LETTER

Enhanced performance of mesoporous NiCo$_2$S$_4$ nanosheets fibre-shaped electrode for supercapacitor

1 | INTRODUCTION

Among various power storage devices, supercapacitors have attracted much attention in the past few years due to their high power density, long-life cycle and short charge-discharge times [1, 2]. Supercapacitors can be classified into Faradaic redox reaction pseudocapacitors (FPCs), electrochemical double-layer capacitors (EDLCs) and hybrid supercapacitors according to their energy store mechanisms [3, 4]. So far, pseudocapacitors have been developed deeply since, FPCs have higher energy density than EDLCs. Electrode materials have vital influence on the electrochemical performance of supercapacitors. NiCo$_2$S$_4$ with many shapes, such as sphere [5], nanoparticle [6], nanowhisker [7] and nanoflake [8], has been widely reported owing to its high electrical conductivity, thermal stability and super electrochemical performance [9]. Sulphur is abundant and less electronegative than oxygen, so transition metal sulphide has more flexible structure and higher electrochemical activity than transition metal oxide or hydroxide. Much work indicated that NiCo$_2$S$_4$ was prepared with two steps: in the first step, Ni–Co precursor was fabricated with solvothermal route and then the precursor was sulphured to obtain NiCo$_2$S$_4$ [10]. NiCo$_2$S$_4$ can inherit the structure of Ni-Co precursor to a large extent. As we know, electrodeposition method can prepare Ni–Co LDH with 3D nanostructure easily. However, Ni–Co LDH prepared using this technique has not been reported to fabricate NiCo$_2$S$_4$ electrode material for supercapacitor.

In this paper, hierarchical Ni–Co LDH precursor on nickel wire was fabricated by a simple electrodeposition process, and an ordinary sulphuration method was employed to prepare NiCo$_2$S$_4$ fibre-shaped electrode. NiCo$_2$S$_4$ electrode showed far higher electrochemical performance than Ni–Co LDH.

2 | EXPERIMENTAL PROCEDURE

Nickel wire with diameter of 100 µm was ultrasonicated in HCl for 5 min to remove the oxide layer. Then the nickel wire was washed with deionized water and alcohol repeatedly and dried in a vacuum oven at 70 °C for further use. To prepare Ni–Co LDH, 2 mmol Co(NO$_3$)$_2$·6H$_2$O, 2 mmol Ni(NO$_3$)$_2$·6H$_2$O and 20 mmol NH$_4$Cl were mixed with 100 mL deionized water and stirred for 15 min with a magnetic stirrer. The Ni–Co LDH was deposited on the surface of nickel wire in an electrochemical work-station for 15 min at the steady current of 0.02 A. Finally, the obtained products were washed for several times with deionized water and ethanol, and dried at 70 °C for 12 h.

2.4 mmol Na$_2$S·9H$_2$O was dissolved in 50 mL deionized water and stirred for 30 min. Next, 30 mL of the solution and the nickel wire coated with Ni-Co LDH were transferred into a Teflon-lined autoclave of 50 mL for sulphuration reaction at 100 °C for 10 h. After that, the nickel wire was taken out and washed with deionized water and ethanol, finally dried at 60 °C for 12 h. During sulphuration process, Ni–Co LDH was transformed to NiCo$_2$S$_4$. The whole fabrication of NiCo$_2$S$_4$ fibre-shaped electrode was shown in Figure 1.

The X-ray diffraction (XRD) analysis with Cu Kα radiation, high-Resolution transmission electron microscope (HREM, Tecnai G² F20), scanning electron microscope (SEM, Hitachi SU-8200) were used to characterize the structure, phase and morphology of the products. X-ray photoelectron spectroscopy (XPS) was carried out to investigate the elemental compositions.

The electrochemical studies of Ni–Co LDH and NiCo$_2$S$_4$ electrodes were tested in a three electrode system in 1 M KOH aqueous solution, in which Ni-Co LDH and NiCo$_2$S$_4$ electrodes were used as working electrode, platinum plate and standard calomel electrode (SCE) as counter electrode and reference electrode, respectively. Cyclic voltammogram (CV) and galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were done in CHI660E electrochemical station at room temperature. The cycle life of the electrodes was measured with repeated GCD test.

