

**Photocatalytic Hydrogen Evolution Based on $\text{Cu}_2\text{ZnSnS}_4$, $\text{Cu}_2\text{ZnSnSe}_4$, $\text{Cu}_2\text{ZnSnSe}_{4-x}\text{S}_x$
Nanofibers**

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S-1. Materials

All chemicals were used without further purification. Copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), zincchloride (ZnCl_2), tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), dimethylformamide (DMF), hydrochloric acid (HCl, 37.5%) and sodium hydroxide (NaOH) were purchased from Merck. Sulfur powder (99.98%) and triethanolmine (TEOA) were purchased from Alfa-Aesar. Trioctylphosphine (TOP, 97%) was purchased from Fluka. Polyacrylonitrile (Mw: 150000), Selenium powder (95+/-%) and Eosin-Y (EY) were purchased from Sigma Aldrich. Ultra-pure water was used throughout the experimental process.

S-2. Instrumentation

Electrospinning process was done by using Spellman SL30 brand DC power supply. New Era pump firm Ne-300 model was used as a syringe pump. We started the process of electrospinning after setting the distance between the collector and a syringe at the optimum point. X-ray diffraction (XRD) pattern of colloidal nanoparticles was recorded with a Bruker Advance D8 XRD (Cu α source with 1.5406 wavelength) in powder mode. ZeissEvo model scanning electron microscope and JEOL JEM-2100F 200kV model transmission electron microscopy were used to obtain SEM and TEM images, SAED pattern and elemental mapping. Solar Light – XPS 300TM was used as a visible light source. The amount of evolved hydrogen were analyzed using a Shimadzu GC-2010Plus gas chromatograph (column temperature, 323 K; carrier gas, Ar; column, RESTEK molecular sieve 5A porous layer open tubular capillary column 30 m 0.53 mmID 50 μm df; detector, TCD) and calculated by calibration using standard samples of H_2 in N_2 .

S-3. Synthesis of Nanofibers

2 mmol Copper(II) chloride, 1 mmol Zinc(II) chloride, 1 mmol Tin(II) chloride, 750 mg of PAN and 15 ml DMF were mixed in a 15 ml bottle and heated to 60 °C for 2h under N_2 flow. The solution was waited for a while at room temperature before electrospinning process was performed. Then, the solution was transferred into a syringe with metallic needle tip. The distance (between the needle tip and the square plate) and flow rate were adjusted as 15 cm and 0.35 ml/h, respectively. The electric field are applied between the needle tip and the square plate; Thus, electrospun PAN/ Cu/ Zn/ S nanofibers were intensified on the grounded square plate. To generate the crystalized CZTS, CZTSe and CZTSeS nanofibers, a mixtures

of Trioethylphospine (TOP) and Sulphur and/or Selenium powder solution (depending upon the desired chemical structures) were gradually dropcasted on the CuZnSn-PAN fibers. The nanofibers were placed a calcination oven at a rate of 5 %/min and maintained for 1 h at 500 °C (S1).

S-4. The SEM Images of the CZTSe and CZTSeS Nanofibers

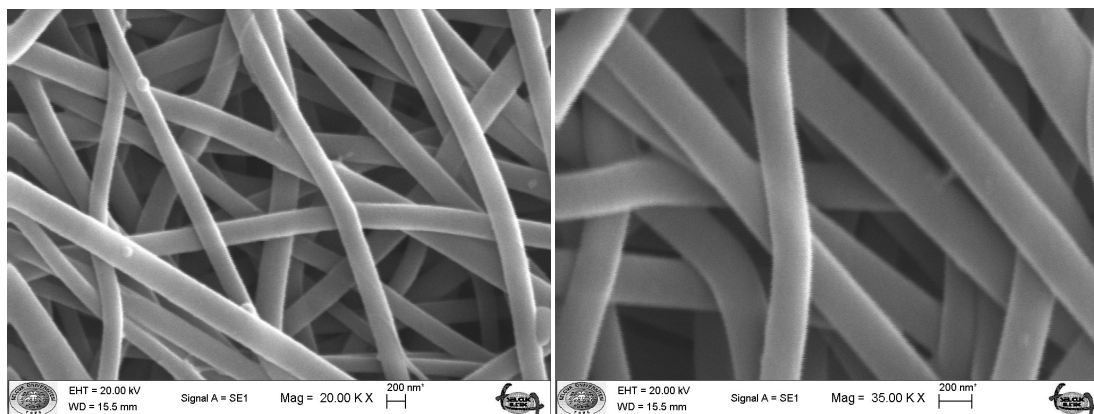


Figure S-1. SEM images of CZTSe (a) and CZTSeS (b) crystalline fibers.

