Supporting Information for

Mechanotunable Microstructures of Carbon Nanotube Networks

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This Supporting Information material includes

- Materials and Methods
- Figures and Captions

Materials and Methods

1. Coarse-grained molecular dynamics. As full-atom molecular dynamics simulations cannot access the carbon nanotube networks with current computing resources, we use a coarse-grained model for the carbon nanotubes. In this model, discrete beads interacting through bond and angle springs provide a description equivalent to the continuum mechanics model with specific tension stiffness, bending rigidity and intertube binding energy. Within each nanotube, the stretching energy contributions of two bonding beads are given by $E_T = k_T(r - r_0)^2/2$, where $k_T = YA/r_0$ is the spring constant relating to the tension stiffness, Y is the Young's modulus of the carbon nanotube, A is the cross-section area and r is the distance between two bonding beads with r_0 equaling equilibrium distance. The bending energy contributions of adjacent beads triplets are given by $E_B = k_B(1 + \cos\varphi)$, where $k_B = 2YI/r_0$ is the angular spring constant relating to the bending stiffness $D = YI$ and φ is bending angle within the triplet. D is calculated by performing full-atom MD simulations. I is the bending moment of inertia. In addition, we define the van der Waals interactions between beads in different carbon nanotubes by the Lennard–Jones formula $E_{pair} = 4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]$. The parameters can be found in Ref. 1.

2. Samples preparation. A two-dimensional periodic boundary condition is used for in-plane directions x and y. The length L and width W of the periodic simulation box are 240 nm and 120 nm respectively. (5, 5) carbon nanotubes with a length of 100 nm are first constructed with a uniform curvature, and deposited in a layer-by-layer manner subsequently.[2] The orientations of the nanotubes are uniformly distributed between 0 and π. The microstructures of the carbon nanotubes network are equilibrated using a Langevin thermostat before mechanical loading. To accelerate the equilibrium process, a

body force is initially applied and a rigid supporting substrate is added below to make the whole structure more compact, following the procedures in experiments.[3] After that, the force and substrate are both removed to maintain the membrane structure. The thermostat at 300 K is maintained for one microsecond till the fluctuation of total energy converges below 0.1%.

For the relatively large supercell used for the network here in our simulation, the distributions of intratube bond distances and angles are isotropic in the *x* and *y* directions. The thickness *h* of a buckpaper in our simulations is defined as the maximum distance in the *z* direction of the sample. We prepare several samples with varying initial carbon nanotube densities *n*. The thickness of the equilibrated network increases as a linear function of the mass density ρ in the beginning and then converges at 0.28 g/cm^3, corresponding to the equilibrium density of the network at the ambient condition. This value of mass density is close to the reported value for single-walled carbon nanotube buckypapers.[4]

3. Mechanical loading. Cycling loads are applied by deforming the simulated supercell. The loading rate *v* is 3 m/s. The equations of motion are integrated using a velocity-Verlet algorithm with a time step of 10 fs that ensures the numerical convergence of integration. The pressure in the transverse *y* direction is restrained as zero during the tensile loading process by using a Berendsen barostat. Tensile stress is calculated from the summation of virial stress over the buckypaper sample and the tensile force is calculated subsequently by multiplying the stress with the cross-section area. The deformation of the simulation box in both *x* and *y* directions is recorded for further strain analysis.

4. Pore size analysis. The pore size distribution of a carbon nanotube network is

analyzed by discretize the whole material into three-dimensional cubic grids. Each grid is denoted by a binary number (1 for carbon nanotubes or filled and 0 for pores or empty). The size of one pore is defined by diameter of the maximum sphere that can be contained in the clusters of empty grids.

References

(1) Cranford, S.; Buehler, M. J., *Nanotechnology* **2010,***21*, 265706.

(2) Xie, B.; Liu, Y.; Ding, Y.; Zheng, Q.; Xu, Z., *Soft Matter* **2011,***7*, 10039-10047.

(3) Xu, M.; Futaba, D. N.; Yamada, T.; Yumura, M.; Hata, K., *Science* **2010,***330*, 1364-1368.

(4) Whitby, R. L. D.; Fukuda, T.; Maekawa, T.; James, S. L.; Mikhalovsky, S. V., *Carbon* **2008,***46*, 949-956.

