

Supporting Information

Anion Exchange Strategy Towards Mesoporous α -Ni(OH)₂ Nanowires with Multinocavities for High-Performance Supercapacitors

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1. Chemicals

Nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, AR), sodium hydroxide (NaOH, AR), ethanol (EtOH, AR), potassium hydroxide (KOH, AR), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, AR), and isopropanol (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. The water used throughout the experiments was distilled water.

2. Synthesis of $\alpha\text{-Ni(OH)}_2$ nanowires

$\alpha\text{-Ni(OH)}_2$ nanowires were synthesized by a modified hydrothermal method.¹ In a typical process, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (9.8 mmol) was dissolved in 40 mL distilled water, and then 4.9 mmol of NaOH was added to the above solution. After 30 min stirring, the mixture was transformed into a 50 mL capacity Teflon-lined autoclave and heated at 120°C for 24 h. After cooling naturally to room temperature, the precipitate was collected by centrifugation. The green paste-like precipitate was subsequently washed three times with distilled water and ethanol, and then dried at 60 °C for 12 h in a vacuum oven. Finally, a green powder was obtained and denoted as S0.

3. Synthesis of mesoporous $\alpha\text{-Ni(OH)}_2$ nanowires

Anion exchange reaction was used to preparation of mesoporous $\alpha\text{-Ni(OH)}_2$ nanowires. 200 mg of $\alpha\text{-Ni(OH)}_2$ nanowires were dispersed into 40.0 mL of Na_2S solution under ultrasonication. After ultrasonicated for 60 min, the mixture was transformed into a Teflon-lined stainless steel autoclave with 50 mL capacity, which was sealed and subsequently heated to 80 °C for 6 h in an oven. After hydrothermal treatment, the precipitates were harvested by centrifugation, washed by distilled water

and ethanol three times. Finally, the sample was dried at 60 °C for 12 h in a vacuum oven. By controlling the concentration of Na₂S at 0.01, 0.03, 0.05, 0.10, and 0.20 mol/L, the as-prepared mesoporous α-Ni(OH)₂ nanowires were denoted as S1, S2, S3, S4, and S5, respectively.

4. Characterization

XRD patterns were recorded on a German Bruker AXS Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Scanning transmission electron microscopy (STEM) image, high-resolution TEM (HRTEM) image, selected area electron diffraction (SAED) pattern, and energy dispersive spectrometry (EDS) mapping were obtained on a FEI Tecnai G2 F30 field emission transmission electron microscopy with an accelerating voltage of 300 kV and equipped with energy dispersive spectrometry. Atomic Force Microscope (AFM) image was recorded on a Bruker dimension edge microscope. X-ray photoelectron spectroscopy (XPS) was measured on a Thermo Fisher Scientific ESCALAB250Xi X-ray photoelectron spectrometer. Pore diameter distribution was obtained from N₂ adsorption-desorption isotherm performed on a Quadrasorb SI analyzer.

5. Electrochemical tests

A three-electrode system was utilized to test the electrochemical properties of the samples. Platinum foil and saturated calomel electrode (SCE) electrodes were used as counter and reference electrodes, respectively. The working electrode was prepared by mixing 80 wt% of active material, 10 wt% of acetylene black, and 10 wt% of polytetrafluoroethylene (PTFE). Isopropanol was then added to the mixture to

produce a homogeneous paste, which was subsequently brush-coated onto nickel foam and then dried at 60 °C for 12 h in a vacuum oven. Cyclic voltammograms (CV), and galvanostatic charge-discharge curves were recorded on a CHI660C electrochemical workstation in a 2 mol/L KOH aqueous electrolyte. Cycling stability was performed on a NEWARE program control test system.

The specific capacitances (C_s) of the samples could be calculated according to the following equation.²

$$C_s = \frac{i\Delta t}{m\Delta V} \quad (2)$$

Where i is the discharge current, Δt is the discharge time, m is the mass of active materials, and ΔV is the range of potential window during discharge.

