3D hierarchical dandelion-like NiCo₂O₄/N-doped carbon/Ni foam for an effective binder-free supercapacitor electrode

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Abstract

In this work, the 3D hierarchical dandelion-like NiCo₂O₄/N-doped carbon/Ni foam has been developed by introducing PANI as the precursor of N-doped carbon. Meanwhile, the NiCo₂O₄/N-doped carbon/Ni foam with a novel 3D hierarchical dandelion-like structure was verified by X-ray diffraction, X-ray photoelectron spectroscopy and scanning electron microscopy, etc. In addition, the NiCo₂O₄/N-doped carbon/Ni foam was directly used as a binder-free supercapacitor electrode and its performances were investigated by cycle voltammetry, galvanostatic charge–discharge and electrochemical impedance spectroscopy. The results show that the obtained NiCo₂O₄/N-doped carbon/Ni foam electrode owns good electrochemical performances, such as high specific capacitance (864 F/g at 1 A/g) and good cycling stability, owing to the porous feature from its novel 3D hierarchical dandelion-like structure.

Keywords:

composite materials; nanostructure; electronic characterization; electrochemical properties

1. Introduction

Supercapacitor, a common renewable energy storage device, plays a very crucial role in coping with the ever-growing energy crisis. The electrode materials, including carbon materials, conductive polymers and metal oxides, are the vital component of supercapacitors. In general, the energy storage mechanisms of these electrode materials are different: carbon materials, such as activated carbon and graphene, derived from the formation of double charge layer on the electrode/electrolyte interface [1-2]; while conductive polymers, like polyaniline (PANI) and polypyrrole, by occurring the redox reactions of N-type or P-type doped and de-doped in the conjugated chain [3-4]; metal oxides, such as NiO, Co₃O₄, MnO₂, RuO₂, etc. based on the redox reactions between electrode materials and electrolyte [5-8].

Among these possible materials, metal oxides have attracted large amounts of attentions, owing to the high theoretical capacity and low cost. Especially, NiCo₂O₄ is identified as the most promising candidate for the next generation supercapacitor electrode materials, considering its exceptional high theoretical capacity, extremely good redox activity and high capability [9]. Unfortunately, the binders in the preparation of electrodes may hinder the diffusion and migration of charge and ions, leading to the unsatisfactory capacitive performance [10]. Therefore, NiCo₂O₄ with different morphologies is directly grown on Ni foam for binder-free electrodes, such as Ni foam supported mesoporous NiCo₂O₄ nanosheets [11], three-dimensional NiCo₂O₄ nanoneedle arrays deposited on Ni foam [12]. In addition, the poor conductivity of NiCo₂O₄ is also an obstacle for its actual application as electrodes. To

1 overcome this issue, carbon materials are often introduced in view of their good
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3 conductivity [13].
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6 In this work, PANI was used as the precursor of carbon materials to prepare 3D
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8 hierarchical $\text{NiCo}_2\text{O}_4/\text{N-doped carbon/Ni foam}$ hybrids. Ongoing researches show
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10 that the interposition of 3D hierarchical network structures in the supercapacitor
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12 electrode material can cause the promising capacitive performances of the electrode
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16 [14]. Surprisingly, the NiCo_2O_4 on N-doped carbon/Ni foam exhibits dandelion-like
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18 shape, leading to the formation of porous structure. Therefore, it is expected that the
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20 3D hierarchical dandelion-like $\text{NiCo}_2\text{O}_4/\text{N-doped carbon/Ni foam}$ exhibits good
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26 supercapacitive performances.
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28 **2. Experimental**

29 **2.1 Materials**

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34 Many reagents, including aniline, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, urea and
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36 cetyltrimethylammonium bromide, were obtained from Tianjin Jiangtian Chemical
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38 Technology Co. Besides, Ni foam was provided by Kunshan dessco Electronics Co.
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41 **2.2 Synthesis of $\text{NiCo}_2\text{O}_4/\text{N-doped carbon/Ni foam}$**

