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### Room-temperature synthesized porous Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> hybrid nanowires as highperformance electrode material for asymmetric supercapacitor

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#### Abstract

Copper-based nanomaterials have attracted significant interest as electrode materials for supercapacitors due to their low cost and environmental friendliness, however, their low capacitances inhibit their commercial applications. Design and application of porous and hybrid 1-D nanostructures as electrode materials is an effective approach to improve their capacitance. In this work, porous Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> hybrid nanowires were synthesized at room temperature using a self-sacrificial template method. They had large surface areas and pore volumes, which provided numerous active sites for faradaic reactions and facilitated fast ion diffusions and electron transports during the charge-discharge processes. The Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowires coated on a nickel foam were used as electrodes without using any conductive agent or binder. Results showed that a high specific capacity of 1610.8 C g<sup>-1</sup> was achieved at a current density of 4 A g<sup>-1</sup> <sup>1</sup>, and a large value of 765.0 C g<sup>-1</sup> was still retained at a higher current density of 30 A g<sup>-1</sup>. An asymmetric supercapacitor assembled using this Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> positive electrode and an active carbon negative electrode demonstrated a high energy density of 48.1 Wh kg<sup>-1</sup> at a power density of 429.3 W kg<sup>-1</sup> and a good cycling stability, suggesting that these porous Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> hybrid nanowires are promising electrode materials for supercapacitors.

Key words: Cu<sub>7</sub>S<sub>4</sub>, Cu(OH)<sub>2</sub>, Porous, Hybrid, Nanowires, Supercapacitor.

#### 1. Introduction

Because of its short charge/discharge time, high power density, excellent cycling stability, safe operation, environmental friendliness and low cost, supercapacitor is regarded as a promising energy storage device and has received tremendous attention in recent years<sup>1, 2</sup>. Recently hybrid supercapacitors<sup>3, 4</sup> which are assembled using a double-layer capacitor electrode and a battery-type electrode, have attracted significant interest. The battery-type electrode can provide a high energy density due to its faradaic reactions<sup>5, 6</sup>. Therefore, many battery-type electrode materials have been investigated, including transition metal oxides and hydroxides (e.g., Co<sub>3</sub>O<sub>4</sub><sup>7, 8</sup>, Co(OH)<sub>2</sub><sup>9</sup>, NiO<sup>10</sup>,  $Ni(OH)_{2}^{11}$ ,  $CuO^{12}$ ,  $Cu(OH)_{2}^{13}$ ,  $Fe_{x}O_{y}^{14}$ ,  $CeO_{2}$ ,  $MnO_{2}^{15, 16}$ ,  $MoO_{3}^{17}$ ), and transition metal chalcogenides (e.g., CoS<sup>18</sup>, Co<sub>9</sub>S<sup>19</sup>, NiS<sup>20</sup>, Ni<sub>3</sub>S<sup>21</sup>, MoS<sup>22</sup>, ZnS<sup>23</sup> and CuS<sup>2, 24</sup>). Among these, copper-based nanomaterials have received considerable attention as high-performance electrode materials for hybrid supercapacitors, and these include  $CuO^{25, 26}, Cu_2O^{27, 28}, Cu(OH)_2^{29, 30}, CuS^{24, 31, 32}, Cu_9S_5^{33}$  and  $Cu_7S_4^{33, 34}$ . They generally have good electrochemical activity, large theoretical capacity and environmental compatibility<sup>35</sup>. In particular, their low cost, abundance and low toxicity are advantageous compared with those of cobalt or nickel-based nanomaterials<sup>36, 37</sup>.

However, these copper-based oxides and hydroxides have low electrical conductivity, which limits their electrochemical capacitances<sup>29, 30</sup>. To overcome this issue, the most commonly adopted approach is to combine the copper-based oxides and hydroxides with advanced carbon nanomaterials. For examples, Pramanik et al<sup>38</sup> reported that the

reduced graphene oxide (rGO) anchored Cu(OH)<sub>2</sub> showed a larger capacitance of 602 F g<sup>-1</sup> than that of the Cu(OH)<sub>2</sub> (419 F g<sup>-1</sup>) at 0.2 A g<sup>-1</sup> in 1 M KOH. However, the low capacitance of carbon nanomaterials will affect the energy density of supercapacitors. Transition metal chalcogenides, with their high theoretical capacitance and metal-like electronic conductivity ( $10^{-3}$  S cm<sup>-1</sup>)<sup>39</sup>, have also been explored to combine with oxides and hydroxides to form hybrid electrode materials for increasing capacitance. For example, Naveenkumar et al<sup>40</sup> prepared CuS/Cu(OH)<sub>2</sub> nanoparticles using a solvothermal method, which showed a higher capacitance of 845.5 F g<sup>-1</sup> at 1 mA cm<sup>-2</sup> than those of Cu(OH)<sub>2</sub> (419.7 F g<sup>-1</sup>) and CuS (738.3 F g<sup>-1</sup>).

