresponding FFT (inset) of the ZnS_{0.8}Se_{0.2} nanosheet.

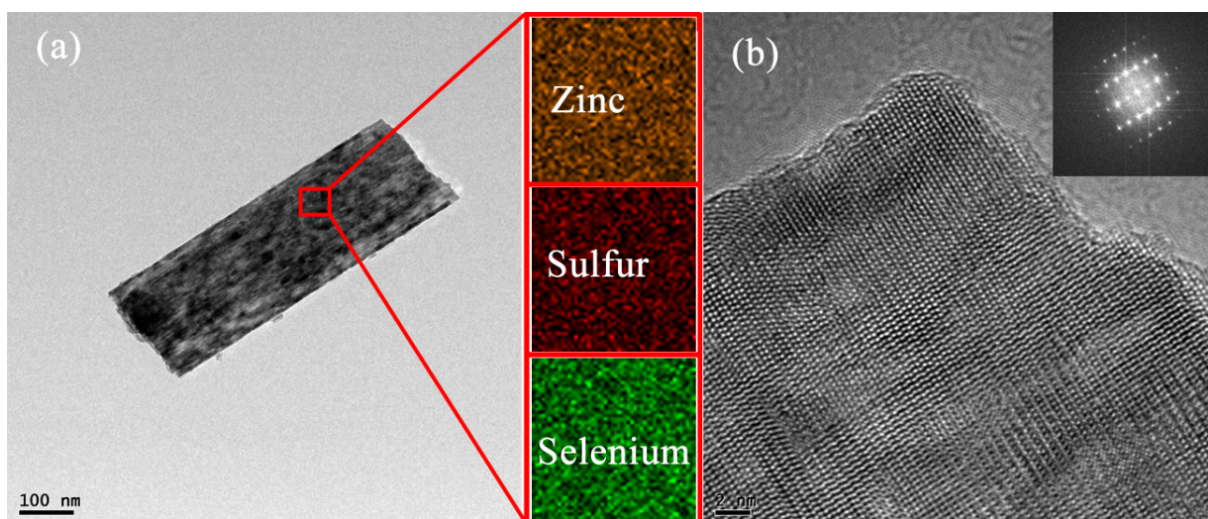


Figure S4. (a) TEM and EDS mapping images of an individual ternary ZnS_{0.6}Se_{0.4} nanosheet. (d) HRTEM image and corresponding FFT (inset) of the ZnS_{0.6}Se_{0.4} nanosheet.

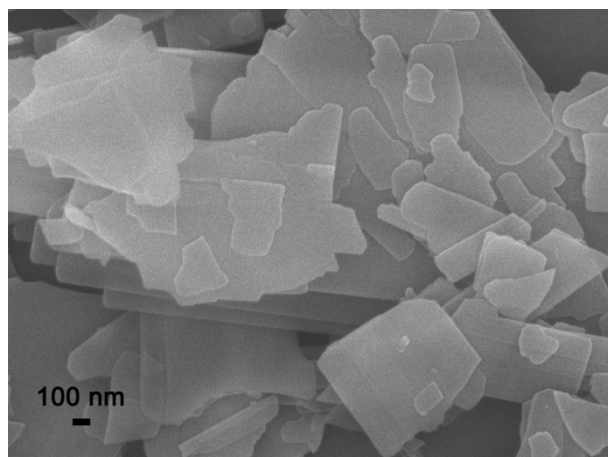


Figure S5. The typical SEM image of the $\text{ZnS}_{1-x}\text{Se}_x \cdot 0.5\text{en}$ precursor.