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45 The deposition of PANI on Ni foam was performed in the mixture of 0.1 M
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47 H_2SO_4 and 0.1 M aniline without oxygen using CV technique. 20 cycles were carried
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49 out in the potential range of -0.66 to 0.5 V vs. $\text{Hg/Hg}_2\text{SO}_4$ at a scan rate of 5 mV/s to
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51 gain PANI/Ni foam. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.5 mmol), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (3 mmol),
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53 cetyltrimethylammonium bromide (1 mmol) and urea (20 mmol) were dispersed into
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58 distilled water (20 mL) and stirred to produce a homogeneous suspension. Then the
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1 solution and PANI/Ni foam were transferred into a Teflon-lined autoclave and
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3 maintained at 120 °C for 5 h. The coated Ni foam was washed, dried and heated at
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6 400 °C for 3h in N₂ atmosphere to obtain the dandelion-like NiCo₂O₄/N-doped
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8 carbon/Ni foam, which was directly utilized as the working electrode. The total
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10 loading mass of N-doped carbon and NiCo₂O₄ is about 1 mg/cm².
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13 14 2.3 Characterization 15

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17 The X-ray diffraction (XRD) pattern of NiCo₂O₄/N-doped carbon/Ni foam was
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19 measured by an X-ray diffractometer (D8-Focus, Bruker, Germany) using a reference
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21 target (Cu Ka radiation) from 10 to 80° (2θ) with steps of 4° min⁻¹. Raman spectrum
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23 of NiCo₂O₄/N-doped carbon/Ni foam was provided by the DXR Raman Microscope
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25 (US). X-ray photoelectron spectroscopy (XPS) was obtained on an X-ray
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27 photoelectron spectrometer (XPS, PHI1600 ESCA System, PERKIN ELMER, USA)
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29 and fitted with a Shirley background using the XPS Peak 4.1 software. The scanning
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31 electron microscopy (SEM) measurement was performed using S4800 microscope
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33 (Hitachi Limited, Japan).
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42 Electrochemical tests, including cycle voltammetry (CV), galvanostatic
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44 charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS), were
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46 made using a three-electrode setup with the Pt foil and Hg/HgO as auxiliary and
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48 reference electrodes in 1 M KOH. The specific capacitances (C, F/g) were evaluated
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50 based on the Equations:
$$C = \frac{i \times \Delta t}{\Delta v \times m} \quad (1)$$

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53 Where i (A) and Δt (s) refer to the discharge current and time respectively, Δv (V)
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55 represents the given potential range, and m (g) is the mass of active materials
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(N-doped carbon and NiCo_2O_4) [15].

3. Results and discussion

The prepared 3D hierarchical dandelion-like NiCo_2O_4 /N-doped carbon/Ni foam was studied by XRD measurement and the resulting XRD pattern was shown in Figure 1a. The three strong peaks at $2\theta = 44.5^\circ$, 51.8° and 76.4° are from Ni foam. The peaks at 18.9° , 31.1° , 36.7° , 59.1° and 64.9° are assigned to the lattice planes (111), (220), (311), (511) and (440) of NiCo_2O_4 (JCPDS No. 20-0781). The peak at about 22.0° stems from the carbon derived from PANI. In addition, the carbon derived from PANI was also characterized by the Raman spectrum of NiCo_2O_4 /N-doped carbon/Ni foam. In Figure 1b, it can be seen that the carbon derived from PANI is amorphous.

Figure 1 XRD pattern (a) and Raman spectrum (b) of the obtained NiCo_2O_4 /N-doped carbon/Ni foam

The accurate composition and atomic oxidation state for the hybrid were further studied by XPS analysis. The elements Ni, Co, O, C and N appear in the survey spectrum of the hybrid (Figure 2a). In Figure 2b, the Ni 2p core level spectrum was

