Supporting information

Effects of chemical composition and vacant oxygen defects on the performance of $Ni(OH)_2$-$Ni_{0.85}Se$ heterostructure nanowires as supercapacitor electrodes

Ziwei Wang[a], Yongjie Zheng*[a], Kun Song*[a], Jianjiao Xin[a], Guangming Yin[a], Guoli Chen[ab]

[a] College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar 161006, Heilongjiang, P. R. China

[b] School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, P. R. China.

* Corresponding author: Tel: +86 452 2738 750; Fax: +86 452 2738 750

E-mail: zyj1964@163.com; sky253838@163.com

Experimental Procedures

Materials and Characterization

Nickel sulfate, sodium hydroxide, Ni foam, sodium selenite and CNTs were purchased from Aladdin. Ethanol, hydrochloric acid and potassium hydroxide were purchased from Tianjin recovery technology development Co.,Ltd. (Tianjin, China). All chemicals used in this study were of analytical grade.

The X-ray diffractometer is the Japanese science SmartLab, the X-ray source is Kα series, the copper target, the maximum test voltage is 45 kV, the maximum current is 150 A, the incident wavelength is lambda =0.1541 nm, the test range is 2θ Angle from 0 to 210, the scanning speed can be set, and the minimum step length of the goniometer is 1/10000 degree. High precision goniometer, goniometer with program variable slit, automatic identification of all optical components sample table, CBO cross light path, provide focused light path and high intensity high resolution parallel light path (with Mirror), multi-purpose film test kit. Powder sample, Measurement and analysis software is SmartLab Guidance, Little error.

The scanning electron microscope (SEM) is a Japanese electronic JSM-7200F, and the electronic optics system of JSM-7200F uses the Japanese electronic flagship. The immersive schottky gun technology of The JSM-7200F, and the standard TTLS (Through-The-Lens System), both under high/low acceleration voltage, the spatial resolution has been greatly improved over the traditional models. The maximum amplification factor of JSM-7200F is 1 million times, and it can obtain both secondary electron image and backscattered electron image. JSM-7200F has objective lens adopts hybrid lens. This hybrid lens is an electromagnetic field superposition objective lens combining magnetic lens and electrostatic lens, which is smaller than the traditional aberration and can obtain higher spatial resolution. Test conditions: Powder sample, the ambient temperature should be controlled at 22-25℃, the relative humidity should be less than 70%, to ensure the laboratory clean and tidy, to avoid loud noise and vibration of magnetic field interference.

The high resolution transmission electron microscope (HRTEM) is Hitachi H-9500 which can quickly conduct sample analysis, sample change in 1 minute. The atomic resolution of HRTEM by is 300 kV, rise to (300 kV) in 5 minutes. The point resolution is 0.18 nm, the lattice resolution is 0.1 nm and the amplification ratio is continuous amplification mode (1000~1500000), selection mode (4000~500000), and low power mode (200~500). The electron gun filament is LaB6 (lanthanum hexboride filament, dc heating), the lens is a four-stage lens, the concentrator aperture is 4-hole variable. Micron beam mode: 0.05-0.2 μm (level 4), nanometer beam mode: 1-10 nm (level 4), electron beam tilting ± 3°, image sway adjustment, positive focus compensation using astigmatism monitor. Image processing: digital CCD camera, effective pixel 1024×1024 pixels. EDS element range: B5~U92, EDS energy resolution: 138 eV. Test conditions: Powder sample, the ambient temperature should be controlled at 22-25℃, the relative humidity should be less than 70%, to ensure the laboratory clean and tidy, to avoid loud noise and vibration of magnetic field interference.

X-ray photoelectron spectroscopy (XPS): Thermo Fisher Scientific ESCALAB Xi X is an integrated test tool with a wide range of analytical techniques. The excitation source is monochromator ALK beam (h =1 486.6ev), power is 250 W, vacuum degree of the analysis room is 5×10^{-10} Mbar, full spectrum scanning range is 0~1350 eV, passing energy is 100 eV, step size is 1.00 eV. The imaging resolution of XPI is up to 1 μm, and the obtained data has no back-bottom feature of the detector and no back-bottom correction is needed to directly obtain the micron-scale resolution of the quantitative element distribution imaging results. During high-resolution fine scanning, the binding energy of samples with a pass energy of 20 eV and a step size of 0.10 eV is used to conduct charge correction on other test spectral peaks by using carbon pollution C1s (284.8 eV). The minimum energy resolution of the instrument is 0.48 eV (Ag 3d 5/2 peak) and avantage software is used for spectral peak fitting and quantification. Powder sample, Avantage analysis software, Little error.

