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Ligand-Free Nano-Grain Cu_2SnS_3 as a Potential Cathode Alternative for Both Cobalt and Iodine Redox Electrolyte Dye-Sensitized Solar Cells

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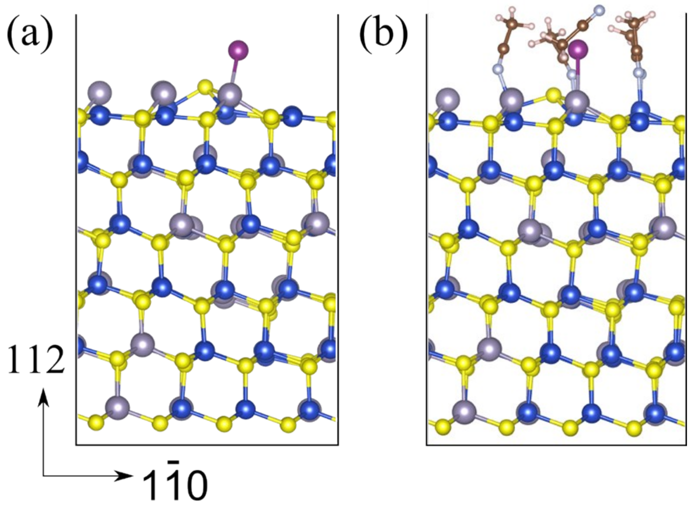

Figure S1. Geometry structure of the adsorption configuration of (a) one I atom with the most strong adsorption (E^{I}_{ad} = -0.95 eV), and (b) the I adsorption configuration together with five around CH_3CN molecules (E^{I}_{ad} = -0.79 eV) on the tetragonal Cu_2SnS_3 (112) surface slab model as examples. The blue, gray, and yellow balls represent the Cu, Sn, and S atoms, respectively. The purple, cyan, brown, and white balls are I, N, C, and H, respectively.

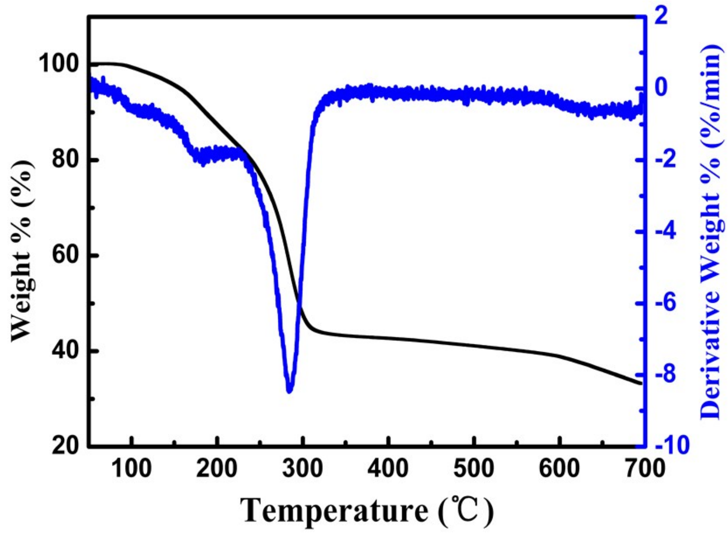

Figure S2. TGA trace of CTS solid precursor, obtained by pre-drying solution at 120 °C. Conditions: 60 mL min^{-1} nitrogen, ramp 10 °C min^{-1} to 500 °C.

