Electronic Supplementary Information

Solar-driven capacity enhancement of aqueous redox batteries with vertically-oriented tin disulfide array as both photo-cathode and battery anode

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Materials and Methods

Preparation of the SnS$_2$ photoelectrode and Super P electrode

The tin disulfide grown on the titanium mesh was prepared by a simple hydrothermal method. In a typical process, 0.7g SnCl$_4$·5H$_2$O and 0.75g thioacetamide were dissolved in 75 mL of anhydrous ethanol and kept stirring for 1 hour to achieve a homogeneous solution. Then, the titanium mesh was washed by ultrasonication in acetone, water and ethanol for 30 min in sequence. The solution and the titanium mesh (wound into a cylinder) above were transferred into a Teflon-lined autoclave and maintained at 180 °C for 12 h. The final mesh products were washed with water and ethanol several times, and then dried in a 60 °C oven over night. The Super P electrode was prepared by mixing the Super P carbon with polyvinylidene fluoride (PVDF) in a weight ratio of 8:2, and the prepared slurry was then cast on a titanium mesh.

Assembly and preparation of the PEARB

The system of PEARB mainly included the SnS$_2$@Ti mesh ‖ anolyte (Na$_2$S$_4$) / Nafion 117 membrane / catholyte (NaI) ‖ Super P@Ti mesh. The anolytes with different concentrations were configured on basis of 1 M Na$_2$S$_4$ aqueous solution which prepared as following steps: 1 M Na$_2$S·9H$_2$0 was first dissolved in a 10 mL DI water and kept stirring to achieve a homogeneous solution, and then 3.2 M sulfur (Wako) was added into above solution. Finally, the solution was kept stirring for 5 hours in a water bath at 80 °C. The Nafion 117 membrane was purchased from Aldrich. First, membranes were treated with 5% H$_2$O$_2$ under 80 °C for 1 h and then were transferred to 5% H$_2$SO$_4$ at 80 °C for 1 h. Finally, 1 M NaCl aqueous solution was used to change the H-type (i.e., proton conductive) Nafion membranes to Na+-type (i.e., Na+ conductive) under 80 °C for 2 h. The cell configuration is H-shaped, which composed of cylindrical quartz bottles. The anolyte and catholyte are injected in an environment that is insulated from air.

Electrochemical and photoelectrochemical measurements

Cyclic voltammogram tests of iodide and polysulfide were conducted using a graphite rod as the counter electrode and an Ag/AgCl electrode as the reference electrode by a CHI760E workstation (CH Instruments, USA). All subsequent three-electrode tests were performed using Ag/AgCl electrode as the reference electrode and graphite rod as the counter electrode (LSV and *I-t* curves). The galvanostatic characterizations of the PEARB were conducted on battery testing system (LAND, CT2001A, Wuhan LAND electronics Co., Ltd). The light source used for the illumination is a Xe-lamp (Perfect Light PLS-SXE 300), and the illumination intensity during the measurement was adjusted to 50 mW cm^{-2}. It is worth noting that all the electrode areas are 1 cm^2 (photoelectrode and Super P electrode) in the whole measurements.

Characterization

Morphologies and elements mapping of samples were inspected using a Scios FEI Scanning Electron Microscopy (SEM). Detailed structures of products were obtained by

a Tecnai G2 F20 S-TWIN Transmission Electron Microscopy (TEM) with an accelerating voltage of 200 kV, which is also capable of imaging in Scanning Transmission Electron Microscope (STEM) mode. X-ray diffraction (XRD) patterns of as-synthesized materials were recorded using a Bruker D8 Advance Diffractometer. The X-ray photoelectron spectroscopy (XPS) spectra were obtained using an Escalab 250Xi Spectrophotometer. And the UV-vis absorption spectroscopy was obtained by a Lambda 750S Spectrophotometer.

