Supporting Information

Photo-electrochemical property and electronic band structure of kesterite copper chalcogenides Cu_2-II-Sn-S_4 (II = Fe, Co, Ni) thin films

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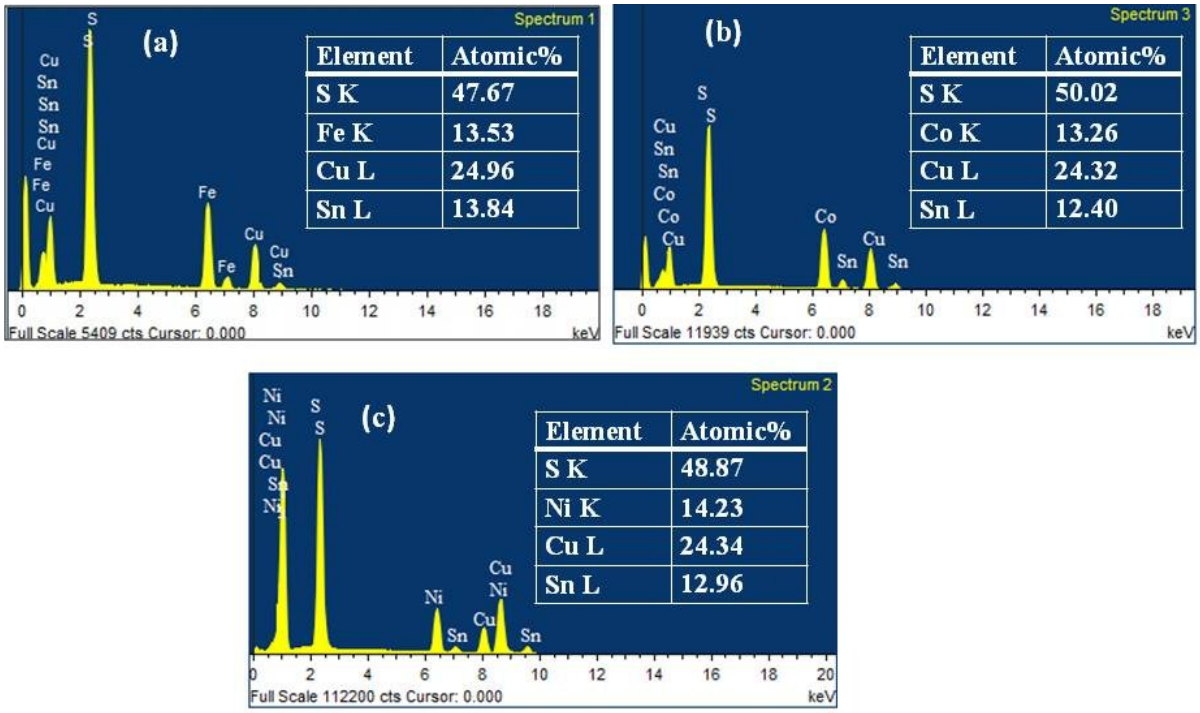

Figure S1: EDX spectra of (a) CFTS, (b) CCTS, (CNTS).

