NiCoO₂ flowers grown on the aligned-flakes coated Ni foam for application in hybrid energy storage

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Abstract

Many NiCoO₂ flowers with an average diameter of about 4 μm were grown on the NiCoO₂ flakes coated Ni foam (denoted as NiCoO₂/Ni foam) through a simple hydrothermal method and confirmed by scanning and transmission electron microscopies, X-ray diffraction and X-ray photoelectron spectrum measurements. The NiCoO₂/Ni foam with high specific area and porosity was directly used as the working electrode without any binders. The measured specific capacitance of NiCoO₂ grown on Ni foam is 756 F/g at 0.75 A/g using a three-electrode setup in 1 M KOH. Considering the high capacity of NiCoO₂ and the good stability of rGO, the NiCoO₂/Ni foam//rGO hybrid supercapacitor combining NiCoO₂/Ni foam and rGO shows very good properties, such as high specific capacitance (82 F/g at 2 A/g based on the total mass of active materials), high energy density (25.7 Wh/kg at 1500 W/kg based on the total mass of active materials), good stability (about 90% capacitance retention after 2000-cycle at 100 mV/s), and low charge ion transfer resistance.

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Keywords: NiCoO₂ flowers; aligned-flakes coated Ni foam; high specific area; porosity; specific capacitance; hybrid supercapacitor

1. Introduction

The clean energy conversion and storage devices, such as supercapacitors, Li-ions batteries and fuel cells, have been vigorously exploited to reach the global excellent environment goal. Especially for supercapacitors, their research interest has been rising at alarming rates in the past several years, and predicted to be still growing at soon in the future, owing to their remarkable superiorities, including short charge time, high power density and long lifetime [1-4].

The properties for supercapacitors greatly depend on the inherent features of electrode materials [5-6]. Transition metal oxides can not only store charge like carbon materials, but also offer rich Faradic redox reactions due to the multiple valence states, which can generate high capacitance. Thus transition metal oxides can be described as alternative electrode materials. Especially, some oxides of inexpensive, abundant and environmentally benign transition metal elements, such as Mn, Co and Ni, have attracted enormous interest. Moreover, the mixed transition metal oxides, such as MnCo₂O₄, NiCo₂O₄, have been investigated to own higher electrical conductivity and capacitance than single components [7]. The mixed nickel cobaltite oxides have been widely studied on account of the co-existence of Ni and Co, that is, Ni²⁺ can replace Co²⁺ in the spinel Co₃O₄ and cubic crystal CoO to form NiCo₂O₄ and NiCoO₂ respectively [8].

Recently, many researches about the preparation and supercapacitive

performances of NiCo_2O_4 have been reported, such as nanoflakes [9], nanoparticles [10], nanowires [11] and flowers [12]. However, few studies on the synthesis and supercapacitor evaluation of NiCoO_2 have been investigated. Du *et al.* prepared NiCoO_2 single-crystalline nanoparticles with a specific capacitance of 184 F/g at 1 A/g [13]. Xu *et al.* synthesized NiCoO_2 nanotubes for supercapacitors based on the template of polymeric nanotubes [14]. Moreover, some NiCoO_2 based composites, like $\text{CoNiO}_2/\text{TiN-TiO}_x\text{Ny}$ composites [15], branched $\text{CoMoO}_4@\text{CoNiO}_2$ core/shell nanowire arrays [16] and N-doped reduced graphene oxide (rGO)/ NiCoO_2 [17], have been also determined to use in supercapacitors. In addition, NiCoO_2 with some other structures, including nanowires [18] and flowers [19], has been used for water oxidation and Li-ion batteries, rather than supercapacitors. Therefore, the supercapacitor performances of NiCoO_2 with the specific structure are worth being researched. It is reported that the hierarchical structures can not only inherit the merits of the single components but also provide novel properties from the synergistic interactions between the nano building blocks [20]. The Ni foam was used to be the template in the preparation procedure of NiCoO_2 . It was surprised to find that the hierarchical NiCoO_2 flowers grown on the aligned-flakes coated Ni foam were formed (denoted as $\text{NiCoO}_2/\text{Ni foam}$) and then it was used for supercapacitors. Compared with the reported similar works [19, 21], the novelties are as follows: (a) the good interconnectivity from flowers grown on the aligned-flakes can promote the charge ion transport; (b) it can be directly used as the electrode without binders, avoiding the contact limitation of active materials with electrolyte from binders; (c)

the flower-like NiCoO_2 is the first time to be used in supercapacitors, to our knowledge.