FIGURE 1 Schematic illustration describing the preparation process of NiCo$_2$S$_4$ fibre-shaped electrode

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3 RESULTS AND DISCUSSION

The crystalline structure of Ni–Co LDH and NiCo$_2$S$_4$ was examined by XRD analysis, as shown in Figure A1. The diffraction peaks at 11.34°, 34.41°, 38.77° and 59.98° were indexed as (003), (012), (015) and (110) planes of Ni(OH)$_2$·0.75H$_2$O and (003), (102), (105) and (110) planes of Co$_5$(O$_{9.48}$H$_{8.52}$)NO$_3$ in Figure A1(a) [11]. The three strong peaks at 44.2°, 51.6° and 76.1° correspond to nickel wire. Several peaks located at 31.6°, 38.3°, 55.3° and 78.1° can be assigned to the (311), (400), (440) and (553) crystal planes of the cubic NiCo$_2$S$_4$ phase as shown in Figure A1(b). It is worth noting that after sulphuration, the peaks of nickel wire became weak obviously and the two peaks at 51.6° and 76.1° cannot be detected almost, meaning that nickel wire was involved in this sulfurization reaction. To further investigate the composition and chemical element of NiCo$_2$S$_4$, XPS spectra are shown in Figure 2.

Figure 2(a–d) shows the XPS spectra of NiCo$_2$S$_4$. The elements C, S, Ni and Co were detected in the full-scan spectrum of the sample (Figure 2(a)). As shown in Figure 2(b,c), the Ni 2p and Co 2p spectra can be fitted with two spin-orbit doublets and two shake-up satellites. In Ni 2p spectrum (Figure 2(b)), the binding energy at 863 eV in Ni 2p$_{3/2}$ and 883.6 eV in Ni 2p$_{1/2}$ agreed with the spin-orbit of Ni$^{2+}$, and the binding energy at 956.12 eV in Ni 2p$_{3/2}$ and 873.97 eV in Ni 2p$_{1/2}$ were the characteristic of Ni$^{3+}$. Figure 2(c) indicates that Co 2p$_{3/2}$ and Co 2p$_{1/2}$ peaks located at the binding energies of 781.13 and 796.86 eV were accompanied by shake-up satellites, implying that the cobalt in NiCo$_2$S$_4$ are Co$^{2+}$ and Co$^{3+}$ states. As for S 2p spectrum in Figure 2(d), the peaks at 161.79 and 168.46 eV corresponded to the S 2p$_{3/2}$ and S 2p$_{1/2}$, respectively, representing the common metal-sulphur bond.

The morphology Ni-Co LDH nanosheets on Ni wire was investigated by SEM (Figure 3(a–c)). Ni-Co LDH was deposited on Ni wire densely and uniformly (Figure 3(a)). From the inset of Figure 3(a), the thickness of Ni-Co LDH can be estimated to be about 11 μm. Ni-Co LDH exhibited nanosheet-like shape with thickness of about 5 nm (Figure 3(b,c)).
Figure 4 (a, b) SEM images of NiCo$_2$S$_4$ at various magnifications, (c) TEM images, (d) HRTEM image of NiCo$_2$S$_4$ and the corresponding SAED pattern (inset)

The structural information of NiCo$_2$S$_4$ was shown in Figure 4. NiCo$_2$S$_4$ displays nanosheet-like shape with 3D network structure, which is extremely similar to that of Ni–Co LDH. This suggests NiCo$_2$S$_4$ inherits the structure of Ni–Co LDH.

