



Highly porous and easy shapeable poly-dopamine derived graphene-coated single walled carbon nanotube aerogels for stretchable wire-type supercapacitors

Gengheng Zhou^{a, e}, Na-Ri Kim^a, Sang-Eun Chun^b, Wonoh Lee^a, Moon-Kwang Um^a,
Tsu-Wei Chou^c, Mohammad F. Islam^d, Joon-Hyung Byun^{a, **, *}, Youngseok Oh^{a, *}

^a Korea Institute of Materials Science, 797 Changwondaero, Changwon 642-831, Republic of Korea

^b School of Materials Sciences and Engineering, Kyungpook National University, Daegu 41566, Republic of Korea

^c Department of Mechanical Engineering, University of Delaware, Newark, DE 19716, USA

^d Department of Materials Science and Engineering, 5000 Forbes Avenue, Carnegie Mellon University, Pittsburgh, PA 15213, USA

^e Division of Advanced Nanomaterials, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou, 215123, PR China

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ABSTRACT

Easy shapeable highly porous and robust three dimensional (3D) nano-carbon architectures (3D NCA) are crucial for the practical applications of electrochemical energy storage devices. Here, a facile easy shapeable nitrogen-doped graphene coated 3D NCA exhibiting an ultra-high specific surface area, remarkable robustness, and excellent aqueous wettability is reported. A 3D single-walled carbon nanotube (SWCNT) hydrogel composed of isolated SWCNTs is first prepared, and then a thin polydopamine (pDA) layer is uniformly coated onto the fabricated 3D SWCNT hydrogel via an *in situ* polymerization of dopamine. A nitrogen-doped graphene-coated 3D NCA is obtained via pyrolysis of the pDA-coated 3D NCA. By decorating this highly porous nitrogen-doped 3D NCA onto helical micro carbon fibers, a highly stretchable (~100% strain) wire-type supercapacitor (WTSC) is fabricated. The areal specific power and energy density of the WTSC are determined to be 2.59 mW cm⁻² and 1.1 μWh cm⁻², respectively. These values are remarkably larger than those previously reported WTSCs. Moreover, our WTSC maintains more than 91% of its capacitance after 10,000 stretch-release cycles at tensile strains of up to 50%. The combination of the easy shapeable, robust and highly porous nitrogen-doped 3D NCA paves a new way for the development of high-performance wearable textile-based energy devices.

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1. Introduction

Three-dimensional (3D) porous nanocarbon architectures (NCAs) such as sponges, foams and aerogels have attracted increasing research interest because of their high specific surface area (SSA), environmental compatibility, chemical stability, and excellent electrical performance [1–10]. Open-cell 3D NCAs are promising materials for numerous applications, including high-performance electrodes in electrochemical energy storage [11–17], supporters [18], templates [19], photocatalysis components [20], membranes [21], stretchable conductors [21,22] and

sensors [23,24].

Typically, 3D NCAs are fabricated by chemical vapor deposition with multi- and single-walled carbon nanotubes (SWCNTs) [25] or sol-gel chemistry, which involves the transformation of carbon precursors into highly cross-linked organic gels, followed by solvent removal via special drying techniques, such as freeze drying and supercritical CO₂ drying [2,3,6,22,26]. However, owing to the difficulties in tuning material shape and physical characteristics, including mechanical behaviors, pore size and electrical performance, the 3D NCAs obtained from these typical fabrication methods are limited in their potential for many applications, especially in electrochemical devices. SWCNTs that have ultra-high strength, elasticity, and electrical conductivity and high SSAs are ideal candidates for fabricating multifunctional 3D NCAs. However, owing to the large bundles resulting from strong van der Waals interactions, typical 3D NCAs made from SWCNTs have low SSAs

* Corresponding author.

** Corresponding author.

E-mail addresses: bjh1673@kims.re.kr (J.-H. Byun), youngsoh@kims.re.kr (Y. Oh).

