

Electronic Supplementary Information

Temperature effect on the binder-free nickel copper oxide nanowires with superior supercapacitor performance

Liuyang Zhang, Chunhua Tang, Hao Gong*

Table 1 Peak positions in the experimental XRD patterns and peak positions of possible materials of $\text{Cu}_{0.2}\text{Ni}_{0.8}\text{O}$ (JCPDF Card No. 25-1049) and Ni_2CuO_3 (JCPDF Card No.40-0959).

Ni_2CuO (PDF Card)(20)	37.025	41.623	43.715	61.935	63.540	72.933	75.939	78.921
$\text{Cu}_{0.2}\text{Ni}_{0.8}\text{O}$ (PDF Card)(20)	37.184	--	43.188	--	62.773	--	75.232	79.233
XRD Peaks	1		2		3		4	5
90 °C	37.2±0.1	--	43.2±0.1	--	--	--	--	--
120 °C	37.1±0.1	--	43.2±0.1	--	62.7±0.1	--	75.2±0.1	79.0±0.1
135 °C	37.0±0.1	--	43.3±0.1	--	--	--	--	--
150 °C	37.0±0.1	--	43.3±0.1	--	--	--	--	--

Table 2 Theoretical ratio of ring diameters from selected electron diffraction pattern of material with FCC (face-centered cubic) structures and the experimental ratio deduced from selected area electron diffraction pattern of Fig3(a, b, c).

(hkl) for FCC structure	$\sqrt{h^2+k^2+l^2}$	$\sqrt{1^2+1^2+1^2}/\sqrt{h^2+k^2+l^2}$	Ring number in experimental SAED patterns	Diameter ratio of ring 1 to ring n (120 °C)	Diameter ratio of ring 1 to ring n (135°C)	Diameter ratio of ring 1 to ring n (150°C)
(111)	1.732	1	1	1	1	1
(200)	2	86.6%	2	86.6%±2%	86.7%±2%	85.7±2%
(220)	2.828	60.82%	3	60.8%±2%	61%±2%	60%±2%
(311)	3.316	51.86%	4	51.8%±2%	51.7±2%	51.6%±2%
(222)	3.464	50%	5	50%±2%	50%±2%	50%±2%
(400)	4	43.3%	6	43%±2%	42.9%±2%	42.9%±2%
(331)	4.358	39.7%	7	39.6%±2%	39.5%±2%	39.4%±2%
(240)	4.472	38.73%	8	38.7%±2%	38.9%±2%	38.8%±2%
(224)	4.898	35.3%	9	--	34.9%±2%	34.9%±2%

Table 3 Lattice spacings (d value) of $\text{Cu}_{0.2}\text{Ni}_{0.8}\text{O}$ and d value calculated from selected area electron diffraction (SAED) patterns of material synthesized at different temperature (Figure 3).

D value of $\text{Cu}_{0.2}\text{Ni}_{0.8}\text{O}$ (PDF Card) (nm)	D value from SEAD (120°C)	D value from SEAD (135°C)	D value from SEAD (120°C)
0.242	0.241±0.002	0.245±0.002	0.244±0.002
0.209	0.209±0.002	0.212±0.002	0.209±0.002
0.147	0.147±0.002	0.149±0.002	0.147±0.002
0.126	0.125±0.002	0.127±0.002	0.126±0.002
0.121	0.121±0.002	0.122±0.002	0.122±0.002
0.105	0.104±0.002	0.105±0.002	0.105±0.002
0.096	0.095±0.002	0.097±0.002	0.096±0.002
0.094	0.093±0.002	0.095±0.002	0.095±0.002
0.085	--	0.086±0.002	0.085±0.002