S-5 Elemental Mapping Images of CZTSeS Nanofibers

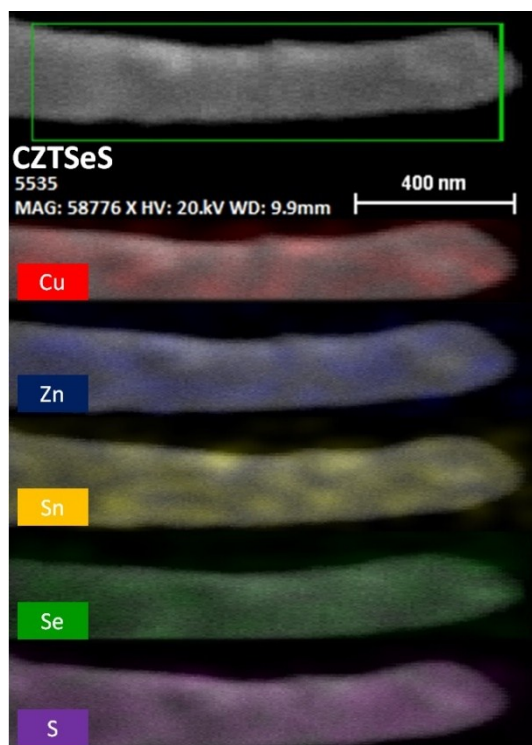


Figure S-2. Elemental mapping images of CZTSeS nanofibers

S-6. EDS Spectrum of CZTSeS Nanofibers

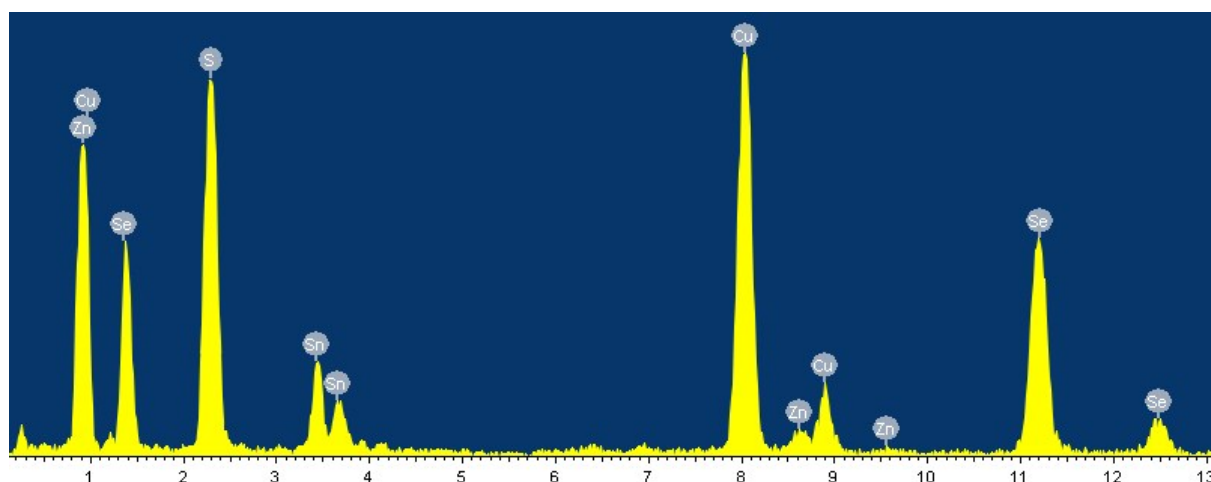


Figure S-3. Energy Dispersive X-Ray Spectrum (EDS) of CZTSeS nanofibers

S-7. The Photocatalytic Hydrogen Evolution by Nanofibers

Triethanolamine (0.33 M) and Eosin Y photosensitizer (0.33 mM) solution (total volume of solution 20 ml) were prepared in the flask and bubbled with N_2 to remove O_2 . Nanofibers (CZTS, CZTSe or CZTSeS, 10 mg) were taken a reaction cell (total volume 135ml) and then, both electron donor solution (TEOA) and nanofibers were taken in the anaerobic glove box system. Solution and catalyst were mixed in the glove box and sonicated to homogenize the solution. Afterward, EY solution was added in the solution-catalyst mix. The reaction flask was sealed tightly with a rubber septum and removed from the glovebox for the light experiments. And then this mixture were stirred vigorously under the visible light source (Solar Light – XPS 300TM) and at room temperature. Then gas sample were taken periodically in the headspace, which is above the solution. The gas in the headspace was analyzed using a Shimadzu GC-2010 Plus gas chromatograph (detector, TCD; column temperature, 323 K; column, RESTEK molecular sieve 5A porous layer open tubular

capillary column 30 m 0.53 mmID 50 μ m df; Ar as a carrier gas) to determine the produced hydrogen.

