Hierarchical Heterostructures of NiCo$_2$O$_4$@XMoO$_4$ (X = Ni, Co) as an Electrode Material for High-Performance Supercapacitors

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Abstract
Hierarchical heterostructures of NiCo$_2$O$_4$@XMoO$_4$ (X = Ni, Co) were developed as an electrode material for supercapacitor with improved pseudocapacitive performance. Within these hierarchical heterostructures, the mesoporous NiCo$_2$O$_4$ nanosheet arrays directly grown on the Ni foam can not only act as an excellent pseudocapacitive material but also serve as a hierarchical scaffold for growing NiMoO$_4$ or CoMoO$_4$ electroactive materials (nanosheets). The electrode made of NiCo$_2$O$_4$@NiMoO$_4$ presented a highest areal capacitance of 3.74 F/cm$^2$ at 2 mA/cm$^2$, which was much higher than the electrodes made of NiCo$_2$O$_4$@CoMoO$_4$ (2.452 F/cm$^2$) and NiCo$_2$O$_4$ (0.456 F/cm$^2$), respectively. Meanwhile, the NiCo$_2$O$_4$@NiMoO$_4$ electrode exhibited good rate capability. It suggested the potential of the hierarchical heterostructures of NiCo$_2$O$_4$@CoMoO$_4$ as an electrode material in supercapacitors.

Keywords: Supercapacitor, NiCo$_2$O$_4$@XMoO$_4$, Heterostructures, Nanosheet arrays

Background
To meet the increasing requirement for portable electronics, hybrid electronic vehicles and other micro- and nano-devices, numerous studies have been carried out to develop many kinds of energy storage systems. As an important energy storage device, the widely studied supercapacitors, also known as electrochemical capacitors, have been believed as a promising candidate due to their high specific power, long cycling life, fast charge and discharge rates, and reliable safety [1–9]. Though these supercapacitors demonstrated these distinctive advantages, as compared with the batteries and fuel cells, the relatively lower energy densities seriously block their large-scale practical application [4, 10]. So far, various electrode materials which include carbon materials [11, 12], transition metal oxides [2, 13–15], and conducting polymers [16, 17] have been designed and synthesized to enhance the electrochemical properties for the practical applications in the supercapacitors.

Recently, some bimetallic oxides, such as NiCo$_2$O$_4$ [15, 17–20], ZnCo$_2$O$_4$ [21, 22], NiMoO$_4$ [23], and CoMoO$_4$ [24, 25], have been developed as a new electrode material used for supercapacitors because of their excellent electrical conductivity and multiple oxidation states (as compared with the binary metal oxides) for reversible Faradaic reactions [26]. For fully utilizing the advantages of active materials and thus optimizing the performance of these materials, plenty of efforts has been devoted, i.e., realizing additive/binder-free electrode architectures, which eliminate the “dead surface” and release complicated process in traditional slurry-coating electrode and meaningfully improve the utilization rate of electrode materials even at high rates [4, 27], constructing 3D hierarchical heterostructures, which can provide efficient and fast pathways for electron and ion transport [20, 28], and exploring smart integrated array architectures with rational multi-component combination, which can achieve the synergistic effect from all individual constituents [29–31]. Taken some successful examples, Co$_{x}$Ni$_{1-x}$DHs/NiCo$_2$O$_4$/CFP composite electrodes were...
prepared by a hydrothermal route and an electrodeposition process, showing high capacitance of \( \sim 1.64 \, \text{F/cm}^2 \) at 2 mA/cm\(^2\), good rate capability, and excellent cycling stability [20]; 3D hierarchical NiCo\(_2\)O\(_4@\)NiMoO\(_4\) core-shell nanowire/nanosheet arrays delivered a high areal capacitance of 5.80 F/cm\(^2\) at 10 mA/cm\(^2\), excellent rate capability, and high cycling stability [32]. Despite these notable achievements, it is still a hard task to design and construct 3D hierarchical heterostructures made of the bimetallic oxides with improved electrochemical properties for the supercapacitors.

