

## Supporting Information

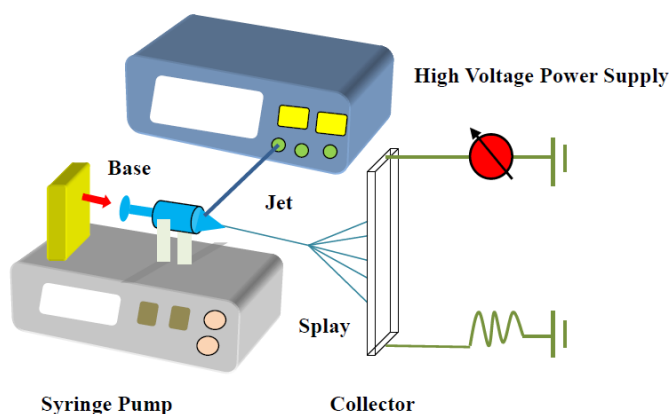
### Compositionally controlled band gap and photoluminescence of ZnSSe nanofibers by electrospinning

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#### Experimental Section

**Materials.** Zinc chloride ( $\text{ZnCl}_2$ , Alfa Aesar, 99.99%), diethylenetriamine (Aldrich, 99%), ethanol (Alfa Aesar, 94%), selenium powder (Sigma-Aldrich, 99.99%), sulfur powder (Sigma-Aldrich, 99.98%), toluene (Sigma-Aldrich, 99.8%), hydrochloric acid (Alfa Aesar, 36.5%), polyvinylbutyral (PVB) (Alfa Aesar, average  $M_v \sim 40\text{kDa}$ ) and trioctylphosphine oxide (TOPO, Sigma-Aldrich, 99%). All chemicals were used without further purification.  $\text{ZnS}_x\text{Se}_{1-x}$  nanofibers were prepared by the electrospinning of a mixture of selenium and sulfur precursor into the zinc precursor based on previously reported methods. First, a mixture of  $\text{ZnCl}_2$  (4 mmole), ethanol (30 mL), hydrochloric acid (1 mg), and 23 wt% PVB (PVB/ethanol content) were heated with stirring at  $80^\circ\text{C}$ , while purging continuously with nitrogen for 1 h. Sulfur and selenium precursors were made separately by dissolving S and Se powder in trioctylphosphine oxide (TOPO) and diethylenetriamine under a nitrogen atmosphere, forming TOPOS and TOPOSe, respectively. These were then mixed with the desired ratios in TOPO to form 1 mL of 1 M TOPOSeS precursor used for sol-gel process. The sulfur to selenium molar ratios used for the TOPOSeS were 1:0, 0.8:0.2, 0.5:0.5, 0.5:0.8, and 0:1. In the electrospinning of polymer solutions, the fiber formation process is characterized by the formation and thinning of the liquid jet and the solidification and deposition of wires on the collection target. A stainless steel electrode was connected to a high voltage power supply, which can generate a DC voltage of up to 30 kV. The applied voltage overcomes the liquid surface tension to form a jet, which then bends and spirals into a large looping path as it thins into fine fibers and solidifies. Also, the precursor solutions are immediately used for solvent evaporation as the production of the fibers becomes more rapid (Figure S1).

The applied voltage between the tip and collector were set at 16 kV with a tip-to-collector distance of 14 cm. Homogenous precursor solutions of PVB/  $\text{ZnS}_x\text{Se}_{1-x}$  composites were prepared and used promptly for electrospinning. Because during this procedure evaporation of solvent occurred and results in a faster increase in the viscosity of the solution. Finally  $\text{ZnS}_x\text{Se}_{1-x}$  nanofibers were obtained after annealing at 600 °C for 2 h. The as-prepared samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). XRD was carried out on a D/MAX-500 X-ray powder diffraction system with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). A scanning rate of  $0.02^\circ$  was applied to record the patterns in the 2 Theta range of  $15\text{--}80^\circ$ . TEM characterization was conducted on a JEM-2000EX system using an acceleration voltage of 160 kV. A Hitachi scanning electron microscopy (SEM) with at an acceleration voltage of 5 kV was employed to characterize the morphology. The quantum yield of the PL emission was measured using the absolute PL quantum yield measurement system



**Figure S1.** Schematic diagram of electrospinning device.

PVB/  $\text{ZnS}_x\text{Se}_{1-x}$  nanofibers (Figure S2(a)) exhibited three steps and a total loss of ca. 28.3%. The first step of ca. 2.2%, from 100 to 357 °C, can be attributed to the loss of volatile water and ethanol solution. The second significant weight loss of ca. 4.7%, between 357 and 405 °C, can be attributed to the loss of crystal water and the decomposition of acetate along with the degradation of PVB by dehydration on the polymer side chain. The third step, which started at about 405 °C and ended at about 505 °C was a weight loss of ca. 21.4%, which was assigned to the release of water formed from the condensation of carbonyl groups in the PVB/  $\text{ZnS}_x\text{Se}_{1-x}$  framework and the decomposition of the excess chalcogen species. The weight loss of PVB fibers (Figure S2(b)) began to occur at approximately 320 °C and was complete at about 560 °C. The temperatures corresponding to the peak maxima were near 400 °C for ions representing aliphatic species and near 410 °C for alkyl aromatics.

