Novel Dealloying-Fabricated NiS/NiO Nanoparticles with Superior Cycling Stability for Supercapacitors

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ABSTRACT: NiS/NiO nanoparticles are successfully fabricated through a simple dealloying method and an ion-exchange process. X-ray diffraction demonstrates the existence of NiO and NiS phases, and scanning electron microscopy and transmission electron microscopy imply the nanopore distribution nature and the nanoparticle morphology of the produced material. The electrochemical behaviors are studied by cyclic voltammetry and galvanostatic charge–discharge measurements. The NiS/NiO electrode shows an enhanced specific capacitance of 1260 F g⁻¹ at a current density of 0.5 A g⁻¹. The NiS/NiO//AC device provides a maximum energy density of 17.42 W h kg⁻¹, a high power density of 4000 W kg⁻¹, and a satisfactory cycling performance of 93% capacitance retention after 30,000 cycles.

INTRODUCTION

The increasing deficiency of fossil energy sources and the serious greenhouse effect have made it urgent to explore renewable energies such as tidal energy, wind energy, and solar energy. However, these renewable energies are unsustainable and limited by time or location; an electrochemical energy storage apparatus is needed to realize their practical application. Among various energy storage apparatuses, supercapacitors have been focused here because of their merits such as fast charging/discharging, superior cycling stability, and long service life. Supercapacitors generally include pseudocapacitors and electrochemical double-layer capacitors (EDLCs) in light of the distinctions between their charge storage mechanisms. Pseudocapacitors and electrochemical double-layer capacitors (EDLCs) in light of the distinctions between their charge storage mechanisms, electrode materials play a fundamental role in the electrochemical performance. As pseudocapacitors have a higher theoretical specific capacitance than that of conventional EDLCs, there has been increasing interest in using pseudocapacitive materials as cathodes for supercapacitor applications.

Over the past few years, transition-metal oxides and sulfides with rich chemical valence states have been extensively investigated and applied as electrode materials for supercapacitors. Among them, NiO stands out because of its merits of low cost, well-defined redox behavior, high theoretical specific capacitance, and environmental friendliness. NiO materials with rich morphologies including nanotubes, nanosheets, hollow spheres, nanofibers, and so forth have been designed as electrodes for supercapacitors and show excellent capacitive performance. However, the comparatively poor electrical conductivity may contribute to a relatively worse electrochemical performance. In order to tackle this problem, some researchers tried to combine NiO with carbon-based conductive materials including graphene and carbon nanotubes to enhance the electrochemical conductivity and thus the overall capacitance. The investigators also introduced transition-metal sulfides such as NiS2 into the NiO system because of their inimitable chemical and physical features, better energy density, as well as superior electrical conductivity. Li’s group fabricated honeycomb-like NiS2/NiO via a hydrothermal process; as the unique structure can help in providing fast electron-transfer paths and large active sites and the lower electronegativity of NiS2 is favorable for the diffusion and association between the electrode and the electrolyte, NiS2/NiO demonstrated a high specific capacitance of 2251 F g⁻¹ at a current density of 1 A g⁻¹. Hou et al. reported a rhombohedral dodecadhedral composite Co$_3$S$_4$@NiO, which shows a specific capacitance of 1877.93 F g⁻¹ at 1 A g⁻¹; after cycling at 5 A g⁻¹ for 10,000 cycles, there was still 92.6% capacitance retained. Huang’s group fabricated NiCo$_2$S$_4$@NiO core–shell nanowires, which showed a high specific capacitance of 12.2 F cm⁻² at 1 mA cm⁻² and good cycling performance.
performance with 89% retention after 10,000 cycles. Among these electrochemical materials, NiS has aroused extensive research interest because of the virtues of cost-effectiveness, high specific capacitance, and environmentally benign.\textsuperscript{33,34} NiO-based compounds have been synthesized by many methods, such as hydrothermal synthesis,\textsuperscript{35} sol–gel\textsuperscript{36} and microwave-assisted methods.\textsuperscript{27} While the reaction process of these methods is comparatively complicated, a soft or hard template is needed to be applied for the preparation of nanoporous-structured materials. Dealloying is a convenient method to regulate the morphology and the composition gradient of noble-metal alloy materials by dissolving the selected elemental components from an alloy.\textsuperscript{37–39} It has proved to be an effective approach to fabricate nanoporous (or microporous) and hierarchical (micro–nano) porous metal structures with novel properties.\textsuperscript{40–42} Nanostructured noble-metal-based alloys (Pt–Au/Ag)\textsuperscript{43} and transition-metal oxides (TiO\textsubscript{2} and Co\textsubscript{3}O\textsubscript{4})\textsuperscript{44} have been widely investigated and showed their potential applications in the energy storage field. It is demonstrated that a nanoporous NiO-based compound electrode can be easily constructed by the dealloying method. The interconnected porous structure obtained from dealloying can improve the electron transport performance of NiO-based compounds, thus enhancing the energy storage density maximally.\textsuperscript{43} However, to our knowledge, nanoporous NiS/NiO prepared by the dealloying method, a facile top-down strategy, has rarely been reported.

