



Self-assembling hierarchical NiCo₂O₄/MnO₂ nanosheets and MoO₃/PPy core-shell heterostructured nanobelts for supercapacitor

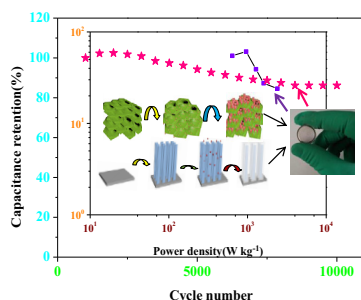
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HIGHLIGHTS

- A novel low-cost high-performance aqueous asymmetric device was designed.
- The device presents a maximum energy/power densities of 60.4 Wh kg⁻¹ and a 2400 W kg⁻¹.
- The capacitance of the device can still maintains 88.2% after 10,000 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

A high energy/power density aqueous asymmetric supercapacitor device is assembled by self-assembled NiCo₂O₄/MnO₂ composite as a positive electrode and MoO₃@PPy composite as a negative electrode in Na₂SO₄ electrolyte. Due to the synergistic effect of electronic conductivity of PPy and high-rate metal oxides, the heterostructure electrodes reveal better charge transport and cycling stability. The overall areal capacitance retentions for the NiCo₂O₄/MnO₂ and MoO₃@PPy electrode materials are 97.5% and 86.2% after 6000 cycles, respectively. Such unique nanoarchitecture in the hybrid device further presents remarkable electrochemical performance with high capacitance and ideal cycle life at high rates. The novel device with an expanded operating voltage window of 1.6 V, presents a high energy density of 60.4 Wh kg⁻¹ and a maximum power density of 2400 W kg⁻¹. The device demonstrates a good cycle life with 88.2% capacitance retention after 10,000 cycles. This strategy for the choice provides a promising route for the next-generation device of energy storage and conversion with high energy, high power density, and long life.

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1. Introduction

With the increasing interests in electric energy storage for portable systems and mobile electronics, many efforts have been dedicated to the new generation energy devices. Among miscellaneous conversion devices and electrochemical energy storage,

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supercapacitors (SCs) is hopeful as energy-type and long life candidates [1–8]. Transition metal oxides as positive electrodes of SCs have been diffusely explored with high energy densities and areal capacitance deriving from faradic redox reactions [9–15]. Among the transition metal oxides, spinel nickel cobaltite (NiCo₂O₄) has been received vast interest recently in supercapacitor applications because of its low-cost, high availability and environmental friendliness [3]. Particularly, NiCo₂O₄ has much higher redox activity and better electrical conductivity compared to cobalt oxides

and nickel oxides [16–21]. At the same time, MnO_2 [22–25] also has been widely investigated as pseudocapacitive material due to its natural abundance, low toxicity and high theoretical capacitance. Therefore, NiCo_2O_4 with higher conductivity can support the active electrode material (MnO_2) forming 3D hierarchical hybrid nanostructure for high-performance supercapacitor device. For the negative electrode, Khomenko's group reported an asymmetric capacitor with manganese oxide/activated carbon [26]. Cheng and his coworkers investigated MnO_2 nanowire/graphene//graphene asymmetric electrochemical capacitors [27]. Liu et al. studied CoO @Polypyrrole nanowire array used in supercapacitor [28].

As is known, metal oxides (MOs) in general exhibit higher electrochemical energy storage ability arising from faradic redox reactions than carbon-based materials. Among various transition metal oxides, MoO_3 with a typical two-dimensional layered structure is one of the most actual interest because of its unique structure is beneficial for small ions to insert/remove such as H^+ , Na^+ and K^+ [29] and multiple oxidation states that enable rich redox reactions to happen for pseudocapacitive [30], which contributes to high specific capacitance. Nevertheless, its poor inherent electrical conductivity usually affects its high performance in device and reduces faradic redox kinetics. To address this problem, an effective way to improve electrochemical performance of MoO_3 is to coat MoO_3 with a conductive polymer. Polypyrrole (PPy) is an interesting conductive polymer due to its high electrical conductivity, low cost and the performance of coating forbidding the structural collapsing happened to transition metal oxide after charge-discharge process [31–33].

Herein, we report a novel low-cost high-performance aqueous asymmetric device with self-assembled $\text{NiCo}_2\text{O}_4/\text{MnO}_2$ composite as a positive electrode and MoO_3 @PPy composite as a negative electrode. And for all we know, this is the first study to report the new design. The device achieves a specific capacitance of 170.1 F g^{-1} with a relatively wide operational voltage of 1.6 V and a high energy density of 60.4 Wh kg^{-1} at a power density of 950.1 W kg^{-1} . For comparison, we also constructed a button cell with $1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ aqueous electrolyte and PVA- Na_2SO_4 gel as solid-state electrolyte, respectively. The results show that the performance of the button cell was much higher in aqueous electrolyte.