Supporting Figures and Table
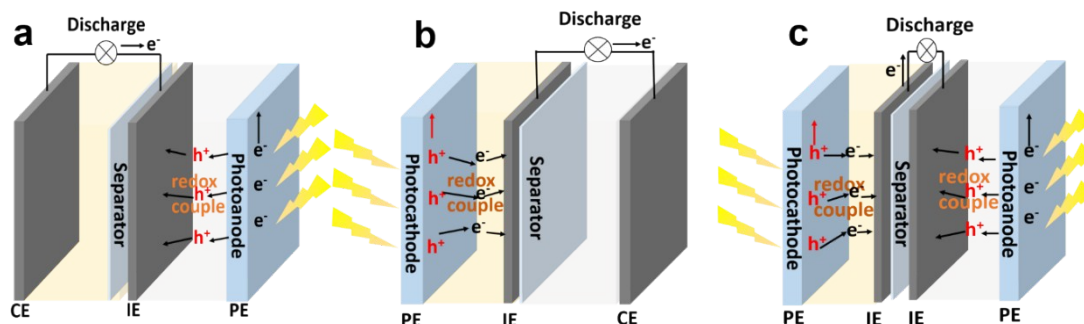
Fig. S1 (a) The typical three-electrodes configuration of photo-assisted redox battery with photo-anode and photo-cathode (b) (PE: photo-electrode, CE: counter-electrode, IE: insert-electrode). (c) The typical four-electrodes configuration of photo-assisted redox battery with photo-anode and photo-cathode simultaneously.

The typical working process of type *a* can be described as follows: in the photo-charging process, the photogenerated electrons and holes are separated under illumination. Then, the photogenerated holes (photoanode) oxidize catholyte ions on the PE and the photogenerated electrons flow to the CE. Finally, reversible redox reaction occurs on the IE and CE for catholyte and anolyte ions in the discharging process. Type *b* functions in the same fashion as type *a* except that it uses photogenerated electrons (photocathode) to reduce the ions on the PE and the photogenerated holes flow to the CE. Type *c* is the simultaneous use of photogenerated holes (photoanode) and electrons (photocathode) to oxidize and reduce ions in the solution, respectively. During the discharging process, the two IEs are connected.
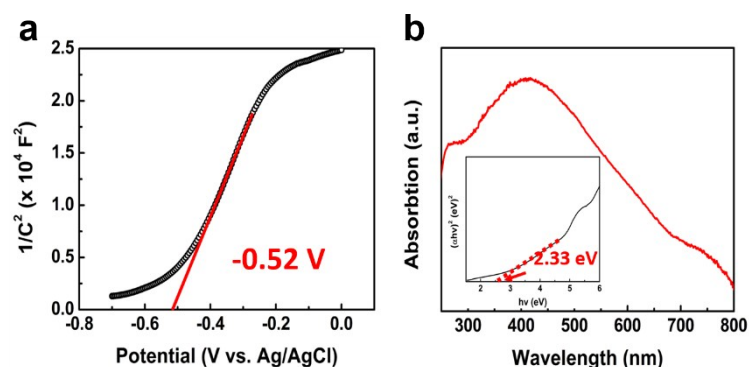
Fig. S2 (a) Mott-Schottky plot in 0.5 M Na_2SO_4 solution (SnS_2@Ti mesh, Ag/AgCl, and graphite rod are used as WE, RE, and CE, respectively in a three-electrode system). (b) UV-vis absorption spectrum (800-250 nm) of SnS_2 powders which were dispersed in ethanol.

Mott-Schottky plot is a quite common method of testing semiconductor flat band potential. There exist reports on employing the flat band potential as the CB potential.[1] In fact, when the semiconductor is in contact with the solution, the band will bend, and the measured flat band potential is slightly lower than the CB potential.[2] In other words, the CB position of SnS_2 is more negative than -0.32 V vs. NHE. From the energy diagram, the more negative CB position means higher reductive activity of photo-generated electrons. Therefore, it is thermodynamically feasible for photo-generated electrons to reduce polysulfides.
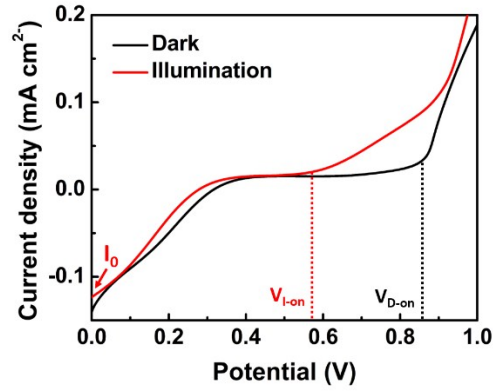
Fig. S3 LSV curves in a two electrode PEARB with SnS_2 as an anode and Super P as a cathode (0.15 M NaI and 0.03 M Na_2S_4).

