Holey nickel-cobalt layered double hydroxide thin sheets with ultrahigh areal capacitance

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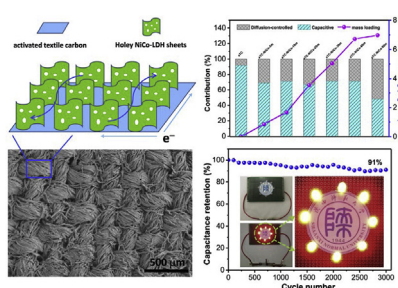
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HIGHLIGHTS

- Holey NiCo-LDH nanosheets are strongly adhered onto cotton-derived carbon cloth.
- Mass loading of NiCo-LDH nanosheets strongly depends on the electrodeposition time.
- It serves as a positive electrode in constructing a flexible asymmetric capacitor.
- The device delivers a high volumetric energy density with good flexibility.

GRAPHICAL ABSTRACT

ABSTRACT

Strong coupling of electroactive components on conductive carbonaceous matrix to fabricate flexible hybrid electrodes represents a promising approach towards high performance supercapacitors. This work reports the fabrication of holey nickel cobalt layered double hydroxide (NiCo-LDH) nanosheets that are vertically grown on the cotton cloth-derived activated textile carbon (aTC). The abundant nanoholes on the thin-sheet NiCo-LDH not only enhance the electrode efficiency for efficient Faradaic redox reactions but also facilitate access of electrolyte to the electrode surface, thus giving rise to 70% capacitance arising from their outer surface. As a result, the aTC-NiCo hybrid electrode is capable of simultaneously achieving extremely high areal capacitance ($6.37\,F\,cm^{-2}$), mass capacitance ($525\,F\,g^{-1}$) and volumetric capacitance ($249\,F\,cm^{-3}$) at a practical level of mass loading ($6.72\,mg\,cm^{-2}$). Moreover, a solid-state asymmetric capacitor built with aTC-NiCo as positive electrode and active carbon-coated on aTC as negative electrode can deliver a volumetric energy density of $7.4\,mWh\,cm^{-3}$ at a power density of $103\,mW\,cm^{-3}$, while preserving a superior power performance, satisfying cycling stability and good mechanical flexibility.

1. Introduction

The ever-increasing energy demand has promoted the rapid development of various wearable energy storage systems [1,2]. Batteries and supercapacitors are two kinds of electrochemical energy storage devices that have received tremendous attentions over the past decades [2]. Particularly, supercapacitors, which can offer higher power density and extraordinary cycling stability, have been widely used as back-up power source for various electric vehicles and portable electronics devices. Supercapacitor stores energy in the form of either fast ion adsorption at the carbon electrode surface or reversible faradaic redox reactions at the electrode/electrolyte interfaces [3]. As compared with the carbon-based double-layer supercapacitors, pseudocapacitors relying on transition metal oxides or conducting polymers can deliver

remarkably higher energy due to significant contribution of pseudocapacitance arising from the reversible redox reactions at or near the surface of the active electrodes [4,5].

Nickel-cobalt layered double hydroxides (NiCo-LDH) have received tremendous attentions in view of their nature abundance, low-cost, nontoxicity and extremely high theoretical capacity [6–12]. However, performance of NiCo-LDH is still unable to meet the practical requirement for high-rate and long-term supercapacitor because of its limited electrochemically active sites, low conductivity and poor cycling stability. To address these issues, pseudocapacitive NiCo-LDH with desirable nanostructures have been integrated with various conductive substrates, including nickel or graphene foam [13–15], reduced graphene oxides [16,17], carbonaceous substrates [18,19], and conductive textile fibers [20] to achieve a better performance. For example, Wong et al. prepared the flower-like NiCo-LDH on the highly conductive nickel foam through the electrochemical deposition technique [14]. The 3D interconnected nickel foam scaffold allows the hybrid to deliver a specific capacitance of 1487 mF cm^{-2} at 5 mV s^{-1} and 702 mF cm^{-2} at 50 mV s^{-1}. Alternatively, a hybrid electrode composed of needle-like NiCo-LDH grown on active carbon fibers is capable of delivering a specific capacitance of 1281 F g^{-1} at 0.5 A g^{-1} and retaining 70% of its capacitance upon increasing the current density to 30 A g^{-1} [21]. Although tremendous efforts have been devoted to boosting its overall performance, the practical application of NiCo-LDH electrode is severely restricted by the extremely low mass loading (usually below 2.0 mg cm^{-2}) [20,22–25]. Moreover, performance measured at low mass loading cannot be readily scaled to that at the commercial level (~10 mg cm^{-2} with typical electrode thickness of 100–200 μm) because both ions penetration and electron motion would encounter larger resistance within the thicker electrode [26,27]. Most recently, it has been demonstrated that two-dimensional graphene electrode consisting of plenty of in-plane nano-holes could potentially improve ion motions [28–30], and graphene architectures assembled with these holey graphene sheets indeed show satisfying rate performance at practical mass loading [31–33]. Inspired by these results, creating nanopores on NiCo-LDH sheets is expected to address the capacitance decay at high mass loading.