It is well known that morphology and microstructure of electrode materials significantly influence their performance. Therefore, exploring various nanostructures of Cu-based hybrid materials with high capacity is desired for the supercapacitor application. In this study, we propose to design porous and hybrid Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowires to achieve good electrochemical performance as the electrode materials for supercapacitors. Firstly, it is well-known that one-dimensional nanostructures (such as nanowires) of the electrode materials can accelerate the transport of electrons and ions along their longitudinal direction. This will reduce the internal resistance and increase their electrochemical performance<sup>41</sup>. Secondly, porous nanostructures can have large surface areas, short ion-transport distance, and more channels for fast electrolyte ion transport. All of these can facilitate the faradaic reactions and achieve the high specific capacitance<sup>42</sup>. Furthermore, the porous structure can withstand the large volume changes during charge-discharge processes, and facilitates the cycling stability of

supercapacitors.

Many methods have been reported to prepare hybrid materials of transition metal chalcogenides and hydroxides, such as hydrothermal process<sup>43</sup>, electrodeposition<sup>39</sup> and chemical bath deposition<sup>44</sup>. However, these synthesis processes are complex, time-consuming and energy-intensive. It is critical to develop a simple and economic process for large-scale preparation of porous Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> hybrid nanowires at room temperature.

In this work, we proposed a fast and facile self-sacrificial template method to develop porous Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowires with a high specific capacity and an excellent rate capability. We then designed an asymmetric supercapacitor (ASC) assembled with Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> and active carbon, and demonstrated that it can achieve a high energy density, power density and good cycling stability.

#### 2. Experimental

#### 2.1 Preparation of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowire electrode



Figure 1. Schematic illustration for the fabrication process of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowire

#### electrode

Fig. 1 illustrates the synthesis processes of porous  $Cu(OH)_2/Cu_7S_4$  nanowire electrode. The [Cu(tu)]Cl·1/2H<sub>2</sub>O (here "tu" means thiourea) precursor was firstly prepared. CuCl<sub>2</sub>·2H<sub>2</sub>O of 2.131 g was dissolved into the mixed solution of 46 mL deionized water and 4 mL ethylene glycol, and then thiourea of 0.163 g was dissolved in another mixed solution of deionized water (46 mL) and ethylene glycol (4 mL). These two solutions were mixed, and the [Cu(tu)]Cl·1/2H<sub>2</sub>O precursor was formed.

After the [Cu(tu)]Cl·1/2H<sub>2</sub>O suspension was placed for 30 hrs. A piece of nickel foam (with a thickness of 1.0 mm and an area of  $1 \times 1$  cm<sup>-2</sup>) was dip-coated in the above suspension, and then dried at 50 °C for 12 hrs in a vacuum oven. Then, it was pressed at a pressure of 10 MPa for about 1 min in order to improve adhesion and avoid shedding of the active material. The thickness of nickel foam was reduced to 0.14 mm. Finally, it was dipped in the 2 M KOH solution for 10 min to obtain the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> electrode.

#### 2.2 Characterizations

Crystalline structures of samples were characterized using X-ray diffraction (XRD, Rigaku D/max-2400, CuK $\alpha$ , 40 kV). Morphology was observed using a scanning electron microscope (SEM, Inspect F50, 20 KV). Nanostructures of the samples were obtained using a high-resolution transmission electron microscope (HRTEM, JEM-2200FS). Dot-mapping of elements (Cu, S, O) in the hybrid nanowires was obtained using an energy-dispersive X-ray spectroscope (EDX). Chemical states of elements (Cu, S, O) on the surfaces of hybrid nanowires were measured using an X-ray photoelectron spectroscope (XPS, Al k $\alpha$ , ESCALAB 250Xi). Nitrogen physisorption apparatus (JW-BK122W, JWGB SCI. TECH.) was used to obtain the N<sub>2</sub> adsorption-desorption isotherms of hybrid nanowires at 77 K. Before N<sub>2</sub> physisorption, the samples were degassed in vacuum at 50 °C for 4 hrs. Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area and Barrett-Joyner-Halenda (BJH) method was used to calculate the pore diameter distribution. The adsorption amount at  $P/P_0$  of 0.99 was used to calculate the total pore volumes (V<sub>total</sub>).

#### **2.3 Electrochemical measurements**

The electrochemical properties were measured using a CHI660E electrochemical workstation. For the three-electrode system, the prepared Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowires on the nickel foam (with a thickness of 0.14 mm and an area of  $1 \times 1$  cm<sup>-2</sup>) and a platinum plate were used as the working electrode and counter electrode, respectively. The reference electrode was a Hg/HgO electrode. The electrolyte was the 2 M KOH aqueous solution.