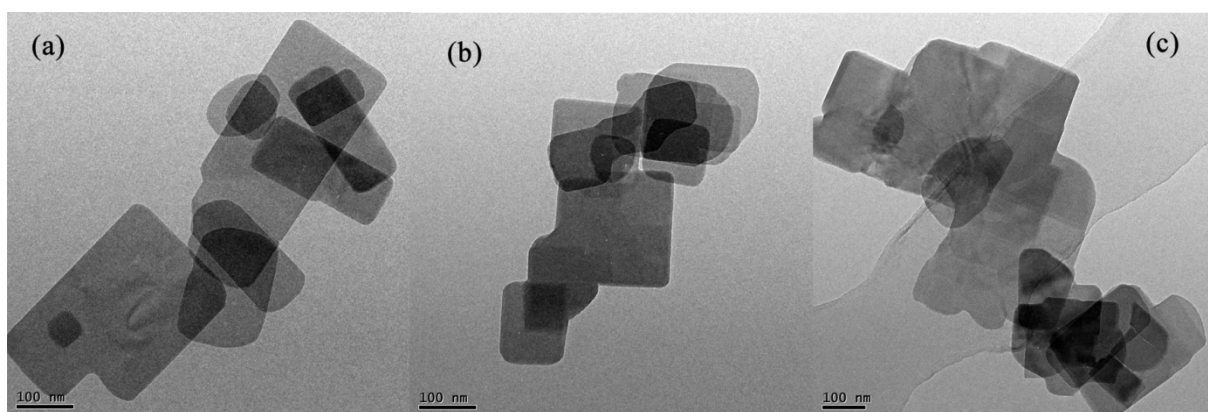


Figure S6. TEM images of as-synthesized $\text{ZnS}_{1-x}\text{Se}_x \cdot 0.5\text{en}$ precursors. (a) $x = 0.2$, (b) $x = 0.4$, (c) $x = 0.6$.

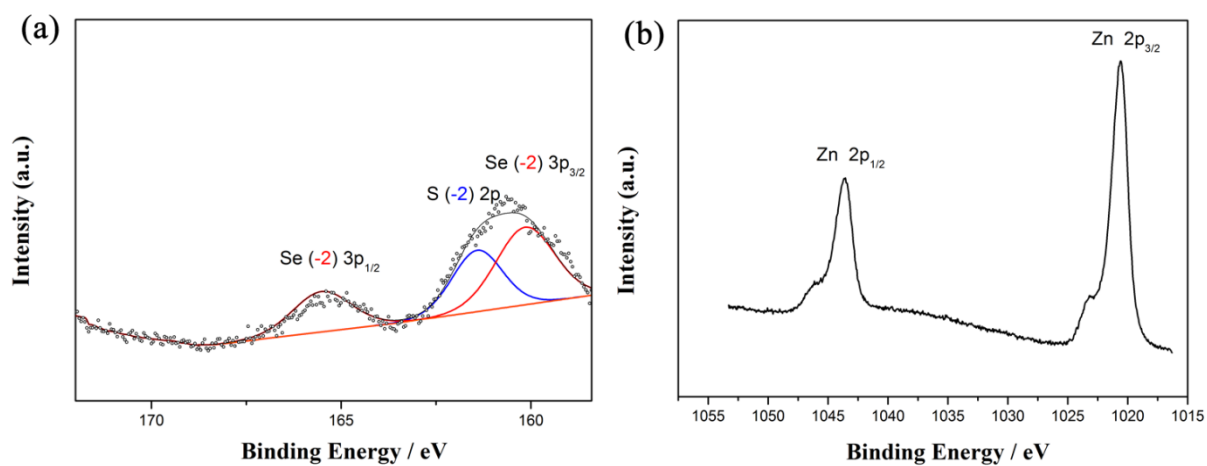


Figure S7. (a) S 2p, Se 3p and (b) Zn 2p XPS core-level spectra of typical $\text{ZnS}_{0.4}\text{Se}_{0.6}$

nanosheets.

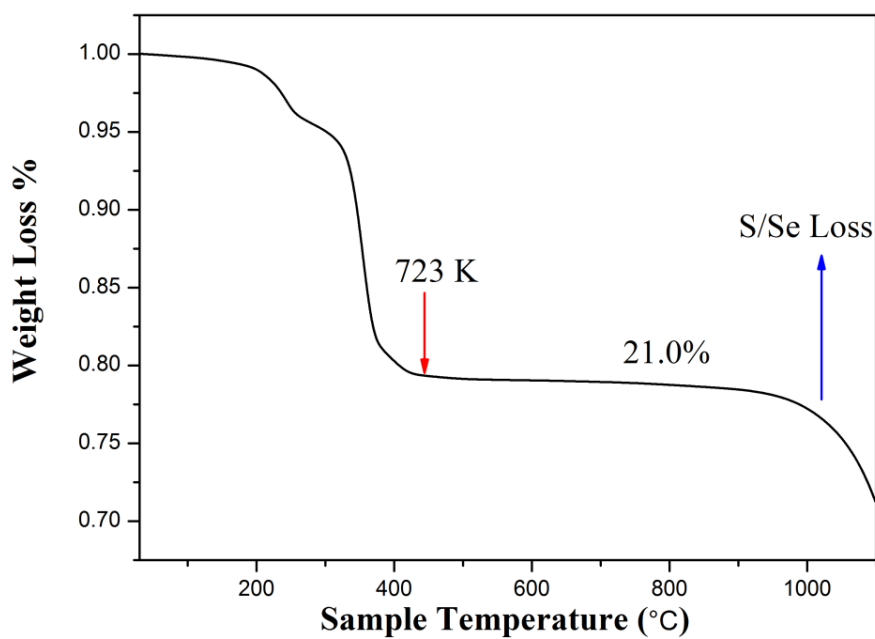


Figure S8. The TG analysis of typical $\text{ZnS}_{0.4}\text{Se}_{0.6}\cdot 0.5\text{en}$ precursors.

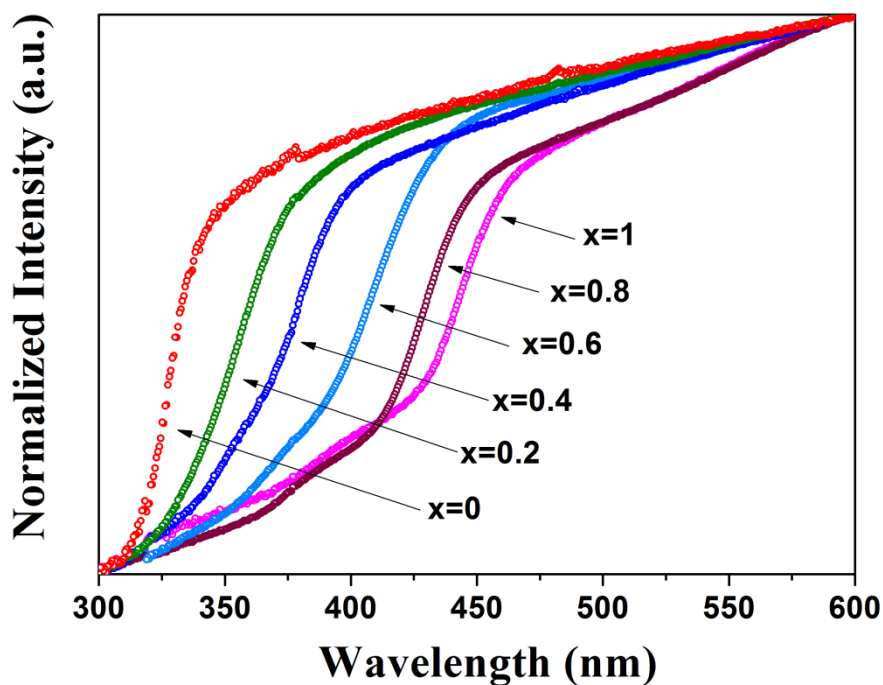


Figure S9. The Normalized UV-vis diffuse reflectance spectra of the $\text{ZnS}_{1-x}\text{Se}_x$ nanosheets with various Se content. The calcination temperature is 723 K.

