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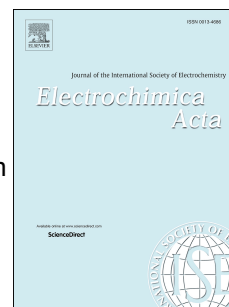
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Please cite this article as: S. Wu, H. Guo, K.S. Hui, K.N. Hui, Rational design of integrated CuO@Co$_x$Ni$_{1-x}$(OH)$_2$ nanowire arrays on copper foam for high-rate and long-life supercapacitors, *Electrochimica Acta* (2018), doi: https://doi.org/10.1016/j.electacta.2018.10.183.

Rapid electron transfer

Facile ion transport

Robust bonding

CuO@Co$_x$Ni$_{1-x}$(OH)$_2$ nanowire arrays on 3D copper foam

Rational Design of Integrated CuO@Co$_x$Ni$_{1-x}$(OH)$_2$ Nanowire Arrays on Copper Foam for High-Rate and Long-Life Supercapacitors

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Abstract

Rational electrode architectural design, favorable electrode composition, and versatile synthesis approach play a significant role in developing advanced electrodes for high-performance supercapacitor. In this work, we report a facile approach for fabricating 1D hierarchical $CuO@Co_xNi_{1-x}(OH)_2$ nanowire arrays grown on 3D highly conductive copper foam. The optimized $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrode delivers an ultrahigh specific capacity of 374.7 mAh g^{-1} at 2 A g^{-1} with exceptional rate capability (301.7 mAh g^{-1} at 50 A g^{-1}) and remarkable cycling stability (95.9% after 10 000 cycles at 50 A g^{-1}). A flexible asymmetric solid-state supercapacitor (ASC) is fabricated using the optimized $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ as the positive electrode, activated carbon-coated nickel foam as the negative electrode, and polyvinyl alcohol/KOH gel as electrolyte. The flexible ASC operating with a potential window of 0–1.6 V delivers an energy density of 46.5 Wh kg^{-1} with a power density of 526.9 W kg^{-1}. The ASC also exhibits excellent cycling stability with a capacity retention of 84.3% after 10 000 cycles at a current density of 7 A g^{-1}.

1. Introduction

The stringent requirements for reliable supercapacitors have increased because of their rapidly growing commercial markets for electronic devices and electric vehicles [1]. Supercapacitors can be divided into two types based on their charge storage mechanism: electrical double layer capacitors (EDLCs) and pesudocapacitors [2]. EDLCs typically use carbon-based electrodes such activated carbon, carbon nanotube (CNT), and graphene to accumulate charges at electrode/electrolyte interface [3]. Pesudocapacitors store energy in rapid redox reactions, intercalation, or adsorption process [4]. One of the key challenges for fabricating reliable supercapacitors is manufacturing electrodes with high electrochemical performance. Carbon-based EDLCs provide ultrahigh power density and long cycle life; however, the obtained specific capacity and energy density are relatively low [5]. Specifically, it is impractical to have a pure EDLC based on carbon-based materials since carbon samples are usually composed of defects, dangling atoms and bonds, functionalized groups, dopants, *etc.* [6]. In this context, pseudocapacitive materials have been widely explored as supercapacitor electrode materials.

Co–Ni hydroxides are the most promising candidates because of their ultrahigh theoretical specific capacity [7-9]. Nonetheless, Co–Ni-based hydroxides suffer from low rate capability and limited cycling performance. For example, Liu et al. utilized coprecipitation to synthesize Co–Ni hydroxides/graphene composites, which exhibit a remarkable capability at 0.5 A g^{-1} but poor cycling performance (~25% decay after 5000 cycles at 20 A g^{-1}) [10]. Huang et al. fabricated Ni–Co@Ni–Co layered double hydroxide (LDH) core/shell nanotube array on carbon fiber cloth. The as-prepared electrode shows

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superior capacity at a current density of 1 A g^{-1}; however, the capacity remains 20% of the original value when the current density was increased from 1 to 20 A g^{-1}, and only 5000 cycles were tested for cycling stability [11]. Chen et al. developed Ni–Co LDH nanosheet/nickel foam electrode possesses a super-high specific capacity but suffers from a low rate capability (capacity retention ~63.6% when the current density was increased to 20 A g^{-1}) [7]. The unsatisfactory rate capability/cycling stability could be attributed to the low electrical conductivity, poor ion transport, and large volume expansion at high rates [12]. Accordingly, tremendous efforts have been devoted to resolve these challenges of Ni–Co hydroxides for high-performance supercapacitors. Liu et al. reported the optimal Ni/Co composition ratio to increase the electrochemical surface active sites and the enhancement in the electroactive sites can be ascribed to the possible valence interchange or charge hopping between Co and Ni cations [13]. Gupta et al. reported the direct growth of Co_xNi_{1-x} LDHs on stainless steel, which led to rapid electron transportation and robust adherence between the active materials and the current collector [14]. Meanwhile, the development of novel current collectors is highly desired. Jiang et al. pioneered the growth of CuO nanowire arrays direct on Cu substrate by an eco-friendly single thermal annealing process [15]. The obtained CuO nanowires were further demonstrated to possess desirable electrical conductivity [16]. However, it is still challenging to combine the aforementioned strategies together.

Inspired by these considerations, herein, we report a two-step facile approach for the synthesis of robust 1D hierarchical $CuO@Co_xNi_{1-x}(OH)_2$ core/shell nanowire arrays directly grown on 3D conductive copper foam (CF) via oxidation followed by electrodeposition. First, CuO nanowire arrays were in situ grown on CF by a facile

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oxidation reaction. The nanowire arrays were chosen as the 1D support for the prominent electroactive $Co_xNi_{1-x}(OH)_2$ nanosheets because of their ease of fabrication via oxidation reaction from CF [17, 18]. Second, ultrathin $Co_xNi_{1-x}(OH)_2$ nanosheets were electrodeposited on the CuO nanowire arrays to form a hierarchical 1D core/shell nanostructure through the fast and well-controllable electrodeposition method [19]. The proposed electrode architectures offers the advantages of fast electron transport of 1D CuO nanowire arrays, high redox active surface areas of $Co_xNi_{1-x}(OH)_2$ nanosheets for electrochemical reaction, and robust oxidation-grown CuO nanowire arrays supported for $Co_xNi_{1-x}(OH)_2$ nanosheets. The molar ratio of Ni/Co in the $Co_xNi_{1-x}(OH)_2$ nanosheets during electrodeposition was optimized to achieve high electrochemical performance. The optimized $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ composite shows remarkable electrochemical performance, including ultrahigh specific capacity (374.7 mAh g^{-1} at a current density of 2 A g^{-1}), excellent rate capability (capacity retention of 80.5% on increasing current density from 2 A g^{-1} to 50 A g^{-1}), and outstanding cycling stability at high current density (retention of 95.9% over 10 000 cycles at a high density of 50 A g^{-1}). A flexible asymmetric solid-state supercapacitor (ASC) was fabricated using $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ as the positive electrode, activated carbon (AC) as negative electrode, and polyvinyl alcohol (PVA)/KOH gel as the solid electrolyte. The flexible solid-state ASC operating at a cell voltage of 1.6 V within a potential window of 0–1.6 V delivers an energy density of 46.5 Wh kg^{-1} and power density of 526.9 W kg^{-1}. The ASC also exhibits excellent cycling stability with capacity retention of 84.3% after 10 000 cycles at a current density of 7 A g^{-1}. Results demonstrate that binder-free 1D hierarchical core/shell nanostructures

grown directly on a mesoporous conductive current electrode are promising materials for high-performance supercapacitors.

