Electronic Supplementary Information

High-Quality Ultralong Copper Sulphide Nanowires for Promising Applications in High Efficiency Solar Water Evaporation

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EXPERIMENTAL SECTION

Chemicals. Oleylamine (OM, 70%, Sigma-Aldrich), CuCl (99.99%, Sigma-Aldrich), sodium diethyldithiocarbamate (NaDDTC, 99%, Sigma-Aldrich), ethanol (AR) and cyclohexane (AR) were used as received without further purification.

Synthesis of High-Quality Ultralong $Cu_{2-x}S$ NWs. For synthesis of ultralong $Cu_{2-x}S$ NWs, 1.0 mmol of copper (I) chloride (CuCl) was added to 10.0 ml of oleylamine (OM) in a three-necked flask (50 mL) at room temperature. The slurry was heated to 130 °C in a vacuum for 60 min to take water and oxygen away and then form an optically transparent solution. Then, the sodium diethyldithiocarbamate (NaDDTC) dispersion formed by ultrasonication of 2.5 mmol of NaDDTC powder in 6.0 ml OM at room temperature and was quickly injected into the aforementioned

solution at 260 °C. The resulting mixture was kept at 260 °C for 15 min, and it turned into greyblack color. After it cooled to room temperature, the ultralong $Cu_{2-x}S$ NWs were precipitated through adding ethanol and collected by centrifugation at 8500 rpm for 10 min. The as-formed ultralong $Cu_{2-x}S$ NWs were easily dispersed in nonpolar organic solvents (such as toluene, cyclohexane). The yields of the obtained ultralong $Cu_{2-x}S$ NWs sample were ca. ~95%.

Fabrication of the Double-Layer Configuration (Ultralong Cu_{2-x}S NWs/Melamine Foam). 200 mg of ultralong Cu_{2-x}S NWs (a length up to tens of micrometers) was dispersed well in 20 mL cyclohexane, under the assistance of ultrasonic bath. The dispersed mixture was deposited on the melamine foam. The ultralong Cu_{2-x}S NWs with a length up to tens of micrometers could easily wrap around the framework of melamine foam to form the double-layer configuration. The performed double-layer configuration was placed in the oven and the temperature was kept at 60 °C for 30 min. After cooling down, the double-layer configuration was stored in a Petri dish for further use.

Characterizations. TEM images were acquired by a Hitachi HT-7700 transmission electron microscope (TEM, Japan) operating at 100 kV. High-resolution TEM (HRTEM) micrographs were obtained with a Philips Tecnai F20 FEG-TEM (The USA) operated at 200 kV. Samples for TEM analysis were prepared by drying a drop of cyclohexane solution containing the nanomaterials on the surface of a carbon-coated copper grid. The XRD patterns were obtained using a Rigaku D/MAX-RB with monochromatized Cu K α radiation (λ =1.5418 Å) in the 2 θ ranging from 20° to 80°. X-ray photoelectron spectra (XPS) were conducted using a PHI Quantera SXM instrument equipped with an Al X-ray excitation source (1486.6 eV). Binding energies (BEs) are referenced to the C 1s of carbon contaminants at 284.6 eV. The Fourier Transform Infrared was recorded on a Nicolet 6700 FT-IR spectrometer. The UV-Vis-NIR absorption spectra were measured on a

Perkin-Elmer Lambda 35UV-vis spectrophotometer. The IR photographs were taken by a Fluke VT04A Infrared Camera. The salinity was assayed by inductively coupled plasma spectroscopy (ICP-OES, IRIS Advantage, Thermo Scientific, 0.1 mg L^{-1} in accuracy).

Water Evaporation. The water evaporation by the double-layer configuration (ultralong Cu₂. _xS NWs/melamine foam) was tested in a 25 mL beaker with an interior diameter of 3 cm. The beaker was wrapped with thermal insulation and stored on an electronic balance to measure the mass of evaporated water. For each cycle, the beaker was filled with 25 mL of distilled water, and the double-layer configuration floated on the water surface. A 300 W Xenon lamp (Perfect Light PLS-SXE300UV, China) was used to simulate the solar irradiance and the aperture diameter was adjusted to be the same as the double-layer configuration. The light intensity is ~1000 W m⁻² to ~8000 W m⁻², which was measured by a PL-MW2000 Photoradiometer calibrated reference. The spectral output was measured with a StellarNetInc spectrophotometer. After certain time intervals, the weights of water in the container were recorded. The thermal efficiency η can then be defined as follows: ^[1]

$$\eta = \frac{\dot{m}h_{LV}}{C_{opt}P_0} \quad (1)$$

In which \dot{m} denotes the mass flux, $h_{\rm LV}$ is the total enthalpy of the liquid-vapor phase change. $C_{\rm opt}$ refers to the optical concentration and P_0 is the nominal solar irradiation power of 1 kW m⁻².

The analysis of heat loss. The heat loss of the solar evaporation device consists of three parts: (a) radiation, (b) convection, and (c) conduction.

a. Radiation:

The radiation loss can be calculated by the Stefan-Boltzmann equation.

$$Q_{\rm rad} = \varepsilon A \sigma (T_1^4 - T_2^4) \qquad (2)$$

Where Q_{rad} denotes heat flux, ε is the emissivity (It is assumed that the absorber has a maximum emissivity of 0.97), A is the surface area (7.065 cm²), σ is the Stefan-Boltzmann constant (5.67×10⁻⁸ W m⁻² K⁻⁴), T_1 is the average surface temperature (≈41 °C) of absorber at steady state condition, and T_2 is the ambient temperature (≈26 °C) upward the absorber under the illumination of 8 Sun solar flux. According to equation (2), the radiation heat loss is calculated to be ~1.1%.

b. Convection:

The convective heat loss is defined by Newton' law of cooling.

$$Q_{\rm conv} = h A(T_1 - T_2) \qquad (3)$$

Where Q_{conv} represents the heat energy, and *h* is the convection heat transfer coefficient (set as 5 W m⁻² K).^[2-7] According to equation (3), the connection heat loss is calculated to be ~0.9%. c. Conduction:

$$Q_{\rm cond} = Cm\Delta T \qquad (4)$$

Where Q_{cond} is the heat energy, *C* is the specific heat capacity of water (4.2 kJ °C⁻¹ kg⁻¹), *m* is the water weight (12 g), and ΔT is the average increased bulk water temperature after 1 h illumination of 8 Sun solar flux (≈ 10 °C). According to equation (4), the conduction heat loss is calculated to be ~2.4%.