An asymmetric supercapacitor (ASC) device was composed of a  $Cu(OH)_2/Cu_7S_4$ positive electrode and an active carbon (AC) negative electrode. The electrolyte are an aqueous solution of 2 M KOH. The active carbon (AC) negative electrode was prepared by coating a nickel foam (1.0 ×1.0 cm<sup>-2</sup>) using a slurry, which ware consisted of active carbon (80 wt%), carbon black (10 wt%) and polytetrafluoroethylene (10 wt%) in ethanol. It was pressed at 10 MPa for 1 min. According to the charge balance theory, the mass ratio of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> and active carbon is about 1:10.5 based on the following formula<sup>45, 46</sup>:

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \tag{1}$$

The cycling performance of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC ASC device was measured using a battery test instrument system (CT3001A, LAND Electronic Co. Ltd).

#### 3. Results and discussion



#### 3.1 Material characterization

Fig. 2 XRD spectra of (a) [Cu(tu)]Cl·1/2H<sub>2</sub>O and (b) Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>.

XRD spectra of samples before and after treatment using the KOH solution are shown in Figs. 2a and 2b, respectively. All the diffraction peaks of the precursor shown in Fig. 2a are corresponding to  $(\bar{1}10)$ , (101),  $(\bar{1}20)$ ,  $(\bar{1}02)$ , (121), (112),  $(\bar{2}22)$ ,  $(\bar{2}31)$ ,  $(\bar{1}03)$ , (040) and  $(\bar{3}31)$  of the [Cu(tu)]Cl·1/2H<sub>2</sub>O (JCPDS card No. 53-0121). After treated using the KOH solution, the [Cu(tu)]Cl·1/2H<sub>2</sub>O precursor was changed into black color as illustrated in Fig. 1. The diffraction peaks in the XRD spectrum of Fig. 2b are attributed to Cu<sub>7</sub>S<sub>4</sub> (JCPDS card No. 23-0958) and Cu(OH)<sub>2</sub> (JCPDS card No. 35-0505), meaning that the black product is composed of Cu<sub>7</sub>S<sub>4</sub> and Cu(OH)<sub>2</sub>. Therefore, it is confirmed that the [Cu(tu)]Cl·1/2H<sub>2</sub>O precursor has been successfully transformed into Cu<sub>7</sub>S<sub>4</sub>/Cu(OH)<sub>2</sub> hybrid materials in the KOH solution based on the following chemical equations:

 $4[CuSC(NH_2)_2]Cl \cdot 1/2H_2O + 12OH^- + O_2 + 4H_2O \rightarrow 4Cu(OH)_2 + 8NH_4^+ + 4CO_3^{2-} + 4Cl^- + 4S^{2-}$ (2)

 $28[CuSC(NH_2)_2]Cl \cdot 1/2H_2O + 40OH^- + O_2 + 28H_2O \rightarrow 4Cu_7S_4 + 56NH_4^+ + 62H_2O - 62H_2$ 



Fig. 3 SEM images of [Cu(tu)]Cl·1/2H<sub>2</sub>O and (b) Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>.



Fig. 4 (a, b) TEM images, (c) HRTEM image, and (d) the elemental mapping analysis of  $Cu(OH)_2/Cu_7S_4$  nanowires.

SEM images of [Cu(tu)]Cl·1/2H<sub>2</sub>O precursor and Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanostructure are shown in Fig. 3. Both of them are composed of nanowires. The average diameter of [Cu(tu)]Cl·1/2H<sub>2</sub>O nanowire is ~89.7 nm. Because the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowires were directly transformed from the [Cu(tu)]Cl·1/2H<sub>2</sub>O nanowires using a self-sacrificial template method in the KOH solution, their average diameter did not show significant changes, which is ~79.6 nm.

TEM images shown in Figs. 4a and 4b further prove that the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> has a nanowire structure, which is composed of nanoparticles with an average diameter size of 11.5 nm. In the HRTEM image shown in Fig. 4c, the lattice spacing of 0.26 nm is corresponding to the (002) plane of Cu(OH)<sub>2</sub> crystals, and another lattice spacing of 0.30 nm is corresponding to the (804) plane of Cu<sub>7</sub>S<sub>4</sub>. EDX elemental mapping analysis was conducted to investigate the distributions of Cu, O and S elements in the hybrid nanowires, and the mapping results are shown in Fig. 4d. All the Cu, O and S elements are uniformly distributed in the hybrid nanowires, indicating that these nanowires are composed of uniformly distributed Cu(OH)<sub>2</sub> and Cu<sub>7</sub>S<sub>4</sub> nanocrystals. Furthermore, many nano-pores were found in the hybrid nanowires, and the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowires were formed by the decomposition of [Cu(tu)]Cl-1/2H<sub>2</sub>O precursor in the KOH solution. During decomposition process, the formation of Cu(OH)<sub>2</sub> and Cu<sub>7</sub>S<sub>4</sub> nano-pores in the hybrid nanowires, thus forming many nano-pores in the hybrid nanowires.