In order to explore the practical value of NiCoO_2/Ni foam, the hybrid supercapacitor (NiCoO_2/Ni foam//rGO) was established with NiCoO_2/Ni foam as the positive material and rGO as the negative material. The 1 M KOH was selected as the electrolyte on account of low cost, safety and environmental friendliness [22]. In view of this design, this hybrid supercapacitor combines the high capacity of NiCoO_2 as well as the good stability of rGO.

2. Experimental

2.1 Materials

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, urea, ethanol, hydrazine hydrate, etc. were purchased from Tianjin Jiangtian Chemical Technology Company without any post-processing. Ni foam was from Kunshan dessco Electronics Company. Graphite was from Qingdao Graphite Factory.

2.2 Preparation of NiCoO_2/Ni foam

The Ni foam was sheared into the pieces ($1.0 \times 4.0 \times 0.15 \text{ cm}^3$, 30 mg/cm^2) and then treated with acetone, ethanol and deionized water under ultrasonic processing to remove the surface oxidation layer. 0.3 mmol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.3 mmol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 3 mmol urea were dissolved into the mixture of ethanol and deionized water (10/10 mL) under stirring to obtain a clear solution. Then the solution and the clean Ni foam were transferred into a Teflon-lined autoclave and maintained

at 100 °C for 8 h. After cooling, the coated Ni foam was picked out, washed with deionized water and dried at 60 °C to obtain NiCoO₂ precursor/Ni foam. The NiCoO₂ precursor/Ni foam was annealed at 300 °C for 3 h in N₂ atmosphere to achieve NiCoO₂/Ni foam.

2.3 Preparation of rGO

The graphite was oxidized into graphene oxide (GO) by a modified Hummer's method [23]. Then GO was reduced into rGO by hydrazine hydrate at 90 °C.

2.4 Characterization

The scanning electron microscopy (SEM) measurement of NiCoO₂/Ni foam and rGO was performed using S4800 microscope (Hitachi Limited, Japan). Transmission electron microscopy (TEM) images of NiCoO₂ and rGO were got using Philips Tecnai G2F20 microscopy (Netherlands). The X-ray diffraction (XRD) patterns of NiCoO₂/Ni foam and rGO were measured with the given step (4° min⁻¹) using a D8 FOCUS diffractometer with Cu K α radiation as reference target. The X-ray photoelectron spectrum (XPS) measurement of NiCoO₂ was conducted using a PHI1600 ESCA System spectrometer (PERKIN ELMER, USA) with Al K α radiation.

2.5 Electrochemical measurement

The NiCoO₂/Ni foam (1×1 cm²) was directly used as the working electrode. The rGO, carbon black and polytetrafluoroethylene with a mass ratio of 75:15:10 were mixed and coated on Ni foam (1 × 1 cm²) and then used as a working electrode. The large-area Pt mesh and HgO/Hg were assigned as counter and reference electrode, respectively. The performance tests of NiCoO₂/Ni foam and rGO single electrodes

were conducted in a three-electrode system in 1 M KOH electrolyte.

The hybrid supercapacitor was assembled with NiCoO₂/Ni foam (1×1cm²) and rGO as positive and negative electrodes, cellulose membrane as separator, KOH (1 M) as electrolyte. Before assembling the device, the two electrodes and separator were immersed into 1 M KOH for 2 h. The performances of this NiCoO₂/Ni foam//rGO hybrid supercapacitor was studied using a two-electrode system.

