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Design and analysis of sandwiched fullerene-graphene composites using molecular dynamics simulations

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ABSTRACT

Computational design of a novel carbon based hybrid material that is composed of fullerene units covalently sandwiched between parallel graphene sheets is presented. In this regard, atomistic models for the proposed novel material structure are generated via a systematic approach by employing different fullerene types (i.e. C_{180}, C_{320}, C_{540} and C_{720}) as sandwich cores. Then, thermodynamic stability of the atomistic structures is checked by monitoring free energy profiles and junctional bond configurations which are obtained through classical molecular dynamics (MD) simulations. Thermodynamic feasibility of all atomistic specimens with different fullerene types is suggested by the energy profiles, because total configuration energies for all systems are minimized and remained stable over a long period of time. Furthermore, mechanical behavior of the nano-sandwiched material system is investigated by performing compression tests via MD simulations and basic deformation mechanisms underlying the compressive response are determined. By detailed examination, it is shown that proposed nano-sandwiched material can be identified as quasi-foam material due to comparable energy absorbing characteristics. Furthermore, regarding the effect of fullerene size on the compressive response, it is found that for a given stress level, specimens with larger fullerenes exhibit higher energy absorbing capacity.

1. Introduction and background

Carbon based nanomaterials including zero-dimensional fullerenes, one dimensional carbon nanotubes (CNTs) and two dimensional graphene are of great interest to a broad range of research communities. Multifunctional characteristics of these nanostructures owing to their extraordinary mechanical [1,2], thermal [3,4] and electrical [5,6] properties stimulate their usage in diverse innovative technological applications ranging from wiring in integrated circuits and nanoscale components to composite materials with improved functional characteristics [7–14]. Being the first carbon nanostructure experimentally observed and produced, due to their excellent structural characteristics, electronic conductivity, mechanical strength and chemical properties, fullerene and its derivatives encouraged researchers to implement them in various fields such as electronics, computers, fuel cell technology, solar cells and field emission technology [15–18]. Furthermore, emergence of fullerenes increased the intensity of attention on nanoscience and nanotechnology, resulting in the discovery of the carbon nanotubes which have been more popular than fullerenes [19]. Following the fullerenes and CNTs, another allotropic carbon nanostructure demonstrating unique physical and chemical properties, graphene, is derived finally as a single mono-atomic layered structure [20].

Apart from the studies focusing on the physical and chemical properties of single fullerenes, CNTs or graphene nanostructures [21–24], after a maturation period followed by their discovery, many other studies on their potential employments within different materials, as fillers, resulting in composite materials with improved properties and increased functionalities are also performed [25–30]. On the other perspective, in order to achieve novel materials with superior characteristics, possibilities of self-establishment of those carbon nanostructures are examined to built-up macroscopic materials [31–38]. Ultralight, highly porous CNT aerogels composed by three dimensional networks of CNTs are one of the examples that can be given for these types of multifunctional novel materials [37,38]. Similarly, a recently synthesized carbon based nanomaterial, namely aerographite, is a cellular

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graphene network material with open cell architecture presented with exceptional characteristics [39]. In addition to those materials consisted of purely CNTs or graphene building units, hybrid nanomaterials made up of different couplings such as CNT-graphene and CNT-fullerene are also proposed and investigated [40–43]. For instance, a novel carbon based hybrid nanomaterial termed as nanobuds, have been synthesized by combining single-walled carbon nanotubes (SWCNTs) and fullerenes into a single structure through covalent bonding formations [43]. In the study reporting the discovery of nanobuds, the hybrid structure of SWCNTs and fullerenes is evidenced through transmission electron microscopy (TEM) images, spectroscopic and spectrometric investigations accompanied by theoretical simulations [43–45]. However, it should be noted here that the first approach of synthesis and characterization of covalently coupled SWCNT-fullerene hybrid structures through a simple mechanochemical reaction was reported in a previous study [46]. Regarding carbon nanotube-fullerene (i.e., C_{60}) hybrid nanostructure, in a very recent study [47], fullerene bombardment on the CNTs is investigated by molecular dynamics simulations. Accordingly, different types of nanobuds formed by C_{60} bombardment on the CNT structure are presented and mechanical properties of those nanobuds are reported by noticing that nanobuds may cause degradation of strength of the CNTs. Being different from the nanobuds where fullerenes are chemically bonded on the outer surface of the CNTs, fullerene-CNT couple is also studied for the oscillatory motion of fullerenes which are located within SWCNTs. In their study, Cox et al. investigated the high frequency oscillation of fullerenes placed in SWCNTs by deriving a mathematical model that is able to capture the essential mechanisms of such gigahertz oscillators [48].

