Supporting Information

Breakdown of Hooke's Law at Nanoscale – 2D Materials-based Nanospring

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S1. Different boundary conditions

Graphene nanosprings (NSs) with two different boundary conditions (B1 and B2) were examined, i.e., introducing a same initial pitch length to one or both boundary coil(s) as shown in **Figure S1**a. The NS has six coils (including the boundary coil) and a width of ~ 1.0 nm. Initial even pitch length of $6.0d_0$ was introduced to the structure (excluding the boundary coils). As shown in Figure S1a, the NSs experience inhomogeneous transition either during energy minimization (B2) or relaxation (B1). This inhomogeneous transition phenomenon is well captured by the potential energy profile (Figure S1b). For instance, for the case of B1, the inhomogeneous transition occurs during relaxation, which induces a clear potential energy drop. To further test that, we also checked these two boundary conditions at a temperature of 300 K, all of which yield to the same results.

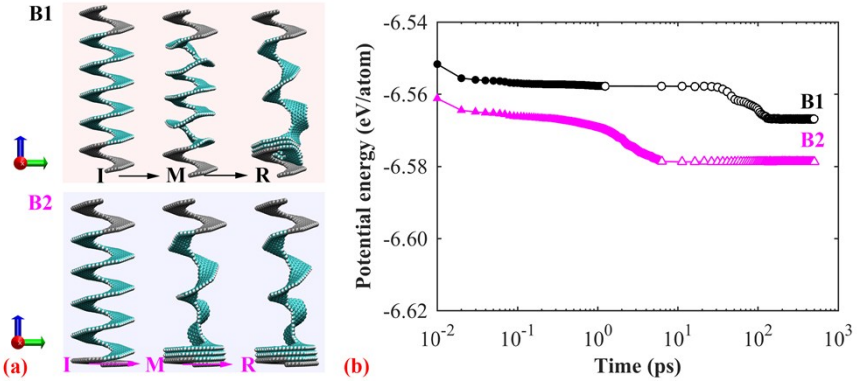

Figure S1. Stable inhomogeneous structural transition. (a) Atomic configurations of the graphene NS with two different boundary conditions (B1 and B2). I, M and R represent the

structure at initial, after energy minimization and relaxation process, respectively. (b) Potential energy profile during structural transition. Solid markers represent energy minimization and open markers denote relaxation process.

S2. Inhomogeneous structural transition

Five additional groups of graphene NSs with different structural parameters were tested. In Group I, we considered NSs having six coils under a temperature from 50 to 400 K and the pitch length ranges from $1.4d_0$ to $10.0d_0$. For Group II, NSs with a coil number of five, seven or eight were considered. An even pitch length ranging from $1.4d_0$ to $10.0d_0$ was applied to each model. For Group III, we kept the NS having six coils but with a randomly distributed pitch length as $\varepsilon_i d_0$ ($\varepsilon_i < 11$, which was chosen to ensure no bond breaking), while keeping the mean pitch length as $4.0d_0$ or $9.0d_0$. Five samples were constructed for each mean pitch length. In Group IV, NSs with varying coil number from 10 to 30 (with a fixed nanoribbon width of ~ 1.0 nm) were examined, and Group V considered the NS with a nanoribbon width ranging from ~ 0.5 to ~ 2.0 nm (with six coils). Each NS has an initial even pitch length about ~ $6.0d_0$. The structural parameters of these NSs are summarised in **Table S1**.

Table S1 Structural parameters of the additional NS models being examined. R represents the NS has a randomly distributed pitch length.