The pseudocapacitive NiCo-LDH has been hybridized with cellulose fibers or carbon fibers paper for flexible energy storage devices [20,34,35]. In most cases, a conductive coating layer is required to modify the surface of cellulose or carbon substrates for favorable deposition of NiCo-LDH [20,23,34,36]. Introduction of this meditated layer not only complicates the overall synthetic procedure, but also lowers the specific capacitance of the hybrid electrodes as meditated layer nearly has no contribution to the specific capacitance.

Most recently, carbon fibers derived from carbonization of natural cotton has been applied as one of promising matrix for growing various electroactive species [21,37]. The significantly improved performances of these pseudocapacitive components are closely related to the unique structure of carbon fibers, including its hollow network, ultralong conductive backbone and favorable ionic pathways [38]. As the textile cotton cloth is weaved by the interconnected cotton threads, carbonization and chemical activation of the cotton cloth could yield activated textile carbon (aTC) that comprises of many interweaved hollow carbon fiber bundles. Herein, we apply the aTC as flexible matrix to grow NiCo-LDH in the presence of hexamethylenetetramine (HMT) through a facile electrochemical deposition technique. Different from the structures of conventional NiCo-LDH, the NiCo-LDH reported herein presents thin sheets morphology with plenty of in-plane nanoholes, which not only increase the electrochemically active surface for efficient faradic redox, but also facilitate ion diffusion across the NiCo-LDH nanosheet. Moreover, the strong interfacial interaction between nanosheets and aTC matrix dramatically improves electron transfer and enhances cycling stability. Accordingly, as a supercapacitor electrode, the aCT-NiCo hybrid exhibits a large areal capacitance of 6.37 F cm^{-2} at a high mass loading of 6.72 mg cm^{-2}, while remaining a good rate performance.

Moreover, a packaged solid-state asymmetric supercapacitor (ASC) device based on aTC-NiCo electrode also exhibits superior power performance together with good mechanical flexibility.

2. Experimental section

2.1. Electrode preparation

The aTC was prepared by carbonization of textile cotton cloth at 800 °C for 1.5 h, followed by chemical activation with KOH (the mass ratio of KOH/precursor is 2:1) at 800 °C for 1 h. After rinsing with copious water to remove impurities, the aTC with geometric size of 2.0 × 1.0 cm^2 was applied as working electrode, Pt foil as counter electrode and Ag/AgCl as the reference electrode. Electrodeposition of NiCo-LDH nanosheets on aTC was conducted at 80 °C by applying a constant potential of −1.0 V (vs Ag/AgCl) in 50 mL growth solution containing 0.6 mmol of Ni(NO$_3$)$_2$·6H$_2$O, 1.2 mmol of Co(NO$_3$)$_2$·6H$_2$O and 0.28 mmol of HMT. The mass loading of NiCo-LDH on aTC before and after electrodeposition was determined by a microbalance with an accuracy of 0.01 mg. Through extending the deposition time from 5 to 120 min, mass loading of NiCo-LDH on aTC varies in the range of 0.86–7.12 mg cm^{-2}. These hybrid electrodes are denoted as aTC-NiCo-xm with x representing the deposition time (min). For comparison purpose, samples prepared without the addition of HMT was also prepared and denoted as aTC-NiCo-xm(conv).

2.2. Materials characterization

The morphologies and the structure of the samples were observed on Field-emission scanning electron microscope (SU8020) and transmission electron microscope (TEM, JEOL 2000) with acceleration voltage of 5 kV and 200 kV, respectively. Nitrogen adsorption/desorption was analyzed on ASAP 2460 analyzer at 77 K. Prior to measurement, samples were degassed at 120 °C for 8 h. The total pore volume was calculated at $P/P_0 = 0.99$, while the specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.2. Phase structure of samples was identified on a DX-2700 X-ray diffractometer (XRD) with Cu Kα radiation (λ = 0.154 nm, 40 kV). X-ray photoelectron spectroscopy (XPS) spectra were collected on an AXIS ULTRA spectrometer (Kratos Analytical) using a monochromatized Al Ka X-ray source (1486.71 eV). The binding energy was corrected by the C 1s line at 284.6 eV.

2.3. Electrochemical measurements

Electrochemical performances of the electrode materials were evaluated in 1.0 M KOH electrolyte by cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) on a Gamry Reference 3000 electrochemical workstation. In a typical three-electrode cell, the flexible aCT-NiCo hybrids were directly used as working electrode without the need of any conductive additives or binders, while Pt foil and Ag/AgCl were used as the counter and reference electrode, respectively. The specific areal capacitance of the electrodes C_s (F cm^{-2}) at different current densities (A cm^{-2}) was calculated by Refs. [39,40]:

$$C_s = \frac{2I_s \int V dt}{V^2 |_{\frac{V_f}{V}}} \tag{1}$$

Where I is the discharge current, S is the geometric area of the electrode, $\int V dt$ is the integral current area of the discharge curves, and V is the potential (V) varying from initial (V_i) to final value (V_f). The volumetric energy density (mWh cm^{-3}) of capacitor device was calculated by integrating the area under the discharge curve [41]: