

Electronic Supplementary Information

Optical photoresponse of CuS/n-Si radial heterojunction with Si nanocone arrays fabricated by chemical etching

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ESI. 1 Preparation of CuS material

All the reagents were of AR grade. Cu powder was obtained from Loba-chemie Indoaustranal Co. NH_4Cl , ethylene diamine and thioacetamide were purchased from SRL company. All the reagents were used without further purification.

In this typical reaction 0.32 gm Cu Powder, 1.54 gm NH_4Cl , 1.0 mL pure ethylene diamine and 20 mL water were mixed and heated at 60-70° C in a conical flux. After 10 hr, a deep blue color copper complex was formed and all Cu powder was dissolved. Then we added thioacetamide (0.75 gm) to the deep blue solution. The deep blue color of the complex was gradually faded and a blue-black material was precipitated, which was separated by centrifuge with 8000 rpm and washed with water for several times and dried at 60°C. By this way we prepared about 10 gm CuS material in different batches. In the second step, all the as-prepared CuS material was heated at 150°C for 2 days in a silica crucible for desorption of absorbed organic material, which resulted in a phase pure CuS material.

ESI. 2 Analytical Instruments

The phase of the synthesized CuS powder and CuS film on Si was studied by X-ray diffraction (XRD) (Philips X-Pert MRD) at a grazing incidence mode using Cu $K\alpha$ radiation (45 kV, 40 mA). Reflectance spectra were measured using DRS (Diffuse Reflectance Spectra) mode with a Cary model 5000 UV-VIS-NIR spectrophotometer. Raman spectra were obtained with a Renishaw Raman Microscope. XPS spectra were recorded with PHI

1 5000 Versa Probe II (ULVAC – PHI, INC, Japan. Surface morphology of Si nanocone
2 structures and Si/CuS heterostructures were characterized by field emission scanning
3 electron microscopy (FESEM) using a ZEISS SUPRA 40 microscope. Temperature-
4 dependent photoluminescence (PL) measurements were carried out using a He-Cd laser as the
5 excitation source operating at 325 nm with an output power of 40 mW. The PL signals were
6 recorded using a TRIAX-320 monochromator and Hamamatsu R928 photomultiplier
7 detector.

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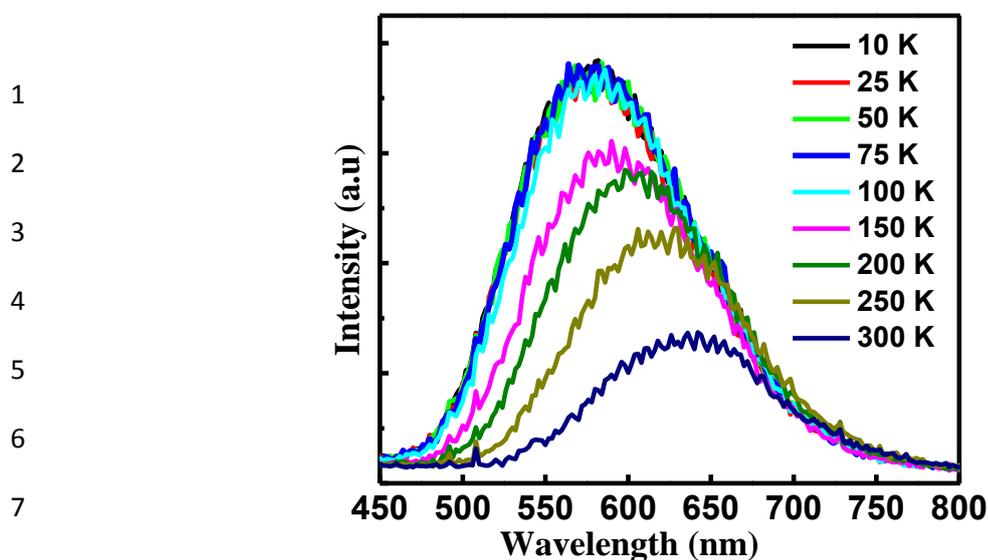
11 **ESI. 3 Temperature Dependent Photoluminescence Measurement**

12 To investigate the optical characteristics of Si nanocones, we have carried out
13 temperature dependent photoluminescence (PL) experiment spanning from 10 K to room
14 temperature (300 K) and the spectra are shown in Figure S2. Orange-red luminescence is
15 observed by naked eyes at 300 K upon illumination of UV excitation pump of 325 nm. A
16 broad emission band with a peak at 652 nm is found at 300 K, whereas the peak position is
17 blue shifted with decrease in temperature. For 10 K, the observed PL peak position is at 590
18 nm. The observed PL is attributed to the porous nature of the nanostructure surface (which is
19 also observed from the FESEM image). Emissions with similar energy have been reported in
20 porous Si NWs¹⁻⁴. The widening of the Si band gap and the reduced electron phonon coupling
21 at a lower temperature results in blue shift of the PL peak with decreasing temperature. The
22 band edge emission near 650 nm affects the electrical properties, which is discussed in the
23 article.

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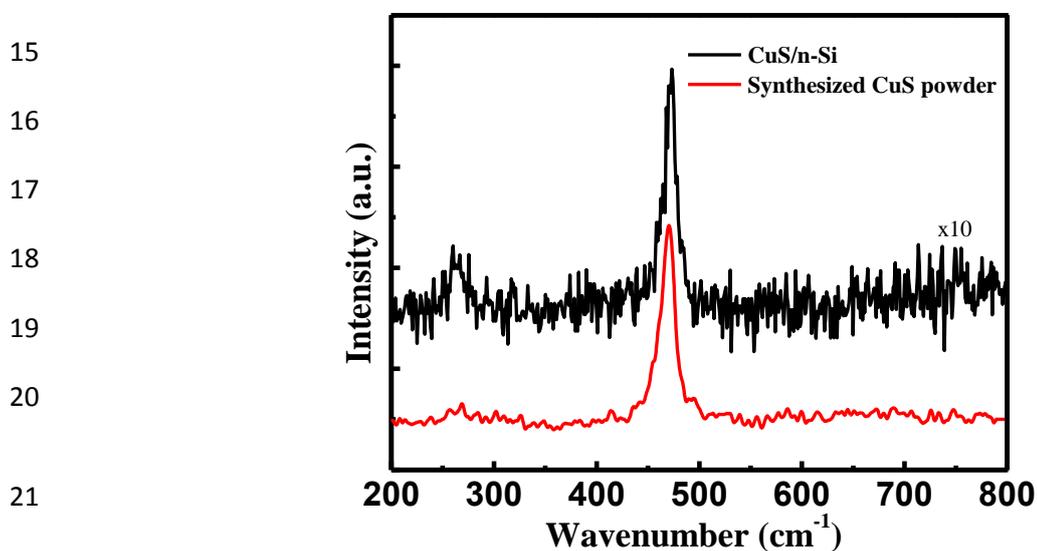
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9 **Figure S1.** Temperature dependent PL spectra of as-synthesized cone-like Si
10 nanostructures

11 **ESI. 4 Raman Spectra**

12 Figure S2 shows the Raman spectra of CuS thin film. The band position at 263 and
13 472 cm^{-1} is assigned to the A_{1g} transverse (TO) and longitudinal (LO) optical modes,
14 respectively, which agrees well with the reported Raman spectra of covellite CuS.⁵)



22 **Figure S2.** Raman spectra of as-synthesized CuS powder and film grown on n-Si substrate .

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