($\sim 500 \text{ m}^2 \text{ g}^{-1}$) far below the theoretical value of the individual SWCNTs ($1315 \text{ m}^2 \text{ g}^{-1}$) [27]. Additionally, control over the wettability of the material is of vital importance for the wide utilization of 3D NCAs in many applications, especially for electrode materials used in charge storage based on ion adsorption, such as supercapacitors (SCs). To enable the full utilization of the high SSA of an electrode, excellent surface wettability and water affinity is required to allow the electrolyte to infiltrate easily into the micropores. Therefore, robust hydrophilic 3D NCAs with high SSAs are the most promising materials and are in high demand for utilization as SC electrodes.

Toward this end, we first fabricated a 3D SWCNT hydrogel composed of isolated SWCNTs using a method we recently developed [3]. Then, a thin polydopamine (pDA) layer was uniformly coated onto the fabricated 3D SWCNT hydrogel via the *in situ* polymerization of dopamine. Finally, a nitrogen-doped graphitic layer-coated 3D NCA was obtained via pyrolysis of the pDA-coated 3D NCA. The mechanical robustness of the 3D NCA was simultaneously enhanced because the nodes, or crosslink points, among individual SWCNTs were anchored by the graphitic layer coating [2]. Therefore, compressible electric double-layer capacitors (EDLCs) can be fabricated from graphene-coated 3D NCA [28]. In addition, the fabricated 3D SWCNT hydrogel can be easily decorated onto other substrates by a simple dip coating. Consequently, the fabricated graphitic layer-coated 3D NCA (3D pDA-Gr NCA) can be decorated onto any substrate with a desired geometry.

Micro carbon fibers (μCFs) can be used as electrode material for supercapacitor [29]. In this work, we fabricated a highly stretchable ($\sim 100\%$ strain) wire-type supercapacitor (WTSC) from micro carbon fibers (μCFs) with a surface decorated by our robust, highly porous nitrogen-doped 3D pDA-Gr NCA. The 3D pDA-Gr NCA has a high SSA of up to $1190 \text{ m}^2 \text{ g}^{-1}$, which is close to the theoretical limit of SWCNTs ($1315 \text{ m}^2 \text{ g}^{-1}$). The areal specific power (P) and energy (E) density of the WTSC were determined to be 2.59 mW cm^{-2} and $1.1 \mu\text{Wh cm}^{-2}$, respectively. These values are remarkably larger than those previously reported for ZnO nanowire-coated polymer fiber SCs ($P = 1.4 \times 10^{-2} \text{ mW cm}^{-2}$ and $E = 2.7 \times 10^{-2} \mu\text{Wh cm}^{-2}$) [30], all-graphene core-sheath microfiber-based SCs ($P = 6\text{--}100 \times 10^{-3} \text{ mW cm}^{-2}$ and $E = 0.4\text{--}1.7 \times 10^{-1} \mu\text{Wh cm}^{-2}$) [31], and CNT fiber-based WTSCs ($P = 4.93 \times 10^{-1} \text{ mW cm}^{-2}$ and $E = 0.8\text{--}2.26 \times 10^{-1} \mu\text{Wh cm}^{-2}$) [32]. Moreover, our WTSC maintains more than 91% of its capacitance after 10,000 stretch-release cycles at tensile strains of up to 50%. These data indicate that our WTSC maintains an ultra-high capacitance, high energy density and excellent cyclability even under large tensile deformation. The combination of the robust and highly porous nitrogen-doped 3D pDA-Gr NCA and the helically wrapped CF substrate with its high resilience paves a new way for the development of cost-effective and high-performance wearable textile-based energy devices.