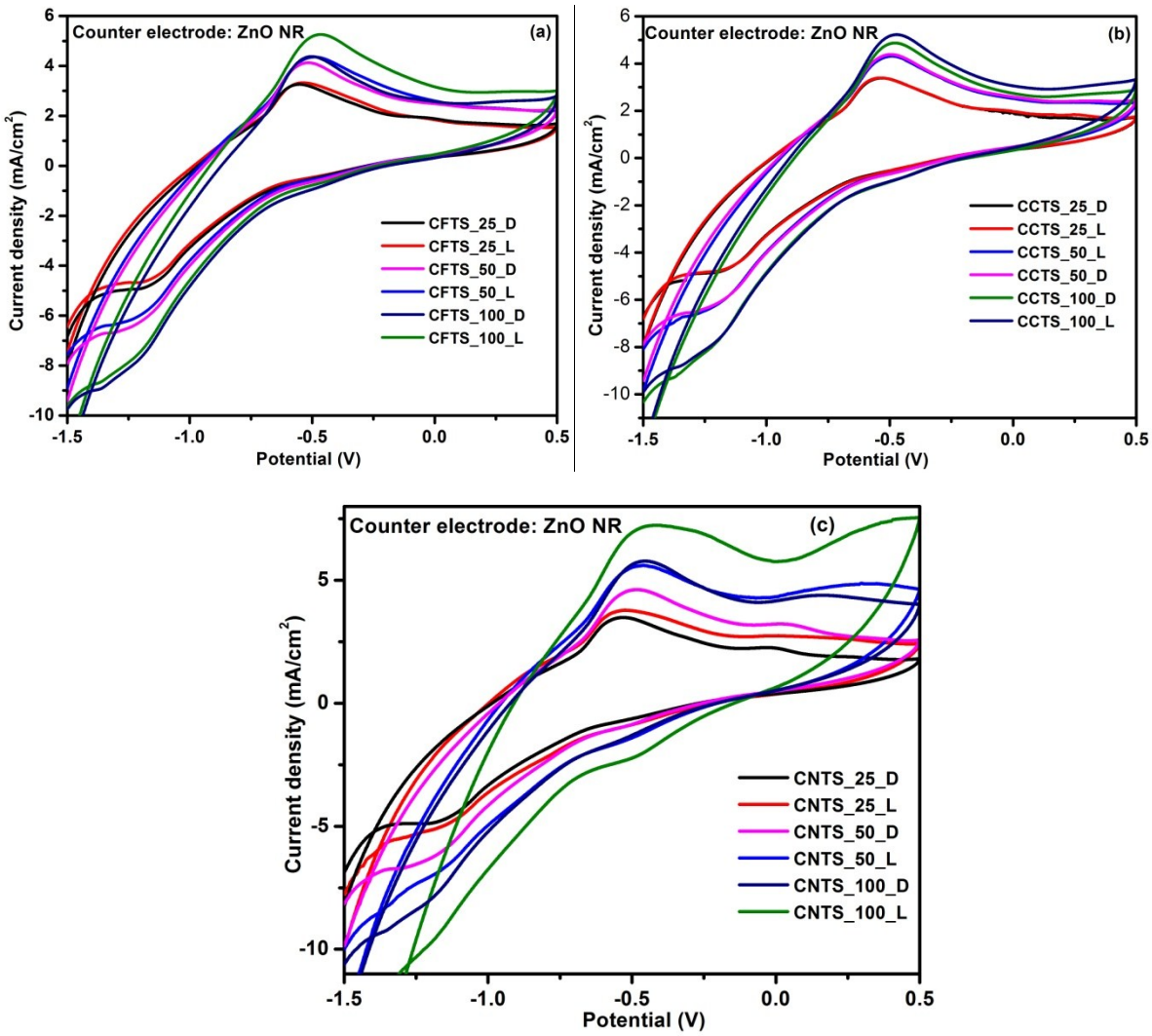

Figure S2. (a-c) Cyclic voltammograms for CFTS, CCTS and CNTS respectively at sweep rate v = 5, 25, 50, 100 mVs^{-1} under dark (D) and visible light (L) illumination using ZnO NR electrode as a cathode electrode.

