1. XPS results

The XPS survey spectrum in Fig. S1 reveals that the obtained sample consists of Cu and S. The binding energies of all spectra were corrected by referencing the C1s value of 284.6 eV. The high-resolution XPS spectra of Cu 2p and S 2p region are shown in figure 1b and 1c. The spectrum of the Cu 2p signal reveals that the binding energy of Cu 2p_{3/2} and Cu 2p_{1/2} is 932.5 eV and 952.2 eV. The sulfur 2p peaks are located at 162.7 eV, which are consistent with the 160-164 eV range expected for S in sulfide phase.\(^1\)

Fig. S1 (a) XPS survey spectrum; (b) and (c) high-resolution XPS spectra of Cu 2p and S 2s.
2. Size distribution

![Size distribution graph](image)

**Fig. S2** Size distribution of (a) the rattle type structure and (b) the core.

3. The reaction between the centrifugated solution and Fe$^{3+}$

The centrifugated solution obtained at 6 hours turn into red for the formation of [Fe(SCN)$_x$]$^{3-x}$. When Fe$^{3+}$ was added into it

![Solution before and after Fe$^{3+}$](image)

**Fig. S3** Digital photo of the solution before and after Fe$^{3+}$ added.

4. The effect of anions
Fig. S4 XRD pattern and SEM image of intermediate obtained at 4 h with (a and b) CuSO₄, (c and d) CuCl₂·2H₂O.

5. SEM evolution process

Fig. S5 SEM image of the evolution process of Cu₁.₈ RTS after (a) 1 h, (b) 6 h and (c) 1 day reaction.
6. Optoelectronic device

Fig. S6 (a) sketch map of setting for photocurrent measurement; (b) SEM image of the prepared Cu$_{1.8}$S film.

References