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RAPID COMMUNICATION

Omnidirectionally stretchable, high performance supercapacitors based on a graphene-carbon-nanotube layered structure

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Abstract
The development of stretchable energy storage systems for fully power-independent and stretchable devices for the next generation is increasing. Here, we report on a graphene-carbon-nanotube-layered structure for use as a stretchable electrode and its application in all-solid-state stretchable supercapacitors and various electronics. In this system, graphene serves as a floating track and carbon nanotubes convert external stress into the stretching motion of the electrode. The structure provides omnidirectional deformation without inhomogeneous interface stress and slip stress between active sites and the stretching passive components. The suggested system offers significant improvement over existing methodologies for fabricating stretchable energy storage systems and electronics in terms of density of capacitance, negligible passive volume, biaxial and twisted deformation, and durability. The integration of stretchable electrodes in various substrates and their application as all-solid-state, stretchable supercapacitors are demonstrated, and a high value of capacitance in the deformed state of 329 F g^{-1} was achieved (based on mass of the graphene). The physical characteristics of the system are also revealed by first-principle calculations and three-dimensional finite-element methods.

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Introduction

Ingenious ideas for fabricating stretchable wavy structures or materials for use in stretchable electronics have been proposed [1]. However, strategies that have been proposed are directed toward only phenomenological characteristics of soft materials with obvious limits, such as the significantly large passive volume of the stretched structure and the low and irreversible performance of stretchable materials [2,3]. Conventional technologies for stretchable electronics are composed of a stretchable bridge and a rigid operating site. Stretchable bridges have successfully conferred deformability to these electronics. However, significant interfacial resistance between the stretchable bridge and the rigid operating site is common, which fundamentally decreases operational stability and durability. Recently, researchers have begun to investigate stretchable supercapacitors in their primary stages [4-8]. Energy storage is of critical importance because it is a limiting factor in achieving complete and independent stretchable electronics for the next generation. Moreover, supercapacitor is one of excellent alternative energy storage systems because of its high power density and device reliability. However, the system also does not circumvent above general limits of the conventional stretching strategies.

To overcome the limitations of stretchable energy storage systems and electronics, we presented first-principle calculations and experimental proof for graphene-carbon-nanotube (CNT)-layered electrodes, a system inspired by the underlying principle of the motion of human muscles. Graphene is one of the best candidate materials in electronic systems, e.g., printed circuit boards, thin-film transistors, light-emitting devices, solar cells, and various sensors [9]. Especially, the low-dimensional material is also considered to be the best candidates currently available for use in supercapacitor electrodes because of their high interface charge separation [10-12]. To fabricate a stretchable graphene structure, several studies have made use of conventional techniques: fabrication of a graphene wavy structure and intensification of its stretchable properties. However, the graphene is brittle, and its advantages, i.e., high electric, mechanical, and thermal properties, diminish abruptly and irreversibly in the deformed state [3,13]. In conclusion, the objective of this study was to investigate the use of the rigid and brittle form of graphene as an operating site for stretchable electronics in an attempt to eliminate the interfacial resistance.

A typical cell in living bodies that undergo semi-permanent and reversible stretching is the sarcomere in muscle tissue [14]. Sarcomeres include myosin molecules that function as molecular motors and actin filaments that act as tracks that direct the motion of the motor assembly [14,15]. In the same manner, undeformable graphene can act as a track, and deformation can be accomplished using a stretching component as a motor riding on the graphene track. It is reasonable to use a CNT cluster as the motor because of their significant stretchability and stability [16,17]. CNT cluster can be attached to the graphene surface with van der Waals interactions caused by graphitic AB stacking [18]. In this system, the graphene serves as a floating track and the CNT cluster converts external stress into the stretching motion of the electrode. The graphene and CNT cluster are bonded to form a two-dimensional homogeneous interface, which can solve the problem of inhomogeneous interface stress. The graphene-CNT structure also has negligible slip stress and no passive surface for stretching utilization. Thus, this structure shows multifunctionality that was previously unachievable, i.e., omnidirectional stretching and energy storage via the formation of a large surface electrochemical double-layer.

Experiments

First-principles calculations and three-dimensional finite-element method modeling

First-principle calculations were carried out on the basis of density functional theory (DFT) using a generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) functional [19]. We used the projector-augmented wave (PAW) method as implemented in the Vienna ab-initio simulation package (VASP) [20]. The van der Waals interactions are described via the DFT-D2 Method of Grimme [21]. A plane-wave basis set with a kinetic-energy cutoff of 600 eV and a $2 \times 2 \times 10$ Monkhorst-Pack k-point mesh was used. The CNT was built into a single-walled armchair nanotube with a (10,10) index (diameter, 13.7 nm), as shown in Figure 1a. The structures are located in the orthorhombic unit cell with a vacuum gap. Lattice constants are a=34.08 Å, b=45.00 Å, and c=2.46 Å (see the Supplementary materials, Figure. S1). Before calculating the binding energy of the graphene-CNT interface, we calculated the variation of the energy along the z-axis by modifying the distance between the graphene and CNT from 5 to 2 Å in steps of 0.2 Å, and the binding energy was maximized at 3.1 Å with structure relaxation (Figure S1b). The structure relaxation well represented the covering state of graphene on the CNT. Calculated energy values were summarized in Table S1. We also developed three-dimensional (3D)-finite element method (FEM) models for numerical structure analysis [22]. All elements of the models were designed by means of a 20-node (Serendipity) hexahedral brick. Near the edges of the model, we used an element size under 2 μm for high accuracy.

Fabrication of graphene-CNT stretchable electrodes

To fabricate the graphene-CNT-layered structure, various elastic supports [rubber, latex, poly(vinyl alcohol) (PVA), etc.] were initially stretched in two dimensions and fixed. Then 10 layers of a 0.5 g/L solution of CNT (ILJIN Nanotech.) ink dissolved in 200 μL of ethanol was spread onto the prestrained substrate. The CNT was pretreated in a 70% HNO_3 solution at 110 °C for 8 h, which resulted in the surface of the CNT being slightly hydrophilic. The HNO_3 treated CNT contains some O-functional groups (8.15 wt%). However, the presence of these did not affect the major interfacial characteristics of the system. Following this process, three layers of a 0.5 g/L graphene ink solution in 200 μL of ethanol was spread onto the CNT layer. The graphene was synthesized from graphene oxide in a microwave oven for 2 min, as suggested in a previous study [23].