NiCo₂O₄ nanowire arrays supported on Ni foam for high-performance flexible all-solid-state supercapacitors†

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Portable electronic devices which are ultrathin, lightweight and even able to roll-up have attracted much attention. Herein, we report the design of flexible all-solid-state symmetric supercapacitors by using two NiCo₂O₄ nanowire arrays supported on Ni foams as the electrodes. The as-fabricated symmetric supercapacitors have excellent electrochemical performance with a high cell areal capacitance of 161 mF cm⁻² at 1 mA cm⁻². Good electrochemical performance stability over 3000 cycles was obtained even when the device was under harsh mechanical conditions including both twisted and bent states. As-fabricated all-solid-state supercapacitors could be charged and power a commercial light-emitting-diode, demonstrating their feasibility as an efficient energy storage component and self-powered micro/nano-system. In addition, we were able to grow NiCo₂O₄ nanowire arrays on many kinds of flexible substrates, including nickel foam, carbon cloth, Ti foil and polytetrafluoroethylene tape. Our work here opens up opportunities for the device configuration for energy-storage devices in the future wearable electronic area and many other flexible, lightweight and high performance functional nanoscale devices.

In general, supercapacitors can be divided into two categories according to the energy storage mechanism: one is the electrochemical double-layer capacitors (EDLCs) that usually use carbonaceous materials with high power density, in which the main mechanism is the accumulation of pure electrostatic charge in the electric double layer formed at the electrode-electrolyte interface; and the other is the Faradaic redox reaction pseudocapacitors, which usually provide very high specific capacitance and rely on the surface or near-surface redox reactions of the electroactive species.† Nanostructure metal oxides, such as MnO₂, WO₃ (ref. 20) and ZnSnO₄ (ref. 21) possessing high capacity, have been widely studied to be used as electrodes for thin, lightweight and flexible supercapacitors. Among metal oxide materials, spinel NiCo₂O₄ holds great promise as an electrode material for supercapacitors, due to its greater electronic conductivity and electrochemical activity than single component nickel or cobalt oxides. Thus, it is highly desirable to develop NiCo₂O₄ materials with different shapes, and orientations and investigate their capacitive properties to fit ultrathin flexible energy-storage device requirements.

In this paper, we report the synthesis of aligned NiCo₂O₄ (NCO) nanowire arrays on nickel foam, which were used as the working electrodes to fabricate high performance all-solid-state supercapacitors. Electrochemical measurements indicated that the as-fabricated SCs can be cycled reversibly between 0 and 1 V and the whole cell exhibits a high areal capacitance of

1 Introduction

Nowadays, portable electronic devices (such as mobile phones, notebook computers, and digital cameras) have attracted much attention due to the increasing demand for sustainable energy in the modern electronics industry. They follow the trend toward small, thin, lightweight, flexible and even roll-up characteristics to meet the rapidly growing demands for personal electronics and modern market. Among various power source devices, the supercapacitor (SC), a circuit component that can temporarily store a large amount of electrical energy and then release it when needed, has been recognized as a future portable energy-storage device due to its high power density, good operational safety and living cycle lifetime, compared with lithium-ion batteries and the conventional capacitors. Flexible all-solid-state supercapacitors can be charged and power a commercial light-emitting-diode, demonstrating their feasibility as an efficient energy storage component and self-powered micro/nano-system. In addition, we were able to grow NiCo₂O₄ nanowire arrays on many kinds of flexible substrates, including nickel foam, carbon cloth, Ti foil and polytetrafluoroethylene tape. Our work here opens up opportunities for the device configuration for energy-storage devices in the future wearable electronic area and many other flexible, lightweight and high performance functional nanoscale devices.

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161 mF cm\(^{-2}\) at 1 mA cm\(^{-2}\). They have superior flexibility and cycling stability that can keep good performance stability over 3000 cycles under harsh mechanical conditions including twisted and bent states. Besides, our method can be easily extended to grow NiCo\(_2\)O\(_4\) nanowire arrays on other flexible substrates for different applications.