2. Experimental

2.1. Fabrication of nitrogen-doped 3D pDA-Gr NCA-decorated CF bundle

Purified CoMoCAT SWCNTs were used to prepare aerogels. CNTs were purchased and used as received from South West Nano Technologies, Inc., (batches of CG200) with a diameter of 0.8–1.4 nm (manufacturer's specifications). The SWCNTs were suspended in Millipore-filtered deionized water at a concentration of 0.1 wt% using sodium dodecylbenzene sulfonate surfactant (Sigma Aldrich) at a 1:10 wt ratio of CNTs to surfactant [33]; different weight ratios of CNTs to surfactant did not alter aerogel quality. Suspensions were then sonicated using a tip sonicator (VCX 500 Sonics & Materials, INC.) for 2 h at 60 W, followed by

centrifugation at 21,000 g for 30 min (Beckman Coulter Allegra 64R) to sediment the CNT bundles. We then collected the supernatants, which contained mostly isolated CNTs. The supernatants were then concentrated by evaporating the water to a final CNT concentration of 6.5 mg mL^{-1} . We degassed the concentrated CNT suspensions to remove any bubbles, as bubbles significantly degrade the mechanical integrity of aerogels, and we then poured the suspensions into cylindrical molds. The CNT suspensions formed hydrogels within 12 h because of the van der Waals interactions among the CNTs. To remove the surfactant from the hydrogels, we washed the obtained hydrogels with 1 M nitric acid at 50°C for 20 min. The acid-washed hydrogels were neutralized by deionized water until the pH equilibrated at 7.

To obtain porous 3D pDA-Gr NCA-coated CF bundle electrodes, we used commercial CF bundles (T300 1K, Toray) composed of 1000 filaments and dipped them into CNT hydrogels that had been tip-sonicated (200 W) for 1 min. The coated CNT suspension on the CF surface formed a hydrogel layer within 12 h because of the strong van der Waals interactions among the CNTs. After surfactant removing process, we then dipped the hydrogel-coated CF bundles into a dopamine solution (3 mg mL^{-1}) for 5 min. Then, we dipped the dopamine-coated fiber bundles into a tris buffer solution with a pH of 8.5 for the *in situ* polymerization of dopamine. We then exchanged the buffer solution with anhydrous ethanol over 32 h (fresh ethanol every 8 h) and critical point dried samples to create pDA-coated aerogels. To convert the pDA into nitrogen-doped graphitic layers, we finally pyrolyzed the pDA-coated fiber bundle at 600°C or 800°C in an Ar atmosphere at 1 atm for 1 h.

2.2. Electron microscopy

The 3D NCA and pDA-Gr NCA were imaged, and EELS spectra were obtained using electron microscopy. We used a Cs-corrected scanning transmission electron microscope (JEM 2100F) operated at 200 kV to collect STEM images, high-resolution TEM images and EELS spectra, as well as a field emission scanning electron microscope (JSM 6700F) to obtain high-resolution SEM images.

2.3. XPS characterization

XPS data was collected using a VG-MKII electron analyzer equipped with a 32-channel detector. We applied a mono-chromatized Al K-line at $h = 1486.6 \text{ eV}$ to excite the sample. The analyzer was operated with a pass energy of 40 eV, yielding a resolution of 0.85 eV.

2.4. Mechanical characterization

To characterize the mechanical properties of the aerogels, we measured compressive stress as a function of compressive strain at room temperature using Instron 5943 with a 50-N load cell. The resolution of the DMA system was $<2 \mu\text{m}$. Cylindrical aerogel samples were loaded between the two compression heads with the top head applying uniaxial compression and release on the sample along the vertical direction.

2.5. Electrochemical performance characterization

All static electrochemical measurements on the fiber SC utilized a three-electrode configuration with 0.5 M Na_2SO_4 aqueous electrolyte and an electrochemical analyzer (Versa stat3, Princeton Applied Research). Dynamic CV measurements were made on a fiber SC by cycling at 10 mV s^{-1} , while the SC was stretched and released at a set strain rate of $15\% \text{ s}^{-1}$ (using a machine constructed in the laboratory for applying tensile deformation). The length of

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