Fig. 5 N2 adsorption/desorption isotherms of Cu(OH)2/Cu7S4 hybrid nanowires (inset is the

pore size distributions).

 $N_2$  adsorption/desorption measurement was further conducted to investigate the porosity of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> hybrid nanowires. As shown in Fig. 5, the type-IV adsorption/desorption isotherm indicates that the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> hybrid nanowires have a mesoporous structure<sup>47</sup>. As shown in Fig. 5b, their pore size distributions are ranged from 1.9 nm to 20.5 nm, with a peak value at around 2.1 nm. Mesoporous nanostructure of the hybrid nanowires show large pore volume and large specific surface area, which are 0.2879 cm<sup>3</sup> g<sup>-1</sup> and 102.8 m<sup>2</sup> g<sup>-1</sup>, respectively.



Fig. 6 XPS survey spectrum of  $Cu(OH)_2/Cu_7S_4$  porous hybrid nanowires (a), and the high

resolution XPS spectra of Cu 2p (b), S 2p (c) and O 1s (d).

Fig. 6a shows the XPS survey spectrum of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> hybrid nanowires, and there are peaks of Cu, S and O which can be observed. The high resolution binding energy spectra of Cu 2p is shown in Fig. 6b, which is composed of Cu 2p<sub>3/2</sub> and 2p<sub>1/2</sub> spin-orbit doublets peaks and their satellite ones. Both the peaks of Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  can be deconvoluted into two sub-peaks, which are corresponding to those of Cu<sup>2+</sup> and Cu<sup>+</sup>, respectively<sup>48</sup>. The binding energies at 952.3 and 932.5 eV are assigned to Cu<sup>+</sup>, whereas those at 954.4 and 934.7 eV are assigned to Cu<sup>2+49</sup>. The Cu<sup>+</sup> should come from the Cu<sub>7</sub>S<sub>4</sub>, and the Cu<sup>2+</sup> should mainly come from the Cu(OH)<sub>2</sub>. The core level spectrum of S 2p is shown in Fig. 6c. The binding energies at 161.8 eV and 163.0 eV are corresponding to the S  $2p_{3/2}$  and S $2p_{1/2}$ , respectively. The binding energy at 164.4 eV should be attributed to S–O bonds<sup>50</sup>, which are resulted from the surface oxidation. The peaks of high resolution XPS spectra of O 1s can be deconvoluted into two peaks at the binding energies of 531.8 eV and 533.4 eV, which are corresponding to the lattice oxygen in Cu(OH)<sub>2</sub> crystals and the –OH groups on the surface<sup>51</sup>, respectively. Therefore, the surface of nanowires is consisted of Cu(OH)<sub>2</sub> and Cu<sub>7</sub>S<sub>4</sub>.

 $150 = 5 \text{ mV s}^{-1}$ 

3.2 Electrochemical performance of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> hybrid nanowires



Fig. 7 (a) CV curves of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowire electrode measured at different scan rates,

(b) The logarithm relationship between scan rate (v) and anodic peak current (i)

Cyclic voltammograms (CV) curves of the nanowire electrodes were measured in a KOH aqueous electrolyte at a voltage window of 0~0.7 V. Fig. 7a represents the CV

curves of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowire electrode at different scan rates (5–50 mV s<sup>-1</sup>). For all the CV curves, a pair of anodic and cathodic peaks can be clearly observed within the voltage window of 0.7 V, which can be linked to the following reversible faradaic redox reactions during the electrochemical processes<sup>38, 52</sup>.

$$Cu_7S_4 + OH^- \leftrightarrow Cu_7S_4OH + H_2O + e^-$$
(4)

$$Cu_7S_4OH + OH^- \leftrightarrow Cu_7S_4O + H_2O + e^-$$
(5)

$$2Cu(OH)_2 + 2e^- \leftrightarrow Cu_2O + 2OH^- + H_2O$$
(6)

The redox peak currents are increased with the increasing scan rates in the CV curves, indicating a good reversibility of these faradaic redox reactions. Due to the polarization effect, the anodic peak and the cathodic peak are shifted to higher voltage and lower voltage with the increasing scan rates, respectively<sup>38, 43</sup>. The reaction kinetics can be analyzed from the CV plots based on the relationship of redox peak current of *i* (A) and scan rate of *v* (mV s<sup>-1</sup>) using the following equation (7)<sup>3</sup>:

$$i=av^b$$
 (7)

where a and b are constant. The b value determines the charge storage behavior of electrode materials. When the b values are 0.5 and 1, they are battery-type and capacitive type, respectively<sup>3</sup>. Fig. 7b shows the obtained plot of log *i* vs log *v* for the nanowire electrode. The obtained b value of 0.495 means that the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowires is a battery-type electrode material, indicating that the charge-discharge mechanism is a diffusion-control process<sup>5</sup>.