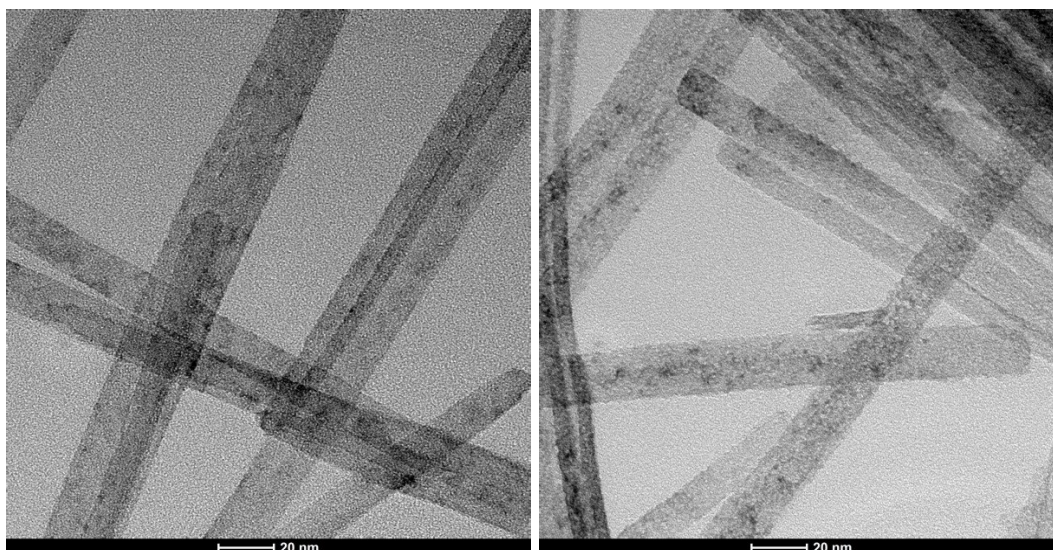
The specific capacitances also can be calculated by integrating the area under the CV curves according the following formula.³

$$C_s = \frac{1}{mv\Delta V} \int_{V_a}^{V_c} iVdV \quad (3)$$

Where C_s is the specific capacitance, m is the mass of active materials, v is the scan rate, ΔV is the range of potential window ($\Delta V=V_a-V_c$), and i is the current.

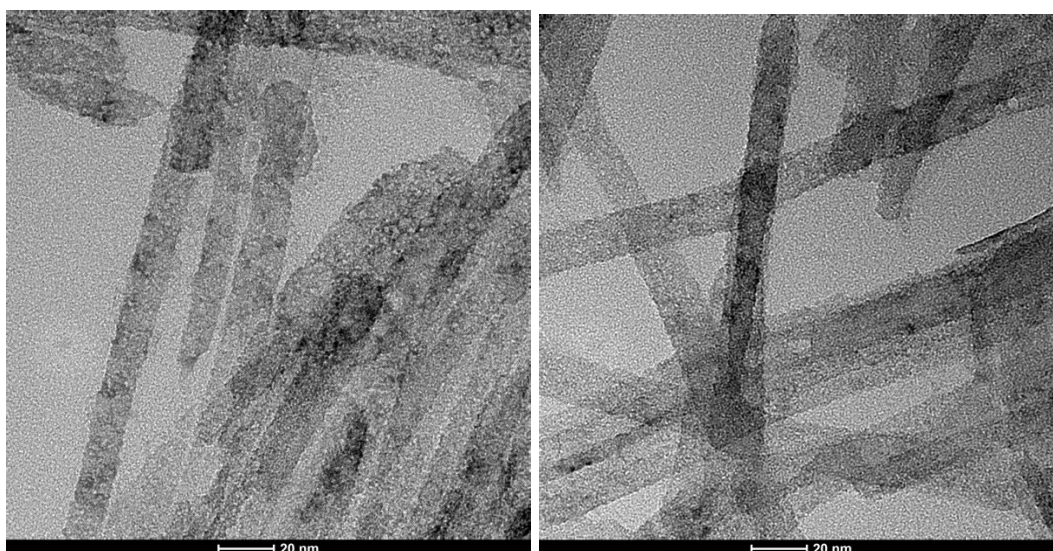
References

- (1) L. Dong, Y. Chu, W. Sun, *Chem. Eur. J.* **2008**, *14*, 5064.
- (2) Z. Sun, X. Lu, *Ind. Eng. Chem. Res.* **2012**, *51*, 9973.
- (3) J. W. Lee, A. S. Hall, J. D. Kim, T. E. Mallouk, *Chem. Mater.* **2012**, *24*, 1158.



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Fig. S1 TEM images of (a) S0, (b) S1, (c) S2, and (d) S4.

