



Rational construction of three dimensional hybrid $\text{Co}_3\text{O}_4@\text{NiMoO}_4$ nanosheets array for energy storage application



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HIGHLIGHTS

- Co_3O_4 NSA can be prepared through a facile chemical etching assistant approach.
- Rational designed 3D hybrid $\text{Co}_3\text{O}_4@\text{NiMoO}_4$ has been successfully constructed.
- The hybrid $\text{Co}_3\text{O}_4@\text{NiMoO}_4$ shows enhanced pseudocapacitive properties.

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ABSTRACT

Electrodes with rationally designed hybrid nanostructures can offer many opportunities for the enhanced performance in electrochemical energy storage. In this work, the uniform 2D Co_3O_4 -based building blocks have been prepared through a facile chemical etching assistant approach and a following treatment of thermal annealing. The obtained nanosheets array has been directly employed as 2D backbone for the subsequent construction of hybrid nanostructure of $\text{Co}_3\text{O}_4@\text{NiMoO}_4$ by a simple hydrothermal synthesis. As a binder-free electrode, the constructed 3D hybrid nanostructures exhibit a high specific capacitance of 1526 F g^{-1} at a current density of 3 mA cm^{-2} and a capacitance retention of 72% with the increase of current density from 3 mA cm^{-2} to 30 mA cm^{-2} . Moreover, an asymmetric supercapacitor based on this hybrid $\text{Co}_3\text{O}_4@\text{NiMoO}_4$ and activated carbon can deliver a maximum energy density of 37.8 Wh kg^{-1} at a power density of 482 W kg^{-1} . The outstanding electrochemical behaviors presented here suggest that this hybrid nanostructured material has potential applications in energy storage.

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1. Introduction

Over the past decades, the growing demand for renewable sources has largely triggered the worldwide research on electrical energy storage devices (EES). As one of the promising candidates for energy storage, supercapacitors (SCs) have been paid great attention due to their excellent properties such as high power density, fast recharge capability and long cycle life [1]. Generally, pseudocapacitors based on transition metal oxides can offer higher capacitance values than carbon materials based electrochemical double-layer capacitors (EDLs) [2]. Therefore, tremendous efforts have been focused on the former type of supercapacitors [3–6].

In order to obtain high-performance of pseudo-capacitors, the structural improvement based on the electrode materials is largely requisite [7–12]. Exploring proper nanomaterials, especially rationally designed three-dimensional (3D) metal oxide hybrid nanostructures (usually, fabricated by certain 1D or/and 2D building blocks), has always been an attractive topic [13–20]. Among various low-dimensional metal oxide building blocks, Co-based nanosheets array has been considered as one of promising electrode materials due to its high theoretical capacitance, environmental benignity and good pseudo-capacitive performance in alkaline solutions [21–24]. Up to now, the synthesis of metal oxide nanosheets array can be generally actualized by two approaches: electro-deposition and hydrothermal synthesis [25–32]. In contrast to electro-deposition, active materials obtained by hydrothermal synthesis can provide uniform and large-scale nanosheets array with numerous large channels, which would facilitate

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the design and fabrication of 3D hybrid nanostructures [21,22,24,25,33]. However, regardless of the type of electrode materials, the capacitance values of 2D building blocks obtained by hydrothermal synthesis are still limited [33–37]. Therefore, it will be meaningful to explore an efficient assistant method to prepare large-scale 2D nanosheets array with the improved pseudo-capacitive performance.

As an attractive member in the class of the AMoO_4 type materials, NiMoO_4 has attracted more and more research interest due to its potential application in electrical energy storage [38,39]. However, the researches on its nanostructure fabrication and pseudo-capacitive performances have been rarely referred to [40,41]. To date, the reported electrode materials based on NiMoO_4 have been usually made by a traditional slurry-coating method, where the involved carbon current collector and polymer binders (or additives) can seriously depress the pseudo-capacitive performance [42–46]. In order to meet the requirement of higher capacitance values, one promising method is to fabricate smartly designed hybrid nanostructures combined with other uniformly low-dimensional building blocks [47,48].

In the present work, we have prepared uniform 2D Co_3O_4 -based building blocks through a facile chemical etching assistant approach, and used this to construct a binder-free electrode with hybrid nanostructured $\text{Co}_3\text{O}_4@/\text{NiMoO}_4$ directly grown on Ni foam. The electrochemical tests showed that this as-synthesized 3D $\text{Co}_3\text{O}_4@/\text{NiMoO}_4$ electrode exhibited a high specific capacitance of 1526 F g^{-1} at 3 mA cm^{-2} , and excellent rate performance (72% capacity retention at 30 mA cm^{-2}). To further evaluate the practical application of this hybrid $\text{Co}_3\text{O}_4@/\text{NiMoO}_4$ NSA in EES, an asymmetric supercapacitor (AS) was also fabricated. The as-fabricated AS achieved a specific capacitance of 121 F g^{-1} at a current density of 5 mA cm^{-2} , and a maximum energy density of 37.8 Wh kg^{-1} at a power density of 482 W kg^{-1} . Such attractive electrochemical performance presented here implies that this hybrid electrode can be a promising candidate for practical applications in supercapacitor.

