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Wearable high-performance supercapacitors based on Ni-coated cotton textile with low-crystalline Ni-Al layered double hydroxide nanoparticles

Haicui Lu [a], Jizhang Chen [a,*], Qinghua Tian [b]

[a] College of Materials Science and Engineering, Nanjing Forestry University, Nanjing, China
[b] Department of Chemistry, School of Sciences, Zhejiang Sci-Tech University, Hangzhou, China

GRAPHICAL ABSTRACT
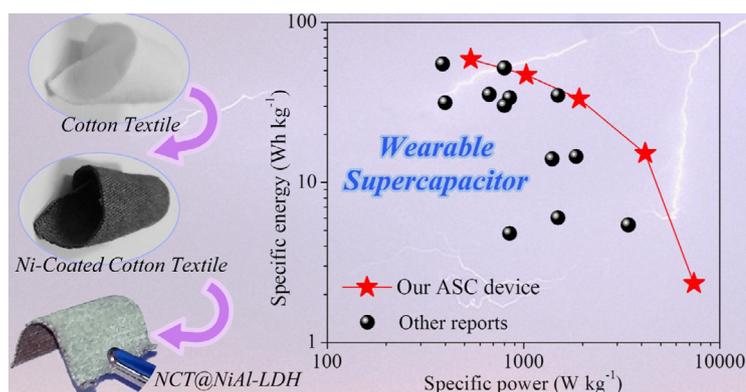
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ABSTRACT

Wearable electronics are developing rapidly in recent years. In this work, we develop a cost-effective, facile, and scalable approach to transform insulating cotton textile to highly conductive Ni-coated cotton textile (NCT). In order to verify the feasibility of NCT as a flexible current collector for wearable supercapacitors, we electrodeposit low-crystalline Ni-Al layered double hydroxide (LDH) nanoparticles onto the NCT. The obtained NCT@NiAl-LDH shows high specific capacitance (935.2 mF cm^{-2}), superior rate capability, and good cyclability. Besides, the asymmetric supercapacitor (ASC) assembled from NCT@NiAl-LDH exhibits high specific energy of 58.8 Wh kg^{-1} (134 µWh cm^{-2}) when the specific power is 539 W kg^{-1} (1228 µW cm^{-2}). The results demonstrate great potential of our methodology.

1. Introduction

The massive usage of fossil fuels has been causing serious consequences, *i.e.*, air pollution, global warming, and geopolitical concerns. Therefore, it is emerging to develop high-performance electrochemical energy storage (EES) devices for renewable energy and electric vehicles, so as to reduce our dependence on fossil fuels [1]. Among various EES devices, electrical double-layer capacitors (EDLCs) are well-known for high specific power (~10 kW kg^{-1}) and extremely long life span (~100 thousand cycles) [2]. However, EDLCs suffer from low specific energy, which originates from their

energy storage mechanism, *i.e.* surface-limited physical ion adsorption [3]. In contrast, pseudocapacitors deliver significantly higher specific energy than that of EDLCs, while their rate capability and cycling stability are much lower [4]. The mechanism behind that is pseudocapacitive materials (*e.g.*, RuO_2, MnO_2, Co_3O_4, $NiCo_2O_4$, $Ni(OH)_2$, $FeOOH$, and MoS_2) store and release charges *via* surface and near-surface redox reactions [5–8]. Among various cathode materials for pseudocapacitors, metallic layered double hydroxides (LDHs) have proven to be highly promising, owing to intriguing layered structure, high redox activity, relatively low cost, and environmentally friendliness [9–12]. LDHs are a class of two-dimensional (2D) layered materials with a general formula of $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot mH_2O$, where M^{II} and M^{III} are divalent and trivalent metal cations, and A^{n-} is the charge-balancing anion. Through varying M^{II} and M^{III}, different types of LDHs, such as Co-Ni LDHs [13], Co-Al LDHs [14], Ni-Mn LDHs [15], and Ni-Al LDHs [16], have been reported as high-performance pseudocapacitive materials. For instance, Li et al. used a homogeneous precipitation approach to obtain a nanocomposite comprised of NiAl-LDH and carbon nanotubes. Their product exhibited a high specific capacitance of 694 F g^{-1} at 1 A g^{-1} [17].

Nowadays, it is a trend to develop flexible, lightweight, and efficient EES devices, in order to satisfy the growing demands for wearable, portable, and smart electronics (*e.g.*, roll-up displays, electronic papers, artificial biosensors, and implantable medical devices) [18–20]. Following this trend, several groups grew LDHs on flexible and conductive substrates, such as carbon cloth [21–23], carbon paper [24], Cu-plated polyethylenterephthalate fibers [25], and reduced graphene oxide thin film [26]. For example, Yu et al. deposited CoNi-LDH nanosheets onto Ag nanowires-fenced carbon cloth, and realized large specific capacitance and high specific energy [22]. Despite great performances achieved by employing the above-mentioned substrates, these substrates are either expensive commercial products or unscalable. Herein, we choose cotton textile as the starting substance for constructing wearable supercapacitors because of its low cost, high flexibility, great strength, good breathability, abundance, renewability, and versatility. As cotton textile is made of cellulose fibers, it cannot be used as a current collector directly due to its insulation nature. To address this point, we introduce a cost-effective, facile, and scalable approach to coat Ni metal onto cotton textile, thus converting insulating cotton textile to conductive Ni-coated cotton textile (NCT). Moreover, this approach is applicable to all kinds of textiles. That is, the preparation of textile-based current collectors is highly tunable. In order to demonstrate the feasibility of NCT as a flexible current collector, we grow low-crystalline NiAl-LDH nanoparticles onto it. The resulting flexible electrode gives good performances in both three-electrode and two-electrode systems. In addition, our methodology can be extended to other pseudocapacitive materials. Therefore, this work offers a new platform in the advancement of wearable supercapacitors.