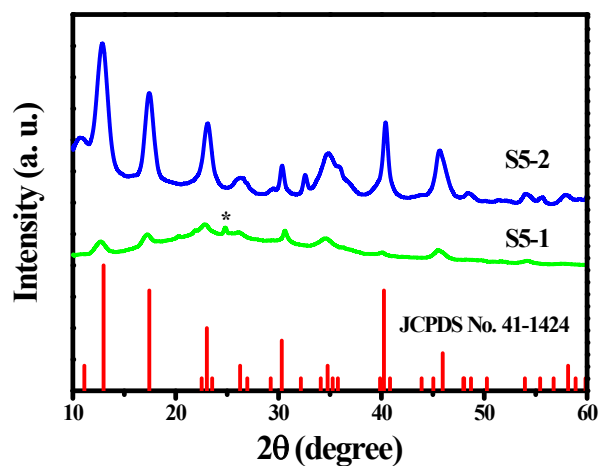


Fig. S2 XRD patterns of S5 obtained at the Na_2S concentration of 0.20 mol/L. S5-1: sample was washed with relatively small amount of water three times; S5-2: sample was washed with large quantities of water six times. The diffraction peaks (marked with *) of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (JCPDS No. 11-0647) as possible adsorbed in pores can be found. This give further proof for the conclusion that SO_4^{2-} anions in $\alpha\text{-Ni}(\text{OH})_2$ nanowires should be replaced by S^{2-} anions.

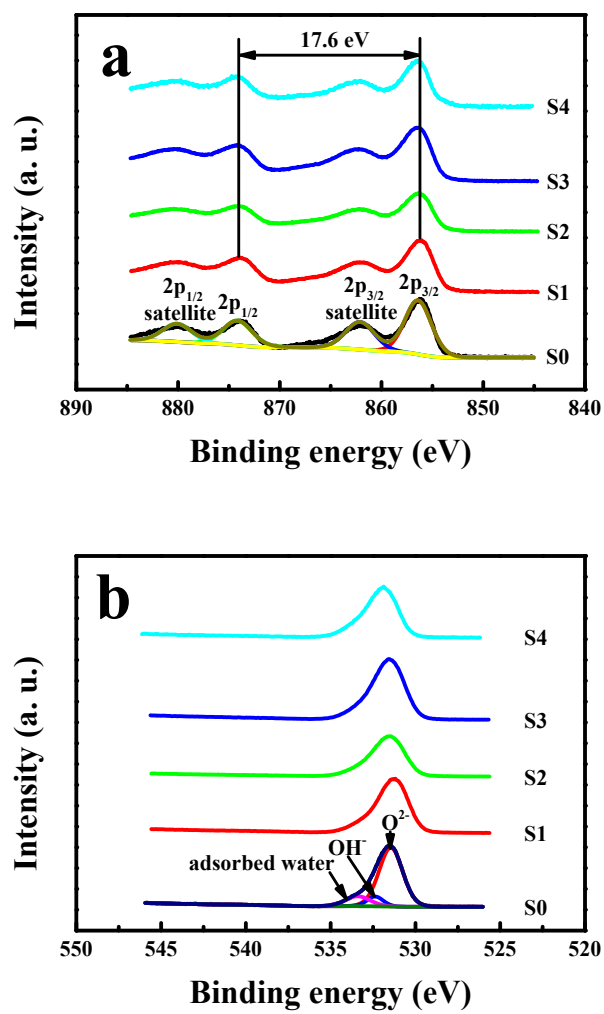
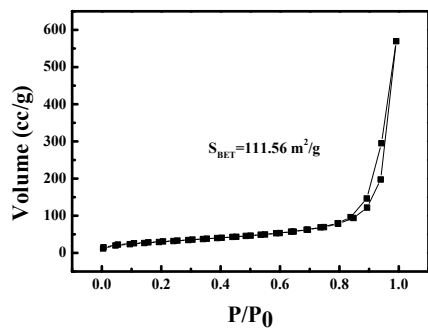
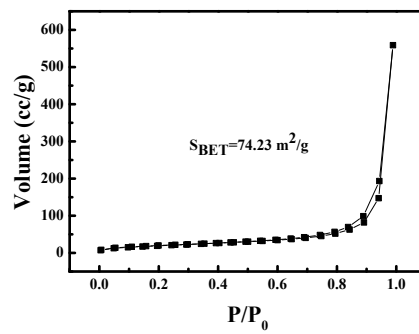


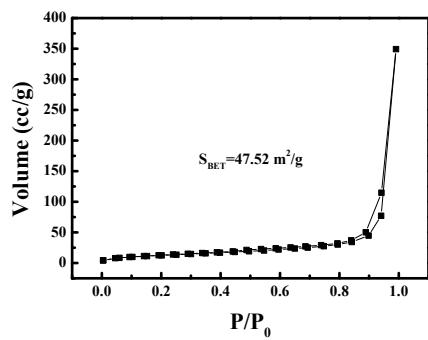
Fig. S3 XPS spectra of (a) Ni 2p, and (b) O 1s for S0, S1, S2, S3, and S4.



