(Supporting Information)

# Chalcogenide Solution-Mediated Activation Protocol for Scalable and Ultrafast Synthesis of Single-Crystalline 1-D Copper Sulfide for Supercapacitor

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## **Experimental Section**

### Material Synthesis

Before sulfur activation, the copper substrates were cleaned with a combination of acetone, alcohol, and distilled water. The entirety of the cleaned copper substrate were directly immersed into the ammonium sulfide solution followed by 10 min of static soaking without any heat treatment in a lab environment at 25 °C. Finally, the copper electrode was washed with distilled water several times. For the roll-to-roll process, the cleaned copper substrate was placed on the roll-to-roll machine and systematically immersed into an ammonium sulfide solution before washing with distilled water.

#### **Characterization**

The nanostructure and crystal structure of the copper sulfide electrodes were characterized using scanning electron microscopy (SEM, Hitachi S-4300), transmission electron microscopy (TEM, JEOL JEM-2200MCO FEGTEM), and high-resolution X-ray diffraction (XRD, Rigaku Medel Smartlab) over a two-theta range of 10-80°. X-ray photon electron spectroscopy (XPS) was conducted using a Thermo Scientific K-Alpha XPS instrument equipped with a micro-focused monochromatic Al X-ray source. The XPS spectrometer was adjusted to align to a binding energy of 284.5 eV for the C 1s line.

## Electrochemical Test

The electrochemical performance of the electrodes was tested in a three-electrode configuration consisting of the sample as the working electrode, a saturated Ag/AgCl electrode as the reference electrode, and a Pt mesh as the counter electrode in a 1.0 M KOH electrolyte. These electrodes were used to analyze cyclic voltammetry (CV, within the range of 0.0-0.6 V),

galvanostatic charge/discharge (GCD, within the range of 0.0-0.5 V), and electrochemical impedance spectroscopies (EIS, in the range of  $10^{-2}$  to  $10^{5}$  Hz) curves using a potentiostat (PGSTAT302N, Metrohm, Autolab). To remove the dissolved oxygen from the KOH solution and to minimize the oxidation damage of the Cu<sub>2</sub>S electrode, we flush the solution with Ar gas before and during the electrochemical test. The AC electrode was constructed by using the active carbon as the anode material, poly (vinylidene difluoride) as the binder, and Ketjen black as the conductive material. This solution was coated onto a compressed Ni foam as the current collector. To design the ASC with the ideal capacitance, the mass of the individual electrodes is optimized according to the following formula.

$$Q_{+} = Q_{-} \rightarrow \frac{m_{+}}{m_{-}} = \frac{C_{-} * \Delta V_{-}}{C_{+} * \Delta V_{+}}$$

where *C*. (~225 F g<sup>-1</sup> at a scan rate of 1.67 A g<sup>-1</sup>) and *C*<sub>+</sub> (~625 F g<sup>-1</sup> at a scan rate of 1.67 A g<sup>-1</sup>) are the calculated capacitance of the negative and positive electrodes, respectively, and  $\Delta V_{-}$  (1.0 V) and  $\Delta V_{+}$  (0.6 V) are the operating potential windows of the negative and positive electrodes, respectively. Therefore, on the basis of *C*. (Active Carbon, (AC)) and the potential window of the AC electrode, the optimum loading ratio of SC-Cu<sub>2</sub>S to AC is 1:1.67.

The Formation mechanism and detailed reaction equations for the Cu<sub>2</sub>S electrode.

It is known that the destabilization of Cu resulting in its corrosion leads to the deposition of  $Cu_2S$ , which is formed on the Cu surface by the dissociation of bisulfide ion (HS<sup>-</sup>) from aqueous ammonium sulfide solutions. Specifically, the chemisorbed species of  $Cu(HS)_{ads}$  react with Cu and HS<sup>-</sup> which are from the Cu matrix and the aqueous solution, respectively. This driving force induces the continuous growth of  $Cu_2S$  on the Cu surface. The detailed reaction equations are as follows:<sup>R1-R4</sup>

#### **Bisulfide formation reaction**

 $(\mathrm{NH}_4)_2\mathrm{S} \text{ (aq)} \rightarrow 2\mathrm{NH}_4^+ \text{ (aq)} + \mathrm{S}^{2-} \text{ (aq)}$  $\mathrm{S}^{2-} \text{ (aq)} + \mathrm{H}_2\mathrm{O} \text{ (l)} \leftrightarrow \mathrm{HS}^- \text{ (aq)} + \mathrm{OH}^- \text{ (aq)}$ 

### **Possible formation reaction**

 $2Cu + HS^{-}(aq) + H^{+}(aq) \rightarrow Cu_2S + H_2(g)$ 

Comparative experiments to control the reaction time and the (NH<sub>4</sub>)<sub>2</sub>S concentration.