2. Experimental Section

2.1 Synthesis of CuO nanowires array

All chemical reagents were of analytical grade and used without further purification. An array of vertically aligned CuO nanowires was fabricated on top of a CF (110 PPI, 1.5 mm thickness, 0.85 g cm^{-3}, Artenano Company Limited, Hong Kong) by in situ oxidation. The CF was sequentially cleaned in an ultrasonic bath with acetone, hydrochloric acid (1.5 M), absolute ethanol, and deionized (DI) water. The CF was dried in a vacuum oven and placed in an alumina crucible. The crucible was placed in a muffle furnace and rapidly heated to 420 °C at a heating rate of 50 °C min^{-1} for 4 h.

2.2 Synthesis of CuO@Co$_x$Ni$_{1-x}$(OH)$_2$ composite

CuO nanowires in situ grown on the CF were used as a scaffold for Co$_x$Ni$_{1-x}$(OH)$_2$ ultrathin nanosheet shell growth through a facile cathodic electrodeposition method. The electrodeposition was carried out in an electrochemical cell with a three-electrode configuration at room temperature (RT). The CuO nanowire array electrode (1 cm × 1 cm) was used as the working electrode, a Pt wire as the counter electrode, and the Hg/HgO electrode as reference electrode. The electrolyte for the electrodeposition of Co$_x$Ni$_{1-x}$(OH)$_2$ was 50 mL of the metal ion solution containing different Co^{2+}/Ni^{2+} molar ratios of 3:1, 2:1, 2:3, 1:4, and 1:7. The deposition was performed at a potential of −1.0 V, and the synthesis duration was 0–200 s. The samples were removed, rinsed with DI water and absolute ethanol several times, and dried in a vacuum oven. The active materials on

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the 3D CF were determined from the mass difference between the CF-supported $CuO@Co_xNi_{1-x}(OH)_2$ and pure CF substrate. The mass was determined using a semi-micro balance with a readability of 0.1 mg. The area density for $CuO@Co_xNi_{1-x}(OH)_2$ was 2 mg cm^{-2}. For comparison, CF-supported $CuO@Co(OH)_2$, $CuO@Ni(OH)_2$, and CF-supported $Co_xNi_{1-x}(OH)_2$ ($CF@Co_xNi_{1-x}(OH)_2$) were also prepared.

2.3 Materials characterizations

X-ray diffraction (XRD) patterns were recorded using a SmartLab HR X-ray diffractometer (Cu-kα radiation, λ = 1.5418 Å, 40 kV, and 40 mA). Scanning electron microscopy (SEM) investigations were performed on a Nova Nano SEM 450&LEO-155 operated at an acceleration voltage of 15 kV. Transmission electron microscopy (TEM) studies, high-angle annular dark-field scanning TEM–EDS (HAADF-STEM-EDS), and elemental mapping were conducted with an FEI Talos microscope operating at 200 kV accelerating voltage. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Thermo VG Escalab 250 photoelectron spectrometer.

2.4 Electrochemical measurements

The electrochemical performance of the as-obtained $CuO@Co_xNi_{1-x}(OH)_2$ hybrid electrode (1 cm × 1 cm) was evaluated using a three-electrode cell configuration on an electrochemical station (ZIVE SP2) at RT in 6 M KOH. A Pt plate and a Hg/HgO electrode were used as counter and reference electrodes, respectively. Cyclic voltammetry (CV) test was performed from 0 V to 0.6 V at various scan rates. Galvanic charging–discharging (GCD) measurements were conducted at current densities from 2 A g^{-1} to 50 A g^{-1}. Electrochemical impedance spectroscopy (EIS) analysis was performed

within 10^{-2} to 10^5 Hz at the open circuit potential with an oscillation amplitude of 5 mV. Cyclic stability was evaluated by GCD measurement at a current density of 50 A g^{-1} for 10 000 cycles. The capacity retention of any cycle was obtained through its discharge time divided by the discharge time of the first cycle. The specific capacity derived from the GCD tests was calculated using $Cs = I\ \Delta t/(m\Delta V)$, where I (A) is the discharge current, Δt is the discharge time, m (g) is the total weight of the $CuO@Co_xNi_{1-x}(OH)_2$ composite, and ΔV is the potential drop during discharge.

2.5 Flexible ASCs

Flexible ASCs were fabricated using $CuO@Co_xNi_{1-x}(OH)_2$ hybrid as the positive electrode, AC (TFB520) as negative electrode, and PVA/KOH film as electrolyte. An AC electrode was prepared by mixing 95 wt% AC and 5 wt% polytetrafluoroethylene and smearing onto nickel foam (110 PPI, 1.5 mm thickness, 0.45 g cm^{-3}, Artenano Company Limited, Hong Kong). The test condition for the electrochemical properties of the individual AC electrode was the same as that of the $CuO@Co_xNi_{1-x}(OH)_2$ hybrid electrode. Solid PVA/KOH gel electrolyte was prepared as follows: 3 g of PVA (molecular weight: 90 000) and 3 g of KOH were dissolved in 30 mL of DI water under vigorous stirring at 90 °C until the solution became clear. The solution was stirred for another 2 h at RT to eliminate bubbles generated during the dissolution. The solution was then poured into watch glasses to obtain ~0.1 mm-thick PVA/KOH gel film. The $CuO@Co_xNi_{1-x}(OH)_2$//AC flexible ASC was fabricated by assembling a PVA/KOH gel film between $CuO@Co_xNi_{1-x}(OH)_2$ electrode and AC electrode. The as-fabricated device was sealed with parafilm to maintain the stable performance of the SC. ASCs were assembled by two electrodes with different charge storage properties to maintain the

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charge balance of the electrodes. The charge balance between the two electrodes follows the relationship of $q^+ = q^-$, and q is calculated in accordance with the equation $q = C_s \times \Delta V \times m$. The mass ratio between $CuO@Co_xNi_{1-x}(OH)_2$ (m_+) electrode and AC (m_-) electrode was obtained using the equation $\frac{m_+}{m_-} = \frac{C_-\Delta V_-}{C_+\Delta V_+}$; thus, the mass ratio of AC to $CuO@Co_xNi_{1-x}(OH)_2$ is 7.3. The electrochemical performance of the devices was evaluated on the same electrochemical workstation. Energy (E, Wh kg^{-1}) and power (P, W kg^{-1}) density were defined as $E = \frac{1}{2}\frac{1000C_s\Delta V^2}{3600}$ and $P = \frac{3600E}{\Delta t}$.