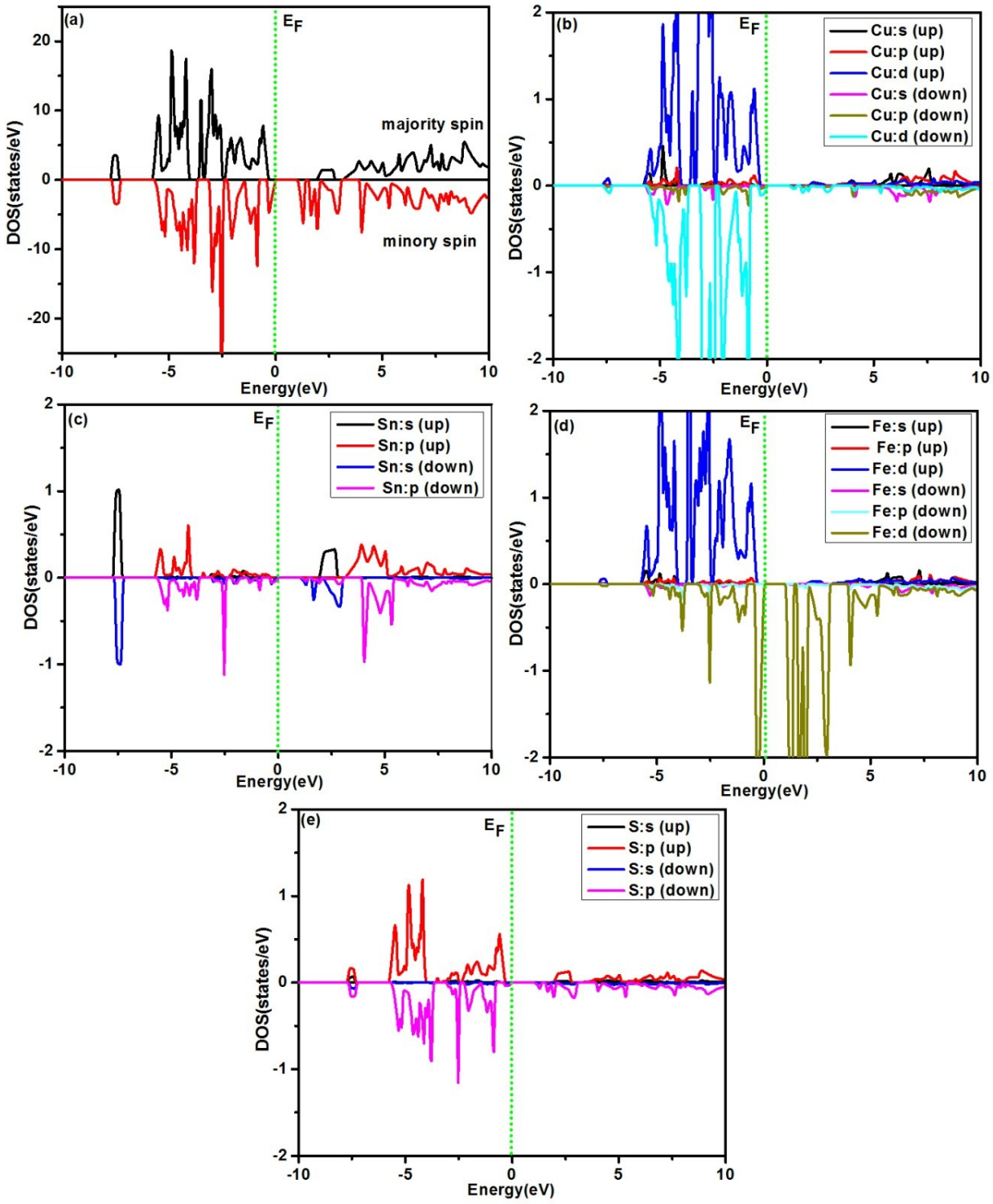

Figure S3: Total and partial density of states (DOS) of Cu_2FeSnS_4 (CFTS).