**Figure S1.** SEM images of the Cu<sub>2</sub>S electrodes synthesized in (a,b) 10 wt%, (c,d) 20 wt%, and (e,f) 40 wt% solution.

First, three different concentrations of the  $(NH_4)_2S$  solution have been employed for the nanostructure growth (10 wt%, 20 wt% and 40 wt%  $(NH_4)_2S$  solutions). The Cu substrates were immersed in each solution for 10 min. As shown in Figure S1, the 20 wt%-Cu<sub>2</sub>S electrode consists of dense 1-D nanorods on the substrate. For the high concentration of 40 wt% solution, there are no 1-D nanostructures on the substrate. Alternatively, for the 10 wt% solution, less dense and smaller nanowires have been synthesized on the substrate. These results might be attributed to the difference in the reactant concentrations being caused by the concentration difference of the  $(NH_4)_2S$  solutions. For example, compared to the 20 wt% solution, the 10 wt% solution is not strong enough to cleave the Cu ion sources (the small amounts of reactants) from the substrate, and the relatively small amounts of Cu<sub>2</sub>S nucleation seeds can be formed.

Conversely, for the 40 wt% solution, the higher activity of the solution can cleave the large amounts of the Cu ions, leading to the relatively large amounts of reactants in the solution. The excessively large amounts of the reactants hinder the formation of the Cu<sub>2</sub>S nanorods with the preferred growth orientation on the Cu mesh substrate. In this regard, the 20 wt% solution was chosen for the comparative reaction time experiments.



**Figure S2.** SEM images of the  $Cu_2S$  electrodes at various growth time in the 20 wt% (NH<sub>4</sub>)<sub>2</sub>S solution.

As shown in Figure S2, the increase in reaction time for the 20 wt% (NH<sub>4</sub>)<sub>2</sub>S solution can produce long and large-diameter Cu<sub>2</sub>S nanorods. After 1 min exposure to the solution (the nucleation stage), the smooth surface of the substrate is converted to a rough surface with many Cu<sub>2</sub>S nucleus seed sites. These seeds are the growth sites for the Cu<sub>2</sub>S nanorods. Increasing the reaction time after the nucleation stage (the growth stage), the length and the diameter of the Cu<sub>2</sub>S nanorods can be increased. After 15 min exposure to the solution, the diameter of the nanorod is about ~1.5  $\mu$ m. The diameters after the 10 min exposure times are too thick for energy storing applications.



**Figure S3.** Cyclic voltammetry of the Cu<sub>2</sub>S electrodes at various growth stages in the 20 wt% (NH<sub>4</sub>)<sub>2</sub>S solution.

Electrochemical tests of the  $Cu_2S$  electrodes at the various growth stages were carried out for the 20 wt% (NH<sub>4</sub>)<sub>2</sub>S solution. As shown in Figure S3, the area bounded by the CV curve of the 10 min-Cu<sub>2</sub>S sample occupies the largest area, indicating the highest value of the electrochemical capacitance. This large CV area might be attributed to the larger surface area of the 10 min-Cu<sub>2</sub>S electrodes. To further demonstrate the cycling stability of the electrodes at the various growth stages, the charge-discharge cycling tests for the 7 min, 10 min and 15 min reaction-time electrodes were carried out.



Figure S4. Cycling stability for the (a) 7 min-, (b) 10 min-, and (c) 15 min-Cu<sub>2</sub>S electrodes at a scan rate of  $10mA cm^{-2}$ .