Numerous fine nanoparticles attached on the nanosheets can be seen clearly in Figure 4(b), which should be the product of sulphuration reaction. Plate-like shape of NiCo$_2$S$_4$ can be also observed in TEM image (Figure 4(c)). In addition, it's found there are many nanopores in the nanosheets, which is different from that of Ni–Co LDH with a relatively smooth surface (Figure A2(a)). NiCo$_2$S$_4$ exhibited clear lattice fringes with interplanar spacing of 0.32 nm in Figure 4d, assigned to the (220) crystal plane of NiCo$_2$S$_4$. SAED pattern of NiCo$_2$S$_4$ also confirms its polycrystalline structure.

Figure 5a shows the typical CV curves of Ni-Co LDH fibre-shaped electrode at the scan rate of 10–80 mV/s in the potential window of 0–0.8 V. Ni–Co LDH shows two distinct pairs redox peaks, revealing that the electrochemical performance characteristics mainly result from Faradaic pseudocapacitance, related to Co$^{2+}$/Co$^{3+}$/Co$^{4+}$ and Ni$^{2+}$/Ni$^{3+}$ redox process [12]. Clear discharge platforms can be observed in GCD curves, in accordance with the reduction peaks (Figure A3(a)).

For NiCo$_2$S$_4$ fibre-shaped electrode, its redox peaks are unconspicuous in CV curves (Figure 5(b)), which exhibit near rectangular appearance. This indicates double-layer capacitance makes larger contribution on its performance. GCD curves of NiCo$_2$S$_4$ electrode with no discharge platform also confirm the dominant charge–discharge mechanism is different from that of Ni–Co LDH precursor (Figure 5(c)). The specific capacitances of Ni–Co LDH and NiCo$_2$S$_4$ fibre-shaped electrodes were calculated based on their GCD curves, as shown in Figure 5(d). NiCo$_2$S$_4$ electrode exhibits specific capacitance of 1974.55, 1800 and 1463.64 mF/cm$^2$ at current densities of 2, 3, 5 mA/cm$^2$, respectively, which is nearly three times than that (630.77, 567.69 and 538.46 mF/cm$^2$) of Ni–Co LDH (Figure A3(b)). At a high current density of 10 mA/cm$^2$, the specific capacitance of NiCo$_2$S$_4$ can reach 1127.27 mF/cm$^2$, while for LDH, the value is only 523.08 mF/cm$^2$. After 5000 cycles at 10 mA/cm$^2$, it's observed that the specific capacitance of Ni–Co LDH electrode decreases rapidly and only 65.3%
capacitance can be retained, while for NiCo$_2$S$_4$ electrode, capacitance retention can reach 86.2% (Figure 5(d)). Evidently, sulphuration treatment generates a positive effect on Ni–Co LDH precursor prepared by electrodeposition technique. This is due to that sulphur-containing functional group in NiCo$_2$S$_4$ has higher pseudocapacitance performance and better structural stability compared with hydroxyl group in Ni–Co LDH. Our work may provide new idea for the performance improvement of LDH used as supercapacitor electrode material.

4 | CONCLUSION

In summary, mesoporous NiCo$_2$S$_4$ nanosheet arrays were successfully prepared through sulfurizing 3D hierarchical Ni–Co LDH, which was fabricated on nickel wire by electrodeposition technique. NiCo$_2$S$_4$ fibre-shaped electrode showed a superior electrochemical performance compared to Ni–Co LDH precursor. The specific capacitance can reach 1974.55 mF/cm$^2$ at 2 mA/cm$^2$ for NiCo$_2$S$_4$ electrode (630.77 mF/cm$^2$ for Ni–Co LDH) and after 5000 cycles, 86.2% capacitance retention can be obtained (only 65.3% for Ni–Co LDH).

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.
APPENDIX A

**FIGURE A.1** XRD patterns of (a) Ni-Co LDH and (b) NiCo2S4 fiber-shaped electrodes

**FIGURE A.2** (a) TEM and (b) HRTEM images of Ni-Co LDH and the insets in (a) display the SAED pattern of Ni-Co LDH

**FIGURE A.3** (a) GCD curves of Ni-Co LDH at different current densities, (b) Specific capacitances of Ni-Co LDH and NiCo2S4 electrodes as a function of current density