First-Principles Calculations. The electronic structure calculations were performed by using the density-functional theory as implemented in the CASTEP code. The electronic structures were studied by using the hybrid function based on the HSE exchange. In the HSE calculation, the structural optimization of electronic self-consistent interactions was performed using a plane-wave cut-off energy of 450 eV, and a Γ -centered Monkhorst-Pack k-point mesh of $1 \times 1 \times 1$ for a conventional unit cell of Cu_{1.75}S.



Figure S1. XRD pattern of ultralong Cu_{2-x}S NWs.



Figure S2. The X-ray photoelectron spectroscopy (XPS) spectra of (a) Cu 2p and (b) S 2p for the ultralong Cu_{2-x}S NWs. As shown in Figure S2a, the Cu 2p peaks at 931.4 eV and 951.2 eV corresponded to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, revealing an oxidation state of Cu⁺.^[8, 9] Figure S2b depicted the S 2p spectrum, where the two peaks of 161.3 eV and 162.9 eV were attributed to S $2p_{3/2}$ and S $2p_{1/2}$, respectively, suggesting the S²⁻ in the ultralong Cu_{2-x}S NWs.^[8]



Figure S3. TEM images of the as-obtained ultralong $Cu_{2-x}S$ NWs product *via* reacting different mole ratios of two precursors in OM (16.0 ml) at 260 °C for 15 min: (a) CuCl (1.0 mmol)/NaDDTC (1.0 mmol) = 1/1; (b) CuCl (1.0 mmol)/NaDDTC (2.0 mmol) = 1/2; (c) CuCl (1.0 mmol)/NaDDTC (3.0 mmol) = 1/3.



Figure S4. TEM images of the as-obtained ultralong Cu_{2-x}S NWs product *via* reacting 1.0 mmol
CuCl and 2.5 mmol NaDDTC in OM (16.0 ml) at different temperatures for 15 min: (a) 120 °C,
(b) 160 °C, (c) 200 °C, (d) 240 °C.



Figure S5. Room temperature UV-Vis-NIR absorption spectrum of ultralong $Cu_{2-x}S$ NWs (black line) and the spectral irradiance of AM 1.5G solar spectrum (blue line).



Figure S6. The melamine foam (a) and the double-layer configuration (ultralong $Cu_{2-x}S$ NWs/melamine foam) (b) floating on top of the water surface.



Figure S7. Fourier transform infrared (FTIR) spectra (Nicolet 6700) of oleylamine and asprepared ultralong $Cu_{2-x}S$ NWs dispersed in cyclohexane. The presence of acyclic C–H stretching at 2926 and 2854 cm⁻¹ indicate the existence of oleylamine. The peaks at 1567 and 1467 cm⁻¹ are assigned to C=C stretch, implying the C=C ligand exists on the NWs surface, and the sharp peak at 1054 cm⁻¹ is indexed to C–N stretch of oleylamine. Based on the FTIR analysis of ultralong $Cu_{2-x}S$ NWs, it is confirmed that NWs are possibly coated by organic molecules, oleylamine. ^[10,11].



Figure S8. Time course contact angles of the hydrophobic double-layer configuration (ultralong Cu_{2-x}S NWs/melamine foam).



Figure S9. Optical photograph of the ultralong $Cu_{2-x}S$ NWs, the $Cu_{2-x}S$ NPs, carbon nanotube and reduced graphene oxide (rGO) coating on the melamine foam.



Figure S10. SEM images of (a) the ultralong $Cu_{2-x}S$ NWs, (b) the $Cu_{2-x}S$ NPs, (c) carbon nanotube and (d) rGO coating on the melamine foam.



Figure S11. (a) Room temperature UV-Vis-NIR absorption spectrum of ultralong $Cu_{2-x}S$ NWs and $Cu_{2-x}S$ NPs. (b) The spectral irradiance of AM 1.5G solar spectrum (black line) and the irradiance absorbed by ultralong $Cu_{2-x}S$ NWs (red line) and $Cu_{2-x}S$ NPs (blue line).

Table S1. Solar water evaporation based on the hydrophobic double-layer configuration (ultralong $Cu_{2-x}S$ NWs/melamine foam) in this work compared with other materials and designs under one Sun.

Sample	Hydropathy	Evaporation rate (kg/m² h)	Efficiency (%)	Ref.
Carbon based DLS	All-hydrophilic	1.2	64	12
Ti ₂ O ₃ NP	All-hydrophilic	1.32	-	13
Carbonized mushroom	All-hydrophilic	1.475	78	5
GO with 2D water path	All-hydrophilic	1.45	80	14
Porous N-doped graphene	N-doping enhance the wettability	1.5	80	15
GDY/CuO	All-hydrophobic	1.55	91	16
Carbon-coated paper	hydrophilic	1.28	88.6	17
Ultralong Cu _{2-x} S NWs/melamine foam	hydrophobic /Hydrophilic nanoporous double layer	0.96	66.83	This work

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