Supplementary Materials

A wide temperature solid-state Li-S battery enabled by plasmon-enhanced copper-silicon nanowire photothermal current collector

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Figure S1. The photo of the solar photothermal solid-state Li-S battery based on the Cu-Si NWs photothermal current collector.

Fig. S1 shows the photo of the soft-pack solar photothermal solid-sate lithium-sulfur (SPT Li-S) battery where the black copper-silicon nanowires (Cu-Si NWs) photothermal current collector is used to harvest solar and convert it into heat to improve the charge transmission and storage in electrolyte/electrodes at extreme temperatures, especially extreme-low temperatures. The preparation process of the soft pack solid-sate Li-S battery is as follows. First, we paste the quartz glass (3*3*0.2cm) on the perforated side (the diameter of the hole is about 0.8cm) of the aluminum plastic film to form an optical window. Subsequently, the SPT Li-S battery was packaged with the Cu-Si NWs photothermal current collector, metal lithium anode, the solid electrolyte based on the PEO and LAGP, and the SKB composite cathode coated on the surface of Al foil. As showed in Fig. S1, the black Cu-Si NWs photothermal current collector with a quartz optical

window is used to harvest solar energy and convert it into heat, and the nickel tab is used as the anode electrode lead lug.

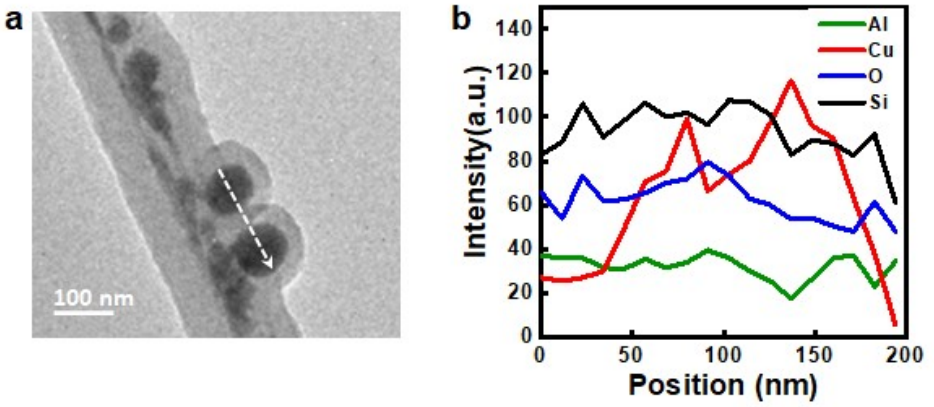
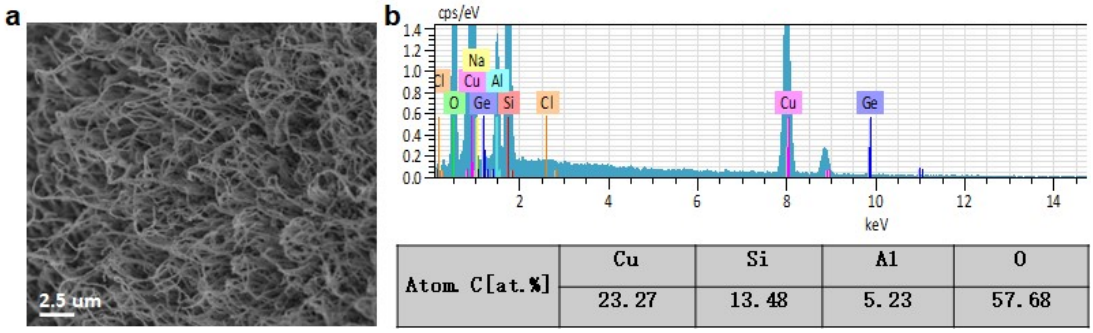


Figure S2. High-resolution TEM (HRTEM) of Cu-Si nanoparticles assembled on Cu-Si nanowire and corresponding EDS line scan analysis.

Fig. S2 shows the high-resolution TEM of hierarchical Cu-Si NWs photothermal current collector. A typical structure that Al_2O_3 coated Cu-Si nanoparticles and Cu-Si nanowire are further demonstrated by the EDS line scan analysis along the while line in HRTEM.



Atom. C[at.%]	Cu	Si	Al	O
	23.27	13.48	5.23	57.68

Figure S3. SEM and EDS of the Cu-Si NWs photothermal current collector. (a) SEM of the Cu-Si nanoparticles assembled on Cu-Si nanowire and corresponding distribution of surface elements (b).