Group	Pitch length (d_0)	Coils No.	Outer radius (nm)	Inner radius (nm)	Width (nm)
I	1.4~10	6	1.84	0.74	0.96
II	1.4~10	5	1.84	0.74	0.96
	1.4~10	7	1.84	0.74	0.96
	1.4~10	8	1.84	0.74	0.96
III	4.0 (R)	6	1.84	0.74	0.96
	9.0 (R)	6	1.84	0.74	0.96
IV	6.0	10	1.84	0.74	0.96
	6.0	15	1.84	0.74	0.96
	6.0	20	1.84	0.74	0.96
	6.0	25	1.84	0.74	0.96
	6.0	30	1.84	0.74	0.96
V	6.0	6	1.84	0.98	0.75
	6.0	6	1.84	1.23	0.53
	6.0	6	2.09	0.74	1.17
	6.0	6	2.34	0.74	1.38
	6.0	6	2.58	0.74	1.60
	6.0	6	3.07	0.74	2.02

All simulations showed a consistent transition phenomenon from homogeneous to inhomogeneous configuration after structural relaxation. These simulation results clearly

verified that the inhomogeneous structure is energetically preferable than its homogeneous counterpart. **Figure S2** compares the potential energy change of the five different samples with a same average pitch length of $9.0d_0$. For illustration, the transition process for three of the tested samples are recorded in:

- **Movie S1**: NS structure with 10 coils – in Group-IV
- **Movie S2**: NS structure with a very small nanoribbon width of 0.53 nm – in Group-V
- **Movie S3**: NS structure with a large nanoribbon width of 2.02 nm – in Group-V

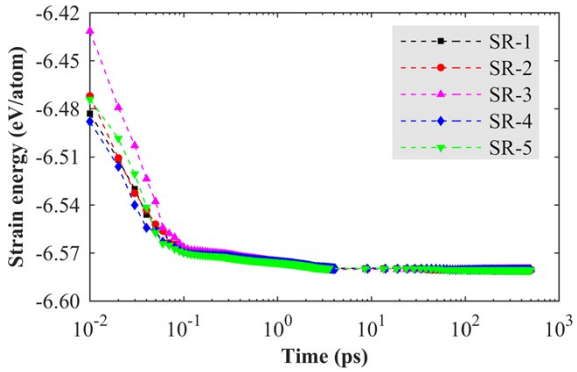

Figure S2. Comparisons of the potential energy of the five NS structures with randomly distributed strain under relaxation (Group-III).

Figure S3 compares the relaxation results for the NS (with six coils) at the temperature of 1 K, 50 K, 100 K, 200 K, 300 K, and 400 K with the pitch length of $5.0d_0$ (in Group I). As is seen, although the morphology has certain degree of difference, the NS retains an inhomogeneous configuration after relaxation.

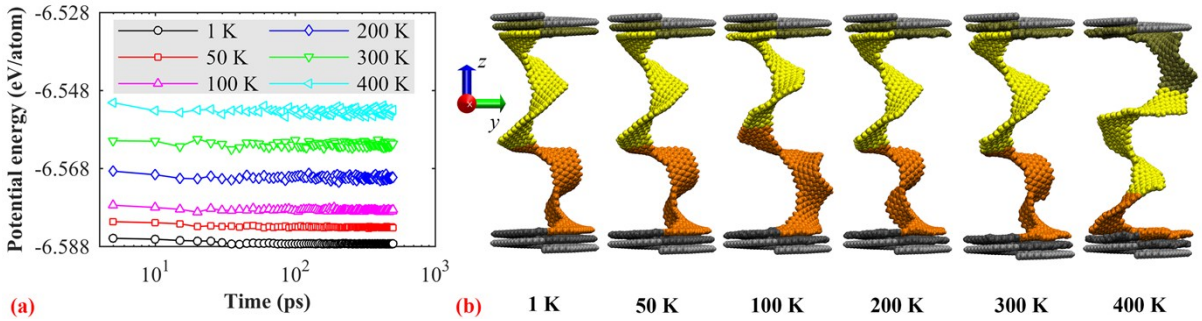

Figure S3. Representative relaxation results of the NS under different temperature. (a) The potential energy as a function of time for the NS under different temperature; and (b) the atomic configurations after relaxation (Group I).