Herein, we report hydrothermal growth of hierarchical heterostructures of NiCo\(_2\)O\(_4@\)XMoO\(_4\) (X = Ni, Co) as an electrode material for the supercapacitors with improved performances. Within these hierarchical heterostructures, high electrochemical activity of NiCo\(_2\)O\(_4\) not only shows outstanding pseudocapacity but also can be regarded as a backbone to provide reliable electrical connection to the XMoO\(_4\) (X = Ni, Co). Between them, the NiCo\(_2\)O\(_4@\)NiMoO\(_4\) electrode material showed a highest areal capacitance of 3.74 F/cm\(^2\) at 2 mA/cm\(^2\), which was much higher than the NiCo\(_2\)O\(_4@\)CoMoO\(_4\) electrode material (2.452 F/cm\(^2\)), and good rate capability, implying its prospect as an alternative electrode material in the supercapacitors.

**Methods**

**Synthesis of NiCo\(_2\)O\(_4@\)XMoO\(_4\) (X = Ni, Co) Composite Nanosheet Arrays**

All the reactants here were analytically graded and used without further purification. The synthesis of the composite nanosheet arrays was described briefly as follows: Firstly, the NiCo\(_2\)O\(_4\) nanosheet arrays were grown on the Ni foam according to a reference [17]. Secondly, the product of as-grown NiCo\(_2\)O\(_4\) nanosheet arrays was put into a 60-mL Teflon-lined autoclave, which contained 0.5 mmol of NiCl\(_2\)·6H\(_2\)O (or CoCl\(_2\)·6H\(_2\)O), 0.5 mmol of Na\(_2\)MoO\(_4\)·2H\(_2\)O, and 50 mL of deionized water. The autoclave was sealed and maintained at 120 °C for 2 h (or 1 h) in an electric oven and then cooled down to room temperature. The NiCo\(_2\)O\(_4@\)XMoO\(_4\) (X = Ni, Co) composites on the Ni foam were carefully washed with deionized water and absolute ethanol, successively, and then dried at 60 °C overnight. Lastly, the samples were annealed at 400 °C for 1 h at a ramping rate of 1 °C/min.

**Material Characterizations**

As-synthesized products were characterized by means of a D/Max-2550 PC X-ray diffractometer (XRD; Rigaku, Cu-K\(_\alpha\) radiation), a scanning electron microscopy (SEM; S-4800), and a transmission electron microscopy (TEM; JEM-2100 F) equipped with an energy-dispersive X-ray spectrometer (EDX).

**Results and Discussion**

In this work, the NiCo\(_2\)O\(_4@\)XMoO\(_4\) (X = Ni, Co) hierarchical heterostructures were successfully synthesized for electrode materials. As depicted schematically in Fig. 1, the synthesis process includes two steps: the hydrothermal growth of NiCo\(_2\)O\(_4\) nanosheets on the Ni foam and subsequent annealing as the first step and the hydrothermal growth of NiMoO\(_4\) or CoMoO\(_4\) nanosheets (coatings) on the NiCo\(_2\)O\(_4\) nanosheet arrays and another annealing process as the second step. Herein, 3D Ni foam, with uniform macropore structure, huge supporting area, and high electrical conductivity, was selected as a current collector for the growth of electrode materials, which can provide efficient electrolyte penetration to enable fast ion diffusion [27, 33]. Meanwhile, the NiCo\(_2\)O\(_4\) nanosheets grown uniformly on Ni foam functioned as the backbone to support and give reliable electrical connection to XMoO\(_4\) (X = Ni, Co) nanosheets, which can contribute to electronic and ionic diffusion and improve the utilization rate of electrode material. More importantly, the NiCo\(_2\)O\(_4\) electrode material with high electrochemical activity can also act as active materials for charge storage and contribute to the capacitance.