3. Results and discussion

We propose a fabrication strategy for $CuO@Co_xNi_{1-x}(OH)_2$ core/shell nanowire arrays on CF (Scheme 1). Vapor–liquid–solid mechanism can be used to account for the growth of CuO nanowires [20]. When CF is oxidized in air, Cu_2O film forms on the CF surface. Cu_2O then serves as the seed for CuO growth [15]. The reaction processes involved in the synthesis can be summarized as

$$4Cu + O_2 \rightarrow 2Cu_2O \tag{1}$$

$$4\ Cu_2O + O_2 \rightarrow 4CuO \tag{2}$$

CuO nanowires grow through the grain-boundary diffusion of Cu ions across the Cu_2O layer [16]. The slow rate of CuO formation ensures continuous growth mode and uniform diameter for the nanowires. $Co_xNi_{1-x}(OH)_2$ ultrathin nanosheets are electrodeposited uniformly on the CuO nanowire by electrodeposition to obtain 1D hierarchical arrays of $CuO@Co_xNi_{1-x}(OH)_2$ core/shell nanowires supported on CF. The reactions at the deposition potential mainly involve the reduction of nitrate ions (NO_3^-), the interaction

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between the cations and OH⁻ generated, and the deposition of double hydroxides on the substrate. During the initial electrodeposition, NO_3^- ions are reduced ($E^0 = -200mV$) on the cathodic surface to produce hydroxide ions (Eq. 3) [21]. Ni^{2+} and Co^{2+} ions and electro-generated OH⁻ form hydroxide deposits and are immobilized on the substrate to offer nucleation sites for hydroxide growth [22]. The electrodeposition process can be expressed as follows:

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^- \tag{3}$$

$$M^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow M(OH)_{2(s)} \text{ where M = Co, Ni, or (Co + Ni)} \tag{4}$$

Fig. 1a and S1 show the top-view SEM of CuO on CF. The fluffy surface of CF indicates that its entire surface is covered by CuO nanowires. The nanowires possess smooth surfaces and are uniformly distributed and separated from one another (Fig. 1b). The interspaces between neighboring CuO nanowires can provide sufficient solution contact, leading to homogeneous $Co_{0.2}Ni_{0.8}(OH)_2$ modification. Fig. 1c shows the low-magnification TEM image of a CuO nanowire; such image is consistent with the SEM observations. The high-resolution TEM (HRTEM) image is presented in Fig. 1d. Lattice fringe corresponding to the interplanar distance of 0.23 nm can be indexed to the (200) plane of monoclinic CuO phase. XRD measurements were conducted to determine the phase structure of the final products. The backbone material, namely, CuO nanowires on CF (CF@CuO, Cu_2O: JCPDS card No. 05-0667; CuO: JCPDS card No. 48-1548), was identified based on the XRD pattern in Fig. 1e (blue line). The $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ scratched from the substrate was identified in Fig. 1e (red line). The peaks appearing at 2θ values of 11.3° (7.91 Å), 22.2° (4.1Å), 34.1° (2.62 Å), and 60.5° (1.52Å) could be due

to the reflections of the planes (001), (100), (101), and (110), respectively, which correspond to α-Co(OH)$_2$ and α-Ni(OH)$_2$ [23, 24]. Differentiating between α-Co(OH)$_2$ and α-Ni(OH)$_2$ phases is difficult because of their similar structures and very close diffraction peaks [25]. α-Co(OH)$_2$ and α-Ni(OH)$_2$ layers are randomly oriented and have a wide interlayer spacing because the interlamellar space contains water molecules bound to the hydroxyl groups by hydrogen bonds; these layers could exhibit superior electrochemical activity [26]. Raman measurements were then conducted on the samples to further explore the properties of the hierarchical hybrid structures (Fig. 1f). The Raman spectrum of CF@CuO shows three peaks at 293.3, 341, and 630.5 cm^{-1}, corresponding to the A_g, $B_g^{(1)}$, and $B_g^{(2)}$ modes, respectively, of the CuO backbone [27]. The band at 530 cm^{-1} in CuO@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ was not found in CuO; this band can be assigned to the stretching of M–O (M = Co or Ni) bond in α-Co(OH)$_2$ and/or α-Ni(OH)$_2$ [28, 29]. After electrochemical deposition, the 3D array of CuO@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ nanowires was obtained (Fig. 1g). Each CuO nanowire is fully and uniformly covered by the Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ nanosheets. The as-obtained array maintains a highly uniform orientation vertical to the substrate. The unique alignment of nanostructures provides a wide electrochemically active surface and short pathways for rapid ion diffusion and electron transport to improve the electrochemical performance [30]. The high-magnification SEM image (Fig. 1h) reveals that the Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ layer is constructed by perpendicularly cross-linked nanosheets, forming a highly porous surface morphology, which plays a vital role in electrolyte penetration [31]. When viewed at higher magnifications, the nanosheets present a smooth surface and a uniform thickness of ~7 nm (Fig. 1i). The

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energy-dispersive X-ray spectroscopy (EDS) map (Fig. S2) demonstrates the homogenous distribution of elements (Ni, Co, Cu, and O).

TEM characterization was performed to elucidate the detailed nanostructure and the phase of the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ core/shell nanowires. Fig. 2a shows the low-magnification TEM image of an isolated nanowire; in the image, the CuO nanowire core and $Co_{0.2}Ni_{0.8}(OH)_2$ shell ($\approx$130 nm) can be clearly distinguished. The gauze-like $Co_{0.2}Ni_{0.8}(OH)_2$ nanosheets were densely grafted along the CuO nanowire uniformly, forming a robust bond to the nanowire. The core/shell feature was verified through cross-sectional analyses by TEM. Fig. 2b shows a typical TEM image of the cross-section of the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ nanowire. Notably, $Co_{0.2}Ni_{0.8}(OH)_2$ nanosheets are not parallel but vertically grown on the CuO nanowire surface. This result is consistent with the above-mentioned analyses. Fig. 2c displays the HRTEM images of the core/shell nanowire. The visible lattice fringes corresponding to the interplanar distance of 0.25 nm can be attributed to the (1, 1, −1) plane of the CuO phase, and the interplanar distance of 0.234 nm matches well with the (101) planes of $Co_{0.2}Ni_{0.8}(OH)_2$. In addition, the lattice distortion for both CuO and $Co_{0.2}Ni_{0.8}(OH)_2$ in the interface region suggests the strong interaction between the core and shell [32]. Elemental mapping analyses were performed by HAADF–STEM–EDS to confirm the structure of the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ nanowire (Fig. 2d). Cu is located in the central part, and Co and Ni are distributed homogeneously in the shell region. The uniform elemental distribution was further identified through the EDS line scan spectra (Fig. S3).

XPS analysis was conducted to characterize the elemental composition and chemical valence states of $CuO@Co_{0.2}Ni_{0.8}(OH)_2$, confirming the existence of Cu, Co, Ni, C, and

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O in Fig. S4. Fig. 2e, f, and g show the high-resolution XPS spectra of Cu 2p, Co 2p, and Ni 2P, respectively. By using the Gaussian fitting method, the XPS spectra for the Cu 2P show the best fit of the spin-orbit split doublet of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ with a separation of 20 eV (Fig. 2e). The fitting peaks at 933.8 and 953.8 eV are indexed to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively [33]. As shown in Fig. 2f, the fitting peaks at binding energies of 855.5 and 873.2 eV correspond to Ni $2p_{3/2}$ and Ni $2p_{1/2}$, respectively, along with two satellite peaks. For the XPS spectra of Co 2p, the two prominent peaks located at 780.7 and 796.5 eV can be attributed to $Co2p_{3/2}$ and $Co2p_{1/2}$, respectively, and two satellite peaks are located at 785.3 and 802.1 eV (Fig. 2g). Hence, Cu, Co, and Ni are present in the form of Cu^{2+}, Co^{2+}, and Ni^{2+}, respectively, in the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ composite.

