# **Tunable Negative Poisson's Ratio of 3D Spanned-Fullerene Nanotube Nanotruss**

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Abstract CNT-based network, as an emerging class of material, attracts extensive research interest in recent years from both the scientific community and industry. In this study we proposed novel covalently bonded bcc-lattice like 3D nanotruss made up of fullerenes spanned by CNTs. The mechanical properties of such architecture are systematically investigated via full atomistic simulation. Our simulations reveal that the CNTs length of the 3D nanotruss plays a significant role on the mechanical properties. This nanotruss network displays orientation dependent deformation behaviour. Under <100> direction tension, negative Poisson's ratio is observed exclusively for the case of N = 0, while a "flipping" behaviour of Poisson's ratio with "Negative  $\rightarrow$  Positive  $\rightarrow$  Negative" appears when the tension is applied along <110> direction. The findings in our work would provide guidance to optimal design of CNT-fullerene based structures towards tailor-made properties.

Keywords Single-walled carbon nanotubes, Fullerene, Nanotruss, Negative Poisson's ratio, Atomistic simulation

## **1. Introduction**

Since their discovery <sup>[1, 2]</sup>, the properties of fullerenes and nanotubes have been extensively studied both by experiment and by simulation. It is found that they, as unique zero-/one-dimensional carbon materials, possess predominant physical, chemical, and mechanical properties combined with a very little weight. To fully exploit their unique properties and explore additional properties, various types of carbon architectures made up of fullerenes and carbon nanotubes (CNTs) have been successfully fabricated and investigated. A hybrid carbon nanostructure termed "nanopeapod" fullerenes are encapsulated in CNTs, has been fabricated, and the nanopeapod exhibits a variety of intriguing physical and chemical properties <sup>[3-6]</sup>. Another nanostructure based on fullerenes and CNTs called "nanobuds" holds exceptional field emission properties <sup>[7]</sup>. A Y-shaped CNT junction displays rectifying and electrical switching properties, such that it can serve as a switching device <sup>[8]</sup>. Moreover, organized 2D and 3D CNT architectures can be fabricated to realize specific functional properties for a variety of meso- and macro-scale engineering applications. Hall et al.<sup>[9]</sup> revealed that the CNT networks can exhibit unusual mechanical properties such as negative Poisson's ratio. By infiltrating a polymer into a reticulate CNT (RCNT) architecture, CNT-network-based reinforced composites are formed to achieve superior mechanical properties <sup>[10]</sup>, originating from strong molecular-level coupling between reticulate CNTs and polymer chains. The RCNTs/polydimethylsioxane with high transparency, high conductivity, and excellent stretchability in addition to the facile fabrication, is a promising candidate as interconnects and electrodes for stretchable intelligent and functional devices <sup>[11]</sup>. Covalently bonded 3D CNT networks have also been produced at large scale <sup>[12]</sup>, in which an effective stress distribution in the network improves the mechanical strength of the materials. Computer-aided design and simulation of 2D and 3D nanostructures consisting of fragments of CNTs-junctions also helps to exploit their potentials <sup>[13-20]</sup>. For example, Romo-Herrera et al. <sup>[14]</sup> showed that 2D and 3D systems can be utilized for complex integrated nanoelectronic circuits due to specific paths of charges flowing through the nodes of the systems, and the 3D super-cubic and super-diamond architectures have the ability of supporting extremely high unidirectional stress. Despite the increasing interest in CNT architectures, nano-joining and assembly conforming 3D networks are still in very early stages.

Accordingly, in the present work we invoke concept of hierarchical nano-joining to propose new architectures comprised of fullerenes and SWCNTs. We present a systematical atomistic simulation study on the mechanical properties of the novel 3D spanned-fullerene nanotruss architecture.

