Electronic Supplementary Material (ESI) for Nanoscale Horizons.
This journal is © The Royal Society of Chemistry 2015

Supporting Information

Integrated copper-nickel oxide mesoporous nanowire arrays for high energy density aqueous asymmetric supercapacitors

Ruizhi Li, Zhijun Lin, Xin Ba, Yuanyuan Li,* Ruimin Ding, Jinping Liu*

I. Experimental Section

1. Material Synthesis

Synthesis of (Cu, Ni)O nanowire array electrode. The precursor (Ni, Cu)$_2$(OH)$_2$CO$_3$ nanowire array was fabricated via a simple hydrothermal method, which was then transformed into (Cu, Ni)O via a post-annealing process. Typically, for molar ratio of Cu: Ni=1:1, 0.246 g $CuCl_2 \cdot 2H_2O$, 0.343 g $NiCl_2 \cdot 6H_2O$ and 0.7 g urea were completely dissolved in 80 mL distilled water. And then, the resulting solution was transferred into a Teflon-lined stainless steel autoclave with a piece of carbon cloth and kept at 120 °C for 24 h. The carbon cloth covered with precursor nanowire array product was collected, dried, and further annealed at 350 °C for 2 h to obtain (Cu, Ni)O nanowire array. The molar ratio of Cu: Ni was controlled by changing the number of moles of the reactants of $CuCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 6H_2O$. The total mole number of Cu+Ni was kept unchanged.

2. Characterization

The electrode products were characterized by using SEM (JSM-6700F), TEM (JEM-2010FEF; 200 kV), XRD (Bruker D-8 Avance) and XPS (Thermo Electron, VG ESCALAB 250 spectrometer).

Pore size distribution was measured by BJH desorption method on a Micromeritics ASAP 2010 analyzer (accelerated surface area and porosimetry system). The mass of the active materials was measured on an AX/MX/UMX Balance (METTLER TOLEDO, Maximum = 5.1 g; d = 0.001 mg).

3. Electrode Preparation and Electrochemical Testing

All the electrochemical measurements were carried out using a CS310 electrochemical workstation. For individual working electrode samples, the performance was conducted in a three-electrode mode with a Pt foil as counter electrode and an Hg/HgO as reference electrode in 3 M NaOH. For device testing, a two electrode mode was used. To fabricate the asymmetric supercapacitor, an activated carbon electrode was firstly prepared by mixing 80 wt% activated carbon and 20 wt% PVA and casting the mixture onto a 1×2 cm^2 carbon cloth. This electrode (negative) was then pressed and paired with a (Cu, Ni)O nanowire electrode (positive) with 3 M NaOH as the electrolyte.

The specific capacitance, energy density and power density were calculated following the equations below：

$$C = I\Delta t / Vm \qquad E = \frac{I\int V(t)dt}{m}$$

$$P = E / \Delta t$$

where I is the discharging current, Δt is the total discharging time, V is the voltage window excluding the IR drop, $V(t)$ is discharging voltage at t, dt is time differential, and m is the total mass of the active materials.

II. Supplementary Results

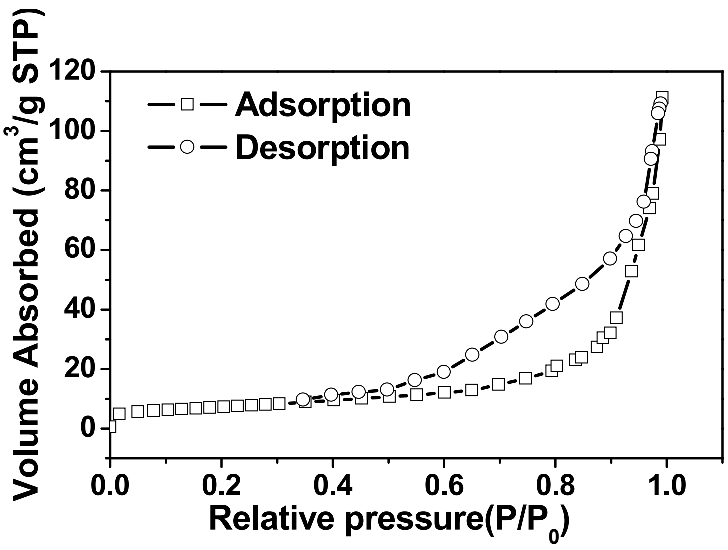

Figure S1. N_2 adsorption-desorption isotherm of the prepared (Cu, Ni)O nanowire array.