2. Experimental

2.1. Synthesis of $\text{NiCo}_2\text{O}_4/\text{MnO}_2$ nanosheet arrays

Firstly, NiCo_2O_4 nanosheet arrays were synthesized on Ni foam (NF) by a facile hydrothermal reaction followed with a simple post-annealing process. In a typical synthesis, 0.2 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.4 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1.2 g NH_4F and 3 g urea were dissolved in 70 mL of deionized water under magnetically stirring for 1 h in air. The as-obtained solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and then a piece of clean NF was immersed into the reaction solution. After that, the autoclave was heated to 120°C inside a conventional oven for 3 h, and then cooled to room temperature. The product on the NF was washed with distilled water repeatedly, and then dried at 60°C for 12 h. Afterward, the sample was calcined at 350°C for 2 h at a ramping rate of 5°C min^{-1} to transform into NiCo_2O_4 nanosheets. Next, the NF was put again into a solution containing $0.1 \text{ mol L}^{-1} \text{ KMnO}_4$ in an autoclave, and the autoclave was subsequently maintained at 180°C for 30 min. Finally, the sample was washed with distilled water, and annealed at 200°C in air for 1 h to obtain $\text{NiCo}_2\text{O}_4/\text{MnO}_2$ nanosheet arrays. The mass loading of the NiCo_2O_4 on the NF was calculated

to be about 2.1 mg. The mass loading of the $\text{NiCo}_2\text{O}_4/\text{MnO}_2$ nanosheets on the NF was about 3 mg.

2.2. Preparation of MoO_3 @PPy nanobelts

The MoO_3 nanobelts were prepared by a hydrothermal method. In a typical synthesis, 40 mL of H_2O_2 (30%) was added dropwise into 4 g of molybdenum powders in the ice-water bath under magnetic stirring for 4 h to remove the redundant H_2O_2 , forming a clear orange solution. The orange solution was transferred and sealed in a 100 mL Teflon-lined stainless autoclave. The autoclave was heated to 180°C for 24 h, then cooled to room temperature. The MoO_3 @PPy nanocomposite was prepared by in situ oxidative polymerization. In a typical synthesis, 0.1 g MoO_3 nanobelts were fully dispersed in 20 mL deionized water at ambient temperature and then transferred into an ice bath. 0.2 mL of pyrrole was added into the above solution and stirred for 30 min. Then, 0.4 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (dissolved in 10 mL of deionized water) was slowly dropped into the above solution. The mixture was kept at ice bath for 4 h under stirring. Finally, the obtained composite was washed with water and ethanol, respectively, and then dried under vacuum at 60°C for 12 h. The mass loadings of the MoO_3 and MoO_3 @PPy on the NF were calculated to be about 1.5 mg and 2 mg, respectively.

2.3. Fabrication of solid-state asymmetric device (AAD)

The AAD were assembled by using MoO_3 @PPy nanobelts as the negative electrode and $\text{NiCo}_2\text{O}_4/\text{MnO}_2$ nanosheet arrays as the positive electrode with a separator (NKK TF40, $40 \mu\text{m}$ thickness, low ESR type, purchased from SCM industrial Chemical CO., LTD) and PVA/ Na_2SO_4 gel as a solid electrolyte. PVA/ Na_2SO_4 gel was prepared as follows: in a typical process, 6 g PVA was dissolved in 60 mL deionized water with stirring at 85°C for 1 h. Then, $1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ was slowly dropped into the above solution at 80°C under stirring until the solution became clear. The $\text{NiCo}_2\text{O}_4/\text{MnO}_2$ electrode, the MoO_3 @PPy electrode and the separator were soaked in the gel for about 3 min, and then were assembled together. The device was kept at 60°C for 12 h to remove excess water in the electrolyte.

2.4. Characterization

The obtained product was characterized by scanning electron microscopy (SEM, Hitachi-4800), and X-ray powder diffraction (XRD, Rigaku Dmax-rB, Cu $K\alpha$ radiation, $\lambda = 0.1542 \text{ nm}$, 40 kV, 100 mA). X-ray photoelectron spectroscopy (XPS) was carried out by using the Physical Electronics PHI model 5700 instrument and a field emission transmission electron microscopy (FETEM) (JEM-2100). Electrochemical characteristics of the as-obtained products were studied on an CHI660 electrochemical work station (Chenhua, Shanghai) using cyclic voltammetry, chronopotentiometry and electrochemical impedance test by configuring the sample into a three-electrode cell, where the sample was used as the working electrode, Pt foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

2.5. Calculation methods

2.5.1. Single electrode

The areal capacitance (C_a) of the electrode could be calculated from its charge/discharge curve by the following equation [5]:

$$C_a = I\Delta t / \Delta V \quad (1)$$

where C (mF cm^{-2}) is areal capacitance, I (mA) represents the discharge current, and S , Δt (s) are designated as the effective electrode area and total discharge time, respectively.

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