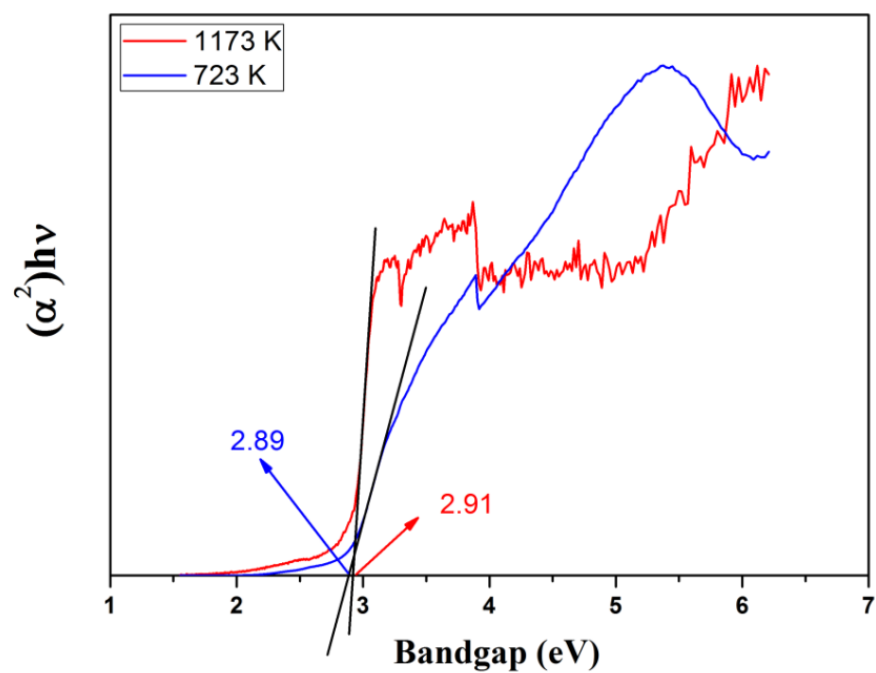
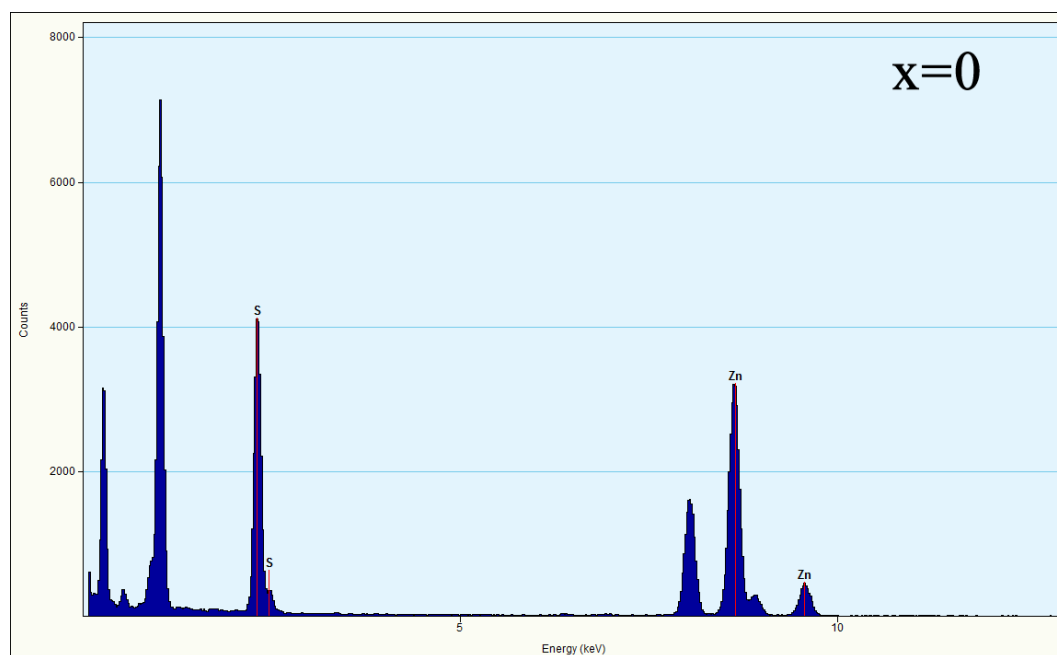