Herein, NiS/NiO was first prepared by dealloying Al\textsubscript{91}Ni\textsubscript{9} melt-spun ribbons and sulfur treatment. Electrochemical analysis results demonstrate that the NiS/NiO electrode possesses a specific capacitance of 1260 F g\textsuperscript{−1} at a current density of 0.5 A g\textsuperscript{−1}. Furthermore, the NiS/NiO//AC hybrid supercapacitor (HSC) shows satisfactory energy density along with outstanding cycling stability (93% capacitance retention after 30,000 cycles).

\section*{RESULTS AND DISCUSSION}

Scheme 1 summarizes the fabrication process of the NiS/NiO sample. The Al\textsubscript{91}Ni\textsubscript{9} alloy ribbon was obtained from Al–Ni ingot through the melt-spinning process. Thereafter, the Ni–O precursor was fabricated by dealloying the Al\textsubscript{91}Ni\textsubscript{9} alloy ribbon in a NaOH solution. After being calcined at 350 °C, NiO nanosheets were obtained. The NiS/NiO nanoparticles were transformed from the NiO sample by the anion-exchange reaction.

The purity and the phase structure of the synthesized samples are investigated by X-ray diffraction (XRD). The XRD patterns of NiO and NiS/NiO are displayed in Figure 1a, which indicate that NiO is successfully prepared by the dealloying and calcination methods, while NiS/NiO is also
obtained from NiO after the sulfuration treatment. The diffraction peaks appeared at 37.25, 43.28, 62.88, 75.41, and 79.41° are indexed to the (111), (200), (220), (311), and (222) planes of NiO (PDF#47-1049), respectively, and the peaks located at 32.2 and 48.8° are ascribed to the (300) and (131) planes of NiS (PDF#12-0041), respectively.

X-ray photoelectron spectroscopy (XPS) spectra are measured and the Gaussian fitting method is used to analyze the elemental composition and the valence state of NiS/NiO. The survey spectrum demonstrates that NiS/NiO consists of nickel, sulfur, oxygen, and carbon; the peaks at 856.2 and 168.7 eV correspond to Ni 2p and S 2p, respectively, as shown in Figure 1b. The emergence of C is ascribed to the fact that NiS is exposed to air. The Ni 2p spectrum shows two spin−orbit doublets located at 853.4 and 870.6 eV, which are ascribed to Ni 2p1/2 and Ni 2p3/2, respectively, and correspond to the characteristic of the NiO phase; the appearance of two shake-up satellites at 856.4 and 874.1 eV ascribed to Ni 2p1/2 and Ni 2p3/2 signals is also seen from Figure 1c. These results demonstrate the characteristic of Ni2+. As for the S 2p spectrum shown in Figure 1d, the spectral peaks at 161.2 and 162.3 eV correspond to S 2p3/2 and S 2p1/2, respectively; the appearance of the peak located at 169.1 eV is ascribed to the shakeup satellite, demonstrating the existence of the S2− signal.

The morphology and the structure of NiO and NiS/NiO are examined by field-emission scanning electron microscopy (FESEM). Figure 2a,b presents the highly magnified surface and side-view SEM images of the NiO precursor. After dealloying and calcination treatments, the NiO particles grow into nanosheet structure, then the nanosheets accumulate in the skeleton structure with pores distributed among them. The nanosheets are ultrathin, which can be beneficial for the full utilization of the active materials. As observed from Figure 2b, the side-view image of NiO shows that the porous structure is present both on the surface and in the interior of the NiO structure. The pores can facilitate the infiltration of the Na2S solution into the interior space and the successful sulfuration of NiO.

