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## **Supplementary Information**

## Isovalent bismuth ions induced growth of highly-disperse Sb<sub>2</sub>S<sub>3</sub> nanorods and their composite with p-CuSCN for self-powered photodetectors

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## Fig. S1-S7



**Fig. S1** SEM images of  $Sb_2S_3$  samples synthesized at different conditions: (a) 170 °C, without Bi ions; (b) 170 °C, 1% Bi; (c) 210 °C, without Bi ions; (d) 210 °C, 1% Bi.



**Fig. S2** TEM and HRTEM images of  $c-Sb_2S_3$  sheaf-like nanostructures (or rod-bundles) synthesized at 210 °C without adding Bi ions. HRTEM image shown in (c) confirms the single-crystal feature and the [010]-oriented growth of individual NRs in the rod-bundles.



**Fig. S3** (a) XPS survey spectrum and (b,c) Sb 3d and S 2p high-resolution XPS spectra recorded on the CuSCN/Sb<sub>2</sub>S<sub>3</sub> composite. The c-Sb<sub>2</sub>S<sub>3</sub> NRs in the composite were prepared at 170 °C with adding 1 atomic% Bi ions.



Fig. S4 (a) XRD patterns of the CuSCN/Sb<sub>2</sub>S<sub>3</sub> composite prepared at different concentrations of CuSCN/DMF solution: 0.002, 0.01, 0.08 mol/L; (b) XRD analysis using MDI Jade 6 of the CuSCN/Sb<sub>2</sub>S<sub>3</sub> composite prepared at the concentrations of CuSCN/DMF solutionof 0.08 mol/L. The peaks marked with asterisks (\*) are the diffractions of  $\beta$ -CuSCN (006) and (012) planes with interplanar spacings of 5.4868 and 3.2974 Å, respectively, which are consistent with the PCPDF standard data (PCPDF# 73-1855).



**Fig. S5** *I*–*t* measurements of the temporal photoresponse of the CuSCN/Sb<sub>2</sub>S<sub>3</sub> composite photodetectors to (a) the torch light of APPLE iphone 7s and (b) 365 nm UV light (3 mw/cm<sup>2</sup>).



Fig. S6 Wavelength-dependency of IPCE spectra of the  $CuSCN/Sb_2S_3$  photodetectors. The measurements were performed under the illumination of 300 W xenon lamp without an applied bias.



**Fig. S7** (a,b) *I–V* and *I–T* curves under the white light illumination for the photodetector made of the CuSCN/Sb<sub>2</sub>S<sub>3</sub> composite that was prepared by using 0.5 mmol/10 mL CuSCN/DMF solution; (c,d) TEM characterization of the above the CuSCN/Sb<sub>2</sub>S<sub>3</sub> composite, from which it is observed that the large amount of CuSCN tiny nanocrystals or clusters cover the surface of Sb<sub>2</sub>S<sub>3</sub> NRs.