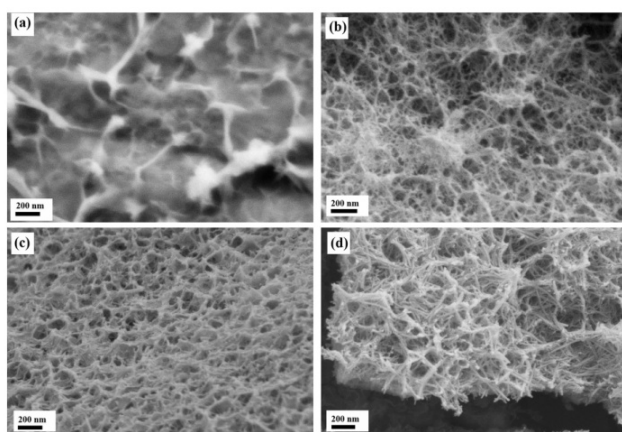


Figure S1. SEM images of the products at different reaction times: (a) 2(b) 4(c) 6(d) 8 hours

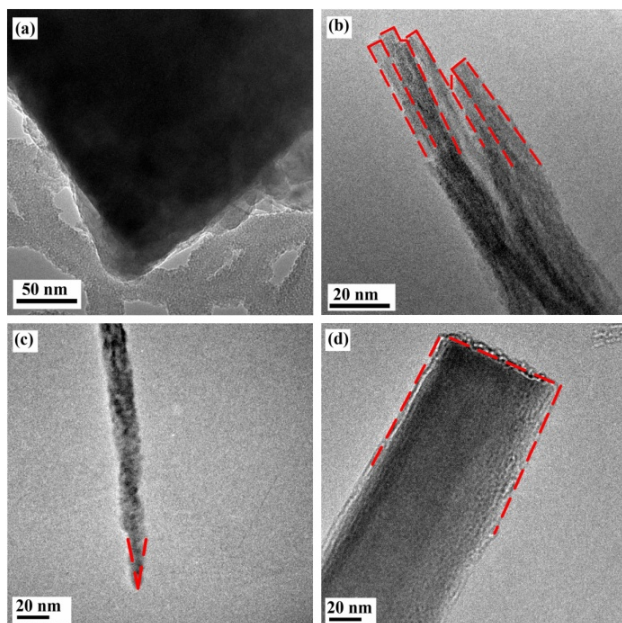


Figure S2. Typical TEM images of products at different temperature.a:90, b:120, c:135, d:150°C.

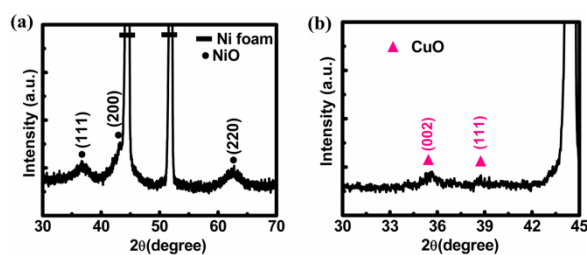


Figure S3. XRD result of the pristine NiO and CuO

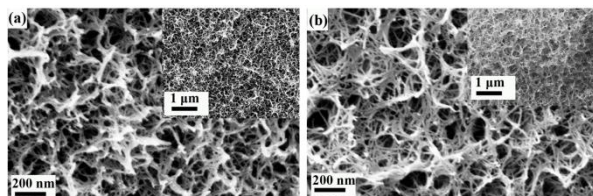


Figure S4. SEM images of the pristine NiO and CuO

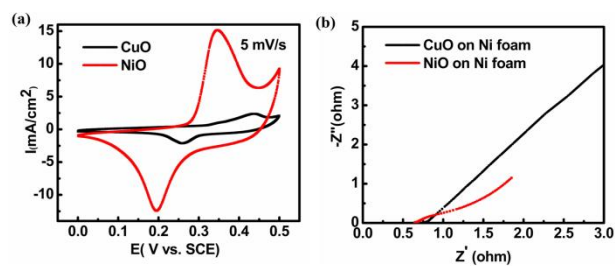


Figure S5. (a) CV curves of pristine NiO and CuO; (b) Electrochemical impedance spectra of pristine NiO and CuO