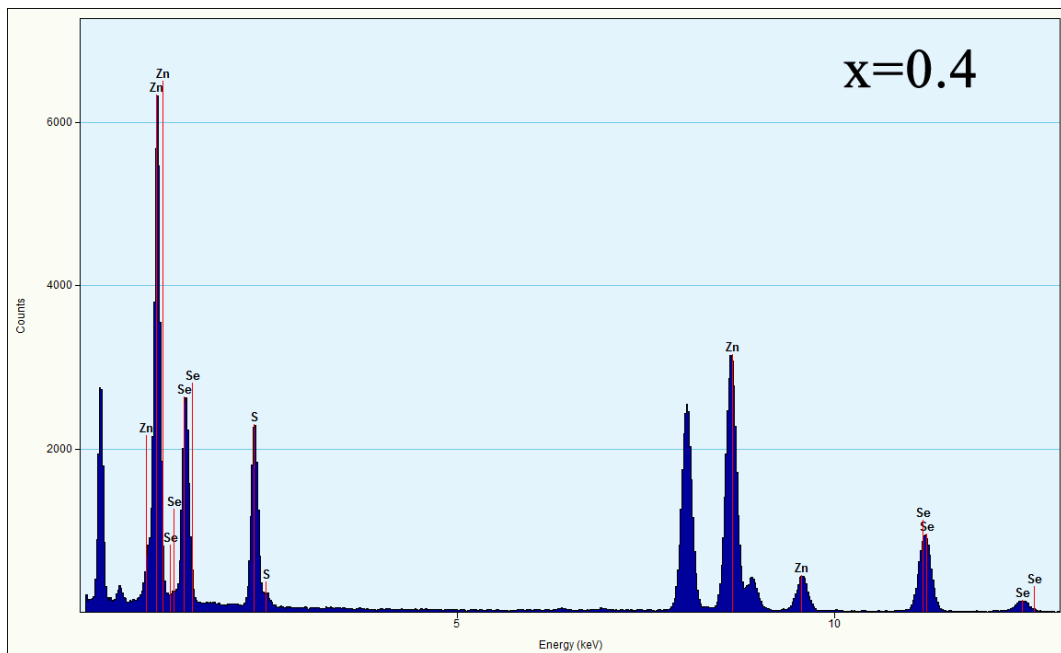
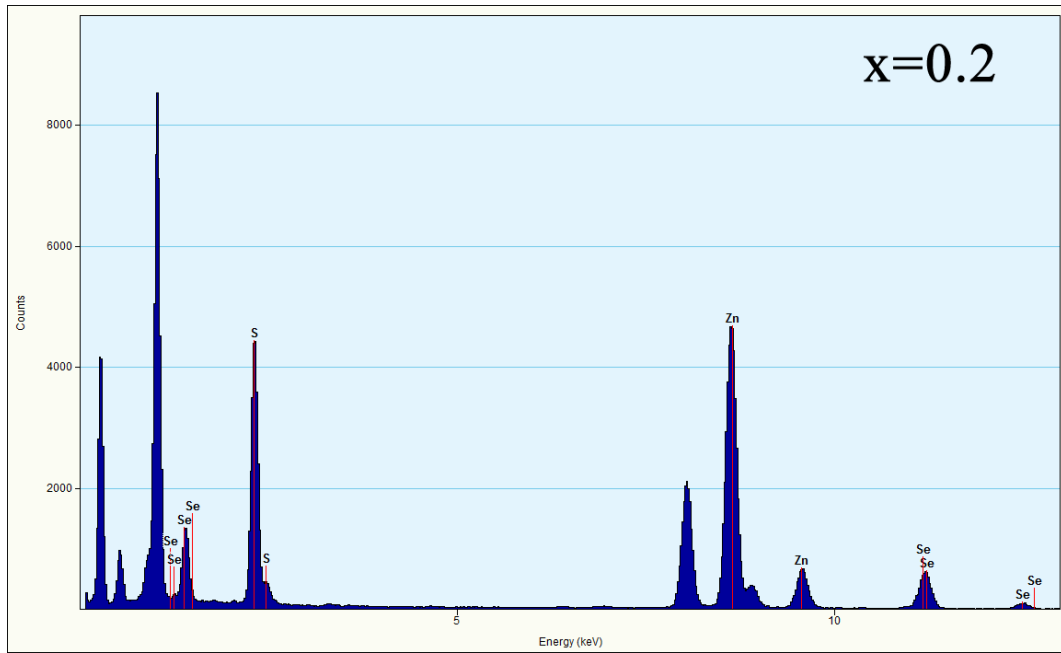