To optimize the electrochemical performance of the 1D hierarchical nanowire electrode, we determined the effect of Co^{2+}/Ni^{2+} molar ratios on the CV and GCD curves. When the other experimental parameters were unchanged, altering the Co^{2+}/Ni^{2+} molar ratios can tune the electrochemical performance of $Co_xNi_{1-x}(OH)_2$. Fig. 3a shows the CV curves of $Co_xNi_{1-x}(OH)_2$, $Co(OH)_2$, and $Ni(OH)_2$ electrodes at a scan rate of 10 mV s^{-1} within the potential window of 0 V to 0.6 V. $Co_xNi_{1-x}(OH)_2$, $Co(OH)_2$, and $Ni(OH)_2$ electrodes show strong redox peaks, which originated mainly from the Faradaic reactions of the surface oxycation species [34]. In the alkaline electrolyte, the Faradaic reactions of $Co(OH)_2$ and $Ni(OH)_2$ were based on the equations [35, 36]:

$$Co(OH)_2 + OH^- \leftrightarrow CoOOH + H_2O + e^- \tag{5}$$

$$CoOOH + OH^- \leftrightarrow Co_2O + H_2O + e^- \tag{6}$$

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^- \tag{7}$$

The redox reactions of $Co(OH)_2$ involve two steps. In particular, two pairs of redox peaks can be observed for $Co(OH)_2$ and $Co_xNi_{1-x}(OH)_2$ due to the existence of Co^{2+}. Notably, the redox peaks are gradually enhanced, and the anodic peaks shift to higher potential with increasing Ni content in the $Co_xNi_{1-x}(OH)_2$ host slabs [21]. Furthermore, the integral area is the largest for the $Co_{0.2}Ni_{0.8}(OH)_2$, suggesting the feasibility of rationally tuning the Co^{2+}/Ni^{2+} molar ratio to optimize the electrochemical performance. Fig. 3b shows the symmetrical GCD curves of the as-prepared electrodes at a galvanic current density of 2 A g^{-1}, indicating good reversible redox reactions. And energy efficiencies of the $Co(OH)_2$, $Co_xNi_{1-x}(OH)_2$, and $Ni(OH)_2$ electrodes were calculated based on the data in Fig. 3b (Fig. S5) [37]. The gravimetric capacity at a current density of 1 A g^{-1} were determined to be 85.0, 106.6, 223.2, 350.6, 374.7, 294.1, and 238.9 mAh g^{-1} for $CuO@Co(OH)_2$, $CuO@Co_{0.75}Ni_{0.25}(OH)_2$, $CuO@Co_{0.67}Ni_{0.33}(OH)_2$, $CuO@Co_{0.4}Ni_{0.6}(OH)_2$, $CuO@Co_{0.2}Ni_{0.8}(OH)_2$, $CuO@Co_{0.13}Ni_{0.87}(OH)_2$, and $CuO@Ni(OH)_2$ (Fig. 3c). Consistent with the CV profiles, the $Co_{0.2}Ni_{0.8}(OH)_2$ electrode exhibits the highest capacity, which is more than 4.4 times higher than that of $Co(OH)_2$ and 1.5 times than that of $Ni(OH)_2$. These results can be attributed to the enhancement of the electro-active sites participating in the Faradaic reactions as a result of possible valence interchange or charge hopping between Co and Ni ions since the electro-active sites in Ni–Co bimetallic hydroxides is tunable through various Ni/Co molar ratio [13, 38]. Therefore, the optimized $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ sample was selected to perform electrochemical tests and fabricate flexible ASC.

Fig. 3d shows the CV curves of CF@CuO (Fig. S6), $Co_{0.2}Ni_{0.8}(OH)_2$ nanosheets grown on CF ($CF@Co_{0.2}Ni_{0.8}(OH)_2$), and $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrodes at scan rate of 10

mV s^{-1} with 6 M KOH as electrolyte. The CV integrated areas of CF@CuO are negligible compared with that of the hybrid electrodes, indicating the negligible contribution of CF@CuO toward the capacity under the conditions adopted in the present work. Moreover, the current density and enclosed CV curve area of the CuO@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ electrode are significantly higher than those of the CF@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ electrode. This finding implies that the CuO@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ electrode possesses high specific capacity and fast redox reaction kinetics because of the synergistic effect of the CuO nanowire arrays and the ultrathin Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ nanosheets [39]. The GCD curves of CF@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ and CuO@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ are symmetric and indicate reversible electrochemistry (Fig. S7). Hence, the discharging time for CuO@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ is higher than that for CF@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$.

Fig. 3e presents the CV curves of the typical CuO@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ electrode at various scan rates ranging from 5 mV s^{-1} to 100 mV s^{-1}. Obvious redox peaks exist in the CV curves, indicating the presence Faradaic reactions between CuO@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ and alkaline electrolytes. With increasing scan rates, the quasi-symmetric redox peaks and similar curve shapes are maintained, implying the prominent reversible redox reaction. The cathodic peak shifts positively, and the anodic peak shifts negatively because of increased ion diffusion resistance [40]. Fig. 3f shows the representative GCD plots of CuO@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ electrode at current densities of 2, 5, 10, 20, 30, 40, and 50 A g^{-1}. The GCD curves remain symmetrical even at current densities as high as 50 A g^{-1}, indicating superior rate capability. The specific capacity of CuO@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ electrode reaches 374.7, 361.2, 347.1, 328.4, 317.2, 308.1, and 301.7 mAh g^{-1}, which correspond to current densities of 2, 5, 10, 20, 30, 40, and 50 A g^{-1}, respectively. The

results reveal that the optimized $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrode can remarkably retain 80.5% of its initial capacity even when the current density was increased by 25 times. Fig. 3g shows the plot of specific capacity versus current density of the $Co_{0.2}Ni_{0.8}(OH)_2$ and $CF@Co_{0.2}Ni_{0.8}(OH)_2$ electrodes. The specific capacity for the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrode increases by 1.5 times compared with that of the $CF@Co_{0.2}Ni_{0.8}(OH)_2$ electrode (244.4 mAh g^{-1}). The capacity retention for the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrode is higher than that for the $CF@Co_{0.2}Ni_{0.8}(OH)_2$ electrode (68.6%) when the scan rates were increased from 2 A g^{-1} to 50 A g^{-1}. EIS analysis was carried out to further understand the exceptional performance of the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrode (Fig. 3h). The Nyquist plots consist of three main distinguishable regions: high-frequency semi-circle, mid-frequency Warburg impedance, and low-frequency capacitive behavior (Fig. S8) [41]. The measured impedance data were analyzed by fitting to an equivalent electrical circuit, which is composed of an equivalent series resistance (R_s, which includes the intrinsic resistance of active materials, ionic resistance electrolyte, and contact resistance at the active material/current collector interface), charge-transfer resistance (R_{ct}), Warburg impedance (W), and constant-phase element. The fitting values from the equivalent circuit are shown in Table S1. The $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrode shows lower equivalent electrical resistance (R_s = 0.16 Ω) than that of the $CF@Co_{0.2}Ni_{0.8}(OH)_2$ electrode (R_s = 0.29 Ω). Meanwhile, $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrode (R_{ct} = 0.23 Ω) possess lower charge transfer resistance than that of $CF@Co_{0.2}Ni_{0.8}(OH)_2$ electrode (R_{ct} = 0.41 Ω). The Warburg impedance is associated with the electrolyte ion diffusion length and diffusivity in the electrode [41]. $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrode exhibits higher CPE-T and CPE-P, and lower Ohmic resistance (W-R) and diffusion time constant (W-T)