The SEM and EDS shown in Fig S3 determined the structure and distribution of surface elements of the Cu-Si NWs photothermal current collector. The uneven size of Cu-Si nanoparticles was caused by the preparation technology. First, copper oxide nanowires (CuO NWs) were directly prepared on the copper foam substrates by a thermal oxidation process. Then, the amorphous silicon (a-Si) film was coated on the CuO NWs to form CuO/a-Si core-shell nanowires in a PECVD system. Subsequently, the Cu-Si nanoparticles was formed during the reduction process of the copper oxide inside the CuO/a-Si core-shell nanowire under an H_2 atmosphere. The uneven size of Cu-Si nanoparticles was caused by the non-uniform diameter of the CuO NWs in the thermal

oxidation process and non-uniform heat distribution and gas flow in the surface and internal of the sample during the reduction process. In particular, the structure of the hybrid Si-Cu nanoparticles was formed due to the uneven size, which enhanced the light absorption and light-to-heat conversion properties of the current collector.

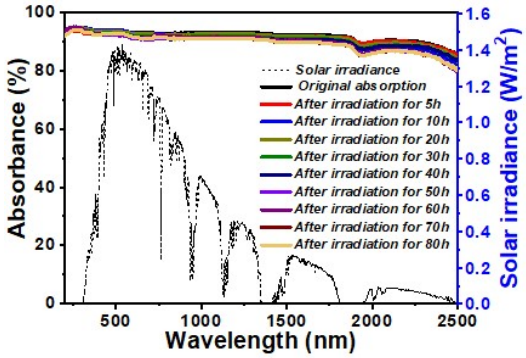


Figure S4. Solar energy absorption spectrum of the Cu-Si NWs photothermal current collector during 80 h solar irradiation (Xe-lamp, 16 kW m^{-2}).

Fig. S4 shows the solar absorption spectrum of the Cu-Si NWs photothermal current collector at a concentrated solar irradiation (16 kW m^{-2}) where the light absorption spectrum of the Cu-Si NWs membrane is tested after 5h, 10h, 20h, 30h, 40h, 50h, 60h, 70h and 80h solar irradiation, respectively. The absorption efficiency of the current collector is ~93% at the initial stage and slightly decreases during high concentrated solar irradiation (16 kW m^{-2}). After 80h solar irradiation, the current collector still demonstrates a high solar absorption (to 91% at 200 nm to 2500 nm) and a high retention of solar absorption efficiency to 98% that indicates a stable and robust solar harvest ability of our copper-silicon photothermal current collector.

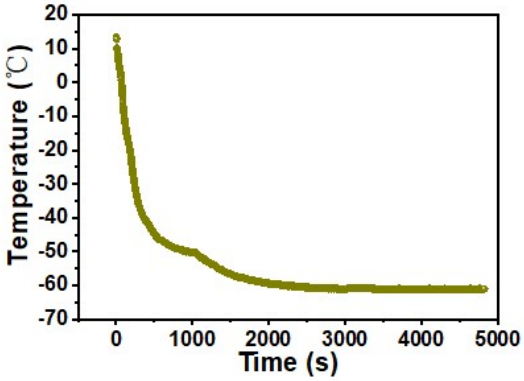


Figure S5. The internal time-temperature curve of the solar photothermal solid-state Li-S battery.

As showed in Fig. S5, the temperature around the battery decreased rapidly in the low-temperature test setup based on the dry ice. The temperature around the battery decreased from 15°C to -30°C in 200 seconds and -60°C in 1500 seconds, and remained stable with the test time

increased.