Figures and Captions

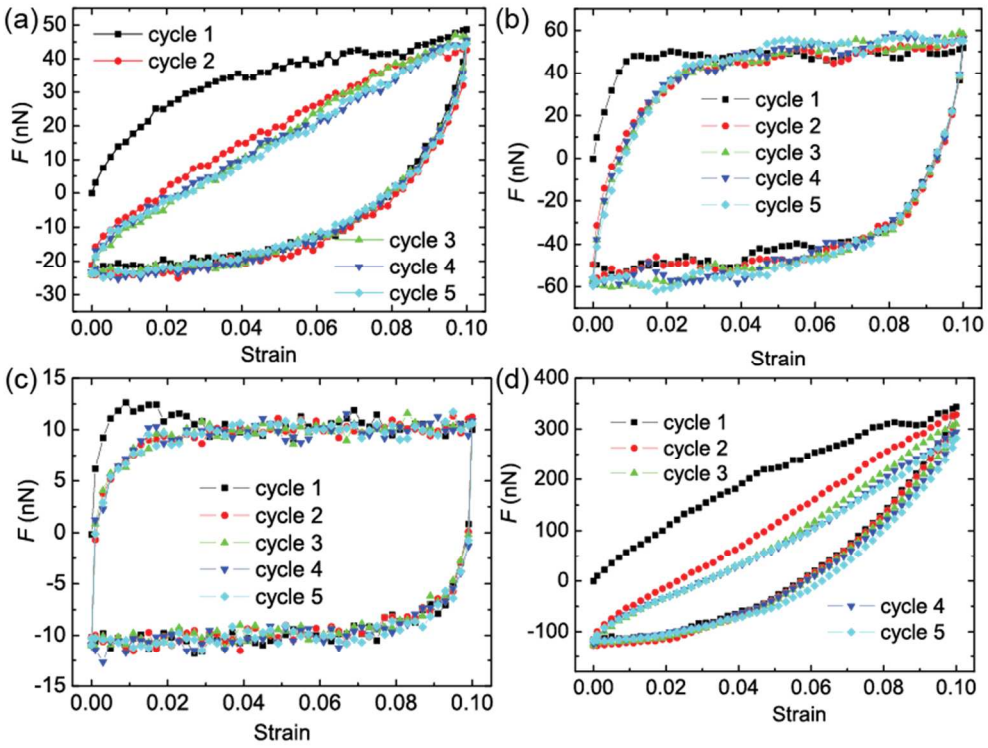

Figure S1. Mechanical responses of carbon nanotube networks in response to cycling strain loading with maximum amplitude 0.1. The bending stiffness D is modified into $0.1D_0$ and $10D_0$ in (a) and (b), and the interfacial cohesion energy γ is modified into $0.1\gamma_0$ and $10\gamma_0$ in (c) and (d), respectively.

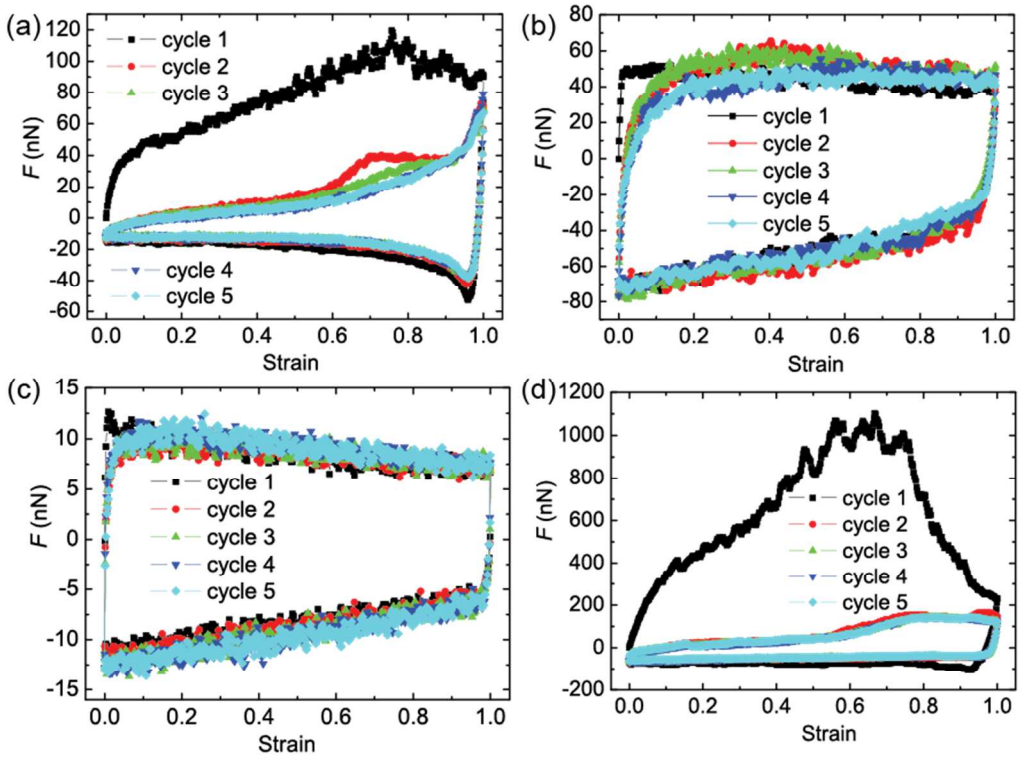

Figure S2. Mechanical responses of carbon nanotube networks in response to cycling strain loading with maximum amplitude 1.0. The bending stiffness D is modified into $0.1D_0$ and $10D_0$ in (a) and (b), and theinterfacial cohesion energy γ is modified into $0.1\gamma_0$ and $10\gamma_0$ in (c) and (d) respectively.