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than that of CF@$Co_{0.2}Ni_{0.8}(OH)_2$ electrode, which implies better capacitive nature and improved diffusion rate of electrolyte ions [42]. The EIS analytical results reveal that the CuO@$Co_{0.2}Ni_{0.8}(OH)_2$ possesses favorable charge-transfer kinetics and rapid electron transport.

The charge–discharge cycling test of 10 000 cycles at 50 A g^{-1} was conducted to evaluate the stability of the CuO@$Co_{0.2}Ni_{0.8}(OH)_2$ electrode (Fig. 3i). The specific capacity of the CuO@$Co_{0.2}Ni_{0.8}(OH)_2$ electrode was maintained as 95.9% after 10 000 cycles. The outstanding durability was evident in the SEM images after long-term cycling (Fig. S9). The image shows the preserved well-ordered array structure and hierarchical morphology of the CuO@$Co_{0.2}Ni_{0.8}(OH)_2$ electrode.

The superior performance of the CuO@$Co_{0.2}Ni_{0.8}(OH)_2$ electrode originates from the architectural exquisiteness of the electrode materials and their concomitant unique properties (Fig. 4). This finding can be explained by the following points. (1) $Co(OH)_2$ and $Ni(OH)_2$ possess intrinsically high pseudocapacitive activities, and the binary metal ions of Ni and Co further enhance the capacitive performance because the mixed valence can increase the number of electro-active sites to superimpose the redox reactions. (2) The 1D hierarchical porous core/shell array configuration leads to an enlarged electrochemically active surface area and multi-access diffusion pathways for facile and rapid ion transport. The ultrathin $Co_xNi_{1-x}(OH)_2$ nanosheet shells are well separated and form a porous layer surrounding the CuO nanowire core, resulting in full access to the electrolyte. The porous and ultrathin morphologies are essential to alleviate volume change under repeated charge–discharge cycles. (3) The CuO nanowire core grown on a conductive substrate offers a direct electrical pathway from active species to the current

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collector. The interfaces of the core/shell are chemically self-assembled and ensure efficient charge transport and good structural integrity. The CuO nanowire core was in situ grown on CF to ensure fast electron transport and excellent structural integrity. (4) Well-aligned $CuO@Co_xNi_{1-x}(OH)_2$ nanowire arrays were grown homogenously on the surface of mesoporous CF current collector to effectively avoid the "dead volume." All the components, i.e., shell, core, and current collector, build a robust one-body structure, which can effectively tolerate any possible structural deformation and accommodate any mechanical stress, thereby ensuring remarkable flexibility and cyclability.

A flexible ASC device was assembled by employing the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ as the positive electrode, commercially available AC pasted on nickel foam as negative electrode(CV and GCD for AC in Fig. S10, Supplementary Materials), and PVA/KOH as solid electrolyte to demonstrate the practical applicability of the well-designed $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrode for flexible supercapacitor applications (Fig. 5a). Given that the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrode and AC electrodes possess stable potential windows of 0 V to 0.6 V and –1 V to 0 V (Fig. 5b), the operating voltage for the assembled ASC could possibly reach 1.6 V. Fig. 5c shows the CV profiles of the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$//AC ASC at a scan rate of 50 mV s^{-1} in different potential windows. The shapes of the CV curves obtained within a wide potential window suggest that both Faradaic reaction and electric double layer contribute to charge storage. The ASC device exhibits stable behavior in the operating window of 0–1.6 V. When the voltage window was further extended to 1.8 V, obvious polarization was observed.

Fig. 5d shows the CV curves of the ASC device measured with a voltage window of 0 V to 1.6 V at scan rates from 5 mV s^{-1} to 100 mV s^{-1}. Unlike the three-electrode

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electrochemical performance featuring obvious redox peaks, the device exhibits a quasi-rectangular CV geometry. With the gradual increase in the scan rate from 5 mV s^{-1} to 100 mV s^{-1}, the CV curve shows the well-maintained shape and excellent fast charge–discharge behavior of the device. The GCD curves of the ASC device at various current densities are illustrated in Fig. 5e. Voltage plateaus were observed in the GCD curves, consistent with the redox peaks in the CV curves. The nearly symmetrical charge–discharge characteristic indicates high Coulombic efficiency and electrochemical reversibility. The specific capacities of the ASC device were calculated from the GCD curves and plotted as a function of current density (Fig. 5f). The device exhibits a high specific capacity of 58.2 mAh g^{-1} based on the total mass of the positive and negative electrodes at 1 A g^{-1} and a high rate capability with a specific capacity of 35.6 mAh g^{-1} at a high current density of 10 A g^{-1}.

To demonstrate the potential application of the ASC in flexible electronic devices, we measured the CV curves under various bending states. The obtained CV curves show no significant change and reveal the excellent flexibility and stability of the device (Fig. 5g). Energy and power densities are two important parameters used to evaluate the performance of energy storage devices. The Ragone plots of CuO@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$ derived from the GCD curves are shown in Fig. 5h. Energy density as high as 46.5 Wh kg^{-1} was obtained at a power density of 526.9 W kg^{-1}, and an energy density of 28.4 Wh kg^{-1} was maintained at a high power density of 7876.9 W kg^{-1}. The CuO@Co$_{0.2}$Ni$_{0.8}$(OH)$_2$//AC ASC device exhibits superior performance to those of other trans-metal-based ASCs, such as NiCo$_2$S$_4$@polypyrole//AC (34.62 Wh kg^{-1} at 120.19 W kg^{-1}) [43], NiCo$_2$O$_4$@CNT/CNT//carbon cloth (27.6 Wh kg^{-1} at 550 W kg^{-1}) [44],