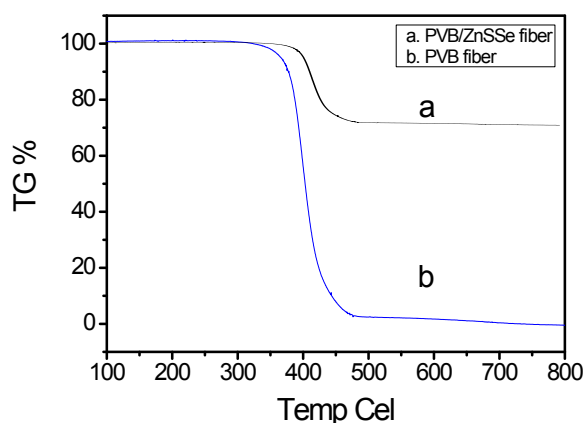
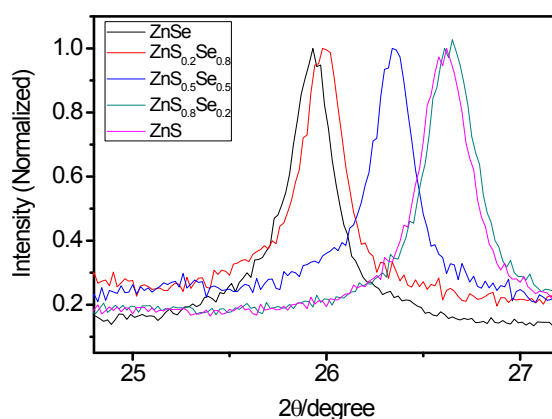
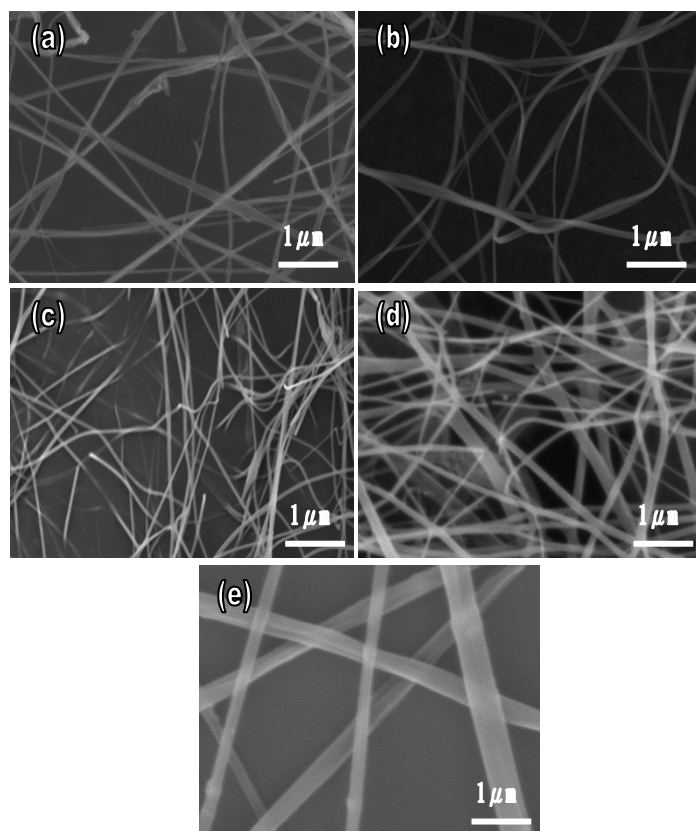


Figure S2. Thermogravimetric analysis (TGA) curves of PVB/  $\text{ZnS}_x\text{Se}_{1-x}$  nanofibers. (a) 23 wt % PVB/  $\text{ZnS}_x\text{Se}_{1-x}$  fiber and (b) pure PVB fiber.

