## Low-cost solution-processed digenite Cu<sub>9</sub>S<sub>5</sub> counter electrode for dye-sensitized solar cells

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> a) b) Cu 2P S 2P raw -raw sum 162.70 sum Cu<sup>+</sup> 931.9 bg bg peak Intensity (a.u.) peak Cu Intensity (a.u.) 161.59 peak 2 peak Cu<sup>2</sup> Cu<sup>2+</sup> 932.85 158 160 162 164 166 168 928 930 932 934 936 938 Banding Energy (eV) Binding Energy (eV)

Fig. S1. (a) and (b) The Cu 2p and S 2p XPS spectrum of Cu<sub>9</sub>S<sub>5</sub> film on FTO substrate.



Fig. S2. EDS elemental mappings of Cu<sub>9</sub>S<sub>5</sub> film on FTO substrate.



Fig. S3. (a) FE-SEM image of Pt CE on FTO substrate; (b) AFM image of Pt CE on FTO substrate.



**Fig. S4.** Cyclic voltammograms for  $Cu_9S_5$  electrode (red line), Pt electrode (black line). (a) cobalt complex-based electrolyte in acetonitrile solution of 20 mM  $Co(bpy)_3(PF_6)_2$ , 5 mM  $Co(bpy)_3(PF_6)_3$ , and 100 mM  $LiClO_4$ ; (b) iodine-based electrolyte in acetonitrile solution of 10 mM LiI, 1 mM I<sub>2</sub>, and 100 mM  $LiClO_4$ ; (c) 50 cycles of CV for as-prepared  $Cu_9S_5$  electrode. The counter electrode was a Pt wire and the reference electrode was Ag/AgNO<sub>3</sub>. The scan rate was 50 mV s<sup>-1</sup>.



**Fig. S5.** Nyquist plots of the prepared Pt CEs in a symmetric sandwich cell configuration with  $[Co(bpy)_3]^{2+/3+}$  and  $I^-/I_3^-$  based electrolytes.



Fig. S6. Tafel-polarization curves of the prepared  $Cu_9S_5$  electrode in a dummy cell with  $[Co(bpy)_3]^{2+/3+}$  and  $I^-/I_3^-$  based electrolytes



**Fig. S7.** Photocurrent density-voltage (*J-V*) curves of DSSCs Pt electrode with  $[Co(bpy)_3]^{2+/3+}$  and  $I^{-}/I_3^{-}$  based electrolytes measured under AM 1.5G simulated sunlight (100 mW cm<sup>-2</sup>) and in the dark.