Figure S10. The normalized UV-DRS of ZnS_{0.4}Se_{0.6} nanosheets under different sintering temperature.





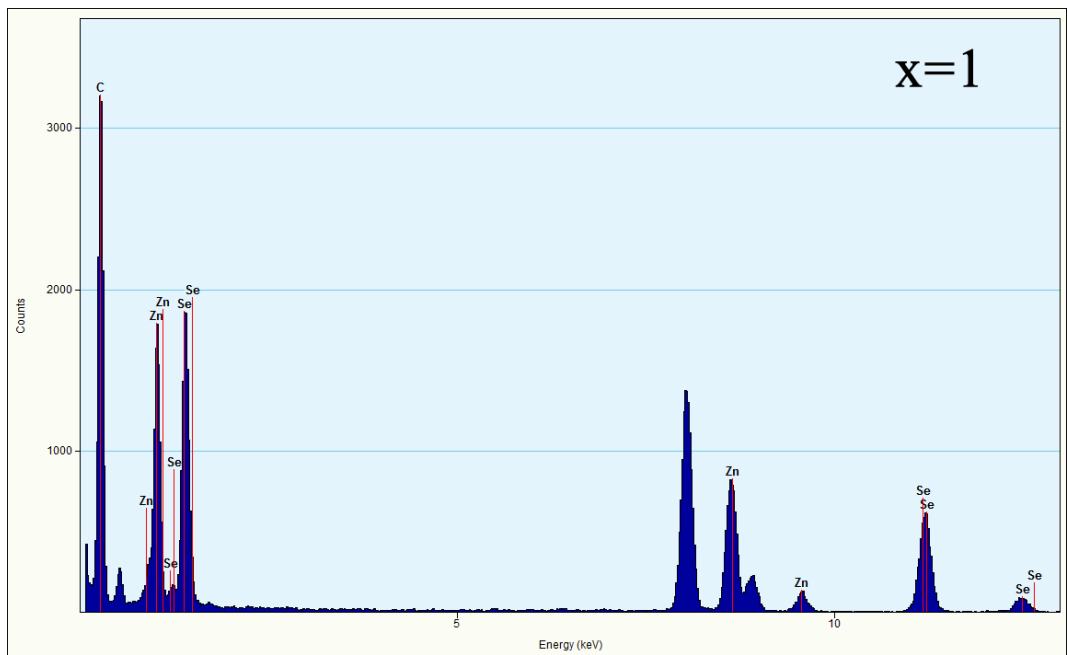
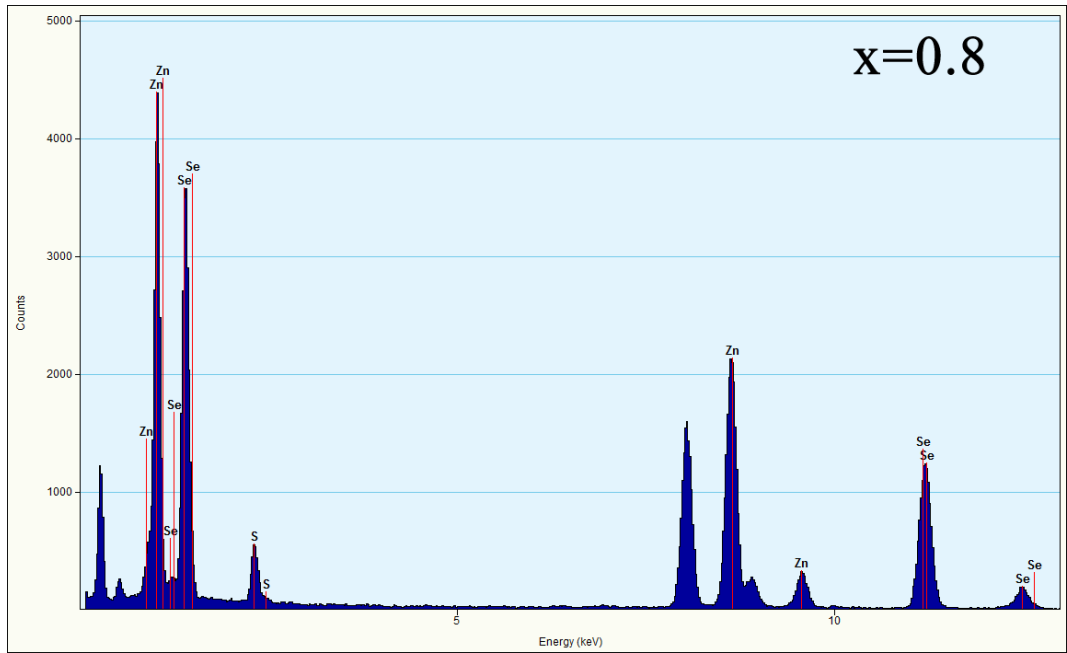


Figure S11. The raw data of EDX spectra.