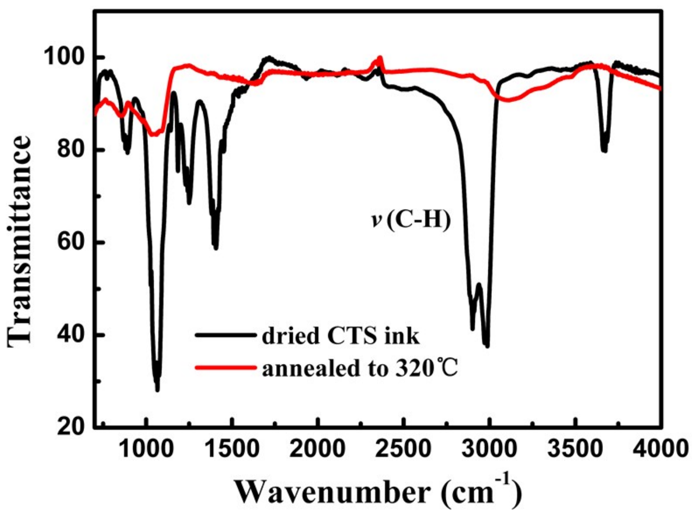

Figure S3. FT-IR spectra of the CTS ink dried to 120 °C for 10 min and after annealing to 320 °C. It was clear that the strong features associated with the *v*(C-H) stretching bands originating from the organic species in the dried films were greatly reduced after annealing to 320 °C, indicating the significant elimination and/or decomposition of the organic species from the dried solid.

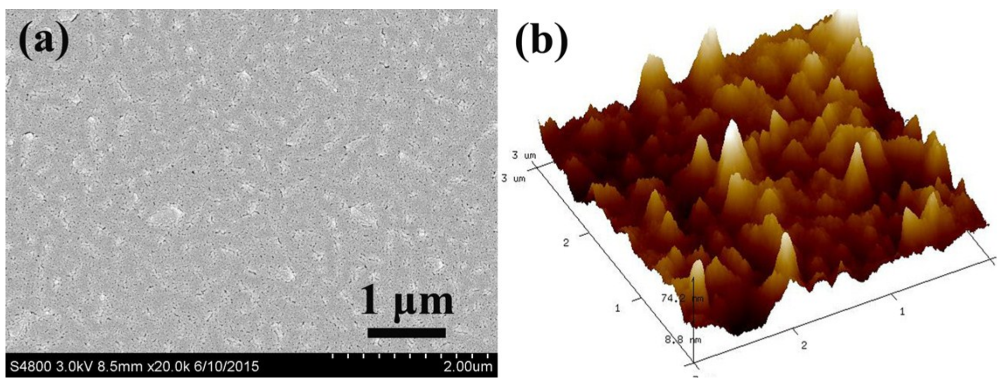

Figure S4. (a) Low-magnification surface SEM image and (b) AFM image of 3 μm by 3 μm surface area of the CTS thin film.

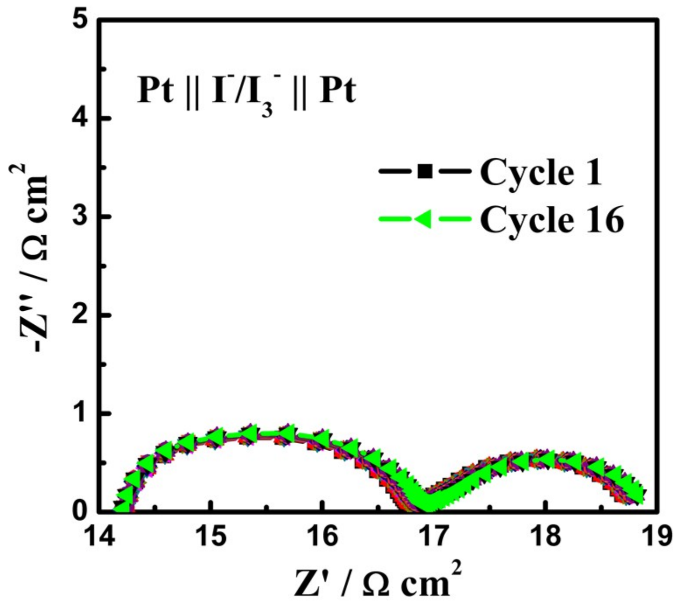

Figure S5. Nyquist plots of EIS for Pt symmetrical cells in iodine electrolyte. This sequential electrochemical test was repeated 16 times.