S3. Tensile deformation of graphene NS

The strain energy curves obtained from the tensile deformation for a graphene NS with only one active coil. The NS has seven turns in a close packed configuration (i.e., pitch length of d_0), with three coils in each end being fixed during the tensile deformation. The

portion of the strain energy curve (due to the covalent bond deformation) when the NS reaches the maximum inhomogeneous structure is used for the fitting to derive the elastic constant k and the equivalent displacement δ_e (for a single coil). In this work, the covalent bond deformation energy is described by the REBO and torsion terms in the AIREBO potential. **Figure S4**a shows the strain energy curve and the fitting result, from which k is around 0.01 eV/Å^2, and δ_e is around 28 Å. Figure S3b shows the tensile force as a function of strain, from which the tensile force is found to increase significantly during the homogeneous deformations stage. At the strain of ~ 11%, the force decreases and the homogeneous deformation starts to transit to inhomogeneous deformation. During the inhomogeneous deformation stage, the tensile force is nearly a constant, which deviates from the Hooke's law.

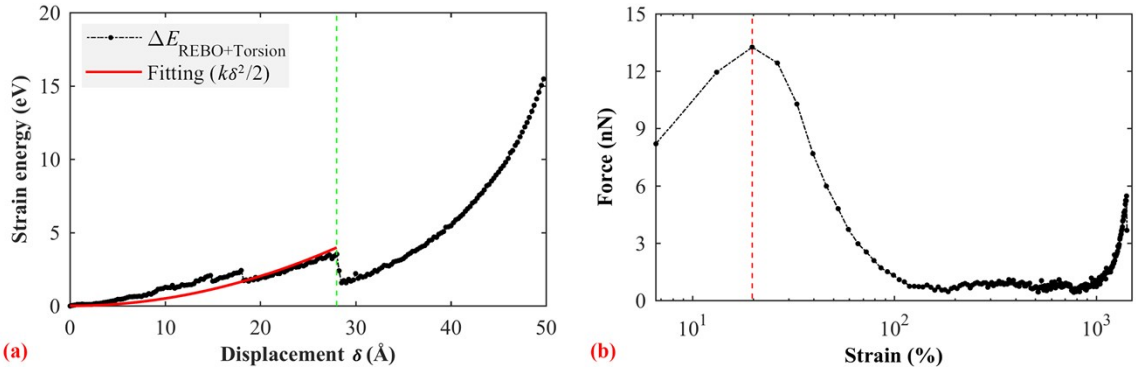

Figure S4. Tensile deformation of graphene NS with a single active coil. (a) Strain energy of as a function of displacement; (b) Tensile force as a function of strain.

S4. Tensile force of graphene NS with different initial pitch length

Figure S5 compares the tensile (stretch) force of the graphene NS with different initial pitch length after structural transition. As is seen, with the same coil number (N), the tensile force is nearly a constant fluctuating around a certain value. More interesting, such feature of the tensile force is not changing for the NS with larger or smaller coil numbers. Recall the series spring model, the nearly constant force indicate that the deflection of each spring element is almost uniform, which does not change with the coil number or the initial pitch length. Refer to the atomic configurations of the NS after structural transition, the final tensile force within the spring is originated from the interactions between the end coils and the boundary coils. Considering the similar boundary configurations after relaxation, it is reasonable to observe a nearly constant tensile force at different initial pitch length (or displacement).

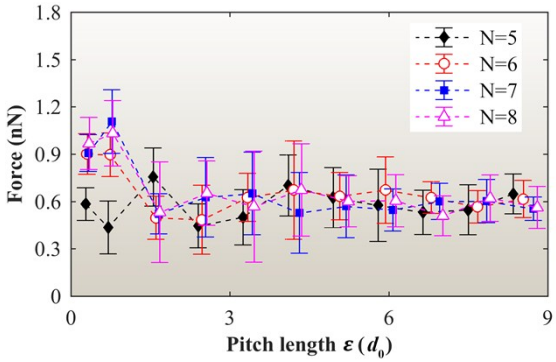

Figure S5. Tensile force of graphene NS with different initial pitch length after structural transition.