Combining the hydrothermal reaction and the annealing process resulted in the NiCo\(_2\)O\(_4\) nanosheet arrays grown on Ni foam. Detailed morphology and microstructure of the NiCo\(_2\)O\(_4\) nanosheets were investigated via the scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 2a, b shows the highly tight NiCo\(_2\)O\(_4\) nanosheets (with a thickness of...
~30–50 nm) that grew uniformly and vertically on the Ni foam and interconnected with each other, resulting in a highly porous structure with an abundant open space. Figure 2c shows a NiCo$_2$O$_4$ nanosheet almost transparent to electron beam, suggesting an ultrathin feature. Intriguingly, numerous mesoporous arrays are distributed uniformly throughout the whole NiCo$_2$O$_4$ nanosheet. The nanosheet arrays were scratched from the Ni foam and were then characterized by X-ray diffraction (XRD) to determine the crystalline phase of the product. As shown in Fig. 2d, all well-defined diffraction peaks can be indexed to the cubic phase NiCo$_2$O$_4$ by referring to the JCPDS card (no. 20-0781).

The NiCo$_2$O$_4$ nanosheet arrays grown on the Ni foam act as an ideal scaffold to load additional electroactive pseudocapacitive materials, thus enhancing the electrochemical performance. Considering this merit, NiMoO$_4$ or CoMoO$_4$ nanosheets were grown on the surface of the NiCo$_2$O$_4$ nanosheets via a hydrothermal reaction and an annealing step similar to the first growth step described above, forming NiCo$_2$O$_4$@NiMoO$_4$ composite nanosheet arrays (a core-shell structure or shaped like caterpillar). Figure 3a, b shows SEM images of the NiCo$_2$O$_4$@NiMoO$_4$ composite nanosheet arrays, in which the ultrathin NiMoO$_4$ nanosheets were uniformly grown on the surface of NiCo$_2$O$_4$ nanosheets and thus plenty of the space among NiCo$_2$O$_4$ nanosheets is utilized abundantly, and a thickness of the NiCo$_2$O$_4$@NiMoO$_4$ composite nanosheets is in the range of ~250–300 nm. Importantly, the integration of the NiMoO$_4$ material into the original NiCo$_2$O$_4$ nanosheet arrays does not destroy the ordered structure. In addition, these NiMoO$_4$ nanosheets are interconnected with each other to form a highly porous morphology, which can provide more active sites for electrolyte ions to transport efficiently. Figure 3c shows the TEM image of the NiCo$_2$O$_4$@NiMoO$_4$ composites. The result shows that the NiMoO$_4$ nanosheets are highly dense but still do not cover the entire mesoporous NiCo$_2$O$_4$ nanosheets fully. Moreover, energy-dispersive X-ray (EDX) spectrum (Fig. 3d) indicates that Ni, Co, Mo, and O can be detected in the composites. Surely, the Cu and C signals come from the carbon-supported Cu grid.

Figure 4 shows the SEM images of the samples, prepared via a different hydrothermal reaction time. It is used to demonstrate the formation process of the samples. Figure 4a depicts the NiCo$_2$O$_4$@NiMoO$_4$ nanosheet arrays formed via 0.5 h of the hydrothermal reaction. It can be seen that the nanosheets’ surface of NiCo$_2$O$_4$ loses their original smooth appearance and was interspersed by many fine NiMoO$_4$ nanosheets. Then, the reaction time was extended to 1 h and the SEM image (Fig. 4b) showed the results. Almost all the naked surface observed before was fully coated by NiMoO$_4$ nanosheets with the thickness increased to ~100–150 nm. As the time of the hydrothermal reaction becomes longer, the composition becomes thicker and at last the whole thickness in Fig. 4d is ~400–500 nm, which leads to a much smaller interspace among the adjacent sheets. But the growth of mass NiMoO$_4$ nanosheets on the NiCo$_2$O$_4$ nanosheets may decay the utilization of the NiCo$_2$O$_4$ (core) materials and even some NiMoO$_4$ (shell) materials.
may be blocked from the access to electrolyte. Therefore, 
the hydrothermal reaction time should be optimized (e.g.,
2 h) to get an improved electrochemical properties.
Hierarchical heterostructures of the NiCo$_2$O$_4$@Co-
MoO$_4$ composite nanosheets were also fabricated as a 
comparison with the NiCo$_2$O$_4$@NiMoO$_4$ nanosheet 
arrays for their usage as an electrode material. Figure 5a,
b shows the SEM image of the NiCo$_2$O$_4$@CoMoO$_4$
composite nanosheets. It clearly confirms that the whole 
surface of the NiCo$_2$O$_4$ nanosheets is homogeneously 
covered by the CoMoO$_4$ nanosheets, and the uniformity 
of these structures is similar to that of the NiCo$_2$O$_4$@Ni-
MoO$_4$ nanosheet arrays. As the TEM image (Fig. 5c) 
demonstrates, the thickness of the CoMoO$_4$ nanosheets 
is about 20–50 nm. Additionally, the composition of the 
as-synthesized NiCo$_2$O$_4$@CoMoO$_4$ composites was con-
firmed by EDX. As shown in Fig. 5d, the peaks of Cu 
and C derive from the Cu grid, and the strong signals of 
Ni, Co, Mo, and O further ascertain the formation of 
NiCo$_2$O$_4$@CoMoO$_4$.