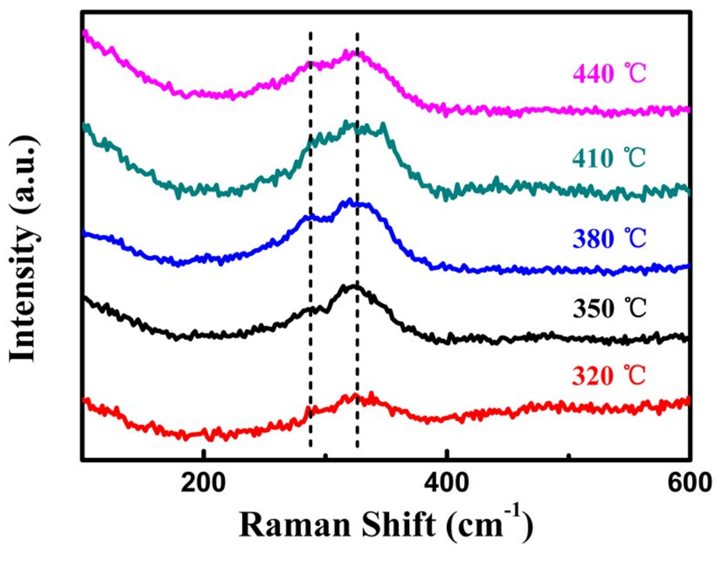

Figure S6. Raman spectra for the sample annealed at different final temperatures of 320 °C, 350 °C, 380 °C, 410 °C, and 440 °C.

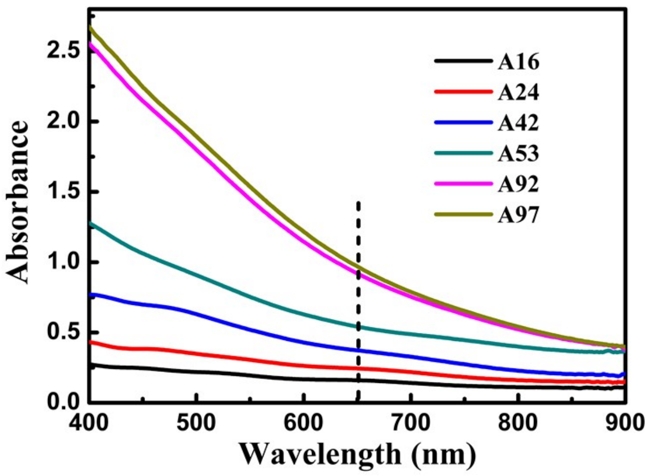

Figure S7. Optical absorbance of CTS films. A16, A24, A42, and A53 electrodes were prepared by spin-coating (3000 rpm, 30s) 0.05, 0.07, 0.1, 0.2 M precursor solution on a FTO glass, respectively, with a heat-treatment at 380 °C. A97 was obtained by drop-casting 0.1 M precursor solution with the same heat-treatment at 380 °C. A92 was obtained by twice spin coating/sintering 0.2 M solution on a FTO glass with the same heat-treatment at 380 °C.

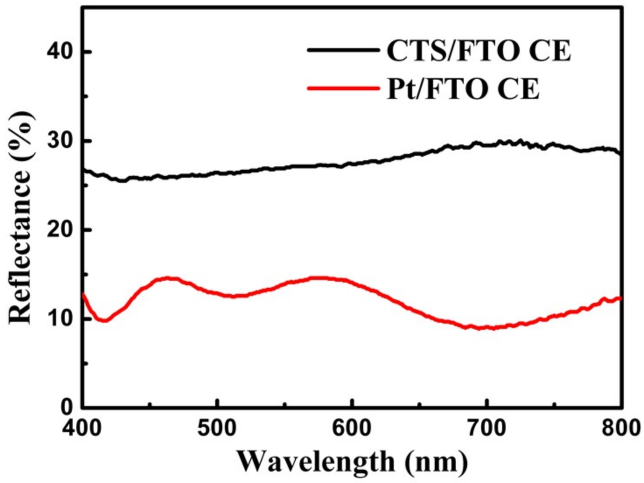

Figure S8. Reflectance of CTS and Pt thin film on FTO glass.