As shown in Figure S4, the 10 min-Cu<sub>2</sub>S electrode exhibits good cycling stability, retaining up to 95.4% after 5000 cycles at a current density of 10 mA cm<sup>-2</sup>. On the other hand, the 15 minand 7 min-Cu<sub>2</sub>S electrodes exhibit cycling stabilities up to ~ 96.4% and ~ 91.0%, respectively. Due to its single crystalline and 1-D nanostructure architecture, all Cu<sub>2</sub>S electrodes exhibit strong mechanical stability. The slight difference in stability across the electrodes might be due to different diameters of nanorods that form the electrodes; the large diameters nanorods can have a stronger rigidity than the small diameter nanorods. Therefore, from the capacity and mechanical stability results, the 10 min-Cu<sub>2</sub>S electrode appears to exhibit well-balanced electrochemical properties due to the large surface area and a reasonable diameter of the Cu<sub>2</sub>S nanorods to ensure mechanical stability.



**Figure S5.** (a) Cu 2p XPS spectra of SC-Cu<sub>2</sub>S nanoarrays. (b) TEM and EDX mapping images of the SC-Cu<sub>2</sub>S nanoarrays. (c) Auger Cu(LMM) spectrum of the SC-Cu<sub>2</sub>S nanoarrays.

An associated Auger XPS line (Cu LMM) at 569.6 eV shows that Cu of the electrode is in the form of Cu (I) state, which is the typical value for  $Cu_2S$  (Figure S5c).



Figure S6. XPS survey of the Cu<sub>2</sub>S electrode.



Figure S7. CV curves of the  $Cu_2S$  electrode and the bare-Cu mesh electrode.



**Figure S8.** (a) GCD curves of the SC-Cu<sub>2</sub>S electrode. (b) Plots of the peak current as a function of the scan rate for the SC-Cu<sub>2</sub>S electrode. (c) Nyquist plots of the SC-Cu<sub>2</sub>S electrode before and after the 20,000 charge/discharge tests.



**Figure S9.** (a) XRD of the  $Cu_2S$  electrode after the cycling test. (b) S 2p XPS of the  $Cu_2S$  electrode after the cycling test.



Figure S10. SEM images of the SC-Cu<sub>2</sub>S NRs (a) before and (b) after the cycling tests.

Figure S10 shows the SEM images of the SC-Cu<sub>2</sub>S NRs after the cycling tests. It can be clearly shown that the structure of the SC-Cu<sub>2</sub>S is found to be unchanged after the charge/discharge cycling tests without a structural collapse, indicating the high structural integrity of the electrode.



**Figure S11.** Plots of  $\Delta J(J_c-J_a)$  versus scan rate for the Cu<sub>2</sub>S nanostructures.

The surface area accessible to electrochemical reactions can be estimated from the electrochemically active surface area (ECSA).<sup>R5-R6</sup> Initially, the non-Faradic capacitive current was obtained from the linear region of the CV curves,

$$\Delta i_{\rm dl} = C_{\rm dl} \times v$$

where  $\Delta i_{dl}$  (J<sub>a</sub>(anode) – J<sub>c</sub>(cathode)),  $C_{dl}$  is the specific capacitance in the non-Faradaic region, and *v* is the scan rate. We calculated the electrochemically active surface area (ECSA) using the following equation:<sup>R7-R9</sup>

$$ECSA = C_{dl}/C_{e}$$

where  $C_e$  is the specific capacitance of the alkaline electrolyte (0.04 mF cm<sup>-2</sup> for an alkaline electrolyte). By plotting  $\Delta i_{dl}$  at 0.15 V versus Ag/AgCl against the scan rate of 10, 20, 40, 60, and 80 mV s<sup>-1</sup> in 1.0 M KOH, the C<sub>dl</sub> of the Cu<sub>2</sub>S nanorods were estimated as shown in Figure

S11. The calculated  $C_{dl}$  is about 3.94 mF cm<sup>-2</sup>, and the overall ECSA of the Cu<sub>2</sub>S electrode (back bone - 1 cm<sup>2</sup>) is about 98.5 cm<sup>2</sup>.



**Figure S12.** (a) GCD curves of the AC//Cu<sub>2</sub>S ASC. (b) Capacitance retention of the AC//Cu<sub>2</sub>S ASC at a current density of 10 mA cm<sup>-2</sup> when subjected to 5000 charge/discharge cycles.