Fig. 3  a, b Low- and high-magnification SEM images of the hierarchical heterostructures of the NiCo$_2$O$_4$@NiMoO$_4$ composite nanosheet arrays on the Ni foam. c TEM image and (d) EDX spectrum of the NiCo$_2$O$_4$@NiMoO$_4$ composite nanosheet arrays

Fig. 4  SEM images of the morphology evolution of the NiCo$_2$O$_4$@NiMoO$_4$ nanosheet arrays formed via different reaction time: (a) 0.5 h, (b) 1 h, 
(c) 2 h, and (d) 4 h
Then, the electrochemical properties of the hierarchical heterostructures of the NiCo$_2$O$_4$@XMoO$_4$ (X = Ni, Co) were investigated to evaluate their applicability as an active material for the supercapacitors, where a three-electrode cell with a saturated calomel electrode (SCE) reference electrode, a Pt counter electrode, and a KOH aqueous electrolyte (3 M) inside was used. As a comparison, the cyclic voltammogram (CV) curves from three electrodes made from NiCo$_2$O$_4$ and NiCo$_2$O$_4$@XMoO$_4$ (X = Ni, Co) materials, respectively, were shown in Fig. 6a. It was recorded with a potential window ranging from 0 to 0.6 V and a scan rate of 5 mV/s. Deduced from the CV curves’ shape, the Faradaic redox reactions associated with M-O/M-O-OH (M = Ni, Co) dominated the capacitance characteristics [18, 20] of these electrodes. Obviously, the surface area of the NiCo$_2$O$_4$@NiMoO$_4$ electrode is higher than that of the NiCo$_2$O$_4$@CoMoO$_4$ electrode and NiCo$_2$O$_4$ electrode, suggesting that the NiCo$_2$O$_4$@NiMoO$_4$ electrode
possessed a greater capacitance than the other two. The high capacitance of the NiCoO₄@NiMoO₄ electrode is mainly attributed to the fact that a highly porous nanostructure that originated from numerous ultrathin NiMoO₄ nanosheets grown on the NiCoO₄ nanosheet surface should provide more active sites for increasing electrolyte ion transportation efficiency to enhance the utilization of the whole electrode. Also, the CV curves of the NiCoO₄@NiMoO₄ electrodes taken via a various scan rate, i.e., 5, 10, 20, and 30 mV/s, were collected, as shown in Fig. 6b. It was noted that the peak position shifted slightly with the increase of scan rate, implying a good capacitive behavior and a high-rate capability of the electrode material. The galvanostatic charge-discharge (CD) method was applied to compare the capacitive ability of the NiCoO₄ electrode and two composite electrodes of NiCoO₄@NiMoO₄ and NiCoO₄@CoMoO₄ at the same current density of 2 mA/cm², as illustrated in Fig. 6c. It was found that the NiCoO₄@NiMoO₄ electrode possessed a longer discharging time than the NiCoO₄@CoMoO₄ and pure NiCoO₄ electrodes, demonstrating that such an electrode has an enhanced capacitance. Moreover, the areal capacitance of the electrode materials could be calculated from their CD curves by this equation: \( C = \int I \cdot d\tau / (S \cdot \Delta V) \), where \( I \) (A) is the current for the charge-discharge measurement, \( \tau \) (s) is the discharge time, \( S \) is the geometrical area of the electrode [31], and \( \Delta V \) (V) is the voltage interval of the discharge. As shown in Fig. 6d, the NiCoO₄@NiMoO₄ electrode always exhibited higher areal capacitances than the NiCoO₄@CoMoO₄ and NiCoO₄ electrodes. The maximal areal capacitance of the NiCoO₄@NiMoO₄ electrode was found to be 3.74 F/cm² at 2 mA/cm², which is much higher than the NiCoO₄@CoMoO₄ electrode (2.45 F/cm²), and 8 times higher than the NiCoO₄ electrode (0.46 F/cm²). In particular, the NiCoO₄@NiMoO₄ electrode still has an areal capacitance of 2.46 F/cm² even if the current density increased to 30 mA/cm², retaining appropriately 66 % of its initial value. However, the NiCoO₄@CoMoO₄ electrode and the NiCoO₄ electrode only showed the areal capacitance of 1.17 and 0.27 F/cm² at a high current density of 30 mA/cm², respectively.