fitted into two spin-orbit couplings, corresponding to Ni^{2+} and Ni^{3+} , and two satellite peaks by using a Gaussian fitting method. As shown in the Co 2p core level spectrum (Figure 2c), there are also two spin-orbit doublets assigned to Co^{2+} and Co^{3+} and satellite peaks. These results indicate that the hybrid includes Ni^{2+} , Ni^{3+} , Co^{2+} and Co^{3+} , which are in good accordance with those of the reported NiCo_2O_4 [16]. In Figure 2d, the O 1s core level spectrum was deconvoluted into two peaks, indicating two existing states of O. The bands at 529.2 and 531.5 eV are referred into the metal-oxygen bond and the surface species including hydroxyls, chemisorbed oxygen, respectively [17]. In Figure 2e, the C 1s core level spectrum contains three fitting peaks located at 284.7, 286.6 and 288.3 eV, in paralleled with C-C/C=C, C-O and C=O, respectively [18]. In the N 1s core level spectrum (Figure 2f), the binding energy at 398.4, 399.3, and 400.5 eV is associated with uncharged deprotonated imine (-C=N-) atoms, neutral nitrogen moieties (-NH-), and positively charged structure (-NH⁺-), respectively [19].

Figure 2 XPS survey spectrum (a); Ni 2p (b), Co 2p (c), O 1s (d), C 1s (e) and N 1s (f) core level spectra for the NiCo₂O₄/N-doped carbon/Ni foam

The SEM images were used to observe the microstructure of the prepared NiCo₂O₄/N-doped carbon/Ni foam. Figure 3 shows the SEM images of NiCo₂O₄/N-doped carbon/Ni foam with the different magnifications. As shown in Figure 3a, many clusters were observed on the skeleton of Ni foam. After the amplification of these clusters, it can be found that these clusters possess the dandelion-like nanostructure (Figure 3b). In Figure 3c and d, it can be seen that the dandelion-like structure is about 10 μm and is composed of some bundles of nano-needles. The assembled dandelion-like structure develops numerous pores, which can access the diffusion of electrolyte into the inner active materials and

Figure 1 consists of four SEM images labeled (a) through (d).
 (a) Low-magnification SEM image showing a dense field of ZnO nanostructures. The scale bar is 50.0 μm. Technical parameters: S-4800 3.0kV 8.8mm x600 SE(U).
 (b) Higher magnification SEM image showing the flower-like morphology of the ZnO nanostructures. The scale bar is 20.0 μm. Technical parameters: S-4800 3.0kV 8.2mm x2.00k SE(U).
 (c) Higher magnification SEM image showing the hierarchical structure of the ZnO nanostructures. The scale bar is 10.0 μm. Technical parameters: S-4800 3.0kV 8.2mm x5.00k SE(U).
 (d) High-magnification SEM image showing the individual petals of the ZnO nanostructures. The scale bar is 5.00 μm. Technical parameters: S-4800 3.0kV 8.2mm x10.0k SE(U).

Figure 3 SEM images of the prepared NiCo₂O₄/N-doped carbon/Ni foam.

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Figure 4 Elemental mapping images of C, N, O, Ni and Co in NiCo₂O₄/N-doped carbon/Ni foam

The synthetic 3D hierarchical dandelion-like NiCo₂O₄/N-doped carbon/Ni foam was directly served as the electrode of supercapacitors, and its electrochemical performances were investigated by CV, GCD and EIS measurements. Figure 5a

provides the CV loops at different scan rates for 3D hierarchical dandelion-like NiCo₂O₄/N-doped carbon/Ni foam. In Figure 5a, a pair of obvious redox peaks are emerged in CV loops, owing to the Faradic redox reactions of MO/MOOH (M = Ni, Co), as follows: $\text{NiCo}_2\text{O}_4 + \text{OH}^- + 2\text{H}_2\text{O} \rightleftharpoons \text{NiOOH} + 2\text{CoOOH} + \text{H}_2\text{O} + \text{e}^-$; $\text{CoOOH} + \text{OH}^- \rightleftharpoons \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^-$ [21-22]. Meanwhile, the shift of redox peaks at high scan rates derived from the increasing internal diffusion resistance in the NiCo₂O₄/N-doped carbon/Ni foam electrode [23].