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MnO_2@polypyrole//AC (25.8 Wh kg^{-1} at 901.7 W kg^{-1}) [45], MnO_2/polyaniline//AC (40.2 Wh kg^{-1} at 340 W kg^{-1}) [46], $CoNi_2O_4$@MnO_2//AC (37.8 Wh kg^{-1} at 187.5 W kg^{-1}) [47], Ni-Co-S/graphene//carbon (43.3 Wh kg^{-1} at 800 W kg^{-1}) [48], $NiCo_2S_4$//graphene (38.64 Wh kg^{-1} at 1330 W kg^{-1}) [49], $Ni/MnO_2//Ni/Fe_2O_3$ (34.1 Wh kg^{-1} at 3197.7 W kg^{-1}) [50], $FeCo_2S_4$-$NiCo_2S_4$//$FeCo_2S_4$-$NiCo_2S_4$ (46 Wh kg^{-1} at 1070 W kg^{-1}) [51], $NiCo_2S_4$//carbon (35 Wh kg^{-1} at 640 W kg^{-1}) [52], g-C3N4@$Ni(OH)_2$//graphene (43.1 Wh kg^{-1} at 1870 W kg^{-1}) [53], and $MnCo_2O_{4.5}$//AC (40.5 Wh kg^{-1} at 376 W kg^{-1}) [54]. The GCD measurement was conducted to evaluate the long-term stability of the ASC device at the current density of 7 A g^{-1}. The results show that 84.3% of the initial capacity was retained after 10 000 cycles, indicating the excellent stability of the as-fabricated CuO@$Co_{0.2}Ni_{0.8}(OH)_2$//AC ASC device. Remarkably, the Coulombic efficiency of the ASC devices stayed ≈97% during the 10 000 charge-discharge cycling test (Fig. S11). For practical application, a red light-emitting diode (LED, 1.9 V) was lit by two flexible ASCs connected in series (Fig. 5i inset).

4. Conclusions

In conclusion, we designed and fabricated 1D hierarchical CuO@$Co_xNi_{1-x}(OH)_2$ core/shell nanowire arrays in situ grown on CF through a facile oxidation process and fast and well-controllable electrodeposition. The resultant CuO@$Co_{0.2}Ni_{0.8}(OH)_2$ electrodes exhibit an ultrahigh specific capacity of 374.7 F g^{-1} at a current density of 2 A g^{-1}, superior rate capability of 80.5% at 50 A g^{-1}, and extremely long cycle stability with capacity retention of 95.9% after 10 000 charge–discharge cycles at 50 A g^{-1}. The superior performance could be attributed to the excellent electrical conductivity of metallic mesoporous Cu foam, 1D electron transport highway of CuO nanowire arrays,

and outstanding pseudocapacitive properties of the $Co_xNi_{1-x}(OH)_2$ ultrathin nanosheets with a large surface area and porous morphology. A flexible ASC device was assembled using $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrodes as the positive electrode, AC on nickel foam as negative electrode, and PVA/KOH as electrolyte to demonstrate the practical application of the high-performance pseudocapacitive electrodes. The maximum specific energy density of 46.5 Wh kg^{-1} and specific power of 7876.9 W kg^{-1} were obtained with an operational potential range of 1.6 V. Hence, the rational design of 1D hierarchical core/shell arrays is an effective approach to realize high specific capacity, high rate capability, and long cycle stability for high-performance supercapacitors. Furthermore, this hierarchical nanostructure arrays may be applicable to other energy conversion and storage systems, such as lithium-ion batteries, water splitting devices, and fuel cells.

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Figure captions

Scheme 1. Schematic of the fabrication process. CuO nanowire array was grown in situ onto the CF through thermal oxidation. $Co_xNi_{1-x}(OH)_2$ ultrathin nanosheets were electrodeposited on CuO nanowire arrays.

Fig. 1. (a, b) SEM images of CF@CuO. (c) TEM and (d) HRTEM images of the CuO nanowire. (e) XRD patterns and (f) Raman spectra of CF@CuO and $CuO@Co_{0.2}Ni_{0.8}(OH)_2$. (g-i) SEM images of $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ with different magnifications. Inset in (i) shows the corresponding magnified nanosheet structure.

Fig. 2. (a) TEM images of $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ at different magnifications. (b) TEM, (c) HRTEM cross-section of the FIB-cut $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ nanowire. (d) Corresponding EDS mapping images for Co, Ni, Cu, and O in the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ nanowire cross-section. High-resolution XPS spectra of Cu 2p (e), Ni 2p (f), and Co 2p (g) core levels in $CuO@Co_{0.2}Ni_{0.8}(OH)_2$.