Figure 7 shows the cycling performance of the NiCoO₄@XMoO₄ (X = Ni, Co) composite electrodes, which was evaluated through 2000 cycles with a scan rate of 60 mV/s. After 2000 cycles, it is found that the total capacitance retention was ~95.5 % for the NiCoO₄@CoMoO₄ electrode and ~83.1 % for the NiCoO₄@NiMoO₄ electrode, respectively. Compared with the NiCoO₄@CoMoO₄ electrodes, the NiCoO₄@NiMoO₄ electrode did not show a better cycling stability, but the characteristics of the high-rate capability and the large areal capacitance make the hierarchical heterostructures of the NiCoO₄@NiMoO₄ a more prospective electrode material. The outstanding capacitive properties of the hierarchical heterostructures of the NiCoO₄@XMoO₄ (X = Ni, Co) electrode are considered to originate from the synergistic effect of its following distinctive compositional and topological features [34–36]. First, within the hierarchical heterostructures, both core and shell are active materials, and the core-shell heterostructures enable easy access of electrolyte. Therefore, both of them can effectively contribute to the capacity. Secondly, the NiCoO₄ is highly conductive, which can provide “superhighways” for the charge in the core-shell structure. The direct growth of the XMoO₄ nanosheets on the NiCoO₄ nanosheet arrays avoids the use of polymer binder/conductive additives and further guarantees the effective charge transport between them. Besides, the high electrical conductivity could decrease the charge transfer resistance of the electrodes, thus leading to an increased power density. Finally, the XMoO₄ nanosheets and the NiCoO₄ nanosheets are mesoporous that increases the electroactive sites.

**Conclusions**

In conclusion, 3D hierarchical heterostructures of the NiCoO₄@XMoO₄ (X = Ni, Co) composite nanosheet arrays have been successfully designed and prepared for the supercapacitors. In such a novel nanostructure, the mesoporous NiCoO₄ nanosheet arrays grown directly on the Ni foam not only acted as a good pseudocapacitive material but also used as a hierarchical framework for loading NiMoO₄ or CoMoO₄ electroactive material. Notably, the NiCoO₄@NiMoO₄ composite electrode showed excellent rate capability as well as a highest areal capacitance of 3.74 F/cm² at 2 mA/cm², which was much higher than the values for the NiCoO₄@CoMoO₄ electrode (2.452 F/cm²) and NiCoO₄ electrode (0.456 F/cm²). The total capacitance retention
of the NiCoO$_2$@CoMoO$_4$ and NiCoO$_2$@NiMoO$_4$ electrodes after 2000 cycles is ~95.5 and ~83.1 %, respectively. Based on these electrochemical properties, the NiCoO$_2$@CoMoO$_4$ and NiCoO$_2$@NiMoO$_4$ composite electrode material may be more appropriate for practical applications.

Competing Interests
The authors declare that they have no competing interests.

Authors’ Contributions
JH designed and performed the experiments. JH, GS, and FQ prepared the samples and analyzed the data. JH, GS, FQ, and LW participated in interpreting and analyzing the data. All authors read and approved the final manuscript.

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