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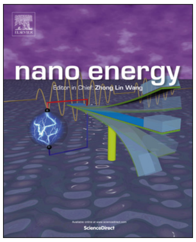

RAPID COMMUNICATION

Resilient aligned carbon nanotube/graphene sandwiches for robust mechanical energy storage

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Abstract

The use of microscale flexible mechanical energy storage devices, instead of traditional electrochemical energy storage devices based on supercapacitors and Li-ion batteries, is highly considered for portable electronics, actuators, and meso-micro scale systems. The selection of resilient and robust building blocks is the first step for high energy-density mechanical energy storage system. Herein, alternative aligned carbon nanotubes (CNTs) and graphene were effectively sandwiched into freestanding sp^2 all-carbon hybrids, rendering the excellent loading transfer in the three-dimensional framework. The millimeter-scale aligned CNT/graphene sandwiches could be repeatedly compressed at high strains ($\varepsilon > 90\%$), with a highest energy absorption density of 237.1 kJ kg^{-1}, an ultrahigh power density of 10.4 kW kg^{-1}, and a remarkable efficiency of 83% during steady operation, providing novel nanocomposites with outstanding mechanical energy storage performance comparable to electrochemical batteries and bridging nanoscopic structures to micro- and mesoscale applications.

1. Introduction

The broad applications of portable electronics and electric vehicles worldwide stimulate the development of energy storage devices or physical media toward higher power density and energy density. Among various strategies, mechanical energy storage that is carried out by conversion into kinetic energy *via* rotating, or potential energy *via* stretching, compression, or elevation has been widely applied nowadays [1]. In fact, the original utilization of mechanical energy storage, the bow, even predates recorded history. While the string of a bow is drawn back, compressive force is exerted on the elastic limbs. The limbs are flexed with higher potential energy, which can be transformed into kinetic energy of the arrow after releasing the string. Consequently, mechanical properties of the

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materials for limbs are of significant importance to the performance of the bow. The combination of materials that are more resilient in compression or tension, such as horn, sinew, fiberglass, and carbon fibers, always brings more powerful bows with better mechanical energy storage and release performances. The pumped hydropower storage system based on mechanical energy storage can also date back to ancient times, and it has still been widely developed and employed in the modern society. Other mechanical energy storage systems, such as flywheels storing mechanical energies by the use of a rapidly rotating flywheel [2], compressed air storing mechanical energies in a confined underground cave or abandoned mine [1], and steel springs storing mechanical energies by their elasticity, were also widely employed. However, the above mentioned mechanical energy storage systems were based on traditional fluid or elastic solids, which offer limited energy density and always operate at a bulk scale. With the increasing requirements on portable electronics, actuators, meso-micro scale systems, the use of microscale flexible mechanical energy storage devices, instead of traditional electrochemical energy storage devices based on supercapacitors and Li-ion batteries, is highly required. Recently, there are breakthroughs on harnessing the fluctuating and transient by “nanogenerators” to realize conversion between mechanical energy and electrical energy using piezoelectric nanogenerator [3,4], triboelectric nanogenerator [5], electromechanical bimorph actuator [6] and free surfaces [7] with unique actuation characteristics and exceedingly high efficiency.

Just like the construction of a stronger bow, the selection of resilient and robust building blocks is the first step for high energy-density mechanical energy storage system. The intrinsic mechanical properties determine their potentials for robust devices with ultra-high energy density and good recovery rate. Both carbon nanotubes (CNTs) and graphene possess exceptional mechanical properties with high tensile strength of 63 and 125 GPa as well as Young modulus of 1.25 [8] and 1.0 TPa [9], respectively. CNT films behave as open-cell foams with nanotubes as elastic struts [10]. The energy storage density of CNT bundles under tensile loading is calculated to be at least three orders larger than that of steel springs, and even under practical considerations, it is still comparable to batteries [11,12]. In theoretical calculations, CNT ropes are also demonstrated to store mechanical energy *via* twisting, stretching, bending and compressing reversibly with a capacity 4 to 10 times higher than that of Li-ion batteries [13]. The individual CNTs have a mechanical energy density as high as 4050 kJ kg^{-1} [14]. The rational combination of CNT sponge with array constructs highly compressible and elastic macroscopic structures with extended energy absorption range and high energy dissipation [15-18]. However, the potential applications in mechanical energy storage for CNTs have greatly suffered from the difficulty of device assembly due to the nano-sized structure.