The nitrogen desorption apparatus is Quadrasorb SI of kantar USA, an automatic specific surface area analyzer. It uses the gas adsorption principle (typically nitrogen) to determine the adsorption desorption isotherm. The BET specific surface area of single point and multi-point can be determined by Langmuir method, and the particle size estimation and true density test porosity and porosity analysis can be performed. The BJH method can also be used for the analysis of mesoporous and macroporous, as well as the determination of the surface area. The micropore area and pore size distribution are analyzed by MP method. It can also be used to analyze the microporous DR theory HK slit hole theory SF cylindrical hole theory, and can be upgraded to calculate the DFT density function theory. Test conditions: before degassing, the sample is degassed at 300 ℃ for 2 h after degassing. The sample is cooled slowly by liquid nitrogen, and the adsorption and desorption experiment is carried out. Powder sample, Microactive Interactive Data analysis software. ST2253 digital four-probe resistivity tester and high-wear-resisting tungsten carbide probe are used to test the resistivity/square resistance of hard materials such as silicon semiconductor metal conductive plastics.

Syntheses of electrodes

Synthesis of NF/4Ni(OH)$_2$-NiOOH nanowires: Firstly, 1 mol L^{-1} solutions of nickel sulfate and sodium hydroxide were prepared. Then, different proportions of nickel sulfate and sodium hydroxide solutions are transferred to the Teflon-lined stainless steel autoclave, where NF (2 cm × 2 cm) is added, and keep the temperature at 120 ℃ for 30 h. The samples were collected and cleaned with DI water for three times, which after the autoclave cooled down to room temperature. Then the samples were dried at room temperature and the product was NF/4Ni(OH)$_2$-NiOOH.

Synthesis of NF/Ni(OH)$_2$ nanowires: Then the above samples NF/4Ni(OH)$_2$-NiOOH, 40 mL DI water and 100 μL hydrazine hydrate were together moved to a 50 mL Teflon-lined stainless steel autoclave and kept at 120 ℃ for 3 h. After the autoclave cooled down to room temperature, the samples were cleaned with DI water for three times, the product was NF/Ni(OH)$_2$.

Synthesis of NF/Ni(OH)$_2$-$Ni_{0.85}Se$ heterogeneous nanowires: Then the above samples

NF/4Ni(OH)$_2$-NiOOH, 0.2 mol/L Na_2SeO_3 solution 40 mL and 100 μL hydrazine hydrate were together moved to a 50 mL Teflon-lined stainless steel autoclave and kept at 120 ℃ for 6 h. After the autoclave cooled down to room temperature, the samples were cleaned with DI water for three times, the product was NF/Ni(OH)$_2$-$Ni_{0.85}Se$.

Elactrochemical Measurement

The NF/Ni(OH)$_2$-$Ni_{0.85}Se$-4h is tailored and applied to working electrodes (1 cm × 1.5 cm, effective worked area of 1 cm × 1 cm). A platinum foil (10 mm × 10 mm) is employed as the counter electrode and Hg/HgO electrode as reference electrode, which apply to a three-electrode system in 3 M KOH solution. The CHI 660D electrochemistry workstation is used to the electrochemical measurements. Cyclic voltammetry (CV) tests are conducted in a potential range of 0−0.6 V (versus Hg/HgO) at scan rates of 10-100 mV s^{-1}. The cycling behavior is particular up to 2000 cycles, and galvanostatic charge–discharge (GCD) tests are carried out at various current densities with a potential range of 0−0.5 V (versus Hg/HgO). EIS (Electrochemical impedance spectroscopy) is implemented to testify the capacitive property at OCV (open circuit voltage) with a frequency from 1 to 10^5 Hz.

The asymmetrical supercapacitors (ASC) are assembled with NF/Ni(OH)$_2$-$Ni_{0.85}Se$-4h heterogeneous-tube as positive electrode and NF/CNTs as negative electrode. To preparing negative electrode could dispersing 80 wt% NF/CNTs is about 8 mg, 15 wt% carbon black is about 1.5 mg and 5 wt% poly (tetrafluoro-ethylene) (PTFE) is about 0.5 mg in ethanol. The mixed solution is fully ultrasonic mixed, divided into two parts on average, and one part is used to make the negative electrode. The homogeneous slurry is pasted onto a Cu foil (1 cm×1 cm) by a spatula, and then dried for 4 h. The actual mass ratio of the positive and negative electrode is 5:1. The active substance of the positive electrode is 2 mg cm^{-2}. The two electrodes of the hybrid flexible supercapacitor are separated by a separator (NKK, MPF30AC-100), and 3 M KOH is used as the electrolyte.

