NiMoO$_4$ nanowires supported on Ni foam as novel advanced electrodes for supercapacitors

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Part I: Experimental

Synthesis of NiMoO$_4$ nanowires on Ni foam:

All the reagents were analytical grade and used without further purification. The nickel nitrate and sodium molybdate were obtained from Tianjin Chemical Reagent Co. NiMoO$_4$ NWs were prepared by a facile hydrothermal synthesis method. Prior to the synthesis, the Ni foam substrate (length × diameter × thickness = 6 × 2 × 0.1 cm) was rinsed with ethanol and water for 30 min respectively, and then placed standing against the wall of a Teflon-lined autoclave. The reaction solution was obtained by mixing 2.5 mmol of Ni(NO$_3$)$_2$·6H$_2$O and 2.5 mmol of Na$_2$MoO$_4$·7H$_2$O in 50 mL of distilled water under constant magnetic stirring and then transferred into Teflon-lined stainless steel autoclave liners. The washed Ni foam substrate was immersed into the reaction solution. The liner was sealed in a stainless steel autoclave and maintained at 150 °C for 6 h and then cooled down to room temperature. After the reaction was over, the Ni foam coated with a light green product was taken out from the autoclave and washed by ultrasound in deionized water followed by acetone for a few minutes in order to remove the residual nanoparticle debris, then dried in an oven at 60 °C for 12 h. Finally, the Ni foam with the as-grown hydrate precursors was annealed at 400 °C for 1 h in pure argon to obtain NiMoO$_4$ NWs.
Characterization:

The crystal structure of the samples was characterized with X-Ray diffraction (XRD, Cu Kα irradiation; λ=1.5418 Å) with a SIEMENS D5000 X-ray diffractometer. The morphology and microstructure of the synthesized sample were characterized by a scanning electron microscopy (SEM, Hitachi S4800) and a transmission electron microscope (TEM; JEOL-2010 with an accelerating voltage of 200 kV).

Electrochemical measurements:

The electrochemical measurements were conducted using a three-electrode mode in a 2 M KOH aqueous solution. The Ni foam supported electroactive material (1 cm² in area) was directly used as the working electrode. A standard calomel electrode (SCE) was used as the reference electrode and a Pt foil as the counter electrode. The mass loading of the NiMoO₄ NWs on Ni foam was about 1.5 mg cm⁻². The area specific capacitance of the electrode was calculated according to the following equations:

\[ C = \frac{i \times t}{\Delta u} \]  

where C is the capacitance of the electroactive materials, Δu is the potential (V), i is the discharging current density (A cm⁻² or A g⁻¹) and t is discharge time (s). Typical CV curves were measured between -0.2 and 0.8 V. All the electrochemical experiments were performed on a CHI660e electrochemical workstation (Chenhua, Shanghai). Electrochemical impedance spectroscopy (EIS) measurements were made with a superimposed 5 mV sinusoidal voltage in a frequency range from 0.01 Hz to 100 kHz at open circuit potential.
Part II: Supplementary Figures

**Fig. S1** (a) SEM image of the as-synthesized NiMoO$_4$ precursor. (b) The XRD pattern of the NiMoO$_4$ precursor scratched from Ni foam.

**Fig. S2** TGA-DSC curves for the precursor NiMoO$_4$.

**Fig. S3** SEM image of the NiMoO$_4$ NWs from the side view.
Fig. S1 (a) showed SEM image of the precursor NiMoO$_4$ and the morphology did not change after calcination. Fig. S1 (b) showed the XRD patterns of the NiMoO$_4$ precursor. All the diffraction peaks of the precursor could be well indexed to NiMoO$_4$·$\text{xH}_2\text{O}$ (JCPDS No: 13-0128). TGA-DSC curves have further demonstrated NiMoO$_4$·$\text{xH}_2\text{O}$ precursor thermal decompose to NiMoO$_4$ nanowires. (Fig. S2). The total weight loss of NiMoO$_4$·$\text{xH}_2\text{O}$ is 16% and the weight becomes stable below 400°C. Fig. S3 showed SEM image of the NiMoO$_4$ NWs from the side view. The length of the nanowires is about 4 μm.

![Graph](image)

Fig. S4 The comparison of the NiMoO$_4$ NWs on Ni foam and bare Ni foam after calcination at 400 °C with the same areal charge–discharge current of 40 mA cm$^{-2}$.

![Graph](image)

Fig. S5 First ten charge/discharge curves of the NiMoO$_4$ electrode at a current density of 40 mA cm$^{-2}$.
**Fig. S6** First ten charge/discharge curves of the NiMoO$_4$ electrode at a current density of 56 mA cm$^{-2}$.

**Fig. S7** First ten charge/discharge curves of the NiMoO$_4$ electrode at a current density of 112 mA cm$^{-2}$.

**Fig. S8** (a) SEM image of the NiMoO$_4$ NWs on Ni foam electrode after 6000 cycles. (b) Electrochemical impedance spectra after 6000th cycles.