The SEM images of NiS/NiO are displayed in Figure 2c,d. After the sulfuration treatment, the nanosheet structure disappeared and transferred into nanoparticles to a large degree (Figure 2c), which makes the surface much rougher when compared with that of the precursor. The coarse surfaces can enhance the surface area and thus the wettability of NiS/NiO samples simultaneously, promoting better electron and electrolyte transmission. Figure 2d further demonstrates the nanoparticle structure of NiS/NiO, which is consistent with previous results.

The transmission electron microscopy (TEM) image in Figure 3a indicates that NiS/NiO consists of nanoparticles with an average diameter of 80 nm; nanopores can be observed among the nanoparticles, as shown from the yellow arrows. The corresponding selected-area electron diffraction (SAED) patterns (Figure 3b) demonstrate the polycrystalline features of NiS/NiO. A set of rings are in line with the (021) and (300) planes of the NiS phase, while (220) and (200) planes correspond to the NiO phase. Figure 3c (enlarged from Figure 3a) further proves that NiS/NiO is composed of nanoparticles, with some pores distributed among nanoparticles. In order to observe the elemental distribution in the nanoparticles, energy-dispersive X-ray spectroscopy (EDS) elemental mapping analysis is performed, with the corresponding results illustrated in Figure S1. As observed, the nanoparticles consisted of Ni, S, and O elements, which are homogeneously distributed in the particle. The ratio of O and S elements is 6:1. The high-resolution TEM (HRTEM) image in Figure 3d demonstrates well-resolved lattice fringes with an interplanar distance of 0.27 nm, which corresponds well to the (300) plane of NiS.

The electrochemical measurements are carried out in a three-electrode device. The cyclic voltammetry (CV) curves of NiS/NiO and NiO at 20 mV s−1 present a pair of redox peaks, demonstrating the pseudocapacitive features of NiS/NiO and NiO electrodes. What is more, the closed area of CV curves is larger for NiS/NiO than for NiO, implying the higher specific
capacitance of the NiS/NiO electrode (Figure 4a). From the galvanostatic charge–discharge (GCD) curves shown in Figure 4b, it can be observed that the NiS/NiO electrode delivers a longer discharge time and exhibits a higher capacitance, which are in agreement with CV results.

Figures 4c and S2a present the CV curves of NiS/NiO and NiO at 2–50 mV s$^{-1}$, respectively. The energy storage of the NiS/NiO electrode is mainly attributed to the pseudocapacitance generated between the redox reaction of Ni$^{2+}$ and Ni$^{3+}$:

$$\text{NiS} + \text{OH}^- \leftrightarrow \text{NiSOH} + e^- \quad (1)$$

$$\text{NiO} + \text{OH}^- \leftrightarrow \text{NiOOH} + e^- \quad (2)$$

Remarkably, due to the existence of the polarization effect, the peaks shift slightly with the changes in the sweep rate, but the shape of the curves did not change too much, implying excellent electrochemical reversibility.

The GCD tests at 0.5–10 A g$^{-1}$ for NiS/NiO and NiO electrodes are conducted with the corresponding results shown in Figures 4d and S2b, respectively. The NiS/NiO electrode presents nonlinear GCD curves with a clear platform, confirming its pseudocapacitive nature in accordance with the CV results. The good symmetry of the GCD curves suggests satisfactory electrochemical reversibility and Coulombic efficiency. Figure 4e reveals the corresponding specific capacitances of NiS/NiO and NiO electrodes against current density; and (f) Nyquist plots.

Figure 4. Electrochemical characterization of NiS/NiO and NiO electrodes. (a) CV curves of electrodes at 20 mV s$^{-1}$; (b) GCD profiles of electrodes at 0.5 A g$^{-1}$; (c) CV curves of the NiS/NiO electrode at 2–50 mV s$^{-1}$; (d) GCD curves of the NiS/NiO electrode at 0.5–10 A g$^{-1}$; (e) capacitance of NiS/NiO and NiO electrodes against current density; and (f) Nyquist plots.
The Nyquist plots of NiS/NiO and NiO electrodes are displayed in Figure 4f. As observed, two EIS plots consist of a quasi-Nyquist plots of NiS/NiO and NiO electrodes are displayed in spectroscopy (EIS) in the frequency range of 0.01 Hz to 100 kHz. The Nyquist plots of NiS/NiO and NiO electrodes are displayed in Figure 4f. As observed, two EIS plots consist of a quasi-semicircle in the high-frequency region and an oblique line in the low-frequency region. The intersection distance on the semicircle helps to understand the charge-transfer resistance ($R_{ct}$). Compared to the NiO electrode, the NiS/NiO electrode possesses smaller $R_{ct}$ and $R_{ct}$ values, implying that the electron can be transferred to the surface of the active material more easily. What is more, the NiS/NiO electrode displays a steep line in the low-frequency region, implying the lower Warburg resistance of the NiS/NiO electrode.