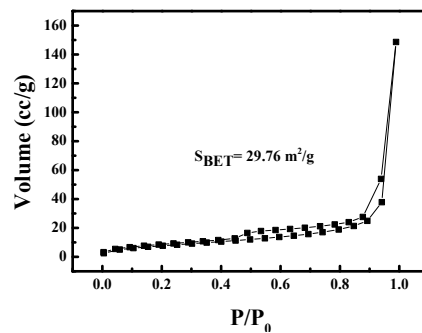
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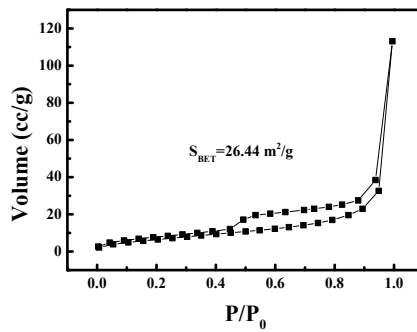
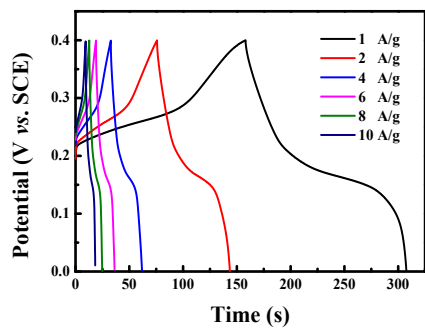
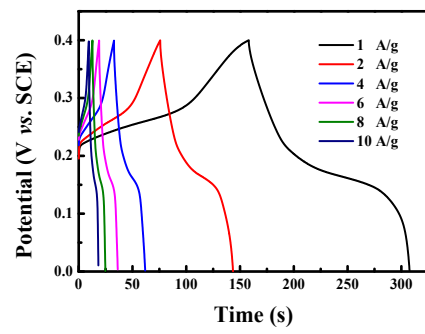


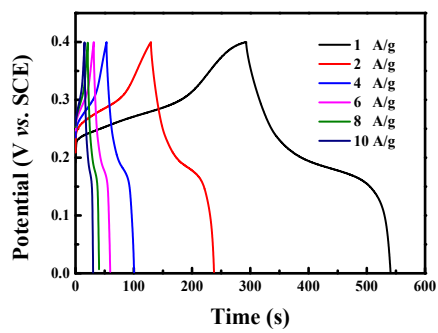
Fig. S4 N₂ adsorption-desorption isotherms of S0, S1, S2, S3 and S4.



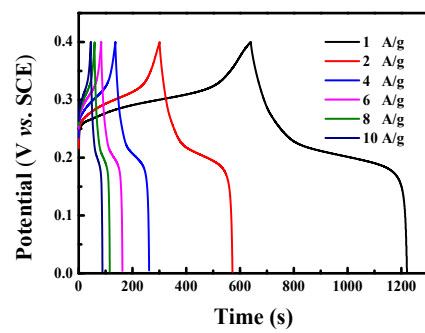
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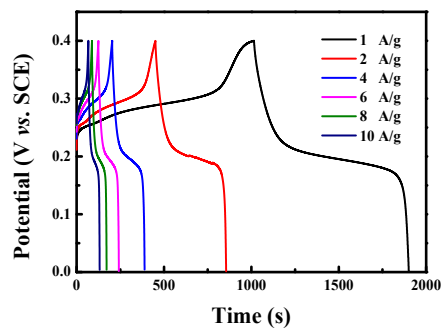
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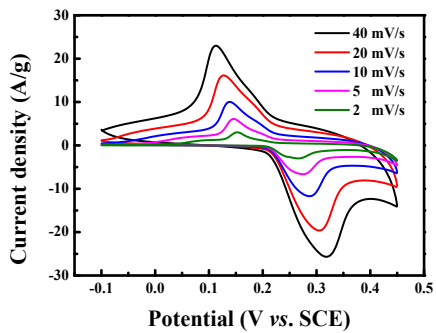


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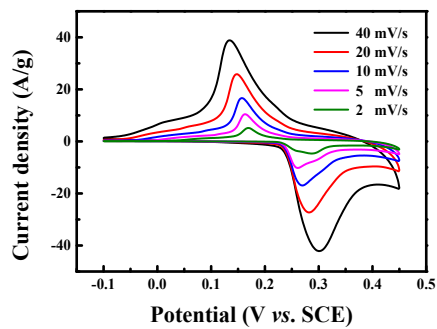