2. Experimental

2.1. Synthesis of NCT

Typically, cotton textile from a *T*-shirt was cut into 4×6 cm^2 slices and immersed into aqueous sensitizing solution containing 0.05 M $SnCl_2$, 0.5 M HCl, and several Sn granules for 5 min. After rinsed with deionized water for 3 times, the cotton textile was immersed into aqueous activation solution containing 20 µg/mL $PdCl_2$ and 0.036 M HCl for 5 min, and was then rinsed with deionized water for 3 times. Subsequently, the cotton textile was immersed into aqueous electroless plating solution containing 0.0712 M $NiSO_4$, 0.561 M NH_4Cl, 0.034 M sodium citrate, and

0.283 M NaH_2PO_2 for 2 h. Before electroless plating, the pH of the solution was adjusted to 9–10 using concentrated ammonia water. After electroless plating, the cotton textile was rinsed by deionized water and ethanol for 3 times, and dried in air overnight. In order to further improve the electrical conductivity, electrodeposition was conducted on a CHI 660E electrochemical workstation using the Ni-plated cotton textile as the cathode, 2×2 cm^2 Pt plate as the anode, and aqueous solution containing 0.15 M $NiSO_4$ and 0.12 M NH_4Cl as the electrolyte. After applying a constant voltage of 2.0 V for 8 min, the cotton textile was rinsed by deionized water and ethanol for 3 times, and dried in a vacuum oven overnight.

2.2. Synthesis of NCT@NiAl-LDH

NiAl-LDH was grown on the NCT through a standard three-electrode set-up. NCT (pretreated with a dilute HCl solution), 2×2 cm^2 Pt plate, and Ag/AgCl electrode were used as the working electrode, counter electrode, and reference electrode, respectively. NiAl-LDH was deposited on the surface of the NCT in an electrolyte composed of 0.1 M KNO_3, 0.075 M $Ni(NO_3)_2$ and 0.025 M $Al(NO_3)_3$ *via* a cyclic voltammetry (CV) method. The CV process was performed at 50 mV s^{-1} for 20 cycles in the potential range of –1.25 to 0 V. After electrodeposition, the product was washed with deionized water and ethanol for 3 times, and finally dried in a vacuum oven overnight. The average mass loading of NiAl-LDH is 1.18 mg cm^{-2}.

2.3. Characterization and electrochemical measurements

X-ray diffraction (XRD) patterns were collected using a Rigaku RU300 diffractometer with Cu Kα radiation source (λ = 0.1540598 nm). The morphology was recorded by a JEOL JSM-7600 field emission scanning electron microscope (FE-SEM). Investigation of the chemical compositions was performed using a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS). The ratio of Ni^{2+} to Al^{3+} was determined by a Varian VISTA-MPX inductively coupled plasma optical emission spectrometer (ICP-OES). Mechanical test was carried out on a tensile testing machine (Instron Model 5966) at a strain rate of 10 mm min^{-1}.

Three-electrode measurements were performed using NCT@NiAl-LDH, 2×2 cm^2 Pt plate, Hg/HgO electrode, and 3 M KOH aqueous solution as the working electrode, counter electrode, reference electrode, and electrolyte, respectively. CV and galvanostatic charging/discharging (GCD) tests were conducted at different scan rates and current densities on a CHI 660E electrochemical workstation. Before the tests, the electrodes were pre-treated by CV scans at 50 mV s^{-1} for 20 cycles. Electrochemical impedance spectroscopy (EIS) measurement was carried out with frequency ranging from 10 mHz to 100 kHz and the amplitude being set as 5 mV. For the two-electrode measurements, NCT@NiAl-LDH, NCT@G-Fe_2O_3, and polyvinyl alcohol (PVA)/KOH gel served as the positive electrode, negative electrode, and electrolyte, respectively. The synthesis process of G-Fe_2O_3 can be found in our previous report [27]. The NCT@G-Fe_2O_3 electrode was prepared by mixing G-Fe_2O_3 with polyvinylidene difluoride (PVDF) and Super P (conductive carbon black) at a weight ratio of 8:1:1 in *N*-methylpyrrolidone (NMP) and then pasting the slurry onto one side of NCT, followed by vacuum drying at 100 °C for 12 h. The preparation of PVA/KOH gel electrolyte and the assembly of solid-state asymmetric supercapacitor (ASC) device were similar to our previous report [28]. Typically, 2 g PVA and 2 g KOH were added to 20 mL deionized water, followed by heating at 85 °C under vigorous stirring until the solution became clear. The obtained viscous solution was dropped onto NCT@NiAl-LDH and NCT@G-Fe_2O_3, and then these two electrodes were assembled