Figure 5b exhibits the GCD curves at different scan rates of the NiCo₂O₄/N-doped carbon/Ni foam electrode. Obviously, the GCD curves with distinct platforms further confirm the Faradic redox mechanism of the NiCo₂O₄/N-doped carbon/Ni foam electrode. The specific capacitances at different current densities of NiCo₂O₄/N-doped carbon/Ni foam were calculated according to Equation (1) and exhibited in Figure 5c. These values are 864, 769, 689, 651, 600, 572, 548 and 525 F/g at 1, 2, 3, 4, 5, 6, 7 and 8 A/g, respectively. It is found that the specific capacitance decreases with the increased current density, because the slow diffusion of protons at a high current density leads to the fact that inner active materials cannot participate in charge storage [24]. The specific capacitances of NiCo₂O₄/N-doped carbon/Ni foam are higher than those of NiCo₂O₄/carbon materials, like NiCo₂O₄/carbon nanotubes doped carbon nanofibers (220 F/g at 1 A/g) [25], NiCo₂O₄/graphitic carbon nitride (253 F/g at 2 A/g) [26] and NiCo₂O₄/ordered mesoporous carbon (577 F/g at 1 A/g) [27], which may be attributed to the porous structure and the absence of binders for the 3D hierarchical dandelion-like NiCo₂O₄/N-doped carbon/Ni foam. Meanwhile, the

specific capacitances of NiCo₂O₄/N-doped carbon/Ni foam in our work are higher than those of the reported NiCo₂O₄/Ni foam in the previous literatures, such as NiCo₂O₄ nanoneedle arrays/Ni foam (655 F/g at 1 A/g [28]), NiCo₂O₄ nanograss/Ni foam (819.2 F/g at about 0.4 A/g) [29].

The long-term cycling stability of the 3D hierarchical dandelion-like NiCo₂O₄/N-doped carbon/Ni foam was evaluated by repeating the CV measurement at a scan rate of 100 mV/s for 1000 cycles [30]. Figure 5d displays the capacitance retention at 1000 cycles and the inset shows the CV loops at given cycles. Very obviously, the capacitance retention is increasing at the initial 400-cycle, owing to the participation of inner active materials into the energy storage along with the cycling going on [31]. However, after 400-cycle, the capacitance retention nearly maintains constant (about 108 %), indicating good cycle stability, which is nearly similar with that of the reported NiCo₂O₄/carbon nanotubes/Ni foam (about 102 %) [32]. Meanwhile, the stability of NiCo₂O₄/N-doped carbon/Ni foam is also superior to those of the reported NiCo₂O₄/Ni foam (about 83% [25]; about 80 % after 1000 cycles [33]).

Figure 5 CV loops at different scan rates (a); GCD curves (b) and specific capacitances at different current densities (c); capacitance retention after 1000-cycle (d) for NiCo₂O₄/N-doped carbon/Ni foam

Figure 6 exhibits the Nyquist plots of the 3D hierarchical dandelion-like NiCo₂O₄/N-doped carbon/Ni foam measured from 0.01 to 10⁵ Hz. The small impedance arc at the high frequency suggests a low charge-transfer resistance. Moreover, the high phase angle (exceeding 45°) at low frequency is related to the low Warburg resistance, which will improve the diffusion of electrolyte into active materials, resulting in a reversible Faradaic redox [34]. The intercept on the real axis represents the solution resistance (1.22 Ω), lower than that of the reported NiCo₂O₄/Ni foam (2.39 Ω [29]). These results confirm the high-performance charge transformation and easy immersion of electrolyte in the 3D hierarchical dandelion-like NiCo₂O₄/N-doped carbon/Ni foam electrode.

Figure 6 Nyquist plots for the 3D hierarchical dandelion-like $\text{NiCo}_2\text{O}_4/\text{N}$ -doped carbon/Ni foam

4. Conclusion

In this work, NiCo_2O_4 was prepared in the presence of PANI/Ni foam and the resulting hybrid coated Ni foam was annealed to receive the $\text{NiCo}_2\text{O}_4/\text{N}$ -doped carbon/Ni foam, which has been confirmed by XRD and XPS. The SEM images show that $\text{NiCo}_2\text{O}_4/\text{N}$ -doped carbon/Ni foam owns the dandelion-like structure. The 3D hierarchical $\text{NiCo}_2\text{O}_4/\text{N}$ -doped carbon/Ni foam was directly used as the supercapacitor electrode and exhibited good electrochemical performances, owing to the hierarchical network structures and the absence of binders, for example, high specific capacitance (864 F/g at 1 A/g), good cycling stability and low charge ion transfer resistance.

Acknowledgements

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