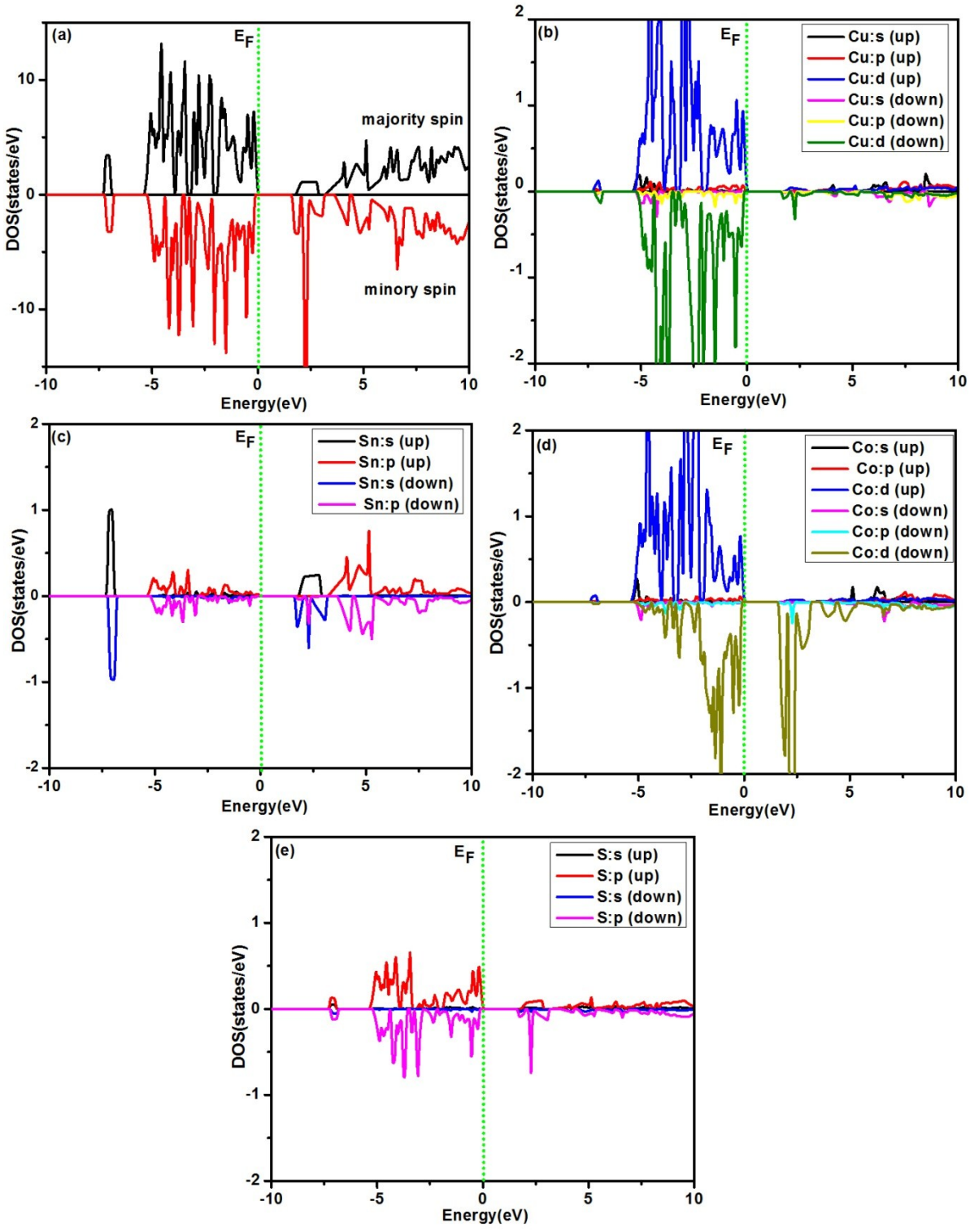

Figure S4: Total and partial density of states (DOS) of Cu_2CoSnS_4 (CCTS).