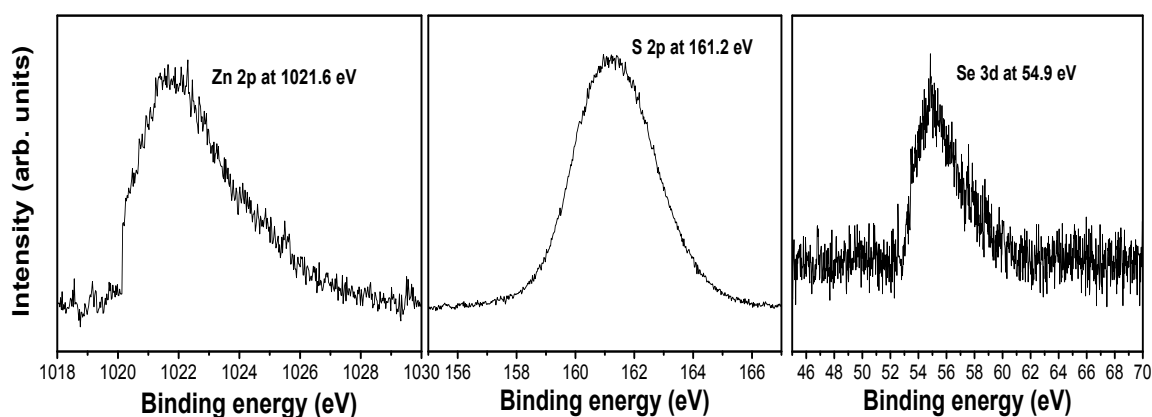


**Figure S3.** (b) X-ray diffraction (XRD) pattern of ZnS (right),  $\text{ZnS}_{0.8}\text{Se}_{0.2}$ ,  $\text{ZnS}_{0.5}\text{Se}_{0.5}$ ,  $\text{ZnS}_{0.2}\text{Se}_{0.8}$ , and ZnSe NWs (left). Change in the (100) crystal plane d-spacing (blue shift) with increasing selenium content.

All the four elements, i.e., zinc, sulfur, and selenium were distributed over the surface and through the bulk of the film. Quantification of peaks gave a ratio of Zn/ S/Se of 1.06: 0.52: 0.42, which is in excellent agreement with the stoichiometry of ZnSSe nanofibers. The optical properties of the  $\text{ZnS}_x\text{Se}_{1-x}$  nanofibers are important for optoelectronic applications. The samples are exposed to air, therefore, C, O-containing species on the surface is possible detected by XPS. To reduce this effect, the samples were purposely cleaned by Ar plasma for 2 min prior to the measurements. The quantitative information from XPS survey was to calculate the film composition using the CasaXPS software. By analyzing XPS data, the composition of the thin film was regarded as ZnSSe by taking Zn as the reference. Relative atomic concentrations of these ZnSSe samples within the probing depth ( $\approx 5$  nm for the taking off angle of  $53^\circ$ ) of XPS were summarized in Figure S4. The average composition of the nanocrystals in the sample has a relative atomic concentrations Zn/S/Se ratio close to 1: x: 1-x with a variation from particle to particle less than the experimental error of ca.  $\pm 5.6$  atom %.



**Figure S4.** SEM images of PVB/  $\text{ZnS}_x\text{Se}_{1-x}$  composite nanofibers electrospinning from 23 wt.% (a)  $x=1$ , (b)  $x=0.8$ , (c)  $x=0.5$ , (d)  $x=0.2$ , and (e)  $x=0$ .



**Figure S5.** Typical XPS spectra of the synthesized wurtzite  $\text{ZnS}_{0.5}\text{Se}_{0.5}$  nanofibers: (a) Zn 2p region spectrum, (b) S 2p region spectrum, and (c) Se 3d region spectrum.

**Table S1.** Measured  $\text{ZnS}_x\text{Se}_{1-x}$  Nanofiber Composition and emission quantum yield in toluene.

Precursor atomic ratio	Measured by EDS <sup>a</sup>	Measured by XPS <sup>b</sup>	Quantum yield (%) <sup>c</sup>
Zn:S:Se	Zn:S:Se	Zn:S:Se	
1:0:1	0.92:0:0.89	0.96:0:0.94	42
1:0.2:0.8	0.88:0.16:0.72	0.98:0.17:0.75	45
1:0.5:0.5	0.95:0.42:0.46	0.95:0.46:0.47	47
1:0.8:0.2	0.94:0.68:0.16	0.96:0.73:0.18	44
1:1:0	0.96:0.92:0	0.97:0.95:0	43

<sup>a</sup> EDS measurements have an error of ca.  $\pm 2$  atom %.

<sup>b</sup> XPS measurement have an error of  $\pm 0.2$  atom % for Zn,  $\pm 0.1$  atom % for S,  $\pm 0.5$  atom % for Se.

<sup>c</sup> The average values obtained are reported with an accuracy within 10% according to the manufacturer.