S5. Factors that determine the initiation of the structural transition

Figure S6 illustrates the combined effects on the transition phenomenon from the equivalent displacement δ_e and elastic constant k as indicated by the two solutions for $\Delta E = 0$ (i.e., δ_e and δ_s). Hereby, we continuously use the graphene NS as the benchmarking system, i.e., the elastic constant k is about 0.01 eV/Å^2 and the cross-sectional area is around 740 Å^2. In general, δ_s decreases when δ_e increases for a given elastic constant, and a larger k leads to a smaller δ_s. As divided by the line of $\delta_s = \delta_e$, in the upper region, δ_s is larger than δ_e, in which case the NS experiences structural transition for any displacement smaller than δ_e, as demonstrated in Figure S5 for the NS with an elastic constant of 2.0k. In the lower region, δ_s is smaller than δ_e, the transition thus occurs only if the displacement is smaller than δ_s. For both cases, the displacement should be larger than a certain value δ_{min}, which is the minimum displacement that triggers the structural transition.

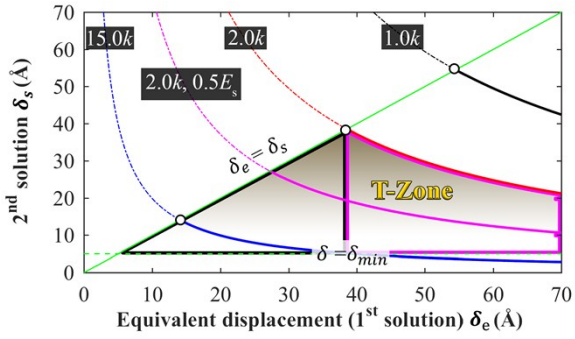

Figure S6. The transition map for the NS with varying elastic constant and maximum displacement. δ_e and δ_s are the two solutions for $\Delta E = 0$. T-Zone denotes the transition zone. A cross-sectional area (~ 740 Å^2) estimated from the examined graphene NS is used in both figures.

It is apparent that to avoid the structural transition, the solutions for $\Delta E = 0$ should be smaller than δ_{min}. According to Figure S5, for the NS with a given elastic constant or surface energy, this means $\delta_s = \delta_e < \delta_{min}$. Simplifying Eq. 4 in main text as

$$\Delta E = a\delta^2 + b\delta + c$$

(S1)

where $a = -nk/2$, $b = (nk\delta_e^2 + 2nAE_s)/2\delta_e$, and $c = -nAE_s$. If the two solutions are the same, then $b^2 - 4ac = 0$. In other words,

$$\delta_e = \delta_s = -b/2a = \delta_e/2 + AE_s/\delta_e k$$

(S2)

Thus δ_e is related with the surface energy and elastic constant by

$$\delta_e = \sqrt{2AE_s/k}$$

(S3)

Therefore, to avoid the structural transition δ_e should be smaller than δ_{min}, i.e., $\delta_{min} > \sqrt{2AE_s/k}$.

S6. Non-Hookean deformation under different temperature

The graphene NS with six total coils were further tested at the temperature of 1 K, 50 K, 100 K, 200 K, 300 K and 400 K. As compared in **Figure S7**, despite certain fluctuations at higher temperature, the strain energy curve is nearly overlapped with each other. Such results indicate the same non-Hookean deformation under different temperatures.

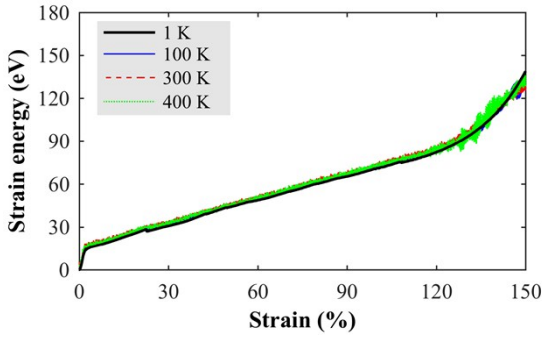

Figure S7. Tensile strain energy of graphene NS as a function of strain at the temperature of 1 K, 100 K, 300 K, and 400 K.