2. Experimental section

2.1. Preparation of uniform 2D Co_3O_4 nanosheets array

The approach for synthesizing uniform 2D Co_3O_4 -based nanosheets array (NSA) has employed the CoAl layered double hydroxides (CoAl LDH) as pristine material, and the CoAl LDH NSA was synthesized by a simple homogeneous hydrothermal method [49–51]. Typically, the reaction solution was obtained by mixing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.5 mmol), NH_4F (5 mmol), and urea (35 mmol) in 50 mL of ultrapure water with $n(\text{Co})/n(\text{Al}) = 2:1$. After being stirred for 1 h, the homogeneous pink solution was transferred into a Teflon-lined stainless steel autoclave, and then a piece of Ni foam was immersed into the reaction solution. Subsequently, the bottle was capped and maintained at 95°C for 6 h in an electric oven and then cooled down to room temperature. After the reaction, the sample was collected and rinsed several times with ultrapure water. The as-prepared precursor on the Ni foam was directly immersed in 5 M NaOH for chemical etching overnight, and then rinsed several times by ultrapure water [52,53]. Finally, the uniform 2D Co_3O_4 -based NSA was obtained by annealing at 300°C for 3 h. For comparison, the sample of CoAl layered double oxides (CoAl LDO) was also prepared under the same annealing conditions.

2.2. Preparation of $\text{Co}_3\text{O}_4@/\text{NiMoO}_4$ hybrid nanostructures

To obtain hybrid nanostructures of $\text{Co}_3\text{O}_4@/\text{NiMoO}_4$, the subsequent hydrothermal growth of NiMoO_4 was processed in 50 mL aqueous solution containing 0.5 M $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 0.5 M

$\text{Na}_2\text{MoO}_4 \cdot 7\text{H}_2\text{O}$ [38,41,46]. The chemical-etched CoAl LDH NSA (before annealing treatment) was directly immersed in the aforementioned reaction solution. The reaction was processed at 140°C for 1 h. After that, the sample was collected and rinsed several times with ultrapure water. For comparison, the aforementioned solution was further used to fabricate other $\text{Co}_3\text{O}_4@/\text{NiMoO}_4$ samples with the reaction times of 0.5 h and 2 h, respectively. Finally, the Ni foam with the as-prepared hydrate precursors was annealed at 300°C for 3 h to obtain hybrid $\text{Co}_3\text{O}_4@/\text{NiMoO}_4$.

2.3. Material characterizations and electrochemical measurements

X-ray diffraction (XRD) patterns were recorded on a Rigaku XRD-2400 diffractometer, using $\text{Cu-K}\alpha$ radiation at 40 kV and 60 mA. The nanostructured samples were observed by using a field emission scanning electron microscope (FESEM, JSM-6701F) and a field emission transmission electron microscope (FETEM, TF20). X-ray photoelectron spectroscopy (XPS) was carried out by using ESCALAB 210 spectrometer (VG Scientific, UK). Nitrogen adsorption/desorption isotherms were measured on an asap 2020 analyzer. All samples were out gassed at 80°C for 6 h under vacuum prior to measurements. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method.

The electrochemical measurements were carried out in a three-electrode electrochemical cell by using the CHI 660E Electrochemical Workstation at room temperature with the 2 M KOH as the electrolyte. The Ni foam supported active materials (Co_3O_4 -based NSA mass $\approx 0.8 \text{ mg cm}^{-2}$, CoAl LDO NSA mass $\approx 1.1 \text{ mg cm}^{-2}$, $\text{Co}_3\text{O}_4@/\text{NiMoO}_4$ NSA mass $\approx 1.75 \text{ mg cm}^{-2}$) were used directly as the working electrodes. A Pt plate and an SCE electrode were used as the counter electrode and the reference electrode, respectively. Electrochemical impedance spectroscopy (EIS) tests were conducted by using a perturbation amplitude of 5 mV in the frequency range from 0.01 Hz to 100 kHz. The galvanostatic charge/discharge tests were conducted on a LAND battery program-control test system. The mass-specific capacitance (MSC, C_s) [F g^{-1}] and areal-specific capacitance (ASC, C_a) [F cm^{-2}] were calculated from the galvanostatic discharge curves using equations as below:

$$C_s = It/m\Delta V$$

$$C_a = It/S\Delta V$$

where I represents the charge–discharge current (A), t is the discharge time (s), ΔV is the potential (V), S is the geometrical area of the electrode, and m designates the total mass of the active materials (g) [13,16,20].

2.4. Fabrication of the asymmetric supercapacitor

The electrochemical performances of asymmetric supercapacitor (AS) were explored under a two-electrode cell in 2 M KOH electrolyte solution [3]. The as-synthesized $\text{Co}_3\text{O}_4@/\text{NiMoO}_4$ NSA on Ni foam was directly used as positive electrode, and the activated carbon (AC) was used as negative electrode. The negative electrode was prepared by a traditional “slurry-coating” method, and the similar process can be found in the references [44,61]. The charge balance between the two electrodes will follow the relationship $q^+ = q^-$. The charge stored (q) by each electrode depends on the following equation:

$$q = mC\Delta V$$

where C represents the specific capacitance of the electrode (F g^{-1}), ΔV is the potential (V), and m designates the total mass of the active

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