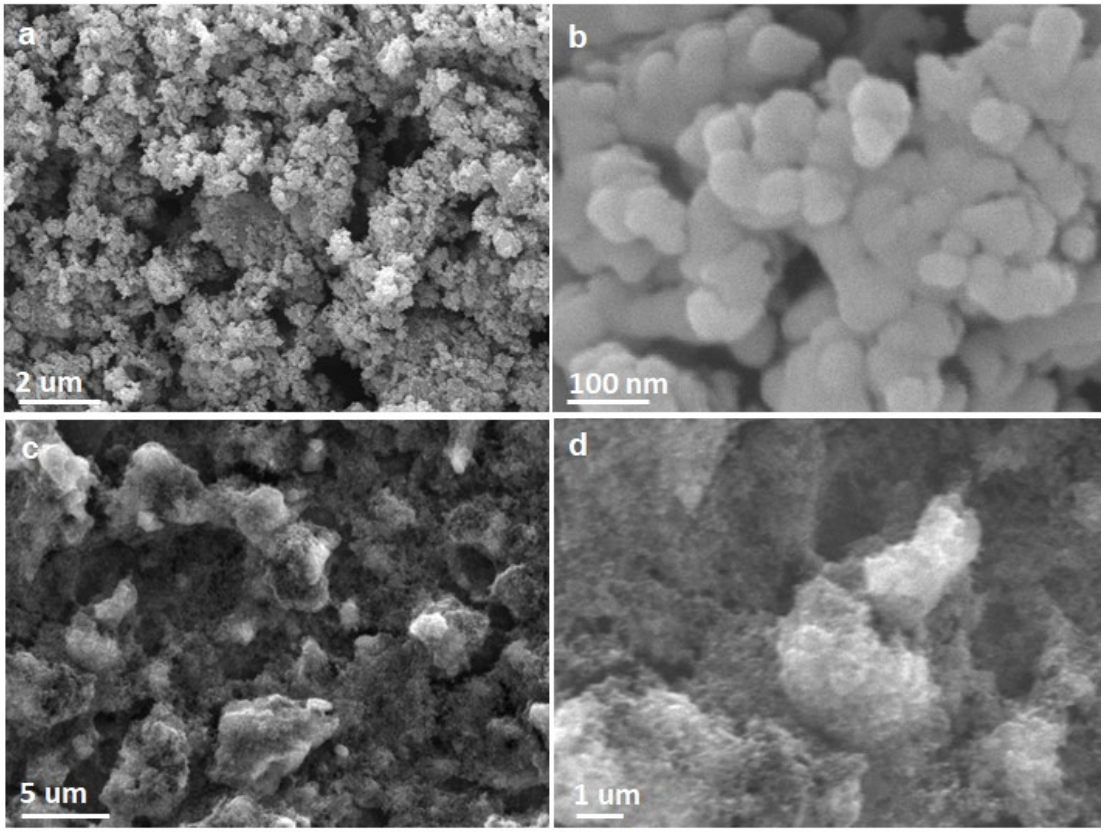


Figure S6. (a, b) SEM image of the prepared SKB composite sulfur cathode powder. (c, d) The SKB composite cathode coated on Al foil.

As showed in Fig. S6, the sulfur (S) can be effectively combined with Ketjenblack (KB) to obtain SKB composite sulfur cathode after grinding and heating. The mass ratio of sulfur in the composite SKB powder is ~68.1% calculated by thermogravimetric analysis. The cathode is porous structure that can relieve the volume expansion of sulfur cathode during cycles.

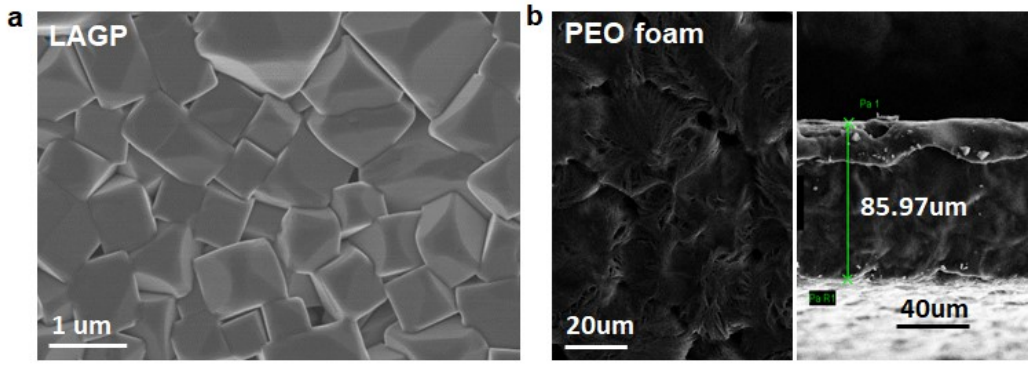


Figure S7. (a) SEM image of the prepared LAGP solid electrolyte. (b) SEM image of the prepared PEO/LiTFSI/Al_2O_3 solid electrolyte.

As showed in Fig. S7, the crystalline grain size of the LAGP solid electrolyte ranges from ~500 nm

to 2.5 µm, and the thickness of the prepared PEO film is about 86 µm.

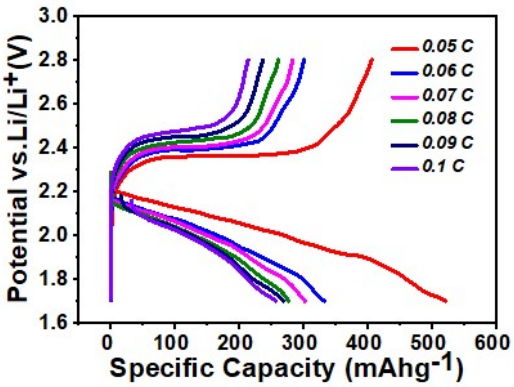


Figure S8. Electrochemical performance of the SSLi-S battery using copper foil current collector at different current density of 0.05C, 0.06C, 0.07C, 0.08C, 0.09C and 0.1C.

Electrochemical performance of the Li-S battery using copper foil current collector based on LAGP electrolyte at high current density were shown in Figure S5. At room temperature, the discharge capacity of the Li-S battery using copper foil current collector gradually increased from ~500 mAh g^{-1} to ~250 mAh g^{-1} when the charge-discharge rate is gradually increased from 0.05C to 0.1C. The Li-S battery using Cu-Si NWs photothermal current collector also showed the same trend of charge-discharge performance.