The red line is under illumination and the black line is at dark. Obviously, the oxidation current density I_0 is < 0 mA cm^{-2} when the potential is = 0 V, which means the battery cannot be charged under illumination without bias voltage. Actually, there are many reasons, such as the recombination of the photogenerated electrons and holes, the recombination of so-called back electron or holes, and the polarization of reaction ions on the surface of electrodes.[3] All of these reasons would cause the actual test results inconsistent with the theoretical scenario. However, some effects about energy band bending has been found. For example, the potential starting to oxide under illumination V_{I-on} is more negative than V_{D-on} (at dark). The more negative starting potential reveals the positive effects of illumination.
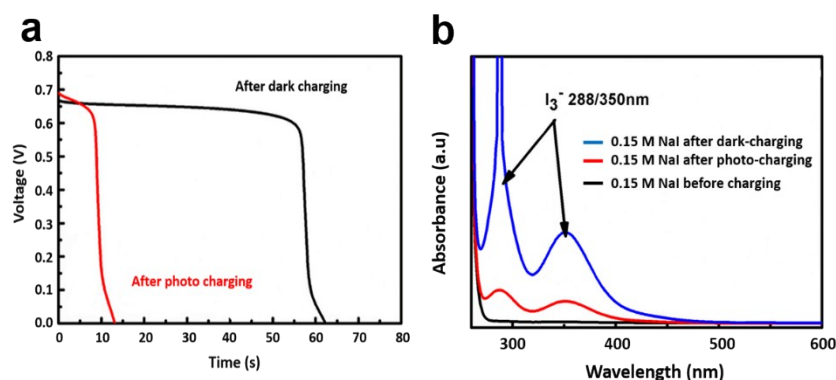
Fig. S4 (a) Galvanostatic discharging curves at a same current density after a 1 V potentiostatic charging for the identical period. Note that the SnS_2 photoelectrode was immersed into a NaI electrolyte. (b) UV-vis absorption spectra of NaI electrolyte after charging at different conditions (black: before charging; red: after photo-charging; blue: after dark-charging).