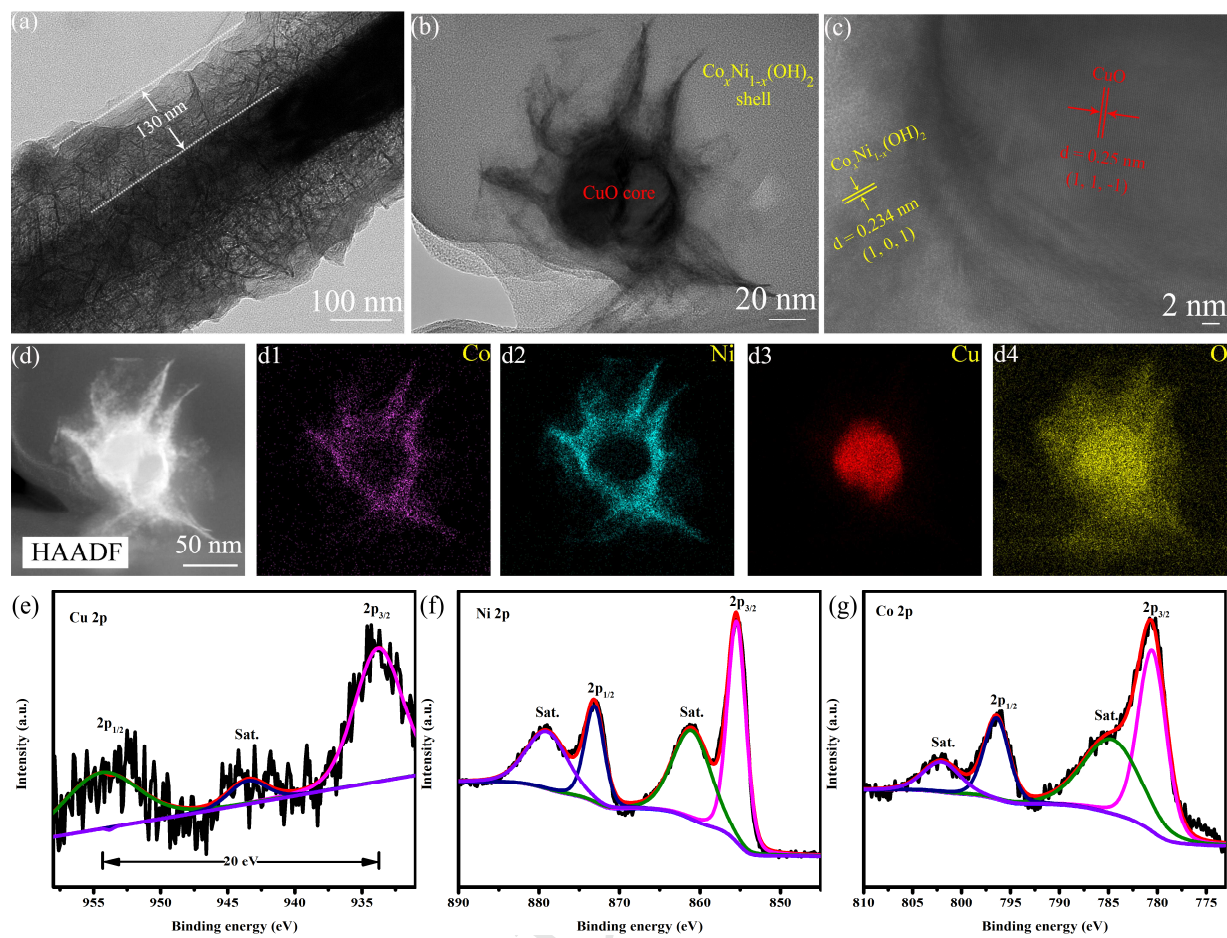**Fig. 3.** (a) CV curves of $Co_xNi_{1-x}(OH)_2$, $Co(OH)_2$, and $Ni(OH)_2$ electrodes at a scan rate of 10 mV s^{-1}. (b) GCD curves of $Co_xNi_{1-x}(OH)_2$, $Co(OH)_2$, and $Ni(OH)_2$ electrodes at a current density of 2 A g^{-1}. (c) Specific capacity of $Co_xNi_{1-x}(OH)_2$, $Co(OH)_2$, and $Ni(OH)_2$ electrodes at a current density of 2 A g^{-1}. (d) CV curves of CF@CuO, $CF@Co_{0.2}Ni_{0.8}(OH)_2$, and $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrodes. (e) CV curves of $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ at different scan rates. (f) GCD curves of $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ at different current densities. (g) Specific capacity of $CF@Co_{0.2}Ni_{0.8}(OH)_2$ and $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrodes at different current densities. (h) EIS curves of $CF@Co_{0.2}Ni_{0.8}(OH)_2$ and $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrodes. (i) Cycling performance of
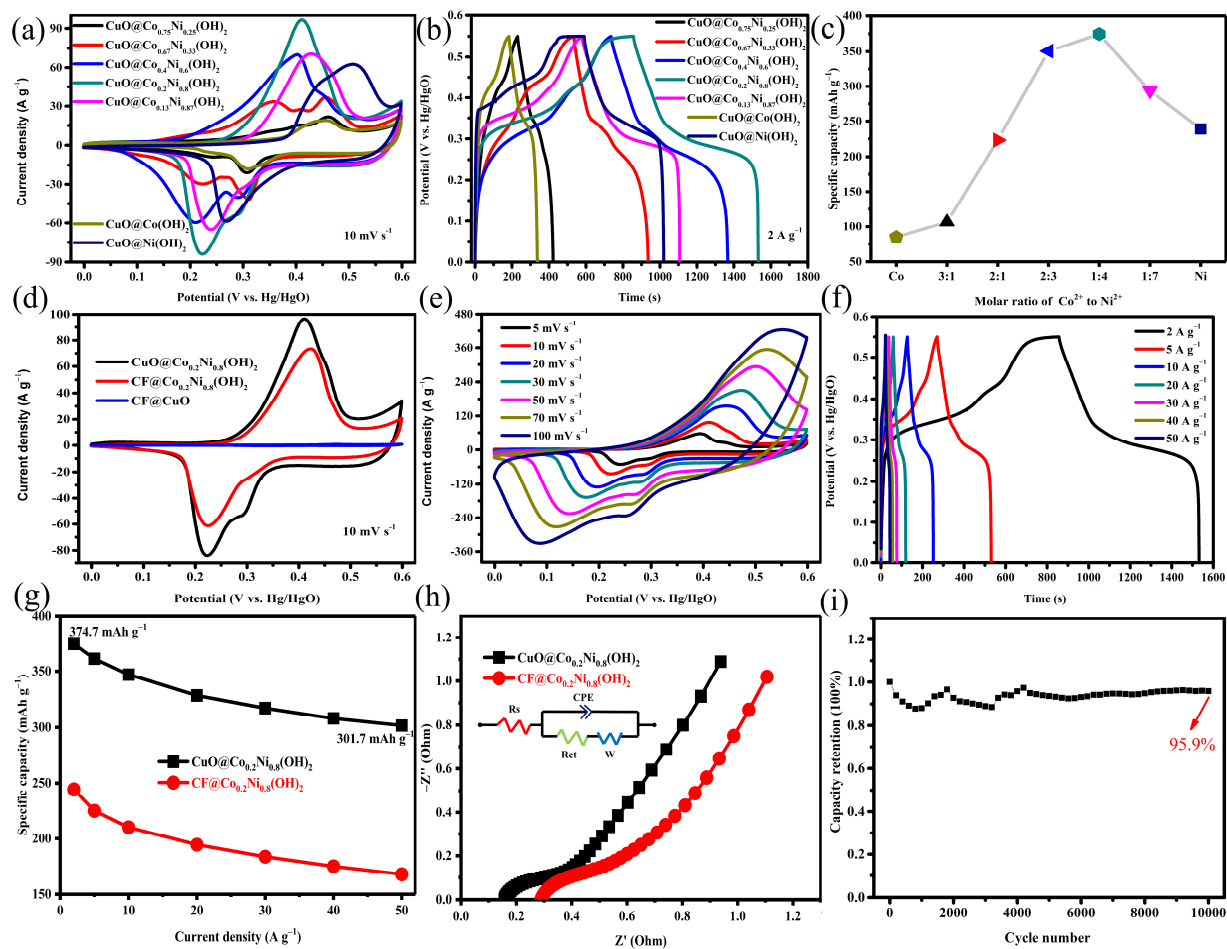
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$CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrode at a current density of 50 A g^{-1} up to 10 000 cycling charge–discharge tests.
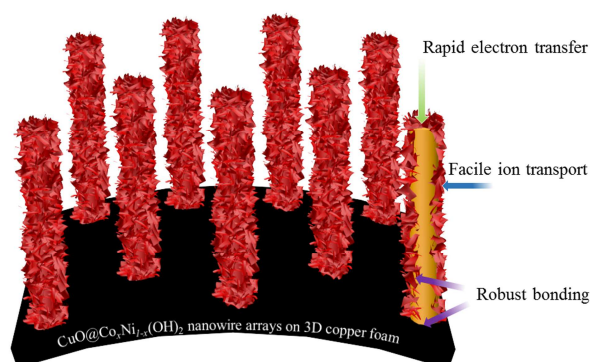
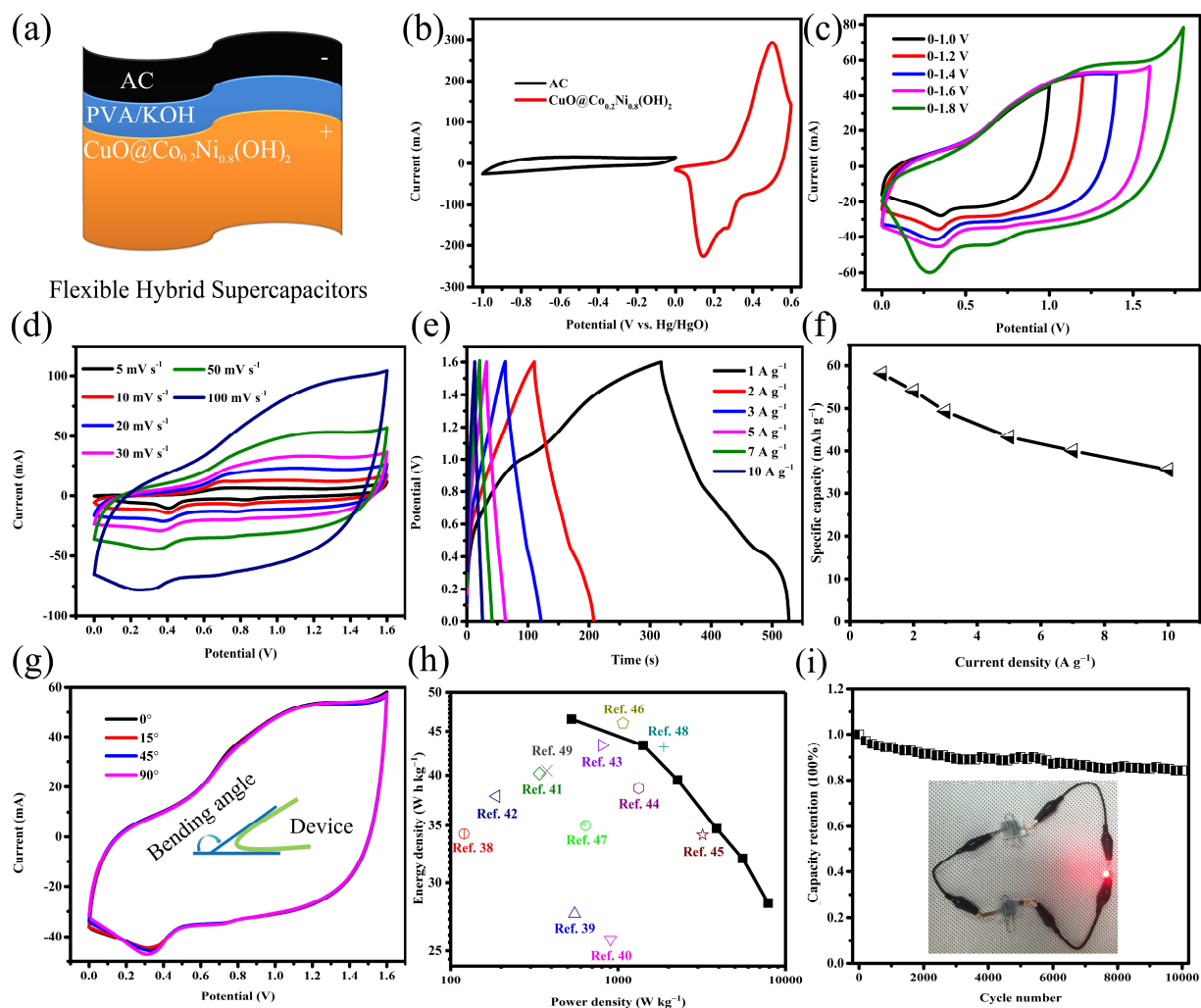**Fig. 4.** Electrode design of $Co_xNi_{1-x}(OH)_2$. Each component provides different functionalities.