One of the initial studies pointing out the idea of coupling the graphene with CNT units investigated hydrogen storage capacity of such a novel three-dimensional network material that consists of pillared CNTs between the stacking of planar graphene layers [49]. Stability of the computational designed pillared graphene network was ensured through theoretical ab initio calculations carried out over single building block which is one graphene sheet and one SWCNT. Computational proposal of such a CNT-graphene hybrid material is followed by several studies [50–52] which introduce several synthesis methods for the forming of CNT-graphene hybrid nanostructures. Among them, a new technique for making the CNT-graphene films, in which vertical CNT units can be patterned in a square way macroscopically is described by Lee et al. [53]. In a more recent study, a synthesizing method to join graphene and SWCNTs seamlessly is reported to be developed, which enables direct growth of CNT forests from graphene sheets [54].

Along the same line with fullerene-CNT and graphene-CNT hybrid nanostructures, graphene-fullerene coupling is also under investigation by continuously increasing attention. One of the successful attempts to covalently attach fullerenes onto graphene sheets is accomplished through monosubstitution of C_{60} units by developing lithiation reactions [55], in which the resultant hybrid structure is employed in solar cells demonstrating the significant improvement of the device performance owing to enhanced electron transport. Similar to that study, there exist a few more experimental works recently established which present novel synthesizing methods to yield fullerene/graphene composites and substantiate their superior capabilities in electrochemical applications such as supercapacitors [56,57].

Considering the recent advances and investigations summarized above, hybridization of carbon based nanostructures (i.e. CNTs, fullerene, and graphene) with each other via chemical couplings is offered as an effective solution to extend the extraordinary properties of those individual nanostructures to bulk material form. Motivated by this fact, in this study a novel carbon based hybrid nanostructure, which can be termed as FullGraph (FG), that is composed of multiple graphene sheets with fullerenes inserted between the graphene layers by covalently fusion is designed computationally and proposed as a new hybrid material. Although other hybridization types such as CNT-fullerene or CNT-graphene composites have been proposed in literature [40–43], graphene-fullerene composition with covalent linkages in a bulk form is computationally presented for the first time. Due to the fact that fullerene grafted single graphene layers can be synthesized successfully by several novel techniques demonstrated in literature [55], manufacturing of FG styled nanoporous hybrid materials seems to be achievable in near future. In the content of computational studies, as a first step, thermodynamic feasibility of FG material is investigated through molecular dynamics simulations by monitoring the energy profile of 3 distinct FG models made up with different fullerene types (i.e. C_{180}, C_{320} and C_{540}). After verifying the thermodynamic stability, mechanical characteristics of FG specimens with different types of fullerene units are probed under compressive loading through molecular dynamics simulations. Under the same compressive loading rates, nominal stress-strain variations of the samples are determined and compared with conventional foamed materials. Furthermore, basic deformation mechanisms underlying the mechanical response of FG samples are investigated and monitored. Based on the simulation results, it has been concluded that the proposed nanostructured hybrid material can be effectively utilized as an energy dissipative structural material especially in aerospace and aeronautical applications due to their ultra-low weight and high damping characteristics. Inherent to carbon based nanomaterials, multi-functional characteristics that can also be imparted to FG composite materials may enable to broaden their application spectrum from structural to thermal and electrical applications.

2. Molecular simulations of fullerene-graphene hybrid foams

Atomistic models of the proposed fullerene sandwiched graphene composites as presented in Fig. 1 are generated by fusing fullerenes randomly dispersed on each different graphene layer. While the locations of the fullerenes are determined randomly, a strict distance control is dictated upon the fullerenes for the sake of avoiding the intersection of the fullerenes. In this respect, primary distance control is performed between the fullerenes located on the same graphene. Additionally, as a secondary distance control, the random locations of the fullerenes on a single graphene sheet are arranged in a way that a fullerene on a layer does not coincide with any other fullerene positioned on the lower and upper neighbor layers. Randomized locations of the holes trimmed on a graphene sheet are shown in Fig. 2. The reason of locating the fullerenes on the adjacent sandwich layers in this way is to prevent overlapping of the fullerene-graphene junctions. This structural design preference will naturally affect the compressive response of the nano-sandwiched material as discussed in the next section.

Regarding generation of welding between carbon-based nanostructures (i.e. CNTs), several strategies including beam irradiation, heat and vibration welding have been proposed to form covalent bonding. Amongst those strategies, in the heat welding method, covalent junctions between CNTs are formed by an annealing process through which the fusion spots are heated up to high temperatures. In this study, for the sake of encouraging the junction formation at lower temperatures than the referenced temperature values (2500–3500 K) for heat welding procedure [58] that is reported to be applicable for CNTs, atoms in a spherical volume centered at the intersecting points is removed to create dangling bonds. Therefore, for fusing fullerenes onto the graphene sheets by forming covalent bonding, both fullerenes and graphene sheets are