It is well accepted that an n-type semiconductor has usually been used as a photoanode to offer photo-induced holes with advanced activity rather than electrons. However, there have been reports on employing n-type semiconductor as a photocathode (e.g., for TiO_2: *J. Catal. 2017, 349, 1-7*),[4] which indicates that the tendency to use the photo-generated holes or electrons really depends upon the investigated systems (configurations, electrolytes, *etc.*) and could indeed vary from case to case. To examine whether our SnS_2, as an n-type semiconductor, is prone to hole-active or electron-active in our PEARB system, we firstly had a shot on inserting the SnS_2 electrode into sodium iodide electrolyte, with the obtained charge/discharge curve shown in Fig. S4a. Under 1 V potentiostatic charging for the same period, it is evident that the discharging time under illumination (red) is much shorter than that in dark (black). In addition, to further probe the evolution of I_3^- ions within the system under illumination and in dark, UV-Vis absorption spectra were collected after photo-charging and dark-charging, respectively (Fig. S4b). It can be observed that the concentration of I_3^- decreases after photo-charging, thereby implying that the photo-generated electrons of SnS_2 reduce the I_3^- to I^- (the external charging has oxidized I^- to I_3^-). This serves as a direct evidence that the photo-generated electrons exhibit higher activities to compete against photo-generated holes. In turn, the illumination had a positive effect when the SnS_2 electrode was placed in polysulfide electrolyte, where highly active photo-generated electrons of SnS_2 enables the reduction of polysulfides to achieve the capacity enhancement. Overall, it could be concluded that such SnS_2 plays a photocathode role in our specific system. Further investigation pertaining to this aspect is currently ongoing in our lab.
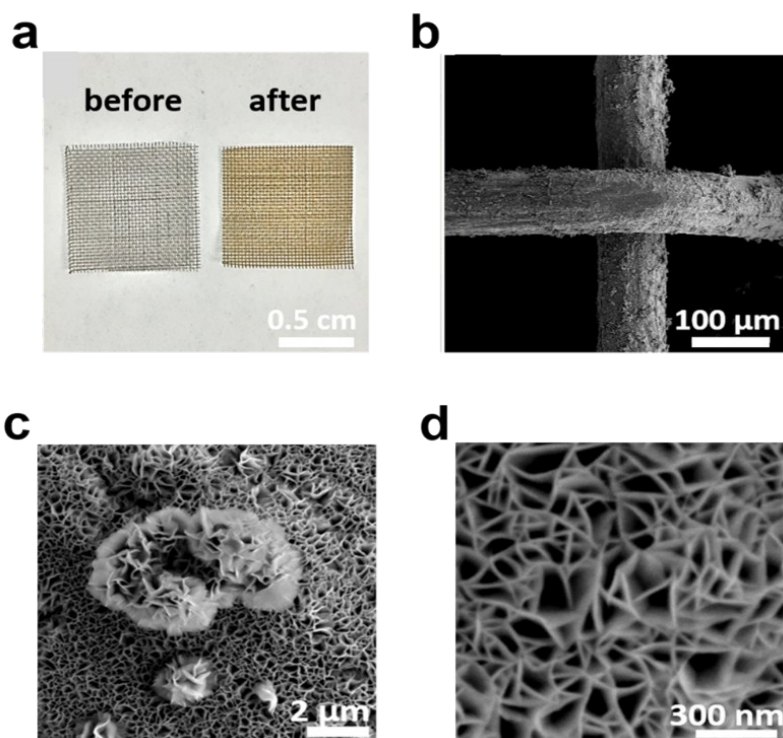
Fig. S5 (a) The digital photographs of new Ti mesh (before) and SnS_2@Ti mesh after hydrothermal reaction (after). (b-d) SEM images of SnS_2@Ti mesh at different magnifications.
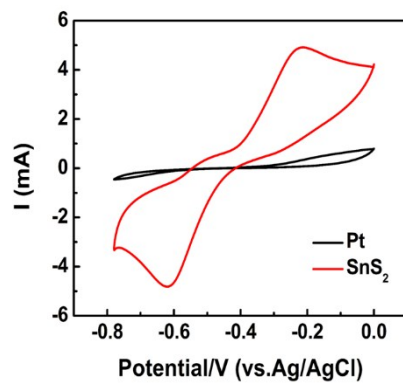
Fig. S6 CV profiles of SnS$_2$ (red color) and metal Pt (black color) in 0.005 M Na$_2$S$_4$ and 0.5 M NaOH solution with a three electrodes system (Scan rate: 10 mV s^{-1}).
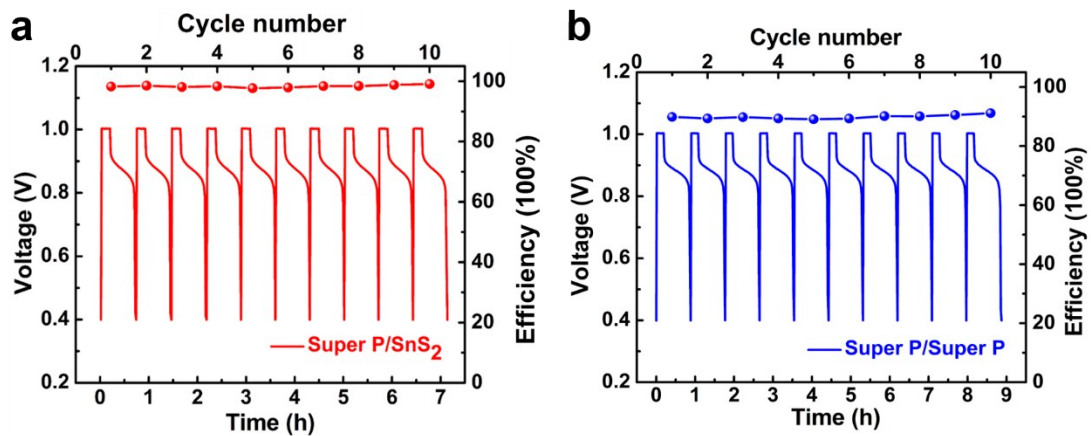
Fig. S7 (a) Charge and discharge cyclic performance at 1 V potentiostatic charge and 0.05 mA cm^{-2} galvanostatic discharge with Super P carbon as cathode and SnS$_2$ as anode in an iodine/polysulfide redox battery. (b) Cyclic performance under the same condition with Super P carbon serving as both anode and cathode.
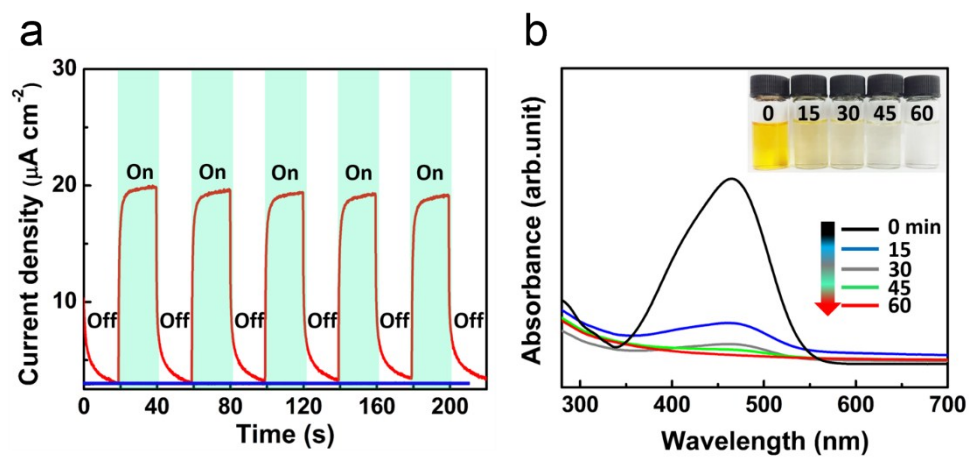
Fig. S8 (a) Photocurrent response of $SnS_2@Ti$ in 0.5 M Na_2SO_4 solution at 0.2 V versus Ag/AgCl reference electrode (the illumination interval was 20 s; the blue line represents the photocurrent response of pure Ti mesh). (b) Photodegradation activities to methyl orange (MO) with different illumination time (the inset picture shows the solution color corresponding to different illumination time).
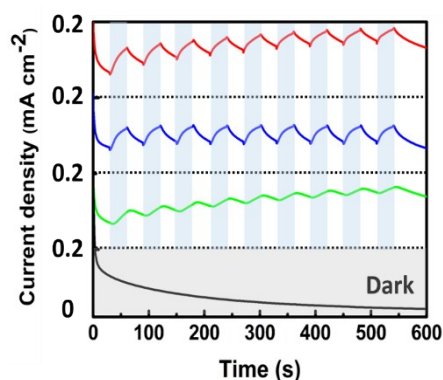
Fig. S9 Current curves under 1 V potentiostatic charge with illumination chopping in a PEARB (the red line is under illumination, the blue line is under illumination with no heat, the green line is under heat without light, the black line is in dark).