Figure S12 shows the performance of the AC//SC-Cu<sub>2</sub>S NR ASC. Before assembling the ASC, we designed the AC anode to ensure charge balance with the SC-Cu<sub>2</sub>S NR electrode. Figure S12a presents the GCD curves of the AC//SC-Cu<sub>2</sub>S NR ASC over a potential range from 0.0 to 1.6 V. The high cyclability of the ASC electrode can be strongly attributed to the benefits of the morphological and crystalline properties of the SC-Cu<sub>2</sub>S electrode, which can tolerate charge/discharge cycling tests (Figure S12b). At fast scan rates ( $5 \sim 40 \text{ mA cm}^{-2}$ ), the coulombic efficiency remains at about 100% during cycling. However, at a low scan rate of 2 mA cm<sup>-2</sup>, there is a little coulombic efficiency drop. This is because the overall performance of the Cu<sub>2</sub>S electrode can be attributed to the diffusion-controlled behavior, inducing the sluggish kinetics, and subsequently resulting in the small coulombic efficiency drop.



**Figure S13.** Plots of current density as a function of voltage of the AC//Cu<sub>2</sub>S flexible asymmetric supercapacitor at different bending states and a scan rate of 50 mV s<sup>-1</sup>.



**Figure S14.** Exemplar results of the SC-Cu<sub>2</sub>S nanoarrays grown on (a) foil and (b) wire substrates. (c) Photographs of the roll-to-roll machine and the solution-immersed synthesis on a Cu foil.



**Figure S15.** (a) CV and (b) GCD curves of the SC-Cu<sub>2</sub>S electrode on a Cu foil after the rollto-roll process. (c) Calculated specific capacitance of the SC-Cu<sub>2</sub>S electrode on a Cu foil following the roll-to-roll process. (d) Capacitance retention of a Cu foil after the roll-to-roll process at a current density of 10 mA cm<sup>-2</sup> for 20000 charge/discharge cycles.

Electrode	Capacitance	Rate retention	Stability	Ref
Our work	<b>0.75 F cm<sup>-2</sup></b> @ 2mA cm <sup>-2</sup>	<b>82.3%</b> (2 - 40 mA cm <sup>-2</sup> )	<b>90.5%</b> @ 20000 cycles	
CuS microspheres	0.57 F cm <sup>-2</sup> @ 0.5 A g <sup>-1</sup>	$\begin{array}{c} 75.9\% \\ (0.5-8\mathrm{Ag^{-1}}) \end{array}$	74% @ 3000 cycles	R10
CuS nanorods	0.37 F cm <sup>-2</sup> @ 2mA cm <sup>-2</sup>	71.2% $(2 - 20 \text{ mA cm}^{-2})$	91% @ 2000 cycles	R11
CuS/CNT	0.83 F cm <sup>-2</sup> @ 5 mA cm <sup>-2</sup>	33.2% (5 - 25 mA cm <sup>-2</sup> )	83% @ 1000 cycles	R12
CuS/polypyrrole	$\begin{array}{c} 427 \ \mathrm{F} \ \mathrm{g}^{-1} \\ @ \ 1 \ \mathrm{A} \ \mathrm{g}^{-1} \end{array}$	74.9% (1 – 8 A g <sup>-1</sup> )	88% @ 1000 cycles	R13
CuS nanowires	305 F g <sup>-1</sup> @ 0.6 mA cm <sup>-2</sup>	73.1% (0.6 – 20 mA cm <sup>-2</sup> )	87% @ 5000 cycles	R14
CuS	717.4 F g <sup>-1</sup> @ 1A g <sup>-1</sup>	74.8% (1 – 8 A g <sup>-1</sup> )	83.6% @ 20000 cycles	R15
CuS nanocages	843 F g <sup>-1</sup> @ 1A g <sup>-1</sup>	59.3% (1 – 10 A g <sup>-1</sup> )	89.2% @ 4000 cycles	R16
Nanoporous CuO	1.51 F cm <sup>-2</sup> @ 1 A g <sup>-1</sup>	70.0% (1- 20 A g <sup>-1</sup> )	93% @ 3000 cycles	R17

 Table S1. Electrochemical performance of other copper-based electrodes.



**Figure S16.** (a) Cycling stability and (b) rate retention radar plot comparison for other copperbased electrodes.

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