Fine combination of one-dimensional (1D) and two-dimensional (2D) building blocks which leads to the formation of hierarchical three-dimensional (3D) composites can usually inherit full advantages of the component materials, or even bring about unexpected properties for unique applications [19-21]. For instance, stable sponge-like structure made of 1D CNTs allows excellent compressibility tunable up to 90% volume shrinkage, and the ability to recover most of volume by free expansion [22]. Graphene has been employed to fabricate multichannel and repeatable self-healing polymeric materials with enhanced mechanical properties and excellent healing efficiency higher than 98%. [23] Chemically converted graphene aerogels with density as low as 3.0 mg cm^{-3} show excellent resilience and can completely recover after more than 90% compression, which are promising as compliant and energy-absorbing materials [24]. The alternate combination of vertically aligned CNTs and 2D inorganic sheets made the resultant 3D hybrid architecture more ductile and resilient [25], and the mechanical energy absorption performances were enhanced greatly in contrast to CNT aggregates [25,26]. 3D CNT/graphene hybrids with extraordinary capacitive performance and storage density were available by facile incorporation of CNTs and graphene through *in situ* growth [27-31]. When the CNTs graft on graphene, they serve as spacers to inhibit the stacking of graphene flakes; meanwhile, the graphene interlinked with CNTs hinders the strong entanglement of tubes [32]. The fine arrangement of 1D CNTs and 2D graphene is highly expected to obtain hybrid sp^2 carbon with ordered structures as well as unique mechanical properties [33], although the current chemical routes *via* self assemble, selective oxidation, electrodeposition, and *in situ* growth [34-39] offer very poor ability to vertically aligned and high-density CNTs on graphene without barriers. It is highly expected to integrate CNTs with graphene into 3D ordered, alternative, highly compressible macroscopic structures instead of entangling or stacking into randomly distributed agglomerates with the potential to full demonstration of the mechanical properties of CNT/graphene hybrids.

In this contribution, we explored the idea of *in situ* CVD of alternative aligned CNTs and graphene sheets to form freestanding 3D sp^2 carbon sandwiches for excellent mechanical energy storage. The reason we selected aligned CNTs rather than entangled CNTs is that aligned CNTs intrinsically exhibit excellent mechanical properties and super-compressible behavior [10,12]. The introduction of strong but flexible graphene sheets to the ends of aligned CNTs renders the resultant composites consisting of dense CNT arrays seamlessly linked by graphene sheets placed vertically to the *c*-axis of CNTs, guaranteeing the excellent stress transfer in the 3D framework. The aligned CNT/graphene sandwiches could be repeatedly compressed at high strains ($\varepsilon > 90\%$), with a highest energy absorption density of 237.1 kJ kg^{-1}, which is about 1700 times that of steel springs (0.14 kJ kg^{-1}) [40], a remarkable efficiency of 83% during steady operation, and an ultrahigh power density of 10.4 kW kg^{-1}. Such excellent mechanical energy storage performance is supposed to be available with particular-designed power supply systems, such as that with escapement mechanisms and piezoelectric cantilevers for CNT springs [12], thereby making this novel composite a new energy storage strategy comparable to electrochemical batteries and perhaps even approaching flywheels.

2. Results and discussion

Our strategy for the fabrication of aligned CNT/graphene sandwiches involves a two-step CVD growth method, which is