The testing technologies contain cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) cycles and electrochemical impedance spectroscopy (EIS). In the EIS measurements, the frequency range is from 10 mHz to 100 kHz with the applied potential amplitude (5 mV). The specific capacitances of the single electrode based on the mass of active materials (C_m , F/g), hybrid supercapacitor device based on the total mass of active materials (C_M , F/g) and hybrid supercapacitor device based on the total mass of the device (C_d , F/g) were determined according to the equations (1), (2) and (3) respectively. The energy density (E , Wh/kg) and power density (P , W/kg) based on the total mass of active materials for the hybrid supercapacitor were calculated using the following equations (4) and (5). The energy density (E_d , Wh/kg) and power density (P_d , W/kg) based on the total mass of the device for the hybrid supercapacitor were also determined using equations (6) and (7).

$$C_m = \frac{i \times \Delta t}{\Delta v \times m} \quad (1)$$

$$C_M = \frac{i \times \Delta t}{\Delta V \times M} \quad (2)$$

$$C_d = \frac{1000 \times i \times \Delta t}{\Delta V \times M_d} \quad (3)$$

$$E = \frac{1000}{2 \times 3600} C_M (\Delta V)^2 \quad (4)$$

$$P = \frac{3600 \times E}{\Delta t} \quad (5)$$

$$Ed = \frac{1000}{2 \times 3600} C_d (\Delta V)^2 \quad (6)$$

$$Pd = \frac{3600 \times Ed}{\Delta t} \quad (7)$$

where i (A), Δt (s), Δv (V) and m (g) refer to the given current, discharge time, potential window and mass of the active material in the single electrode (NiCoO₂ or rGO); ΔV (V), M (g), and Md (cm²) are the voltage, the total mass of active materials (NiCoO₂ and rGO), the total mass of device (~ 0.218 g) for the hybrid supercapacitor.

3. Result and discussion

3.1 Characterization of NiCoO₂/Ni foam

The schematic illustration of the formation process for flower and flake-like NiCoO₂ on the Ni foam and the relevant digital photos are shown in Figure 1. The needle-like NiCoO₂ precursor on the Ni foam was firstly formed in the hydrothermal course. Then the needle-like NiCoO₂ precursor was transferred into flake-like NiCoO₂, and some NiCoO₂ flakes were assembled into the NiCoO₂ flowers in the heat-treatment. Moreover, from Ni foam to NiCoO₂ precursor/Ni foam and to NiCoO₂/Ni foam, the color of the sample changed indicating that the NiCoO₂ has been grown on the Ni foam. The mass loading of NiCoO₂ per area on the Ni foam is estimated 2 mg/cm² through the weight difference value.

Figure 1 The preparation process of $\text{NiCoO}_2/\text{Ni foam}$; Digital photos of Ni foam, NiCoO_2 precursor/Ni foam and $\text{NiCoO}_2/\text{Ni foam}$

In the low-magnification SEM image of $\text{NiCoO}_2/\text{Ni foam}$ (Figure 2a), many flowers with a diameter of about $4\text{ }\mu\text{m}$ are grown on the aligned flakes coated Ni foam. The high-magnification SEM images of the NiCoO_2 flowers are shown in Figure 2b and c to observe those flowers clearly. Obviously, these NiCoO_2 flowers are composed of many interconnected flakes. In addition, Figure 2d and e also show the magnifying images of the NiCoO_2 flakes coated on Ni foam and these flakes are also connected intimately. But the size of these flakes (Figure 2d) is different from that for flakes from flowers (Figure 2c). Such a structure of the NiCoO_2 flowers grown on the aligned flakes can facilitate the penetration of the electrolyte OH^- into the NiCoO_2 active material, leading to the redox reactions. Figure 2f provides the TEM image of

the NiCoO₂ peeling off Ni foam. The lattice fringes with the interplanar distance of 0.244 nm are assigned to (111) phase of NiCoO₂, confirming that the sample is NiCoO₂.

Figure 2 SEM images (a-e) of NiCoO₂/Ni foam; TEM image (f) of NiCoO₂

The end-product NiCoO₂/Ni foam was confirmed by XRD analysis. In Figure 3a, the three obvious peaks at $2\theta = 44.9^\circ$, 52.2° and 76.8° are belonged to the substrate (Ni foam). The other peaks at $2\theta = 36.8^\circ$, 42.8° and 61.8° are assigned to the crystal planes (111), (200) and (220) of NiCoO₂ (JCPDS: 10-0188). These results further confirm the successful formation of NiCoO₂/Ni foam. The sample stripped from NiCoO₂/Ni foam was used for XPS measurement to analyze its composition and the binding energy of atoms. The Ni, Co, O and C atoms are observed in the XPS spectrum of sample (Figure 3b), and the C stems from the absorbed organic matter. The calculated atomic ratio of Ni and Co (Ni/Co) is 1.08, which is on the verge of the stoichiometry of NiCoO₂. In Figure 3c, the Ni 2p core level spectrum contains a main

peak at 855.4 eV, implying that Ni exists in form of divalent state [24]. In Figure 3d, the peak appeared at 855.4 eV on the Co core level spectrum corresponds to $\text{Co}2p_{3/2}$, which is the typical characteristic of the +2 oxidation state [25]. All these results confirm the formation of NiCoO_2 .

Figure 3 XRD pattern of NiCoO_2/Ni foam (a); XPS spectrum (b), Ni 2p (c) and Co 2p (d) core level spectra of NiCoO_2 .

The capacitive performances of NiCoO_2 grown on Ni foam were investigated using a half cell in the three-electrode setup. Figure 4a exhibits the typical CV profiles of the NiCoO_2 grown on Ni foam in the potential ranging from 0 to 0.7 V at various scan rates. A pair of redox peaks exists in these CV profiles, indicating the Faradaic redox energy storage mechanism of the NiCoO_2 [26]. Moreover, the positive shifted

oxidative peaks and negative shifted reductive peaks under the increasing scan rate are rooted in the augment of internal diffusion resistance in the NiCoO₂/Ni foam electrode [27]. Figure 4b shows the GCD profiles of the NiCoO₂ grown on Ni foam in the potential ranging from 0 to 0.5 V at different current densities. The GCD curves contain some platforms, which is parallel with the redox peaks in the CV curves. Meanwhile, the nearly symmetric charge and discharge curves reflect the high coulombic efficiency and low polarization of the NiCoO₂/Ni foam electrode [28]. The specific capacitances of the prepared NiCoO₂ grown on Ni foam were calculated from the GCD measurement using the equation (1) and shown in Figure 4c. The capacitance values are 756, 640, 568 and 555 F/g at 0.75, 1.25, 2 and 2.5 A/g. The specific capacitances of NiCoO₂ grown on Ni foam are superior to those of pure NiCoO₂ (about 150 F/g at 0.2 A/g), and even to those of nitrogen doped reduced graphene sheets-NiCoO₂ (508, 490 and 386 F/g at the discharge currents of 0.5, 1 and 2 A/g) [29]. In addition, Table 1 shows the specific capacitances of NiCoO₂ in this work and the reported literatures, as well as the theoretical capacity. These NiCoO₂ flowers and flakes hold high surface area and pores, which can promote the access of electrolyte ions to inner active materials, leading to high capacitance. The Nyquist plots shown in Figure 4d feature the small radius and high phase angle, in parallel with the low charge transfer resistance and Warburg resistance, indicating the fast charge and ion transfer behavior of the NiCoO₂/Ni foam electrode [30].

Figure 4 CV profiles at different scan rates (a); GCD profiles at different current densities (b); specific capacitances (c); Nyquist plots (d) for the NiCoO_2 grown on Ni foam in the three-electrode setup.

Table 1 Specific capacitances of NiCoO_2

Specific capacitance (F/g)	Reference
756 F/g at 0.75 A/g	Our work
~130 F/g at 1 A/g	[29]
184 F/g at 1 A/g	[13]
1468 F/g at 2 A/g	[14]
~2032 F/g	Theoretical capacity

3.2 Characterization of rGO

The rGO was prepared through the reduction of GO by hydrazine hydrate. In Figure 5a, the diffraction peak of GO is situated at $2\theta = 10.8^\circ$, and shifted to 21.9°

after reduction, confirming the formation of rGO [31]. In addition, the Raman spectra (Figure 5b) of GO and rGO contain two bands (D and G), and the relative intensity of the D and G bands (D/G) for rGO is higher than that for GO, which is also the characteristic phenomenon [32]. It is found that the rGO is lamellar structure from the SEM and TEM images of rGO (Figure 5c and d).