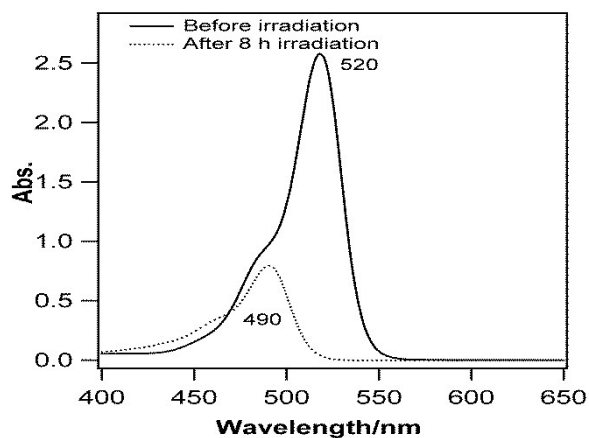


Figure S-4. UV-vis absorption spectra of the solutions before and after photocatalytic hydrogen evolution system containing 10 mg CZTS, Eosin Y ($3.25 \cdot 10^{-4}$ M) and TEOA (5%) in 20 ml H_2O at pH=9.

S-8. The cyclic voltammetry measurements

Cyclic voltammetry is a useful tool to study the behavior of semiconductors. Cyclic voltammetry measurements were taken using Bu_4NPF_6 solution as a support electrolyte in acetonitrile. The cyclic voltammograms of nanofibers were shown at Figure S-5. We had to notice that the potential of Ag/AgCl electrode was considered to be 0.211 V versus standard hydrogen electrode (SHE). Electrochemical energy levels of nanofibers were calculated from the first reduction peak potentials. The onset points of peaks were accepted for calculations. The energy levels versus vacuum level were calculated according to the following equation.

$$E_{LUMO} = -e(E_{onset.red} + 4,75)$$

LUMO energy levels of CZTS, CZTSe and CZTSeS were calculated -4,08 eV, -3,92 eV and -3,94 eV respectively. Subsequently, band gaps of CZTS, CZTSe and CZTSeS nanofibers were determined by UV-vis-NIR data 1,49 eV, 1,17 eV and 1,39 eV respectively. HOMO energy levels were found by subtracting the band gap LUMO levels. HOMO energy levels of CZTS, CZTSe and CZTSeS nanofibers were -5,572 eV, -5,09 eV and 5,33 eV respectively.

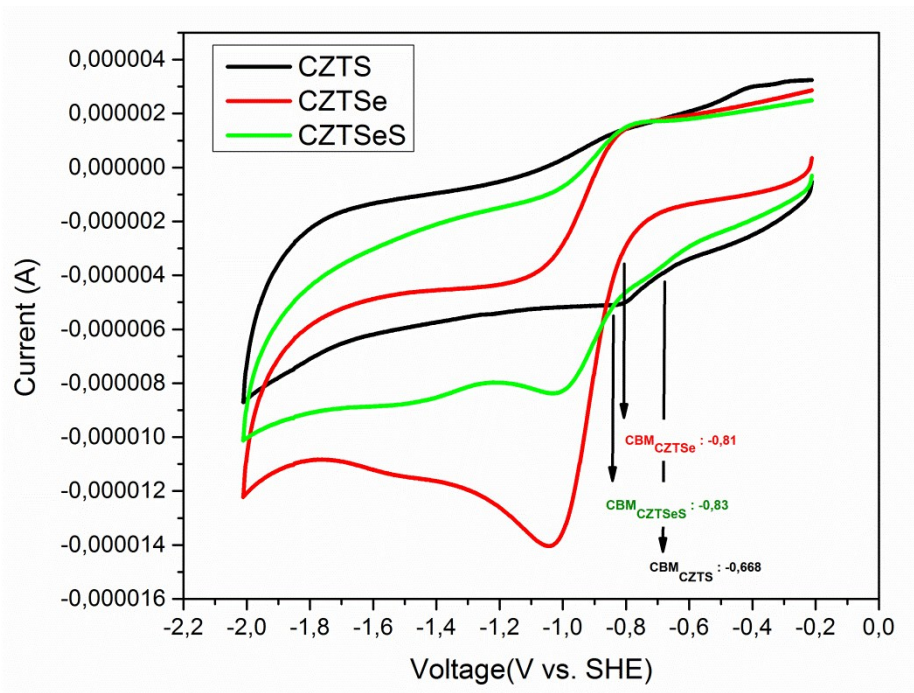


Figure S-5. Cyclic voltammograms of CZT(S/Se/SeS) nanofibers.

