Nano Energy (2015) 11, 568–578

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/nanoenergy

RAPIDCOMMUNICATION

Foldable supercapacitors from triple networks of macroporous cellulose fibers, single-walled carbon nanotubes and polyaniline nanoribbons

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Received 3 August 2014; received in revised form 7 September 2014; accepted 8 November 2014
Available online 20 November 2014

KEYWORDS
Foldable supercapacitor;
Macroporous cellulous fibers;
Polyaniline nanoribbons;
Carbon nanotubes;
Interpenetrating network

Abstract
We report foldable supercapacitor electrodes using a macroporous cellulose fiber network, Kimwipes®, as the scaffold through a simple "dip-absorption-polymerization" method. Single-walled carbon nanotubes (SWCNTs) wrapped around the cellulose fibers as the conductive skin, while ultrathin (~50 nm) and ultralong (tens of microns) polyaniline (PANI) nanoribbons were synthesized in situ between macroporous cellulose fibers and interpenetrated within the SWCNT network. The hybrid material showed good volumetric (40.5 F/cm^3) and areal capacitance (0.33 F/cm^2), which was attributed to the synergistic effect between electron transport within the SWCNTs network and fast charge transfer of the PANI nanoribbons. The paper-based hybrid electrode was highly flexible and compliant; it could be folded back and forth as an origami crane up to 1000 times without mechanical failure or loss of capacitance. We believe that the combination of triple networks and the unique morphology of PANI nanoribbons played critical roles to the repeated foldability. Finally, we assembled six all-solid-

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http://dx.doi.org/10.1016/j.nanoen.2014.11.023
2211-2855/

state supercapacitors based on the SWCNT/PANI nanoribbon paper electrodes connected in series, which lighted LED before, during and after folding for 500 times.

Introduction

The growing interests in portable and wearable electronic devices have driven the search for low-cost, flexible, lightweight, and environmentally friendly energy storage devices such as supercapacitors (SCs), which bridge the gap between rechargeable batteries and conventional high power density electrostatic capacitors [1-5]. Typically, the capacitance and cyclability of SCs for such applications should be comparable to conventional SCs. Furthermore, because the devices will be wrapped around an object (e.g. body) or folded into a small piece, which can be reopened later when needed, the SC electrodes should be lightweight and flexible, and more importantly, bendable to a large extent (e.g. with sharp folds) without losing their electrical performance. This has been proved to be a major challenge. Although free-standing graphene and carbon nanotube (CNT)-based composite films have been studied extensively in literature [2,6-14], many suffer from poor mechanical reliability [13,15] in addition to complicated preparation procedures and high material cost. Recently, much attention has been paid to the use of low-cost, flexible substrates, such as paper [16-22], fabrics [3,23-27], and cellulose nanofibers [28] as templates or scaffolds for depositing active conducting materials.

Paper, consisting of cellulose fibers (diameter ranging from tens to hundreds of microns) interconnected with each other, is by far the cheapest and most exploited substrate for flexible SCs. There are two types of paper investigated in literature for SCs, including printing paper, which is rather nonporous, and filter paper and wipes, which are highly porous with macron-sized interconnected pores. Printing paper has been used as a supporting substrate to draw or deposit conducting materials [18-21], followed by in situ polymerization of nanostructures, for example, polyaniline (PANI) nanowires [18] and polypyrrole nanoparticles [19]. Filter paper, on the other hand, has been used to absorb active materials, for example, graphene nanosheets, which fill the voids between the cellulose fibers [16]. Ethylene-vinyl acetate (EVA) copolymer/CNT has been coated on the surface of lens cleaning paper, followed by electrodeposition of MnO_2 [29]. However, very few have reported the capacity of the flexible electrodes after bending. Weng et al. bent graphene-cellulose paper one time [16] and Yuan et al. bent polypyrrole-coated paper 100 times [19], showing almost no change of the electrical performance. It has also been shown that 85% of initial capacitance is retained after bending 800 times from MnO_2/EVA/CNT paper with moderate curvature [29]. It remains unclear, however, whether these devices can survive repeated folding/unfolding, and sometime twisting at much larger curvatures, where the active materials could be detached or even destroyed at the interface if they are only deposited on the surface of paper [30].

Conducting polymers, such as polyaniline (PANI), are promising electrode materials because of their high specific pseudocapacitance, good environment stability, redox reversibility and low cost [31-33]. Nanostructured PANIs of different morphologies (e.g., nanofibres [34], nanorods [35], and nanowire arrays [36]) and their composites with carbon based materials (e.g. CNTs [37] and graphene [7]) have been synthesized. It has been suggested that the morphologies of nanostructured PANIs and their aggregations play important roles in energy storage, including material utilization, electron transport/ion diffusion pathways, and mechanical properties [38-40]. It is known that networks of high-aspect-ratio nanostructured materials (e.g., nanofibers, nanowires, and nanotubes) can be easily percolated, thus, offering improved mechanical strength and electrical conductivity.[6,41,42] Recently, we showed that dual-interpenetrating networks of single-walled carbon nanotubes (SWCNTs) and ultrathin PANI nanoribbons can be prepared as free-standing, flexible lithium ion battery (LIB) electrodes with high capacity and good cyclability.[40] The SWCNT aerogel and surfactants assembled on SWCNTs are critical to the formation of PANI nanoribbons. It will be attractive to exploit the macroporous network of cellulose fibers to grow SWCNT/PANI nanoribbons, and study the resulting electrical and mechanical performance, specifically, foldability and cyclability.

Here, we coated the macroporous cellulose fibers (Kimwipes®) with SWCNTs, followed by infiltration and in situ polymerization of aniline monomers. The SWCNTs were found wrapping around the interpenetrating cellulose fibers, and ultrathin and ultralong PANI nanoribbons were formed within the network of SWCNTs. The prepared SC electrodes were lightweight ($0.34\ g/cm^3$), and exhibited fairly high capacitance ($40.5\ F/cm^3$ or $0.33\ F/cm^2$). The electrodes could be folded/unfolded repeatedly up to 1000 times without mechanical failure or loss of capacitance, which was in sharp contrast to SWCNT/PANI nanoparticle paper SCs with 35% loss of capacitance.

Experimental

Materials

All reagents were used without further purification. Commercial Kimwipes® (KIMTECH Science* brand delicate task wipers, Kimberly-Clark Corporation) with density of $\sim 0.25\ g/cm^3$ or $2\ mg/cm^2$ was used. Single walled carbon nanotubes (SWCNTs) were purchased from Cheap Tubes Inc. (purity $>$ 90% with ashes $<$ 1.5 wt%) with diameter of $1 \sim 2$ nm and length of $5 \sim 30\ \mu m$. Sodium dodecylbenzene sulfonate (SDBS), aniline (An), camphorsulfonic acid (CSA), ammonium peroxydisulfate (APS), isopropyl alcohol (IPA), and ethanol were obtained from Sigma-Aldrich.