Figure 5 XRD pattern (a) and Raman spectra (b) for GO and rGO; SEM (c) and TEM (d) images of rGO

Figure 6a and b show the CV and GCD loops of the prepared rGO measured in a three-electrode system. The shape of CV loops is close to rectangle, confirming the energy storage mechanism of double electric layer for rGO [33]. The specific capacitances of rGO based on Figure 6b (using equation 1) are 198, 170, 131 and 117

F/g at 0.6, 1, 2 and 2.6 A/g (Figure 6c). From the Nyquist plots of rGO (Figure 6d), it is observed that rGO holds low charge transfer resistance and Warburg resistance.

Figure 6 CV loops at different scan rates (a); GCD loops at different current densities (b), specific capacitances (c); Nyquist plots (d) for the prepared rGO in a three-electrode system

3.3 Hybrid supercapacitor based on NiCoO₂/Ni foam and rGO

The NiCoO₂/Ni foam//rGO hybrid supercapacitor was established combining the NiCoO₂ with the energy storing mechanism of Faradic redox and rGO with double electric layer mechanism. The mass ratio of loading NiCoO₂ to rGO (NiCoO₂/rGO) was estimated to be 0.5 based on the stored charge balance at positive and negative electrodes, where the potential range and specific capacitance are from the three-electrode system [34]. The schematic illustration of this hybrid supercapacitor is

shown in Figure 7a. Figure 7b shows the CV curves obtained at different potential ranges. Here, the potential range from 0 to 1.5 V was selected. Figure 7c and d give the CV and GCD curves of the NiCoO₂/Ni foam//rGO hybrid supercapacitor. The similar CV curves at all scan rates and GCD curves at all current densities reflect good supercapacitive properties [35]. In Figure 7c, the two reduction peaks at voltage positions about 0.43 and 0.73 V during the cathodic process may be assigned to the reduction of Co²⁺ to Co, and Ni²⁺ to Ni [36]. The specific capacitances of the hybrid supercapacitor based on the total mass of active materials through the Equation (2) are 82, 74, 68, 59, 55 and 51 F/g at 2, 2.4, 3, 3.6, 4 and 4.4 A/g respectively (In Figure 7e) (details about the calculation shown in Table S1). It is found that the NiCoO₂/Ni foam//rGO hybrid supercapacitor owns higher specific capacitances by comparing with other hybrid supercapacitors (copper cobalt carbonate hydroxides/Ni foam//graphene/Ni foam supercapacitor: 61 F/g at 0.25 A/g [37]; hybrid activated carbon-NiCo₂O₄: 54 F/g at 0.5 A/g [38]). To facilitate the understanding about the fabrication of hybrid capacitor, the specific capacitances to the total mass of the device were also determined using equation (3) and shown in Figure 7e. They are about 2.26, 2.04, 1.87, 1.62, 1.50 and 1.41 F/g at 0.055, 0.066, 0.083, 0.099, 0.110 and 0.121 A/g (details about the calculation shown in Table S2).

Figure 7f exhibits the Ragone plots about energy and power densities based on the total mass of active materials for the NiCoO₂/Ni foam//rGO hybrid supercapacitor (details about the calculation shown in Table S1), as well as some reported hybrid supercapacitors. It is found that the energy density based on the total mass of active

materials for the hybrid supercapacitor is 25.7 Wh/kg at 1500 W/kg, and retains 16 Wh/kg at 3300 W/kg. The energy and power densities of the given hybrid supercapacitor are higher than those of other reported hybrid supercapacitors, such as activated carbon//MnO₂ hybrid supercapacitor (17.5 Wh/kg at 135 W/kg) [39], β -Ni(OH)₂//activated carbon asymmetric supercapacitor (10.5 Wh/kg at 690 W/kg) [40]. Such high energy density is also competitive with the reported hybrid supercapacitors based on Co-Ni-O and carbon materials, including activated carbon-NiCo₂O₄ asymmetric supercapacitor (14.7 Wh/kg at 175 W/kg) [38], Ni-Co oxides//Activated carbon (10.8 Wh/kg at 474.4 W/kg) [41], NiCoO₂ nanoparticles//Activated carbon (24.0 Wh/kg at 415.4 W/kg) [13]. In addition, the energy densities and power densities to the total mass of the device were also shown in Table 2 (details about the calculation shown in Table S2).