## 2. Model and Methodology

We adopt a CNT (6,6) and a giant fullerene  $C_{372}$  with  $D_{2d}$  molecular symmetry as parent bricks for constructing novel covalent bonded 3D nano-truss systems. As illustrated in Figure 1, 3D nanostructures are built from a fullerene  $C_{372}$ . Three atomic pairs are added as patches (red atoms in Figure 1b) in the face of fullerene (green atoms in Figure 1a and 1b) to create an open-cage cluster with a terminal. This terminal is able to coaxially dock a (6,6) CNT segment (purple atoms in Figure 1c), forming three octagon rings dispersed at the junction. The truss-like 3D network with an all-sided coalescence of fullerenes with (6,6) CNTs is finally created as shown in Figure 1d, resembling a body center cubic (bcc) lattice. The mechanical responses of as-generated 3D nano-truss under tension are systematically investigated with respect to the connection CNT length *N* varying from 0 to 10.



Figure 1 (a) (d) Schematic illustration for constructing the unit of 3D spanned-fullerene nanotube nanotruss. (e) Perspective of 3D architecture models with  $3 \times 3 \times 3$  unit cells.

The full atomistic simulations are carried out using LAMMPS software package capable of running on large computing clusters. The adaptive intermolecular reactive empirical bond-order (AIREBO) potential <sup>[21]</sup> is used for carbon atomic interactions in the simulations. The cutoff parameter for the REBO part of the potential is set to be 2.0 Å as described by Shenderova <sup>[22]</sup> in order to avoid the spuriously high bond forces and nonphysical phenomenon during the fracture process. As-constructed architecture models with  $3 \times 3 \times 3$  unit cells (Figure 1e) are first quasi-statically relaxed by minimizing the total potential energy through a conjugate gradient method. The mechanical loads of uniaxial tension under deformation-control as our previous study <sup>[23]</sup>, are performed on 3D equilibrated structures until complete rupture of each specimen. The samples are deformed with a reasonable strain rate 0.0001/ps based on Nosé-Hoover thermostat. Stresses and strain are calculated every 1000 steps.

The nominal strain parallel to the direction of deformation is defined as

$$\varepsilon = \frac{L - L_0}{L_0} = \frac{\Delta L}{L_0},\tag{1}$$

where  $L_0$  and L are the equilibrium and the current length of the entire systems in the direction of loading.

Under uniaxial tension, the transverse repositioning of nanostructures perpendicular to the load axis gives a measure of the strain from which the Poisson's ratio can be calculated

$$\nu = -\frac{d\varepsilon_{\rm T}}{d\varepsilon_{\rm I}},\tag{2}$$

where  $\varepsilon_{\rm T}$  and  $\varepsilon_{\rm L}$  are the transverse and longitudinal strains, respectively.

#### **3. Results and Discussions**

A uniaxial tension test has been carried out to study the mechanical properties of fullerene 3D foam-like nanostructures formed by CNTs and fullerene. The basic 3D bcc-lattice nano-truss unit is displayed in Figure 1d. Figure 2 shows the stress-strain evolutions of 3D nanotruss with CNT length N varying from 0 to 10. Except for small N where linear elasticity was observed, the 3D nanostructures exhibits nonlinear elasticity and the CNT length plays a key role on the mechanical properties. The dense 3D network (small N) has more constraints that limit the realignment and bending of CNTs, and results in a linear behavior. A nonlinear up-swing behavior appears in the sparse network due to the increase of CNTs length, as in Figure 2. Such nonlinear stiffening behavior results from the different deformation mechanisms at different strain level, such as realignment and bending dominated deformation at smaller strain, and the stretching dominated deformation at larger strain. Subsequent sharp stress load drop reveals a permanent failure due to bond-breaking at the junction for all tests.



Figure 2 Stress–strain curves of 3D nano-truss networks with *N* varying from 0 to 10 under uniaxial tension.



Figure 3 Deformation dependence of the ratio of the transverse and longitudinal strains for the 3D networks under uniaxial tension.

An in-depth investigation on the Poisson's ratio is then performed. Figure 3 presents the calculated strain-dependent Poisson's ratio of the 3D networks. It can be seen that the CNTs length dominates the Poisson's ratio of the 3D networks. With N = 0, the 3D covalent pack of fullerenes exhibits a negative Poisson's ratio. The negative Poisson's ratio of 3D network is attributed to a reduction of absolute curvature in fullerene hub due to high constraint from direct covalent connection between fullerenes without participation of CNTs. The linkage of CNTs would actively involve the bending and stretching dominated deformation, and causes a different stress concentration on the fullerene

hub. The Poisson's ratio is strikingly strain-dependent, sign change from negative to positive when an extensional strain reach around 0.09, which suggests that the transverse strain begins to act in an opposite sense to the longitudinal strain.