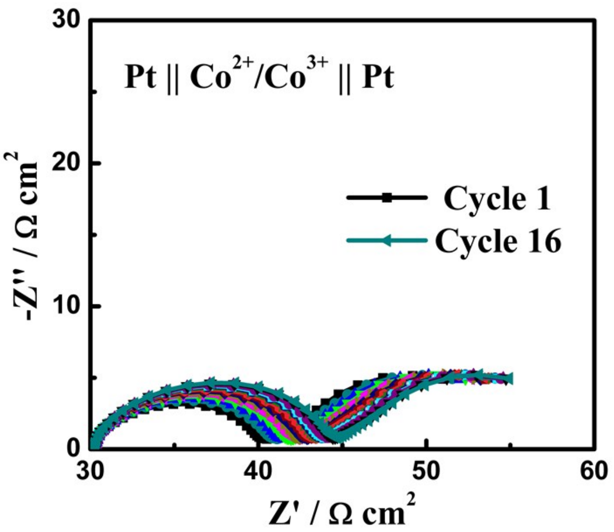

Figure S9. Nyquist plots of EIS for Pt symmetrical cells in cobalt electrolyte. This sequential electrochemical test was repeated 16 times.

Table S1. The adsorption energy and site (on Cu or Sn) of one iodine atom of all the adsorbed configurations.

Config.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
E_{ad}^{I} /eV	-0.95	-0.87	-0.85	-0.83	-0.82	-0.75	-0.72	-0.72	-0.71	-0.67	-0.66	-0.64	-0.61	-0.60	-0.60	-0.50
site	Sn	Sn	Cu	Cu	Sn	Cu	Cu	Cu	Cu	Sn	Cu	Sn	Cu	Cu	Cu	Cu

Table S2. The adsorption energy and site (on Cu or Sn) of one CH_3CN molecule on the tested adsorbed configurations. The adsorption energies are calculated according to:

$$E_{ad}^{CH_3CN} = E_{tot}(CH_3CN_{(N)}\,/\text{surface}) - E_{tot}(CH_3CN_{(N-1)}\,/\text{surface}) - \frac{1}{2}E_{tot}(CH_3CN,\text{gas})\,.$$

Here, $E_{tot}(CH_3CN_{(N)}/\text{surface})$, $E_{tot}(CH_3CN_{(N-1)}/\text{surface})$, and $E_{tot}(CH_3CN, \text{gas})$ are the energies of N CH_3CN molecule(s) adsorbed on the Cu_2SnS_3 surface system, the surface with the N-1 number of adsorbed CH_3CN molecules, and CH_3CN in the gas phase, respectively. In this table, N=1, without iodine together.

Config.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
E_{ad}^{I} /eV	-0.50	-0.48	-0.48	-0.44	-0.42	-0.42	-0.41	-0.41	-0.39	-0.38	-0.31	-0.18	-0.17	-0.16	-0.14	-0.12
site	Cu	Cu	Cu	Cu	Cu	Sn	Cu	Cu	Cu	Cu	Cu	Sn	Sn	Sn	Sn	Sn

Table S3. The adsorption energy and number (N) of CH_3CN molecules referring to the lowest energy I adsorption configuration with (N-1) CH_3CN molecules. There are five Cu sites around iodine atom in this I adsorption configuration. The corresponding E_{ad}^{I} energies are also presented.

N	$E_{ad}^{CH_3CN}$	E_{ad}^{I}
1	-0.78	-1.25
2	-0.66	-1.25
3	-0.45	-1.14
4	-0.46	-1.09
5	-0.39	-0.79