The red line is chopping curve under illumination which is produced by the combination of light and heat. Moreover, the curves under illumination without heat and under heat without light have been tested (blue and green). Obviously, the curve (under illumination without heat) is consistent with our experiment. However, the heat also has a positive effect on our PEARB. The main reason is the ions diffuse faster under heat and polarization resistance becomes smaller. In summary, the light is the main factor driving current change and heat has positive effects on the PEARB.
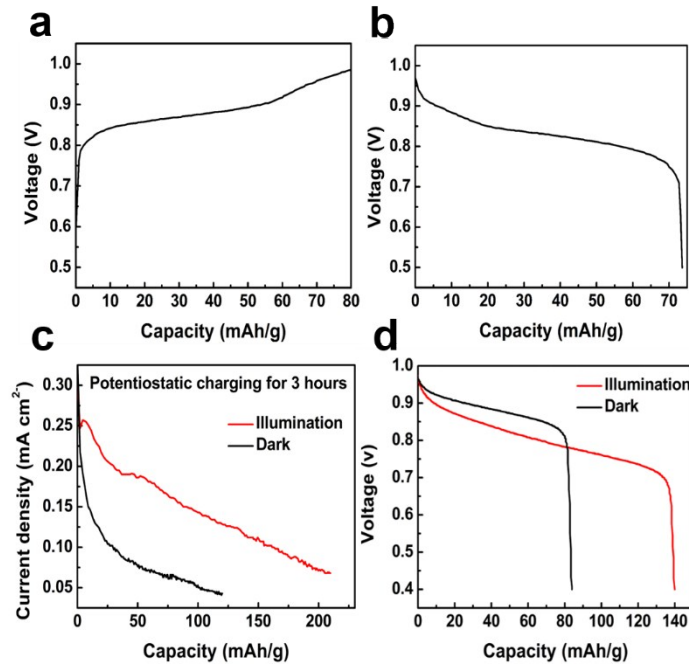
Fig. S10 Charge and discharge capacity curves of a relevant redox battery (a-b: Super P carbon electrode is used as both of cathode and anode, 0.005 M NaI+0.5 M NaCl / 0.03 M Na_2S_4) and a PEARB (c-d: the red line is under illumination and the black line is in dark). It is evident that the specific capacity of PEARB is 140 mAh g^{-1} under illumination and 85 mAh g^{-1} in dark.