Fig. 8 (a) GCD curves and (b) specific capacity values of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> electrode at different current densities, (c) Nyquist plots of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> electrode and (d) the corresponding equivalent circuit.

The galvanostatic charge/discharge curves (GCD) of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowire electrode were measured with the maximum voltage of 0.55 V. Fig. 8a shows the GCD curves of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> electrode obtained at different current densities. For all GCD curves, there are clear voltage plateau in the charge-discharge process, which is resulted from the faradic reactions<sup>34</sup>. This further proves the battery-type characteristic of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> hybrid nanowires. The specific capacity of *C* (C g<sup>-1</sup>) can be calculated according to the GCD curves based on the following formula<sup>53</sup>:

$$C = \frac{I \times \Delta t}{m} \tag{8}$$

where I (mA),  $\Delta t$  (s), and m (mg) are the discharge current, discharge time, voltage window and mass of the electrode material, respectively. Due to the unique architecture of porous hybrid nanowires, the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> electrode has a very large specific capacity of 1610.8 C g<sup>-1</sup> at the discharge current density of 4 A g<sup>-1</sup>. Because the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> is a battery-type electrode material, its rate capability is not good enough. Its specific capacity at 30 A g<sup>-1</sup> is ~47.5 % of that at 4 A g<sup>-1</sup>. However, its high specific capacity still remains high at high charge-discharge current densities, which are 1421.4, 1287.2, 1185.0, 1009.5, 894.0 and 765.0 C g<sup>-1</sup> at 6, 8, 10, 15, 20 and 30 A g<sup>-1</sup>, respectively.

The composition and the electrochemical performance of samples prepared in 2 M KOH solution at different reaction temperatures and reaction times were investigated, and the results are summarized in Table S1. Based on the XRD spectra of samples in Fig. S1 of the ESI, the product is identified to be Cu<sub>7</sub>S<sub>4</sub> when prepared at 50 °C, but it is the composite of Cu<sub>7</sub>S<sub>4</sub>/CuS<sub>2</sub> when prepared at 80 °C. Only prepared at room temperature of 25 °C, the product is Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>. The CV, GCD curves and specific capacity values of these samples are presented in Fig. S2, Fig. S3 and Fig. S4. The specific capacity values of samples prepared at 50 °C and 80 °C are 864.0 and 675.0 C g<sup>-1</sup> at 10 A g<sup>-1</sup>, all of which are much less than 1185.0 C g<sup>-1</sup> of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> prepared at room temperature.

The XRD spectra shown in Fig. S5 indicate that the products prepared in 10 and 30 minutes at room temperature are Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>. However, the product prepared in 5 minutes is Cu<sub>7</sub>S<sub>4</sub>. It can be found from the Fig. S6 that the sample prepared in 5 minutes has a specific capacity of 778.0 C g<sup>-1</sup> at 10 A g<sup>-1</sup>, which is much less than 1185.0 C g<sup>-1</sup> of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> prepared in10 minutes. However, the product prepared in 30 minutes showed almost same CV curve, GCD curve and specific capacity value (1176.0 C g<sup>-1</sup>)

with the sample prepared in 10 minutes. Therefore, when the reaction time is longer than 10 minutes at room temperature, phase of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> with a stable capacity can be obtained.

Compared with the other copper-based electrodes reported in literature (e.g. CuO<sup>12, 25</sup>, Cu(OH)2<sup>29, 31</sup> and CuS<sup>32, 48</sup> electrodes), the Cu(OH)2/Cu<sub>7</sub>S<sub>4</sub> nanowire electrode developed in this study has a significantly larger specific capacity as listed in Table 1. Furthermore, the specific capacity of Cu(OH)2/Cu<sub>7</sub>S<sub>4</sub> electrode are also much larger than those of other copper-based hybrid materials, including CuO-SnO<sub>2</sub> reverse cubic heterojunctions<sup>36</sup>, rGO-Cu(OH)2 composite<sup>38</sup>, lotus-like CuO-Cu(OH)2 hybrid material<sup>52</sup>, etc. They all show much smaller specific capacities than that of the Cu(OH)2/Cu<sub>7</sub>S<sub>4</sub> electrode reported in this study.

