Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2017

# **Supporting Information**

## A cellulose fibers-supported hierarchical forest-like cuprous oxide/copper array

### architecture as a flexible and free-standing electrode for symmetric

### supercapacitors

Caichao Wan, Yue Jiao, Jian  ${\rm Li}^*$ 

Material Science and Engineering College, Northeast Forestry University, Harbin

150040, China

\*Corresponding author at: Northeast Forestry University, No.26 Hexing Road

Xiangfang District, Harbin 150040, China.

TEL./FAX.: +86 45182192399

E-mail addresses: wancaichaojy@163.com (Caichao Wan)

yjiao123@126.com (Yue Jiao)

lijiangroup@163.com (Jian Li)

#### Calculation process of Cu<sub>2</sub>O theoretical specific capacitance

The theoretical pseudocapacitance of metal oxide can be calculated as (J. Mater. Chem. A, 2014, 2, 18229-18235; Adv. Mater., 2014, 26, 1044-1051):

$$C = \frac{n \times F}{M \times V} \tag{1}$$

where *n* is the mean number of the electrons transferred in the redox reaction, *F* is the Faraday constant, *M* is the molar mass of the metal oxide and *V* is the operating voltage window. Then, we obtained the theoretical capacitance of Cu<sub>2</sub>O:  $(2\times96485.3383/0.65/143.091)$  F g<sup>-1</sup>  $\approx$  2075 F g<sup>-1</sup>.

#### Calculation process of mass loading of Cu<sub>2</sub>O

The mass of Cu<sub>2</sub>O was calculated according to the following steps. Firstly, the mass of the Cu<sub>2</sub>O/Cu/cellulose hybrid paper was weighed (coded as  $m_1$ ) by electronic balance. Secondly, this electrode was dipped into a N<sub>2</sub>-saturated 0.1 M HCl solution for about 10 min until no obvious color change occurred. During this step, the Cu<sub>2</sub>O layer was removed by the HCl. The resultant was washed with a large amount of distilled water and completely dried at room temperature, and then weighed again (coded as  $m_2$ ). Finally, the mass of Cu<sub>2</sub>O attached on the electrode was calculated to be ( $m_1$ - $m_2$ ). The mass loading of Cu<sub>2</sub>O per area is 0.26 mg cm<sup>-2</sup>.

Calculation process of Brunauer–Emmett–Teller (BET) surface area of Cu<sub>2</sub>O component The BET surface areas of the Cu/cellulose paper and Cu<sub>2</sub>O/Cu/cellulose hybrid paper are 16.6 and 13.2 m<sup>2</sup> g<sup>-1</sup>, respectively. In addition, the mass percent of Cu<sub>2</sub>O in the

2

Cu<sub>2</sub>O/Cu/cellulose hybrid paper is around 1.3%. Therefore, we can roughly calculate the surface area of Cu<sub>2</sub>O component: [(16.6-13.2)/1.3%] m<sup>2</sup> g<sup>-1</sup>  $\approx$  261.5 m<sup>2</sup> g<sup>-1</sup>.

Table S1. Comparison of specific capacitance, specific energy and cycling stability of

Electrodes	Туре	Maximum specific capacitance (F g <sup>-1</sup> )	Specific energy (W h kg <sup>-1</sup> )	Cycling stability	Potential range (V)	Electrolyte	Refs
Cu₂O@Cu nanoneedle arrays//active carbon	Asymmetric	77 (5 mV s <sup>-1</sup> )	35.6 (0.9 kW kg <sup>-1</sup> )	92% (10000 cycles, 1 A g <sup>-1</sup> )	0–1.8	1 М КОН	[54]
Rose rock-shaped nano-Cu <sub>2</sub> O anchored graphene	Symmetric	92 (1 A g <sup>-1</sup> )	25 (0.6935 kW kg <sup>-1</sup> )	-	0–1.4	6 М КОН	[52]
Cu <sub>2</sub> O-Cu(OH) <sub>2</sub> nanoflakes/graphene/stainles s steel	Symmetric	104 (5 A g <sup>-1</sup> )	20.4 (3.6 kW kg <sup>-1</sup> )	87% (2000 cycles, 10 A g <sup>-1</sup> )	0–1.2	0.5 M Na <sub>2</sub> SO <sub>4</sub>	[57]
Graphene/polypyrrole/Cu <sub>2</sub> O– Cu(OH) <sub>2</sub> /Ni foam	Symmetric	225 (10 A g <sup>-1</sup> )	20 (8 kW kg <sup>-1</sup> )	90% (2000 cycles, 10 A g <sup>-1</sup> )	0–0.8	0.5 M Na₂SO₄	[58]
Cu <sub>2</sub> O/CuO/Co <sub>3</sub> O <sub>4</sub> core-shell nanowires//activated graphene	Asymmetric	-	12 (0.162 kW kg <sup>-1</sup> )	-	0–1.4	3 М КОН	[56]
Forest-like Cu <sub>2</sub> O/Cu array structure	Symmetric	409 (1.9 A g <sup>-1</sup> )	24.0 (0.625 kW kg <sup>-1</sup> )	90.2% (10000 cycles, 30.8 A g <sup>-1</sup> )	0–0.65	1 M KOH	This work

some Cu<sub>2</sub>O-based symmetric/asymmetric supercapacitor devices.



Figure S1. Optical photographs of the cellulose paper, Cu/cellulose paper and

Cu<sub>2</sub>O/Cu/cellulose hybrid paper.



Figure S2. Cross-section SEM image of the cellulose paper to present its three-

dimensional fibers framework structure.



Figure S3. Barrett–Joyner–Halenda (BJH) desorption pore size distribution of the



Cu<sub>2</sub>O/Cu/cellulose hybrid paper.

Figure S4. High-resolution XPS spectrum of Cu 2p core level of the Cu<sub>2</sub>O/Cu/cellulose

hybrid paper after the electrochemical tests to demonstrate the plentiful generation

of CuO or Cu(OH)<sub>2</sub>.



Figure S5. (a) CV curves of the platinum sheet at various scan rates measured in a

three-electrode configuration. (b) CV curves of the platinum sheet and

Cu<sub>2</sub>O/Cu/cellulose hybrid paper-based symmetric supercapacitor device at the scan

rate of 5 mV s<sup>-1</sup>.



Figure S6. Areal and specific capacitances of the  $Cu_2O/Cu/cellulose$  hybrid paper-

based symmetric supercapacitor device at various current densities