2 Experimental section

2.1 Materials and methods

The synthesis was modified according to our previous work.\(^6\) All the reagents used in the experiment were of analytical grade and used without further purification. Prior to the synthesis, the Ni foam was degreased with acetone, etched with 6 M HCl for 20 min, and washed thoroughly with deionized water and absolute ethanol. Hierarchical NCO nanowire array/Ni foam was synthesized via a simple hydrothermal process. In a typical procedure, 2.37 g of CoCl\(_2\)·6H\(_2\)O, 1.185 g of NiCl\(_2\)·6H\(_2\)O and 0.9 g of urea were dissolved in 75 mL of DI water and the mixture was stirred to form a pink solution in the 100 mL Teflon-lined stainless autoclave. Then, a piece of the pre-treated Ni foam was put in the above autoclave, heated to 120 °C, and kept at that temperature for 6 h. After it was cooled down to room temperature, the product supported on the Ni foam was washed with DI water and ethanol several times and calcined at 400 °C in air for 3 h. For comparison, a piece of pre-treated Ni foam was treated in the same conditions without cobalt and nickel sources.

2.2 Fabrication of flexible all-solid-state supercapacitors

The PVA–KOH polymer electrolyte was prepared as follows: in a typical process, 6 g PVA was dissolved in 60 mL DI water with stirring at 100 °C for 2 h. Then, 3 g KOH was dissolved in 20 mL DI water. Finally, the two aqueous solutions were mixed together at 80 °C under vigorous stirring until the solution became clear.

The all-solid-state supercapacitor was prepared by the assembly of PVA–KOH gel electrolyte with two pieces of NCO nanowire arrays electrodes face-to-face. Prior to fabrication, the two pieces of electrode (an aluminum strip as the current collector was joined to one edge of each electrode, which facilitates the electrical contact of the electrode with the alligator clip connecting the electrochemical testing machines) were pressed under pressure of about 2 MPa for 1 min by a sheeting presser. Then, they were immersed into the PVA–KOH solution for 8 min. After evaporation of the excess water at room temperature, the two electrodes were assembled. When the PVA–KOH gel solidified, the final all-solid-state supercapacitor was prepared.

2.3 Characterization

The synthesized products were characterized with an X-ray diffractometer (XRD; X’Pert PRO, PANalytical B.V., the Netherlands) with radiation from a Cu target (K\(_\alpha\), \(\lambda = 0.15406 \text{ nm}\)), field emission scanning electron microscopy (FESEM; JEOl JSM-6700F, 5 kV), and transmission electron microscopy (HRTEM; JEOl, JEM-2010 HT). The electrochemical characteristics were studied on an electrochemical workstation using cyclic voltammetry (CV) and galvanostatic charge/discharge (CD). Specific and areal capacitances were calculated using eqn (1) and (2), respectively.

\[ C_{sp} = I \times \Delta t (m \times \Delta V) \]  
\[ C_a = I \times \Delta t (S \times \Delta V) \]

where \( I \) (mA) represents the constant discharge current, \( m \) (mg), \( \Delta V \) (V) and \( \Delta t \) (s) designate the mass of active materials, potential drop during discharge (excluding the IR drop) and total discharge time, respectively. \( S \) is the geometrical area of the electrode.

3 Results and discussion

Fig. 1a shows a representative low-magnification field emission scanning electron microscopy (FESEM) image of the pristine Ni foam with smooth surface before nanowire growth. After nanowire growth, the surface of the whole Ni foam becomes rough as revealed in Fig. 1b, indicating the growth of the target materials over a large area. Fig. 1c and d show the higher magnification SEM image of the product, where numerous nanowires were found grown vertically on the whole Ni foam to form highly aligned nanowire arrays. Typical nanowires have the lengths of about 3 μm with an average diameter of 80–200 nm. Transmission electron microscopy (TEM) was also used to study the microstructures of the as-obtained NCO nanowires. A typical selected-area electron diffraction (SAED) pattern taken from an individual nanowire is depicted in Fig. S1,† indicating the formation of porous nanowires. A high-resolution TEM (HRTEM) image taken from a single nanocrystal within a NCO nanowire is depicted in Fig. 1e. A lattice fringe of 0.24 nm was observed, corresponding to the (311) planes of spinel NCO material. The composition of the obtained product was studied by XRD and the corresponding XRD pattern is shown in Fig. 1f. All the diffraction peaks can be readily indexed to the spinel NCO, indicating the formation of pure NCO nanowires (JCPDS Card no. 73-170).