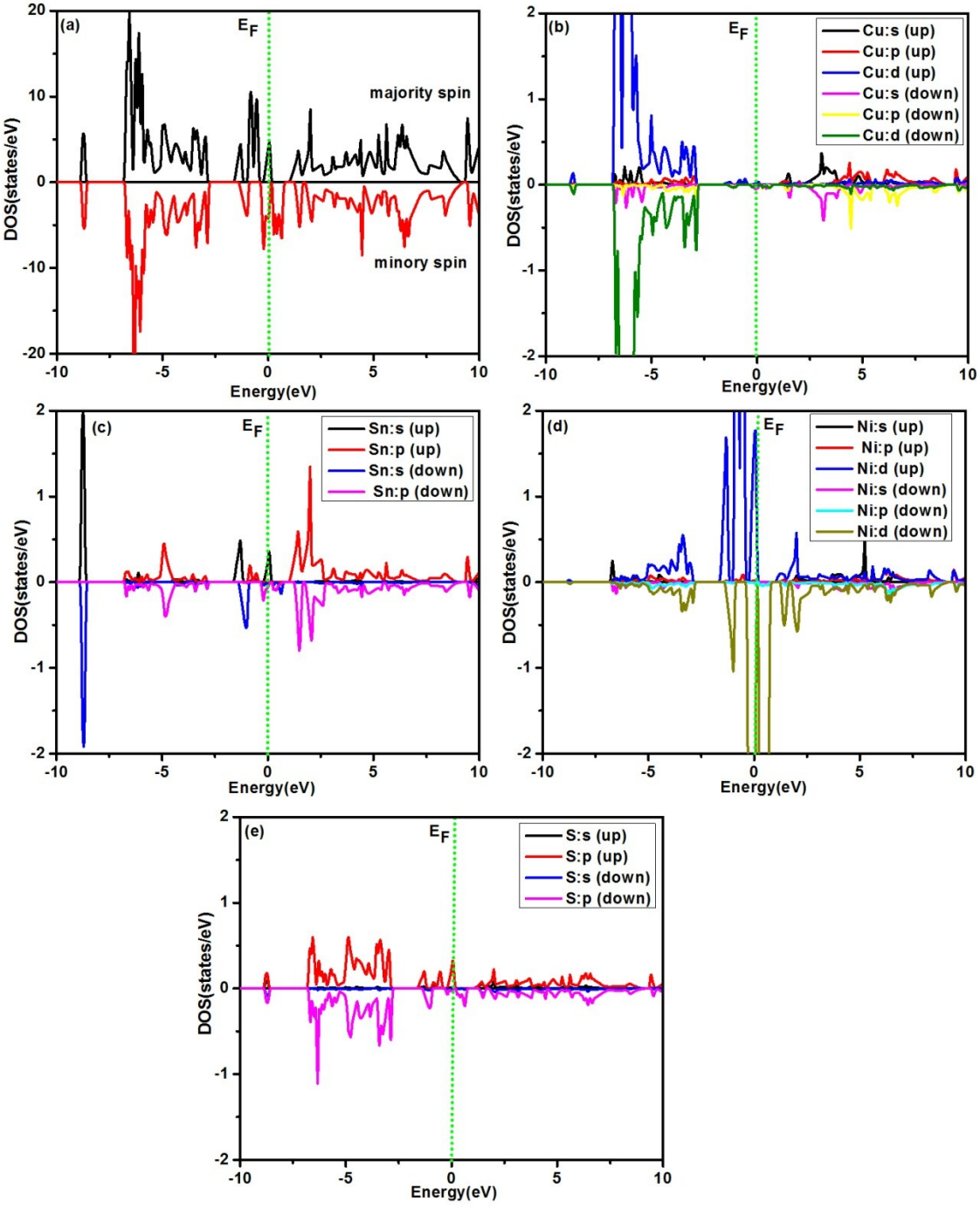

Figure S5: Total and partial density of states (DOS) of Cu_2NiSnS_4 (CNTS).

ZnO nanorod preparation and characterizations

To synthesize the ZnO nanorod arrays on ITO glass substrates hydrothermal route was used as reported previously by several researchers. Before starting hydrothermal deposition, the ITO glass substrates were cleaned by an ultrasonic cleaner with dilute HCl, acetone, 2-propanol, ethanol for each 20 min, then cleaned with deionized water and dried. Zinc acetate dihydrate, 2-methoxethanol and monoethanolamine (MEA) were used as the starting material, solvent and stabilizer, respectively. First, zinc acetate dihydrate was dissolved in the mixture of 2-methoxyethanol and monoethanolamine. The molar ratio of MEA to zinc acetate was maintained at 1.0, and the concentration of zinc acetate was 0.5 M. Then, the resulting mixture was stirred at 60 °C for 2 h until a clear and transparent homogeneous solution was formed. Finally, the solution was aged for 24 hours at room temperature. Then, the solution was spin coated at a rate of 3000 rpm for 30 s using a spin coater. The as-deposited thin film was heated in an oven at 150 °C for 10 min to remove the solvent. After repeating the spin coating and drying procedures for five times to yield the required thickness, the resulting thin film was annealed at 450 °C for 1 h to obtain the ZnO seed layer.

After the formation of seed layer, ZnO nanorod arrays were formed by suspending the ZnO seed layer upside-up in a glass beaker filled with the aqueous solution of 50 mM zinc nitrate hexahydrate and 50 mM hexamethylenetetramine (HMT) heated at 90 °C for 5 h, then cleaned with distilled water and dried.

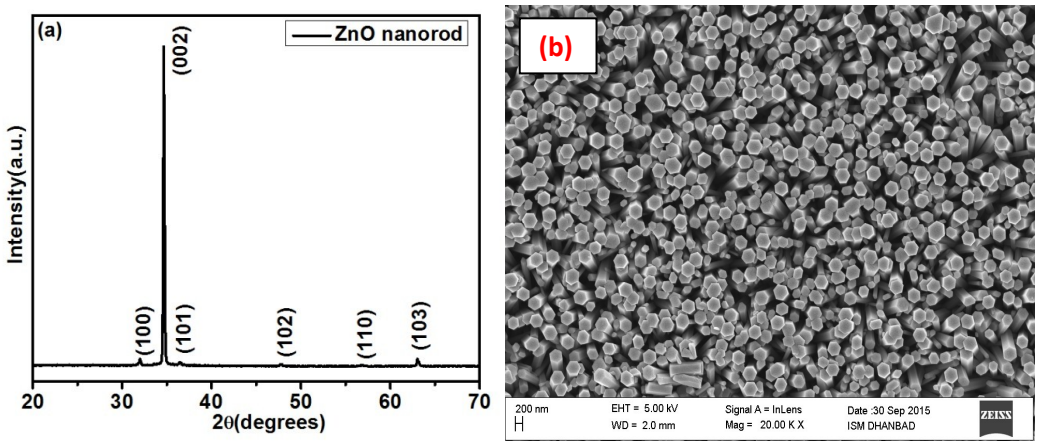

Figure S6. (a) XRD and (b) FESEM image of ZnO nanorods.