Many cubic metals when stretched along the specific 110 off-axis direction become auxetic <sup>[24]</sup>. Accordingly, we conduct tension tests on the bcc-lattice 3D nano-truss network along the <110> orientation and the resulting stress–strain relations with *N* varying from 0 to 10 are shown in Figure 4. We again see clearly that the CNT length dominates the mechanical properties. The tensile stress, tensile stain and stiffness all decreases with the increase of the segment length *N* for the case under tension along the <110> direction. Compared with the Figure 3 we observe that both the tensile strain and tensile stress are smaller than those under <100> direction, resulting from a pure stretching of octagon rings in the fullerene hub. For large CNT segment length of nanotruss, the fracture strain, however, is significantly larger than those under <100> direction.



Figure 4 Stress-strain curves of 3D nano-truss networks with N varying from 0 to 10 under uniaxial tension.

The corresponding Poisson's ratio is determined and plotted in Figure 5. It can be seen that this bcc-latticed 3D network also exhibits a negative Poisson's ratio when tension is applied along the <110> direction. Figure 5c and 5d compare the value of  $-\varepsilon_{<-110>}/\varepsilon_{<110>}$  and  $-\varepsilon_{<001>}/\varepsilon_{<110>}$  as a function of CNTs length at a specific small strain  $\varepsilon_{<110>} = 0.01$ . It must be noted that this 3D network yields a very wide range of Poisson's ratios that are both controlled and tunable by virtue of the microstructural parameter — the length of CNTs. The magnitude of  $-\varepsilon_{<-110>}/\varepsilon_{<110>}$  and  $-\varepsilon_{<001>}/\varepsilon_{<110>}$  roughly covers a wide range from 0.4 to 0.3, and from 0.1 to 1.2, respectively. The spectacular change of  $-\varepsilon_{<001>}/\varepsilon_{<110>}$  appears in this 3D network exceeds 0.5, which is the threshold value for isotropic materials in the theory of elasticity. Interestingly, a dramatic "flip" behaviour of the Poisson's ratio from negative  $\rightarrow$  positive  $\rightarrow$  negative with increase of CNTs length appears (Figure 5c). The findings can be utilized on tailor-making auxetic CNT-fullerene networked nanostructures with the wanted properties. Two different mechanisms, involving curvature flattening and rigid mechanical model, are identified to be responsible for the "flipping" of Poisson's ratio.



Figure 5 (a) and (b) Deformation dependence of the ratio of the transverse and longitudinal strains,  $-\mathcal{E}_{<-110>} / \mathcal{E}_{<110>}$ and  $-\mathcal{E}_{<001>} / \mathcal{E}_{<110>}$  for the 3D networks under uniaxial tension, respectively. (c) and (d) Ratio of transverse and longitudinal strains as a function of CNT segment length *N* at  $\mathcal{E}_{<110>} = 0.01$ .

Visualizing the detailed structural evolutions of this 3D nano-truss provides insights on the structural and mechanical properties, such as the deformation mechanism, the negative Poisson's ratio and fracture modes. Figure 6 displays straining direction dependence of the representative atomic structural development of the 3D nano-truss. For N = 0, the initial side-view shows the porosity of the 3D nanostructures, analogous to the zeolite structure <sup>[25]</sup>, offering a possibility for molecular storage and filters. During the deformation, three stages can be identified: firstly, there is a curvature flattening process with the increase of the strain, as presented in the zoomed-in local structures of Figure 6a and 6c, which results in a negative Poisson's ratio. In this stage, the curvature-flattening dominates the deformation with no irreversible structural changes, triggering an expansion of pore between fullerenes as well as the fullerene cages. Secondly, the subsequent graphitic structure with negative curvature ultimately causes a contraction when the strain approaches a critical value. This is confirmed by the change of Poisson's ratio from negative to positive as shown in Figure 3. Finally, an additional strain increment leads to a fracture at the weak octagon rings at the junction. The fracture propagates in the plane perpendicular to the strain direction towards complete rupture, in which a number of monoatomic carbon chains formed, similar to what is widely observed in the stretching of pure CNTs. A longer CNT for spanning the fullerenes is exploited to tune the properties of this 3D networks. Particularly, sequential deformation configurations of the 3D network with N = 10 are displayed in Figure 6b and 6d. It can be noticed that the long length of CNTs brings a sparse 3D network, and orientation dependence of deformation mechanism on the 3D network with long CNTs length is also clearly observed. In addition, a different deformation mechanism is revealed by comparing with that of N = 0.