Figure 7 The schematic diagram of the NiCoO₂/Ni foam//rGO hybrid supercapacitor (a); CV curves at different potential ranges (b) and scan rates (c) based on the total mass of active materials; GCD curves at different current densities (d) based on the total mass of active materials; the specific capacitances (C_M and C_d) (e); Ragone plots (f) for the hybrid supercapacitor

Table 2. Ed and Pd for the hybrid supercapacitor

Pd (W/kg)	Ed (Wh/kg)
41.28	0.71
49.54	0.64
61.93	0.58
74.31	0.51
82.57	0.47
90.83	0.44

To understand the electrochemical stability of the NiCoO₂/Ni foam//rGO hybrid supercapacitor, the CV test was conducted by repeating for 2000 cycles at a scan rate of 100 mV/s in the operating potential range. Figure 8a shows the capacitance retention and CV curves at first and 2000th cycles (the inset). It is observed that the hybrid supercapacitor possesses good cycle stability where maintains about 90% of

the first capacitance after 2000 cycles. This retention is better than those of previous reported similar hybrid supercapacitors, such as Fe₃O₄/graphene//3D graphene hybrid supercapacitor (70% after 1000 cycles) [42], Ni-Co oxide//activated carbon (85% after 2000 cycles) [41] etc. The good stability may be due to the interconnected and porous structure of the NiCoO₂ flowers and flakes on Ni foam along with the good conductivity of rGO.

Figure 8b presents Nyquist plots before and after cycles of the NiCoO₂/Ni foam//rGO hybrid supercapacitor at the open circle voltage (0.58 V). Obviously, the small radius at high frequency and high phase angle (exceeding 45°) at low frequency in the Nyquist plots reflect the low charge transfer resistance and Warburg resistance, leading to fast charge ion transfer capability [43]. Moreover, the phase angle becomes higher after cycles, which may be attributed to the fact that the electrolyte ions can be more easily access to the active material with the increasing cycles. In addition, the Nyquist plots of the hybrid device at 0.42 and 0.69 V were also performed and shown in Figure 8c. The Nyquist plots of the device at 0.42, 0.58 and 0.69 V were also fitted and the fitted data is shown in Table S3. Figure 8d provides the fitted equivalent circuit of the hybrid capacitor.

Figure 8 Capacitance retention at a function of cycle number at 100 mV/s (a); Nyquist plots before and after cycles (b); Nyquist plots in the different voltages (c) and fitted equivalent circuit (d) for the NiCoO₂/Ni foam//rGO hybrid supercapacitor

4. Conclusion

In this investigation, NiCoO₂ flowers with a diameter of about 4 μm were grown on the aligned NiCoO₂ flakes coated Ni foam to obtain NiCoO₂/Ni foam. The NiCoO₂/Ni foam was directly used as the working electrode without any binders. The specific capacitance values of NiCoO₂ grown on Ni foam in a three-electrode setup are 756, 640, 568 and 555 F/g at 0.75, 1.25, 2 and 2.5 A/g. To evaluate practical application of NiCoO₂/Ni foam, the NiCoO₂/Ni foam//rGO hybrid supercapacitor was established combining the NiCoO₂ with the energy storing mechanism of Faradic redox and rGO with double electric layer mechanism. The hybrid supercapacitor possesses very good properties, for example, high specific capacitance (82 F/g at 2 A/g based on the total mass of active materials); high energy density (25.7 Wh/kg at 1500 W/kg, and retains 16 Wh/kg at 3300 W/kg based on the total mass of active materials); good stability (about 90% capacitance retention after 2000 cycle at 100 mV/s); low charge

transfer resistance and Warburg resistance.

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