The photo-electron conversion efficiency is calculated using the following formula:

$$\eta = \frac{E(photo) - E(dark)}{Pt(solar\ light)}$$

where E(photo) is the discharging energy under illumination; E(dark) is the discharging energy in dark at the same charging condition. P represents the incident intensity of sunlight in the system, and t is the illumination time.

E(photo) = 140 mAh g^{-1}*0.005*149.89*4*10-3*1=0.42 mWh

E(dark) = 85 mAh g^{-1}*0.005*149.89*4*10-3*1=0.25 mWh
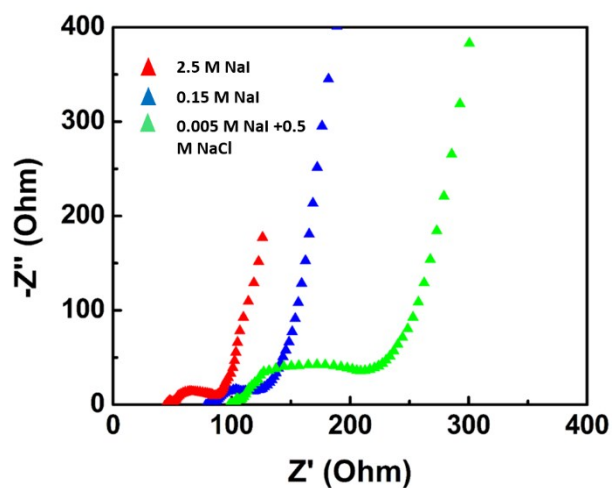
P = 50 mW cm^{-2}

t = 3 h

η = 0.11%

Fig. S11 Electrochemical impedance spectroscopy of a PEARB with different concentrated NaI (2.5 M, 0.15 M, and 0.005 M + 0.5 M NaCl) and identically concentrated Na_2S_4 (0.03 M).

The resistance increases with the concentration reducing. The main reason is that the transportable ions are reduced, which increases the resistance of the solution. Although NaCl has been added into our catholyte, the number of active ions remains unchanged. Therefore, the large resistance can explain that the Coulomb efficiency (in Fig. S10) is lower than Fig. S7.
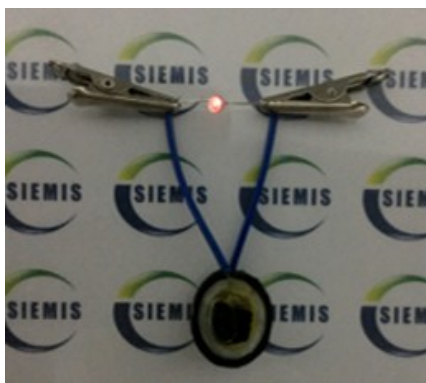
Fig. S12 A proof-of-concept demonstration of a PEARB after photo-charging (powering a red light-emitting-diode (LED) indicator *via* connection in series).

References.

1.   G. Zhang, Z. A. Lan, L. Lin, S. Lin and X. Wang, *Chem. Sci.*, 2016, **7**, 3062-3066.

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