Table 1. Comparisons of specific capacitance of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowire electrode

Materials	Morphology	Specific capacity	Voltage window (V)	Electrolytes	Ref
Cu(OH) <sub>2</sub>	Nanowire arrays	511.5 F g <sup>-1</sup> at 5 mA cm <sup>-2</sup>	0-0.4	6M KOH	31
3D Cu(OH)2	Nano-flowers	1332 F g <sup>-1</sup> at 2 A g <sup>-1</sup>	-0.1-0.4	1M KOH	29
Cu <sub>7</sub> S <sub>4</sub>	Nanowires	400 F g <sup>-1</sup> at 10 mV s <sup>-1</sup>	0-0.8	1M KOH	34
CuS	Nanoporous spheres	814 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	-0.2-0.4	6M KOH	32
Cu <sub>1.96</sub> S	Nanoparticles	1928.6 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	0-0.5	1 M KOH	48
CuS	Nanowire arrays	295 F g <sup>-1</sup> at 1 mA cm <sup>-2</sup>	0-0.5	1M NaOH	1
CuS	Nanosheets	713 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	0-0.45	ЗМ КОН	54
CuS	Hollow nanocages	843 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	0-0.5	2M KOH	55
Ni-CuS	Nanoparticles	753 F g <sup>-1</sup> at 5 mA cm <sup>-2</sup>	0-0.55	2M KOH	56
CuO	Nanoparticles	571.3 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	0-0.8	1M KOH	57

with other electrodes based on copper-based materials

CuO	Nanorod arrays	594.3 F g <sup>-1</sup> at 2 mA cm <sup>-2</sup>	0-0.5	6M KOH	25
CuO	Bamboo leaf-like	269.6 F g <sup>-1</sup> at 0.25 A g <sup>-1</sup>	-0.1-0.4	6M KOH	12
CuO/Cu(OH)2	Lotus-like	278 F g <sup>-1</sup> at 2 mA cm <sup>-2</sup>	0-0.55	5M NaOH	52
CuO–SnO <sub>2</sub>	Cubic	1972 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	-0.2-0.5	6M KOH	36
Cu(OH)2@rGO	Bundled nanorods	$602 \text{ F g}^{-1} \text{ at } 0.2 \text{ A g}^{-1}$	0-0.47	1M KOH	38
ACET/CuS	Nanosheets	2891 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	-0.2-0.4	6M KOH	58
rGO/CuS	Hollow spheres	2317.8 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	-0.2-0.4	6M KOH	59
Graphene-CuS	Nano-flowers	249 F g <sup>-1</sup> at 4 A g <sup>-1</sup>	0-0.55	ЗМ КОН	60
CuS/MWCNTs	Sheets	2831 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	-0.2-0.4	6M KOH	61
$Cu_2SnS_3$	Micro-flowers	183 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	0.1-0.6	1M KOH	62
Ni <sub>3</sub> S <sub>2</sub> -Cu <sub>1.8</sub> S	Nanosheets	1686 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	0-0.5	2M KOH	63
Cu <sub>7</sub> S <sub>4</sub> /NiS	Hollow cubes	1204 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	0-0.45	ЗМ КОН	64
CuS/CuSCN	Particles/nanorods	1787.3 F g <sup>-1</sup> at 1.11 A g <sup>-1</sup>	0-0.7	ЗМ КОН	65
Cu(OH)2/Cu7S4	Porous nanowires	1610.8 C g <sup>-1</sup> at 4 A g <sup>-1</sup>	0-0.55	2М КОН	This
		(2980.8 F g <sup>-1</sup> )			work

The interfacial electrochemical kinetics of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> electrode in KOH electrolyte were further investigated using electrochemical impedance spectroscopy (EIS), measured with an open circuit voltage of 5 mV at a frequency range of  $0.01 \sim 10^5$  Hz. The obtained Nyquist plot is shown in Fig. 8c. A small semicircle and a straight line can be found in the high-frequency and the low frequency region, respectively. The diameter of the semicircle corresponds to the charge-transfer resistance (R<sub>ct</sub>), which should be resulted from the faradaic reactions between the electrode active materials and the electrolyte ions. The intercept at the x-axis is the internal resistance (R<sub>s</sub>), including the contact resistance of electrode materials. The slope of the straight line at the lower frequency region should be attributed to the Warburg impedance behavior (Z<sub>w</sub>),

which is related to ion diffusion in the electrolyte<sup>2, 66</sup>. The internal resistance (R<sub>s</sub>) and charge-transfer resistance (R<sub>ct</sub>) of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> electrode calculated from the EIS result are 0.86  $\Omega$  and 1.99  $\Omega$ , respectively. The low values of R<sub>s</sub> and R<sub>ct</sub> indicate that the high electrical conductivity and the fast electron transport kinetics of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowires electrode in KOH electrolyte<sup>3, 67</sup>.