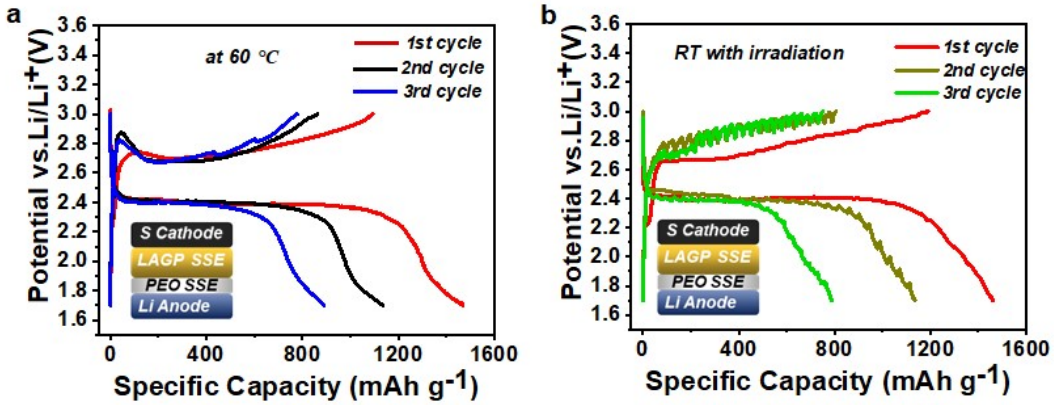


Figure S9. The cycling performance of solid Li-S batteries based on the solid electrolyte composited with PEO/LiTFSI/Al_2O_3 and LAGP and Cu-Si NWs photothermal current collector at room temperature with simulated solar irradiation (a, Xe-lamp, 5 kW m^{-2}) and 60℃ (b) at 0.05C.

The cycling performance of solid Li-S batteries based on the solid electrolyte composited with PEO/LiTFSI/Al_2O_3 and LAGP and Cu-Si NWs photothermal current collector are studied as a typical representative. As showed in Figure S9, The SPT Li-S battery at room temperature with simulated solar irradiation (~5 kW m^{-2}) exhibits a similar discharge/charge behavior compare to the battery at 60℃ in the high temperature system. This indicates that the Cu-Si NWs photothermal current

collector can provide an effective energy supply for the SPT Li-S battery operating at room temperature. However, the discharge and charge stability of the SPT Li-S battery is greatly affected by the irradiation light source, which is also the work that needs to be studied in the future.

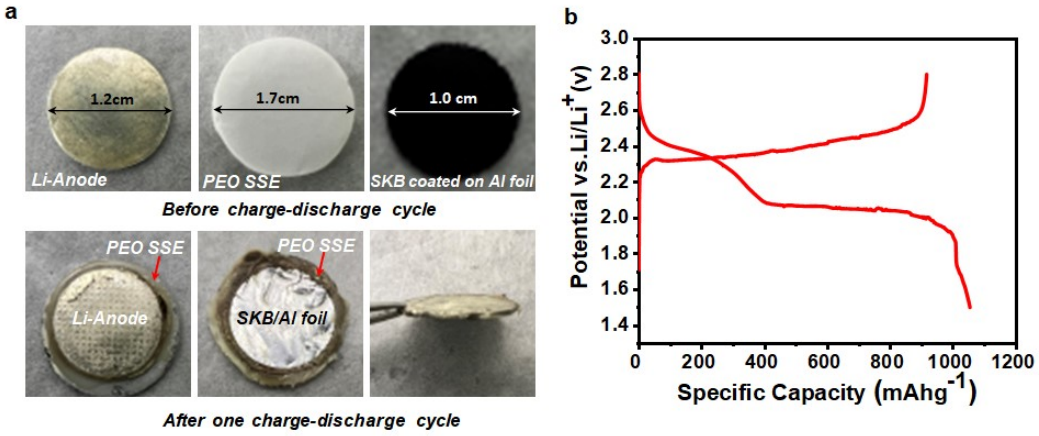


Figure S10. The interface state between electrode and electrolyte before and after one charge-discharge cycle.

As showed in Figure S10, the SPT Li-S battery based on PEO SSE was used as a representative to characterize the interface state between Li-Anode and PEO SSE before and after one charge-discharge cycle. During the discharge and charging process of the SPT Li-S battery, the solar-thermal current collector absorbed sunlight and converted it into heat to maintain a high temperature of about 60 °C inside the battery. Under this temperature condition, the PEO solid electrolyte was converted from a solid film to a gel state, and the metal Li anode and the SKB cathode were tightly bonded together.