To study the electrochemical properties of the as-grown NCO nanowire arrays on Ni foam, the electrochemical measurements were performed with a three-electrode system in 3.0 M KOH solution by both voltammetry and galvanostatic charge–discharge cycling. Fig. 3a shows the CV analysis (mass \( \approx 3 \text{ mg cm}^{-2} \)) measured at various scan rates ranging from 10 mV s\(^{-1}\) to 20 mV s\(^{-1}\) to 40 mV s\(^{-1}\) in a potential window of 0 to 0.45 V (vs. SCE), respectively. Clearly, a pair of well-defined redox peaks is visible in all the CV curves as a result of the Faradic capacitive behavior. The shapes of these CV curves do not significantly change as the scan rate increases from 10 to 40 mV s\(^{-1}\), revealing the ideal capacitive behaviors of the NCO nanowire arrays on Ni foam.

A galvanostatic charging–discharging test was conducted in a stable potential window between 0 and 0.45 V at various current densities ranging from 2 to 8 A g\(^{-1}\), respectively, as shown in Fig. 2b. It is exciting to find that the NCO nanowires...
supported on Ni foam exhibited wonderful pseudocapacitor behaviours with specific capacities of 2681, 2524 and 2305 F g\(^{-1}\) at current densities of 2, 3 and 8 A g\(^{-1}\), respectively. Compared with the previously reported data for NCO nanostructures, the capacitance values of our current NCO nanowire array structures on Ni foam are much higher.\(^{23-28}\) Such superior performances can be attributed to the highly aligned arrays supported on Ni foam that can provide a high surface area and shorten the ion diffusion path. Based on these results, the NCO nanostructures are excellent candidates with superb performance for supercapacitors.

To test their feasibility for flexible all-solid-state capacitance applications, a simple all-solid-state supercapacitor was also presented by assembling two pieces of the as-grown NiCo\(_2\)O\(_4\) nanowire electrodes. The inset in Fig. 3a displays a schematic illustration of the device structure model of the all-solid-state supercapacitor. Fig. 3a shows the CV curves at scan rates of 10–80 mV s\(^{-1}\). From which we can see that increasing the scan rate leads to further augmentation of the CV curve, indicating that the reactions of NCO are rapid. The galvanostatic charge–discharge behavior at different current densities is demonstrated in Fig. 3b. Fig. 3c illustrates the current density dependence of the areal capacitance, which is calculated from the charge–discharge curves. The device shows an excellent rate capability and the capacitance can still be maintained at 137 mF cm\(^{-2}\) even when the current density increased 8 times from 1 to 8 mA cm\(^{-2}\). The results presented here are much better than many previously reported values. For example, conventional carbonaceous materials have a capacitance of 10–40 mF cm\(^{-2}\), TiO\(_2\) nanotube films only have a capacitance of 0.538–0.911 mF cm\(^{-2}\),\(^{29}\) TiO\(_2\)/NiO nanotube arrays have a capacitance of 2.9 mF cm\(^{-2}\) at 0.4 mA cm\(^{-2}\),\(^{30}\) and Ni–NiO core–shell inverse opal films have a capacitance of 8–9 mF cm\(^{-2}\) in capacitance.\(^{31}\) The excellent capacitance and rate-capability of the NCO nanowire electrodes can be attributed to their unique structural features. First, the highly conductive and 3D macroporous Ni foam enable efficient charge transport and accessible diffusion of electrolyte. Second, there is good electrical contact between the current collector and the nanowires so that much more active material can contribute to the capacity. Finally, well-ordered arrayed architecture offers large surface area for Faradaic reactions, which allows abundant adsorption of ions as well as enables fast intercalation/de-intercalation of ions and charge transport. More significantly, of the present flexible all-solid-state supercapacitors are binder-free, which enables a low interfacial resistance and fast electrochemical reaction rate. Also, it was found that pure Ni foam had a small area surrounded by CV curves and short duration time of NCO/Ni foam curves (in Fig. S2†), suggesting that the capacitance contributions from the annealed Ni foam should be minimal.
To further evaluate the electrochemical behavior of the flexible device, electrochemical impedance spectroscopy (EIS) was performed. As shown in Fig. 3d, in the high frequency region, the intercept of the semicircle with the real axis represents the ESR including the resistance of the electrolyte solution, the intrinsic resistance of the active material, and the contact resistance of the interface active material/current collector, the ESR value is 0.86 U.

Fig. 3  (a) CV curves obtained from the flexible devices with different scan rates. (b) Galvanostatic charge–discharge curves measured at different current densities of 1, 2, 3, 5, 8 mA cm\(^{-2}\). (c) Dependencies of the areal capacitances of the device on various current densities ranging from 1 to 8 mA cm\(^{-2}\) for charge–discharge behavior. (d) Nyquist plots of the all-solid-state supercapacitor device. (e) Leakage current of the all-solid-state supercapacitor over 8000 s. (f) Self-discharge curves of the device after charging at 1 V.