The good electrochemical performance of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> should be attributed to the following reasons. Firstly, there is a synergetic effect<sup>68</sup> in the heterostructures of Cu(OH)<sub>2</sub> and Cu<sub>7</sub>S<sub>4</sub> active materials, which can improve the electrochemical performance of electrodes. TEM analysis showed that the Cu(OH)<sub>2</sub> and Cu<sub>7</sub>S<sub>4</sub> nanocrystals are homogeneously mixed in the hybrid nanowires. The Cu<sub>7</sub>S<sub>4</sub> nanoparticles with good conductivity<sup>39</sup> can effectively improve the electron transfer rate to reduce the internal resistance of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> hybrid nanowires as presented in the ESI analysis. Moreover, the heterogeneous composition of Cu(OH)<sub>2</sub> and Cu<sub>7</sub>S<sub>4</sub> nanocrystals in the hybrid nanowires can generate abundant reactive sites due to generation of rich defects and disordered structures on the heterogeneous interfaces<sup>3</sup>, which are beneficial to the faradic redox reactions.

Secondly, the good electrochemical performance of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> is also attributed to its unique porous nanowire architecture. These porous nanostructures constructed by hybid Cu(OH)<sub>2</sub> and Cu<sub>7</sub>S<sub>4</sub> nanocrystals can provide numerous channels for fast transport of electrolyte ions and efficient contact with electroactive sites<sup>42</sup>. Moreover, the one-dimensional hybrid nanowires can accelerate the transport of electrons and ions along their longitudinal direction, which can reduce the internal resistance and increase their electrochemical performance.

Thirdly, the specific capacity can be significantly enhanced due to the large specific surface areas and pore volumes of active materials<sup>42</sup>, which can provide abundant active sites. The specific capacity, pore volume and specific surface area of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowires were compared with those of copper-based materials reported in literature, and the results are listed in the Table S2. It can be seen that larger pore volumes and larger specific surface areas can lead to large specific capacity<sup>29, 32, 34, 59</sup>. Compared to the other reported copper-based materials, the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowires and larger specific surface areas, which should be the two key factors for significantly enhancing its specific capacity.

# 3.3. Electrochemical Performance of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC asymmetric supercapacitors (ASCs)



Fig. 9 Schematic illustration of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC ASC device.



Fig. 10 (a) CV curves of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> and AC electrodes at 50 mV s<sup>-1</sup> measured using a three-electrode configuration, (b) CV curves of the ASC at 50 mV s<sup>-1</sup> at different voltage windows, (c) GCD curves at 1 A g<sup>-1</sup> in different voltage windows, (d) CV curves at various scan rates, (e) GCD curves at different current densities, and (f) specific capacity of the

#### Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC ACS device.

To further assess the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> nanowire electrode for practical supercapacitor applications, we have fabricated asymmetric supercapacitors (ASC) using the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> positive electrode and active carbon (AC) negative electrode, which is schematically illustrated in Fig. 9. Fig. 10a presents the CV curves of active carbon and Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> electrodes measured using the three-electrode system at a voltage range from -1.0 to 0.7 V. Figs. 10b and 10c illustrate the CV and GCD curves for the asymmetric supercapacitor in the voltage range from 0.8 to 1.7 V in 2M KOH electrolyte, respectively. The shapes of CV and GCD curves can be well kept with the increased voltage. Therefore, this ASC device can perfectly work at a wide voltage window of 1.7 V without apparent oxygen evolution<sup>53</sup>. Moreover, all the GCD curves are almost symmetrical, indicating that the ASC exhibits good capacitive properties.

Fig. 10d shows the CV profiles of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC ASC at different scan rates in a voltage window of 1.7 V. It shows an electrical double-layer capacitive characteristic at a lower voltage region and a faradaic behavior at a higher voltage region. With the change of the scan rate from 5 mV s<sup>-1</sup> to 50 mV s<sup>-1</sup>, no obvious distortion and polarization of the CV curves is observed, suggesting the good capacitive characteristic of this Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC ASC device. Based on the capacity formula (8), the specific capacity ( $C_{ASC}$ ) of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC ASC was calculated according to the GCD curves shown in Fig. 10e, and the obtained value is as high as 201.8 C g<sup>-1</sup> at 0.5 A g<sup>-1</sup> as presented in Fig. 10f. Here, It should be noticed that *m* in formula (8) is the total mass of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> and active carbon in two electrodes.