Figure 6 Size- and orientation- dependence on the atomic structural development of 3D networks under uniaxial straining. (a) Sequential deformation snapshots of 3D networks with N = 0 under <100> directional tension. The zoomed-in local atomic structures clearly illustrate the mechanism of negative Poisson's ratio. (b) Sequential deformation snapshots of 3D networks with N = 10 under <100> directional tension. The zoomed-in local atomic structures distinctly display the buckling of fullerene in the node of 3D network prior to the fracture. (c) Sequential deformation snapshots of 3D networks when N = 0 under <110> directional tension. The negative Poisson's ratio is explained by the zoomed-in local atomic structures. (d) Sequential deformation snapshots of 3D networks when N = 10 under <110> directional tension. The negative Poisson's ratio is explained by the zoomed-in local atomic structures. (d) Sequential deformation snapshots of 3D networks when N = 10 under <110> directional tension. The local potential energy shows how the high amount of stress during uniaxial tension resides on the fullerene nodes.

Three deformation stages are also observed from the overall tension processes for both loading directions. Straining along the <100> direction involves direct stretching of all the CNTs in the network, whereas half of CNTs in the network when deformed along <110> undergo direct tension because the axis of other CNTs is perpendicular to the tension direction. For the former case, straining along <100>, an initial tension of the system induces the angles change between CNTs, accompanying with the structural transformation of fullerene hub where the negative curvature structures become either flattening or more curved as in the zoomed-in local structure of Figure 6b. As clearly shown in the second zoomed-in local motif of Figure 6b, an excessive straining induces a striking inversion of a two-pentagon without bond breaking, which is similar to the inversion of a

two-pentagon nanocone via an indenter compression <sup>[26]</sup>. Finally, one octagon ring initially develops to a clean cleavage followed by rest fracturing, and the formation of monoatomic carbon chains. For the latter case of straining along <110>, an incipient straining also induces the change of angles as well as the structural change of the fullerene hubs. As expected, the zoomed-in top-viewed snapshots covered by dash square in Figure 6d show that the tension in <110> direction increases the view-plane-distance between fullerene hubs as a result of rigid mechanical models, indicating a negative Poisson's ratio. The mechanism of this negative Poisson's ratio differs with the case of N =0 in the absence of CNT segments. Beyond the tensile limit, excess angle change and the octagon rings damage occurs, generating morphology as displayed in third snapshot of Figure 6d, similar to a metallic plastic deformation. Further straining results in compete rupture with a clean cleavage. As a whole, the strong correlation between deformation mechanism and organizational parameters demonstrates a close structure–property relationship in this 3D nano-truss network.

## 4. Conclusions

Carbon-based nanomaterials have attracted significant attention due to their unique optical, electrical, thermal and mechanical properties. In our study, 3D nanotruss architecture is constructed by spanning fullerenes with single-walled carbon nanotube (SWCNT) super-bonds. The mechanical properties of this novel architecture are systematically investigated by full atomistic simulation. The deformation and fracture behavior of 3D periodic graphitic nanostructures are largely dictated by the inter-fullerene distance and loading orientation. Surprising negative Poisson's ratio observed in this 3D network is revealed to originate as a result of curvature-flattening or rigid mechanical model. The magnitude of Poisson's ratio is strongly dependent on the level of strain and CNT length. The insight on the deformation mechanism of these periodic graphitic nanostructures will facilitate the integration of low-dimensional materials towards high-dimensional organized structures to realize targeted multi-functional properties.

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