In the three-electrode system, saturated standard calomel electrode (Hg/HgO) and a piece of Pt foil (1 × 1 cm^2) were used as the reference electrode and counter electrode, respectively. An aqueous solution of KOH (3 mol L^{-1}) was used as the electrolyte in the three electrode. The mass specific capacity (Cm, F g^{-1} or Csp, C g^{-1}) of a single electrode is following the equation:

$$Cm = \frac{I \times \Delta t}{m \times \Delta V} \qquad \text{(F1)}$$

$$Csp = \frac{I \times \Delta t}{m} \qquad \text{(F2)}$$

Where Δt is discharge time, I is the discharge current and m is the active mass of the electrode, ΔV is the potential range of the electrode.

The mass specific capacity (C_{ASC}, F g^{-1}) of the hybrid supercapacitor is following the equation:

$$C_{ASC} = \frac{I \times \Delta t}{2 \times M \times \Delta V} \qquad \text{(F3)}$$

Where M is the total mass of the positive and negative electrode active materials, I is the discharge current, Δt is the discharge time, ΔV is the potential range of the electrode of the ASC.

The specific energy density E and power density P are following the equation:

$$E = \frac{0.5 \times C_{ASC} \times \Delta V}{3.6} \quad \text{(F4)}$$

$$P = \frac{E \times 3600}{\Delta t} \quad \text{(F5)}$$

Where C_{ACS} is mass specific capacity of the asymmetric supercapacitor, Δt is the discharge time, ΔV is the potential of the ASC.

Results and Discussion

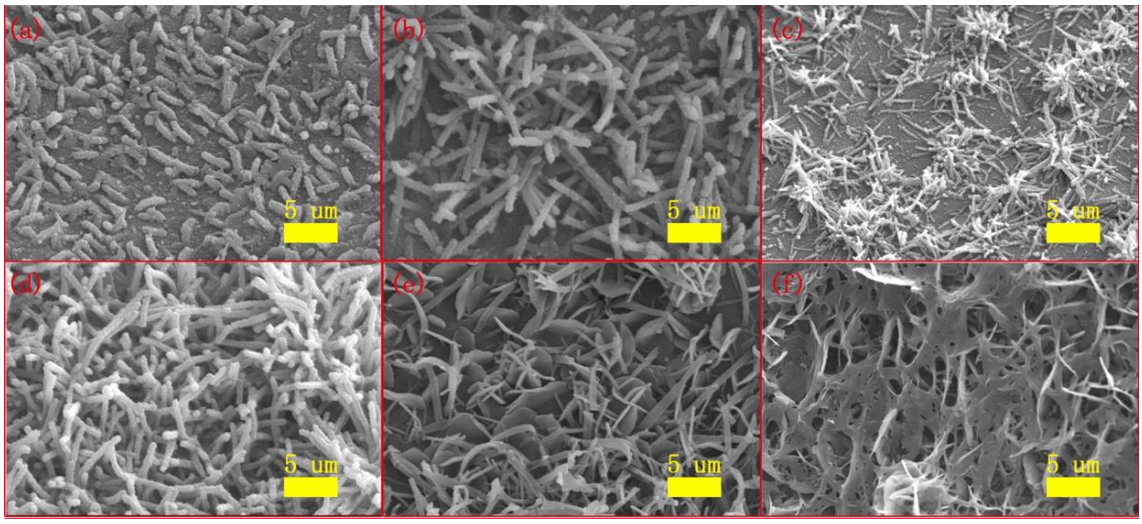

Figure S1. SEM images of $4Ni(OH)_2$-NiOOH nanowire with various reaction times of (a) 10 h, (b) 16 h, (c) 24 h, (d) 30 h, (e) 36 h, (f) 40 h.