Experimental Sections

Materials Preparations

All chemicals were of analytic grade and used as received without further purification. The Ni-Cu composite was prepared by a simple hydrothermal method. Important parameters, including the ratio of Ni/Cu, the

concentration of urea, the reaction time and temperature, were altered in a series of parallel experiments to acquire the optimal results. In a typical preparation, 0.5 m mol of CuCl_2 , 0.75 m mol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and 5 m mol of urea were dissolved in 25ml deionized water by continual stirring. Ni foam was cleaned by acetone, ethanol and deionized water. After stirring for 30 min, the homogeneous solution was transferred into a Teflon-lined stainless steel autoclave (45 mL) and hereafter a piece of clean Ni foam ($2 \times 2 \text{ cm}^2$) was immersed into the reaction solution. Then, the liner was sealed and heated at 120°C for 4h. The substrates were taken out of the bath and washed by repeated rinsing in double-distilled water. Finally, the sample was annealed at 350°C for 60 min, and the final product was denoted as sample-NCO-120. A series of Ni-Cu-O samples was prepared at different reaction temperatures (90, 135, and 150°C), and denoted as NCO-x, where x represent the reaction temperatures.

In addition to Ni-Cu-O samples, carbon black coating on Ni foam was also prepared, as carbon black served as cathode and Ni-Cu-O as anode in our asymmetric supercapacitor. The carbon black coating was prepared by uniformly mixing 70 wt% of active carbon, 25 wt% of acetylene black, and 5 wt% of polytetrafluoroethylene (PTFE) and coated on nickel foam. After at 120°C for removing moisture, carbon black was coated on Ni foam.

Characterization techniques

The morphology of the prepared samples was examined by using a scanning electron microscope with an X-ray energy dispersive spectrometer (SEM, Zeiss SUPRA40). The crystal structure was identified using X-ray diffraction. Transmission electron microscopy and electron diffraction (TEM, JEOL 2000FX) were employed to obtain high resolution image and structural information.

Electrochemical Measurements

In the three electrode configuration, the NCO-x coated on $2 \times 2 \text{ cm}^2$ nickel foam acted as the working electrodes, Pt foil as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. Measurements were performed using 1M KOH as the electrolyte. Electrochemical impedance spectroscopy (EIS) measurements were conducted by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz at the open circuit potential.

Calculation

The specific capacitance can be calculated from the CV curve using the following equations

$$C = \frac{\int i v d v}{2 \mu m \Delta V} \quad (1)$$

$$C = \frac{I t}{m \Delta V} \quad (2)$$

where i and v are the current and potential in the CV test (A and V), μ is the scan rate (V/s), m is the mass of active materials (g), ΔV is the potential window of discharge (0.5V here), I is the constant discharge current and t is the discharge time (s).

The specific capacitance, power density and energy density are calculated based on the galvanic charging-discharging curves using the equation as follows:

$$C = \frac{I \Delta t}{m \Delta V} \quad (3)$$

$$E = \frac{1}{2} \times C \times \Delta V^2 \quad (4)$$

$$P = \frac{E}{\Delta t} \quad (5)$$

where C (Fg^{-1}) is specific capacitance, E (Whkg^{-1}) is energy density, P (Wkg^{-1}) is power density, ΔV is potential window (here 1.3 V), I (A) is discharge current, Δt (s) is discharge time, m (g) is the sum of the masses of the cathode (NCO-120, here 4mg) and anode (activated carbon, here 16mg).

The theoretical capacitance of the asymmetric full cell is

$$\frac{1}{C_T} = \frac{1}{C_P} + \frac{1}{C_N} \quad (6)$$

where C_T is the total capacitance of the cell, C_P is the capacitance of the positive electrode (NCO, here 1497F/g as seen in Fig.6b), C_N is the capacitance of the negative electrode (active carbon, here 140F/g)

The formula is based on the book Conway, B. E. Electrochemical supercapacitors: Scientific fundamentals and technological applications; Kluwer Academic/Plenum Publishers: New York, 1997. and some journals such as Liang Huang, Dongchang Chen, Yong Ding, Shi Feng, Zhong Lin Wang, and Meilin Liu Nano Lett. 2013, 13, 3135–3139