Discussion: This isotherm profile can be categorized as type IV with an obvious hysteresis loop observed at a relative pressure of 0.5-1.0, indicating the presence of a mesoporous structure. As a result, our (Cu, Ni)O nanowire array has a high specific surface area of 53 m^2 g^{-1}, which is comparable to that of mesoporous NiO nanorings (55.4 m^2 g^{-1}, 350 ^{o}C, Ref.1), and much superior to mesoporous CuO nanowires (13.05 m^2 g^{-1}, 350 ^{o}C, Ref.2) and mesoporous Co_3O_4 nanowire array (16.3 m^2 g^{-1}, 400 ^{o}C, Ref.3).

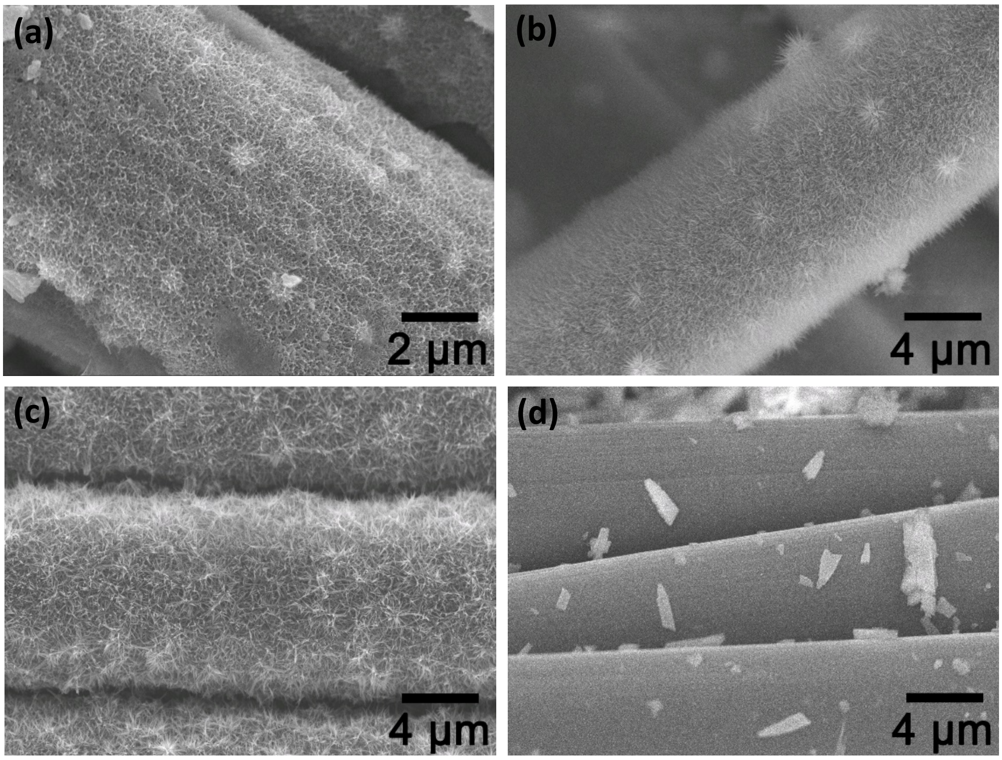

Figure S2. SEM images of (Cu, Ni)O electrodes with different Cu:Ni molar ratios: (a) 0:1, (b) 1:2, (c) 2:1 and (d) 1:0.

References

1 D. S. Wang, R. Xu, X. Wang and Y. D. Li, *Nanotechnology*, 2006, **17**, 979.

2 L. J. Wang, K. Zhang, Z. Hu, W. C. Duan, F. Y. Cheng and J. Chen, *Nano Research*, 2014, **7**, 199.

3 Y. G. Li, B. Tan and Y. Y. Wu, *J. Am. Chem. So*c., 2006, **128**, 14258.