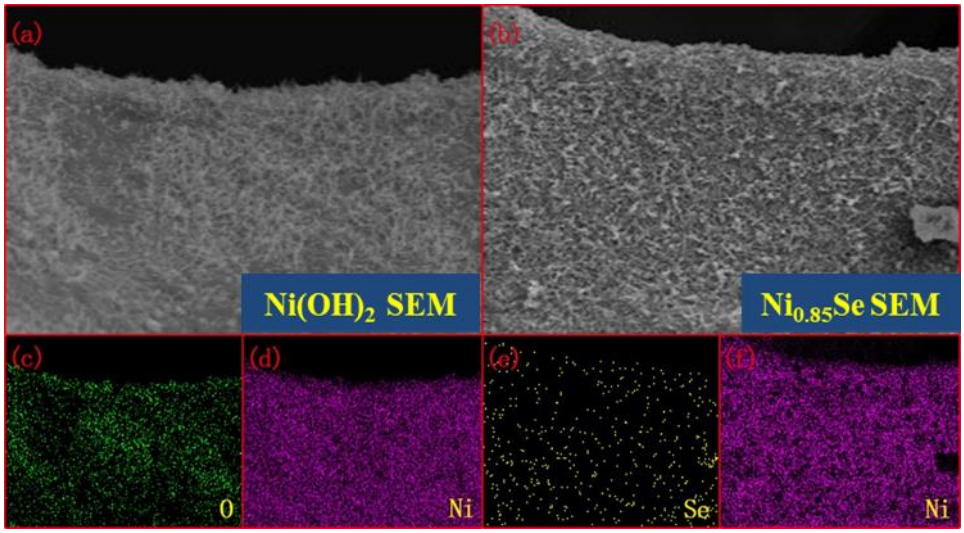

Figure S2. SEM images of (a) $Ni(OH)_2$ and (b) $Ni_{0.85}Se$ with (c) O, (d) Ni, (e) Se, (f) Ni.

Table S1. Comparisons of different reaction times, specific capacitance and retention rate.

Materials	Reaction time (h)	Discharge time (s)	Discharge voltage (V)	Specific Capacitance ($F\ g^{-1}$ at $1\ A\ g^{-1}$)	Retention rate after 2000 cycle (%)
$Ni(OH)_2$	6	70	0.5	140	89.8
	12	135	0.5	270	90
	20	150	0.5	300	90.1
	24	216	0.5	432	90.3
	30	700	0.5	1400	91.8
	36	630	0.5	1260	91.4
	40	364	0.5	728	90.7

Table S2. Data analysis of nitrogen absorption and desorption of selenides at different reaction times.

Materials	Reaction time (h)	S_{BET} ($m^2\ g^{-1}$)	Band gap (eV)	Average Pore Size (nm)	Total Pore Volume (cc/g)
NF/$Ni(OH)_2$-$Ni_{0.85}Se$	0	78.1	0.97	2.75	7.659e-01
	1	91.5	0.83	2.94	9.341 e-01
	2	94.9	0.76	3.05	10.221 e-01
	4	96.2	0.75	3.91	13.089 e-01
	6	92.6	0.68	4.23	15.221 e-01
	8	90.2	0.68	5.14	15.204 e-01

S_{BET}: surface area.

Table S3. The content of selenium and conductivity of samples.

Sample	Reaction time (h)	Se At% of EDS test	Resistance (Ω)	Resistivity (Ω m)	Conductivity (S m^{-1})
NF/$Ni(OH)_2$-$Ni_{0.85}Se$	0	0	4.8	4.8×10^{2}	2.083×10^{-3}
	1	10.5	4.7	4.7×10^{2}	2.128×10^{-3}
	2	19.9	4.7	4.7×10^{2}	2.128×10^{-3}
	4	32.7	4.6	4.6×10^{2}	2.174×10^{-3}
	6	35.9	4.4	4.4×10^{2}	2.273×10^{-3}
	8	61.3	4.2	4.2×10^{2}	2.381×10^{-3}
	10	61.3	4.1	4.1×10^{2}	2.439×10^{-3}
	14	61.3	4.1	4.1×10^{2}	2.439×10^{-3}

The Formula for calculating the Conductivity of sample is $R=\rho L/S$, $\sigma=1/\rho$ where R is the Resistance, S is the area, L is the length, ρ is Resistivity and σ is Conductivity of samples, respectively.

Table S4. Comparison of Se content, proportion of each component and specific capacity.

Materials	Reaction time (h)	Se At% of XPS test	Proportion of $Ni(OH)_2$ (%)	Proportion of $Ni_{0.85}Se$ (%)	Specific Capacity ($F\ g^{-1}$ at $1\ A\ g^{-1}$)
$NF/Ni(OH)_2$	-	0	100	0	1400
$NF/Ni(OH)_2$-$Ni_{0.85}Se$	1	10.1	89.5	10.5	1592
$NF/Ni(OH)_2$-$Ni_{0.85}Se$	2	19.7	75.1	24.9	1983
$NF/Ni(OH)_2$-$Ni_{0.85}Se$	4	32.5	55.6	44.4	2480
$NF/Ni(OH)_2$-$Ni_{0.85}Se$	6	35.8	49.4	50.6	2461
$Ni_{0.85}Se$	8	61.2	0	100	1861
$Ni_{0.85}Se$	10	61.3	0	100	1655
$Ni_{0.85}Se$	14	61.3	0	100	1586