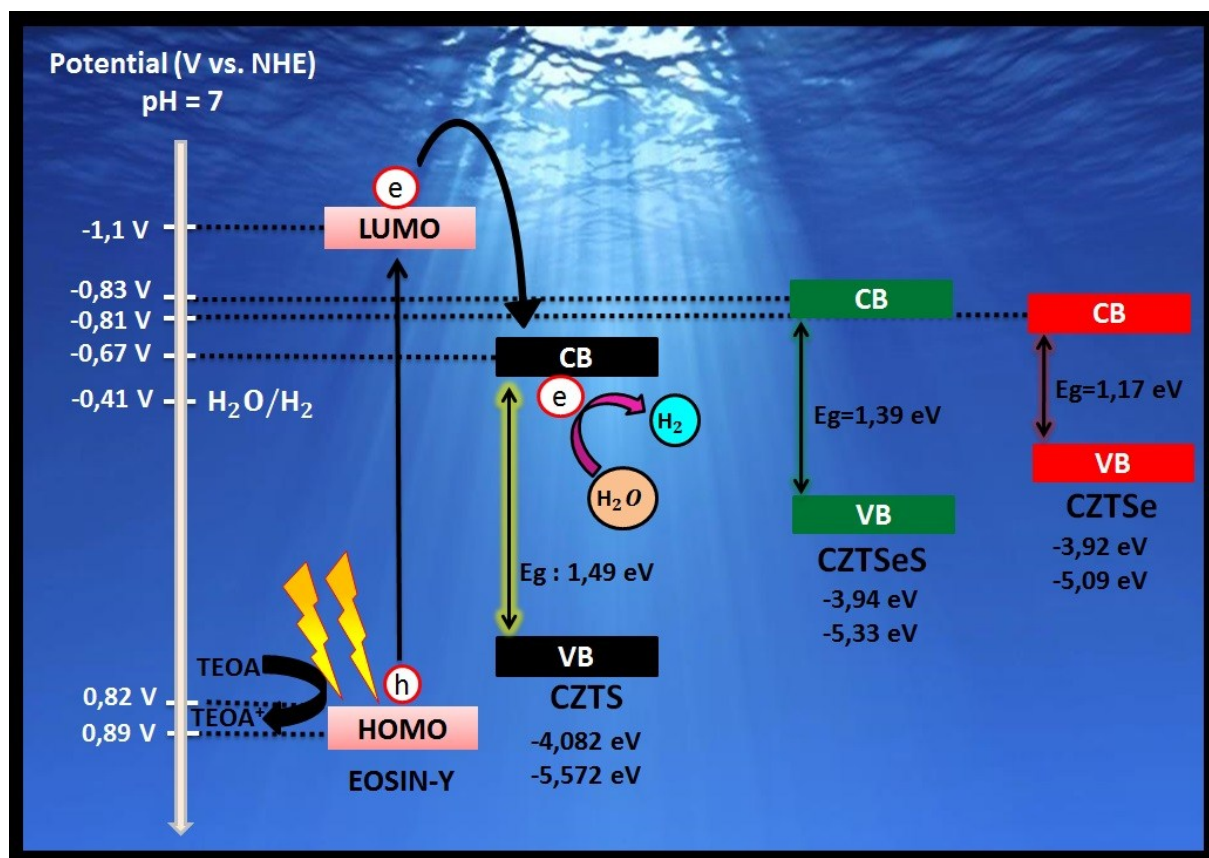


Figure S-6. Mechanism of hydrogen production and energy diagram

- 1** Ozel, F., Kus, M., Yar, A., Arkan, E., Yigit, M.Z., Aljabour .A., Büyükcelebi, S., Tozlu, C. and Ersoz, M., 2015. Electrospinning of $\text{Cu}_2\text{ZnSnSe}_{4-x}\text{S}_x$ nanofibers by using PAN as template. *Materials Letters*. 140, 23.