Fig. 11 (a) Ragone plot, (b) GCD curves before and after 80000 cycles, and (c) cycling performance and coulombic efficiency at  $6 \text{ A g}^{-1}$  of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC device (the inset

#### is the lighting LED by the ASC device).

The energy density (*E*) and power density (*P*) of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC ASC device can be calculated from the GCD curves according to the formula (9) and  $(10)^{69, 70}$ .

$$E = \frac{C_{ASC} \times \Delta V}{2 \times 3.6} \tag{9}$$

$$P = \frac{E \times 3600}{\Delta t} \tag{10}$$

The Ragone plots of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC ASC are shown in Fig. 11a. This ASC device exhibits a high energy density of 48.1 Wh kg<sup>-1</sup> at a power density of 429.3 W kg<sup>-1</sup>. It presents a high powder density of 7956.0 W kg<sup>-1</sup> at the energy density of 21.2 Wh kg<sup>-1</sup>. The obtained energy and power density for this ACS device are higher than those of ASC devices based on other copper-based materials reported in literature as shown in Fig. 9a, which include CuS<sub>1.96</sub>//AC (10.5 Wh kg<sup>-1</sup>at 750 W kg<sup>-1</sup>)<sup>48</sup>, CuCo<sub>2</sub>S<sub>4</sub>//AC (15 Wh kg<sup>-1</sup> at 400 W kg<sup>-1</sup>)<sup>71</sup>, CuS//AC (16.0 Wh kg<sup>-1</sup> at 185.4 W kg<sup>-1</sup>)<sup>24</sup>, Cu(OH)<sub>2</sub>//AC (18.3 Wh kg<sup>-1</sup> at 326 W kg<sup>-1</sup>)<sup>31</sup>, CuS//AC (26.0 Wh kg<sup>-1</sup> at 2700 W kg<sup>-1</sup>)<sup>72</sup>. Even compared with those made of copper-based hybrid materials such as Ni<sub>3</sub>S<sub>2</sub>-Cu<sub>1.8</sub>S//AC (30.9 Wh kg<sup>-1</sup> at 798 W kg<sup>-1</sup>)<sup>63</sup>, CuS@MnS//AC (20.17 Wh kg<sup>-1</sup> at 224.67 W kg<sup>-1</sup>)<sup>73</sup>, CuCo<sub>2</sub>S<sub>4</sub>//AC(23.2 Wh kg<sup>-1</sup> at 402.7 W kg<sup>-1</sup>)<sup>69</sup>, the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC ASC

prepared in this study also shows higher energy and power density.

The cycling performance of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC ASC device was tested by recording the GCD curves at a current density of 6 A g<sup>-1</sup> for 80000 cycles. No obviously changes can be observed for the shape of the GCD curves as shown in Fig. 11b before and after 80000 cycling testing. The corresponding specific capacity values and coulomb efficiency are shown in Fig. 11c. The specific capacity value suffers an apparent decrease within the initial 2500 cycles, which is due to the serious structural collapse (Fig. S7). However, it is then increased and becomes stable until up to 55000 cycles. This is because there are lots of nano-pores in the Cu(OH)2/Cu7S4 hybrid nanowires, therefore, the electrolyte is infiltrated into these mesopores during the charge-discharge processes, thus resulting in significantly more electrochemical reactions inside the electrode materials<sup>74</sup>. Therefore, the specific capacity of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC ASC device is improved. After 80000 cycles, the capacity value is 105.7% of its initial value at 6 A g<sup>-1</sup>. During the whole cycling testing process of the Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC ASC device, the columbic efficiency maintains at about 99.5%, indicating that the good reversibility of these charge-discharge processes.

#### 4. Conclusion

In summary, Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> porous hybrid nanowires have been synthesized at room temperature by self-sacrificial template method using [Cu(tu)]Cl·1/2H<sub>2</sub>O nanowire precursors. This binder-freed Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> on nickel foam was directly used as electrodes and exhibited a high specific capacity of 1610.8 C g<sup>-1</sup> at 4 A g<sup>-1</sup>. The Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub>//AC ACS device showed a high energy density and power density. The excellent electrochemical performance is attributed to the unique architecture of Cu(OH)<sub>2</sub> and Cu<sub>7</sub>S<sub>4</sub> nanocrystals, porous and hybrid nanowires, large BET specific area and large pore volume, which provided numerous active sites for faradaic reaction and facilitated fast ion diffusion and electron transport during the charge-discharge processes. The good electrochemical performance of Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> should be mainly attributed to and the porous nanowire architecture. Due to the good electrochemical performance, fast and facile preparation process, low cost and low toxicity, this Cu(OH)<sub>2</sub>/Cu<sub>7</sub>S<sub>4</sub> porous hybrid nanowires should have a promising application prospects as high performance supercapacitors.

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#### **Conflicts of interest**

There are no conflicts to declare.

#### Footnote

<sup>†</sup> Electronic supplementary information (ESI) available: Experimental details and electrochemical measurements; Fig. S1–S7 and Tables S1 and S2.

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