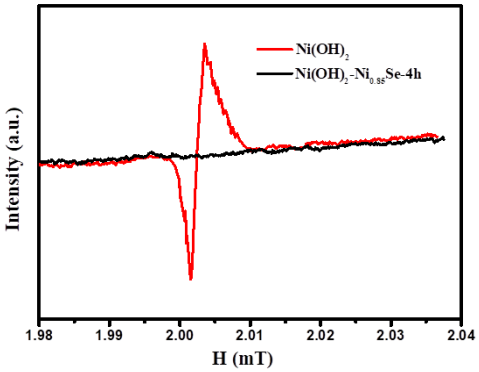

Figure S3. The room-temperature EPR spectra of $Ni(OH)_2$ and $Ni(OH)_2$-$Ni_{0.85}Se$-4h.

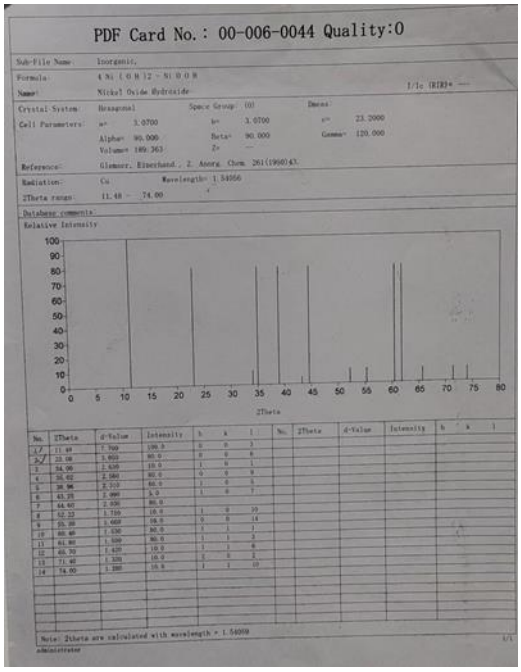

Figure S4. Photo image of the standard PDF card (00-006-0044).

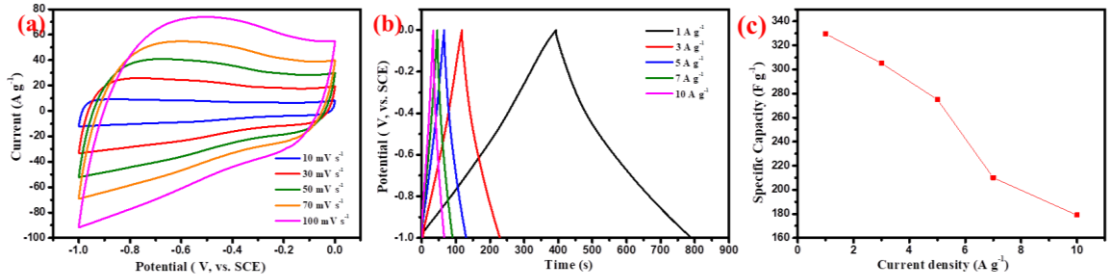

Figure S5. (a) CV curves, (b) GCD curves and (c) specific capacity of NF/CNTs.

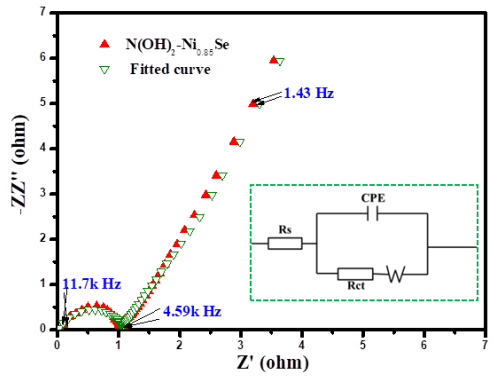

Figure S6. Nyquist plots and fitting curves.

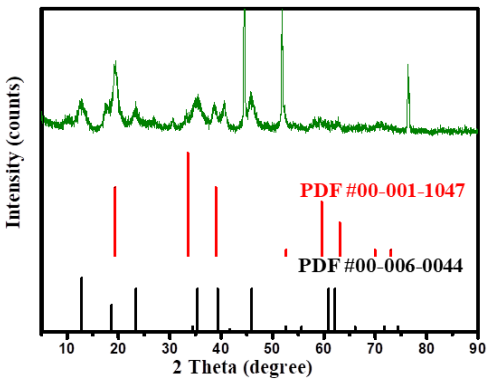

Figure S7. XRD pattern of NF/4Ni(OH)$_2$-NiOOH-40h.