Previous research studies have revealed that the pseudocapacitance-like contribution includes diffusion-controlled Faradaic behavior and capacitive capacity. For the sake of better understanding the reaction kinetics of NiS/NiO and NiO materials, kinetic analysis is performed. The relationship between the current and sweep rate can be expressed as follows:

$$i = a v^b$$

where $a$ is a constant, $i$ stands for the current, and $v$ stands for the sweep rate. If the value of $b$ equals 0.5, the redox reaction is controlled by semi-infinite linear diffusion; What is more, $b = 1$ implies that kinetics is surface-controlled. The plot of log $i$ versus log $v$ is presented in Figure S4. In the aqueous electrolyte, NiS/NiO and NiO electrodes show values of $b$ 0.49 and 0.71, respectively, demonstrating the diffusion-controlled behavior of electrodes.

To illustrate the potential application of the NiS/NiO, a HSC is assembled using NiS/NiO as the cathode and AC as the anode (Figure 5a). As shown in Figure S5, the active carbon (AC) exhibits a rectangular shape in CV curves and linear in GCD curves, demonstrating a representative EDLC behavior. At current densities of 0.5, 1, 2, 5, and 10 A g$^{-1}$, the specific capacities of AC are 110.5, 91, 80.4, 70, and 59.1 F g$^{-1}$, respectively. Because the charge between the cathode and the anode should be balanced ($q^+ = q^-$), the optimal mass ratio between NiS/NiO and AC is 0.22 according to the equation $m^+/m^- = C^+/C^-$. Figure 5b displays the CV curves of the AC and NiS/NiO electrodes recorded at 10 mV s$^{-1}$, which demonstrate that the operating potential window of the HSC device can reach 1.8 V. Figure 5c displays the CV curves of NiS/NiO//AC with potential windows ranging from 1.4 to 1.8 V. As observed, the shape of CV curves was maintained well even when the operating voltage is extended to as high as 1.6 V. The CV curves of NiS/NiO//AC with scan rate ranges from 5 to 30 mV s$^{-1}$ are displayed in Figure 5d. It is worth noting that the CV curves display the common feature of pseudocapacitors and EDLCs at different scan rates, and the shape of CV curves is maintained well without too much change even at high scan rates, implying a high $I$–$V$ response, a fast charge/discharge process, and a superior capacitive behavior of the HSC device.

The GCD tests are conducted at varied current densities to assess the electrochemical properties of the NiS/NiO//AC device (Figure 5e). The superior symmetric GCD curves at a high cell voltage indicate the excellent electrochemical reversibility of the device. As seen from Figure 5f, the specific capacitances obtained from GCD results of Figure 5e, the NiS/NiO//AC device provides specific capacitances of 49, 45, 35, 32, and 25 F g$^{-1}$ at current densities of 0.2, 0.5, 1, 2, and 5 A g$^{-1}$, respectively. The cycling property is investigated by GCD tests at a current density of 5 A g$^{-1}$ for 30,000 cycles, as observed in Figure 5g. The corresponding first 10 and last 10 cycles of GCD curves are displayed in Figure S6. Noteworthily, after 30,000 cycles at 5 A g$^{-1}$, about 93% capacitance retention can be achieved, demonstrating the outstanding cycling stability of the NiS/NiO//AC device.

The energy density and power density should be highly valued when evaluating the practical application of the device (Figure S7). In our work, the fabricated HSC reaches a maximum energy density of 17.42 W h kg$^{-1}$ at a power density of 160 W kg$^{-1}$ (and 8.9 W h kg$^{-1}$ at 4000 W kg$^{-1}$), which outperforms many literature reported devices such as Ni–Co oxide//AC (10.8 W h kg$^{-1}$ at 0.47 kW kg$^{-1}$),$^{56}$ Ni$_3$S$_2$//AC (10.01 W h kg$^{-1}$ at 150.12 W kg$^{-1}$),$^{54}$ and Ni$_3$S$_2$//AC (18.62 W h kg$^{-1}$ at 150 W kg$^{-1}$).$^{55}$
Figure 5. (a) Schematic of the assembled HSC configuration adopting the NiS/NiO positive electrode and the AC negative electrode; (b) CV curves of the NiS/NiO and AC electrodes; (c) CV curves of NiS/NiO//AC obtained at 10 mV s$^{-1}$ in a varied voltage window of 1.4–1.8 V; (d) CV curves of NiS/NiO//AC at 5–30 mV s$^{-1}$; (e) GCD curves of NiS/NiO//AC at 0.2–5 A g$^{-1}$; (f) specific capacitance vs. current density curve; and (g) cycling performance of NiS/NiO//AC at 5 A g$^{-1}$. 
**CONCLUSIONS**