Fig. 4  (a) Optical photographs of the fabricated solid-state supercapacitor device. The top right image shows the flexibility of the device, the bottom image demonstrates a light-emitting-diode (LED) powered by two pieces of supercapacitors in series. (b) Typical charge–discharge characteristics of the device before and after bending for 0, 30 and 60 cycles, respectively.
determining the charge–discharge rate and the power density of a supercapacitor. The relatively small ESR is due to the network structure facilitating the efficient access of electrolyte ions to the active material surface and shortening the ion diffusion path. In addition, the slope of the straight line in the low frequency region is larger than that of the 45° straight line, indicating typical capacitor behavior.

The leakage current that is ascribed to the self-discharge course for the flexible device was very small and the value is about 47 μA for a long time beyond 8000 s, as shown in Fig. 3e. Such a small value of leakage current means fewer shuttle reactions caused by the impurities in the capacitor materials and/or electrolyte in the device. Besides, the flexible device exhibited typical rate of self-discharge and about 0.23 V retained after 22 h, as shown in Fig. 3f, which is similarly to the previously reported values.

The inset in Fig. 4a shows the optical image of the as-fabricated device after packing with aluminium–plastic foils, revealing its excellent flexibility. To demonstrate its practical applications, two pieces of the as-fabricated flexible all-solid-state supercapacitor were used to control a commercial LED in series, as shown in Fig. 4a. Since the NCO-based all-solid-state supercapacitors are lightweight and have excellent flexibility, it is expected that they can be repeatedly bent without significant variations in electrochemical properties. Fig. 4b shows the charge–discharge curves of the flexible device after being bent for different cycles to further evaluate the folding endurance. The electrochemical stability of the device was examined at a scan rate of the 3 mA cm⁻². From the curves, it can be seen that mechanical bending does not have significant influence on the ion transport in the gel electrolytes or the quality of interface between the gel electrolyte layer and the NCO/Ni foam, verifying their excellent flexibility and stability, also the SEM image of the NCO/Ni foam after the bending test can be seen in Fig. S3 †.

The long-term cycling stability of the flexible device was further studied by checking its capacitance retention under different bending states since it is of paramount importance in flexible devices. The long-term cycling stability was tested through a cyclic charge–discharge process at the constant current density of 3 mA cm⁻². Fig. 5 shows the corresponding results when the device was in its normal state, bent state and twisted state, respectively. The electrochemical performances of the device do not significantly change in both the twisted and bent states, further confirming its super mechanical stability.

From the above results, we can conclude that NCO nanowire arrays on Ni foam are promising candidates for flexible all-solid-state supercapacitors. To be fit for other flexible device applications, it is quite important to grow nanostructures on diverse flexible substrates. In our work, we found that we can easily grow aligned NiCo₂O₄ nanowire arrays on many flexible substrates, including carbon cloth, Ti foil, and non-stick tape. Fig. 6 shows the NCO nanostructures grown on carbon cloth (Fig. 6a–c), Ti foil (Fig. 6d–f) and polytetrafluoroethylene tape (Fig. 6g–i), respectively, all of which indicate the growth on aligned NCO nanowires arrays on a large scale. The wonderful versatility of the novel NCO material on diverse flexible substrates provides a promising way to develop devices for application in the fields of flexible LIB, flexible electronic devices and many other emerging research fields.

4 Conclusion

We have presented a facile and high-efficiency hydrothermal method for the direct growth of NCO nanowire arrays on various flexible substrates. The synthesis route presented here is robust and may be extended to fabricate other nanowire arrays for various applications in electrochemical energy storage and optical devices. The NCO nanowire arrays supported on Ni foam were fabricated into highly flexible solid-state supercapacitors.
and they have demonstrated excellent electrochemical performance with a high areal capacitance of 161 mF cm$^{-2}$ at 1 mA cm$^{-2}$, also they have superior flexibility and cycling stability that can maintain good performance stability over 3000 cycles under harsh mechanical conditions including twisted and bent states. Furthermore, our as-fabricated solid-state supercapacitors could be charged and power a commercial light-emitting-diode, demonstrating their feasibility as an efficient storage component and self-powered micro/nano-systems. Our work here opens up opportunities for device configuration for energy-storage devices in the future wearable electronic area and many other flexible, lightweight and high performance functional nanoscale devices.

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**Notes and references**