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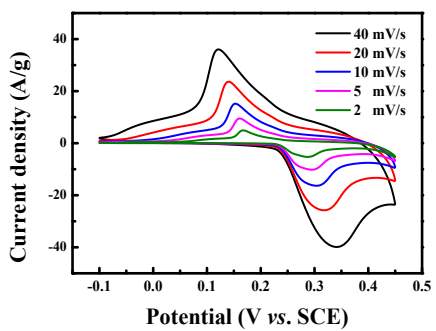
Fig. S5 GCD curves at different current densities. (a) S0, (b) S1, (c) S2, (d) S3, (e) S4.



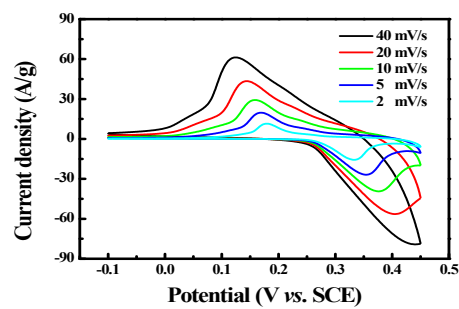
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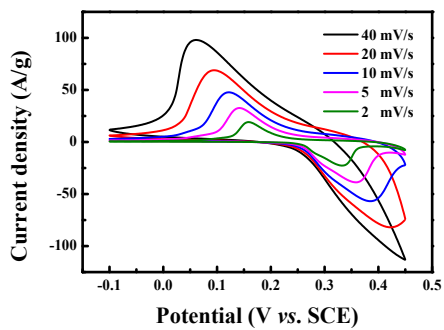
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Fig. S6 CV curves of (a) S0, (b) S1, (c) S2, (d) S3 and (e) S4.

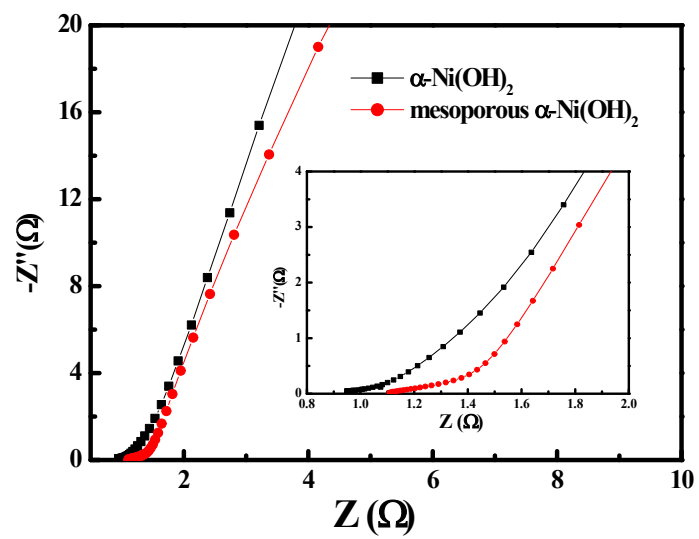


Fig. S7 Nyquist plots of $\alpha\text{-Ni(OH)}_2$ and mesoporous $\alpha\text{-Ni(OH)}_2$ (S3).

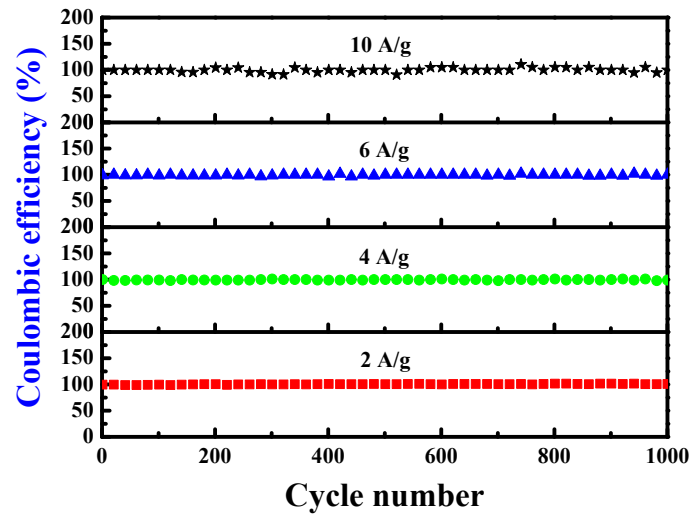


Fig. S8 Coulombic efficiency of the S3 electrode at different current densities.