In conclusion, NiS/NiO nanoparticles were successfully fabricated by a facile dealloying treatment followed by a hydrothermal process. The NiS/NiO electrode exhibits a high specific capacity of 1260 F g⁻¹ at 0.5 A g⁻¹ because of the distribution of nanopores among nanoparticles. Noteworthily, the NiS/NiO//AC HSC device delivered a satisfactory energy density of 17.42 W h kg⁻¹ at a power density of 160 W kg⁻¹. The device also shows outstanding cycling performance with approximately 93% capacitance retention after 30,000 cycles. This research demonstrates that NiS/NiO materials can be synthesized by dealloying on a large scale for supercapacitors.

**EXPERIMENTAL SECTION**

**Preparation of the NiO Nanoporous Structure.** The Al₂Ni₃ alloy was obtained from pure Al (99.90 wt %) and pure Ni (99.99 wt %) by arc-melting under a high-purity Ar atmosphere. Subsequently, the obtained alloy was re-melted and heated in a quartz tube to get the metal solution, which was then blown onto the surface of the melt-spinning roller. The melt-spun ribbons were 20–40 μm in thickness and 3–4 mm in width. The resulting ribbons were dealtloyed in 20 wt % aqueous sodium hydroxide solution at 80 °C for 10 h to harvest a black precipitate. The precipitate was rinsed in deionized water and ethanol in turns, then dried at 80 °C, and calcined in a muffle furnace at 350 °C for 2 h to obtain NiO.

**Preparation of NiS/NiO.** The harvested NiO precursors were added to an aqueous sodium sulfide solution and stirred for 5 min. Then, the mixed solution was transferred to an autoclave and kept in the oven at 90 °C for 9 h. Finally, NiS/NiO was obtained after careful cleaning and vacuum-drying.

**Materials Characterization.** The phase composition of the fabricated materials was tested using an X-ray diffractometer (Shimadzu, XRD-6100). The valence state and the chemical composition of the electrode materials were characterized by XPS (ESCALAB Xi+). The morphology and the microstructure of the products were investigated by FESEM (JEOL, JSM-7000F) and HRTEM (JEOL, JEM-2100).

**Electrochemical Characterization.** The electrochemical tests were performed with a Versa STAT MC electrochemical workstation. A three-electrode system is utilized in CV, EIS, and GCD measurements. In the three-electrode configuration, active materials served as the working electrode, a saturated calomel electrode acted as the reference electrode, and a Pt foil was utilized as the counter electrode, and 2 M KOH was used as the electrolyte. The working electrode was prepared by dissolving a homogeneous mixture of fabricated materials, acetylene black and polyvinylidene fluoride at a 8:1:1 wt ratio in N-methyl-2-pyrrolidinone first, then pasting the slurry onto pretreated foamed nickel, and drying in a vacuum for 12 h.

The specific capacitance \( C \) was calculated by the formula as follows

\[
C = \frac{I \Delta t}{m \Delta V}
\]

where \( I \), \( \Delta t \), \( m \), and \( \Delta V \) are the applied current (A g⁻¹), discharge time (s), active material mass (g), and voltage window (V), respectively.

The electrochemical performance of the NiS/NiO//AC HSC was characterized in a two-electrode system. NiS/NiO and AC were employed as the positive electrode and the negative electrode, respectively. The preparation of the negative electrode was similar to that of the NiS/NiO electrode. An Arbin BT-2000 battery system was employed to test the cycling property. The energy density \( E \) (W h kg⁻¹) and the power density \( P \) (W kg⁻¹) were calculated from the following equations

\[
E = \frac{C \Delta V^2}{2}
\]

\[
P = \frac{3600E}{\Delta t}
\]

where \( C \), \( \Delta V \), and \( \Delta t \) are the specific capacitance (F g⁻¹), voltage window (V), and discharge time (s), respectively.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01717.

TEM–EDS characterization and performance analyses including CV curves, GCD curves, cycling performance, Ragone plot, and plots of log(peak current) versus log(sweep rate) (PDF)

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Notes

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