Fig. 5. (a) Schematic of the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$//AC flexible ASC configuration. (b) CV curves of the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ electrode and AC electrode in separate potential windows at a scan rate of 50 mV s^{-1}. (c) CV curves of the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$//AC in different voltage windows at a scan rate of 50 mV s^{-1}. (d) CV curves of the flexible device at different scan rates. (e) GCD curves at various current densities. (f) Specific capacity at different current densities. (g) CV curves of the flexible device under different bending conditions at a scan rate of 50 mV s^{-1}. (h) Ragone plot of the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$//AC flexible ASC and previously reported SCs in literature. (i) Cycling performance of the $CuO@Co_{0.2}Ni_{0.8}(OH)_2$//AC flexible ASC at a current density of 7 A g^{-1} for 10 000 cycles; inset shows an LED lit by the ASC devices connected in series.

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Rapid electron transfer

Facile ion transport

Robust bonding

CuO@Co$_x$Ni$_{1-x}$(OH)$_2$ nanowire arrays on 3D copper foam

CF $\xrightarrow{\text{Heat treatment}}$ **CF@CuO** $\xrightarrow{\text{Electrodeposition}}$ **CuO@Co$_x$Ni$_{1-x}$(OH)$_2$**
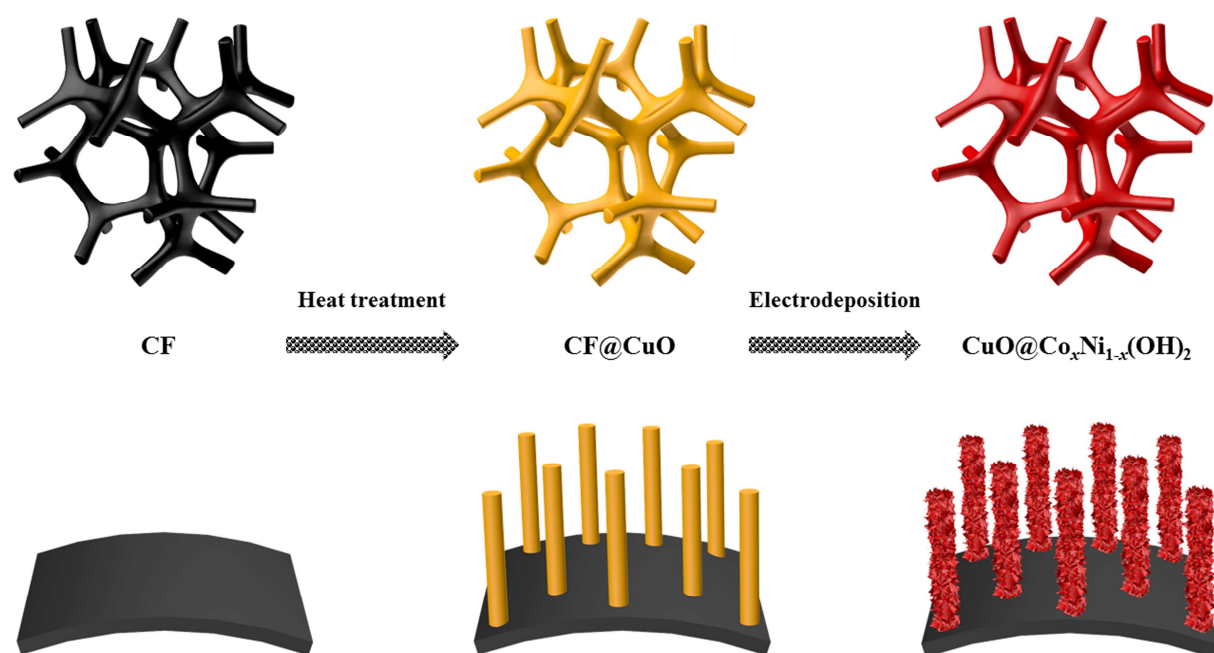
Highlights

- $CuO@Co_xNi_{1-x}(OH)_2$ nanowire arrays grown on 3D copper foam was fabricated.

- The architecture delivered an ultrahigh specific capacity.

- Flexible hybrid supercapacitor using $CuO@Co_{0.2}Ni_{0.8}(OH)_2$ was assembled.

- The flexible devices displayed excellent electrochemical performance.