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Predicted Confinement-Enhanced Stability and Extraordinary Mechanical Properties for Carbon Nanotube Wrapped Chains of Linear Carbon

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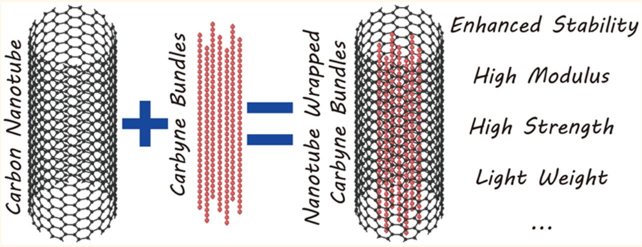

ABSTRACT: The demand for high-modulus, high-strength, lightweight materials has continuously driven the bottom-up assembly of carbon nanostructures into high-performance bulk carbon materials, such as graphene sheets and carbon nanotube yarns. Carbyne, often called linear carbon, has a higher predicted gravimetric modulus and gravimetric strength than any other form of carbon, but possibly reacts under near-ambient conditions because of the extended sp^1 hybridization. The successful fabrication of carbon nanotube wrapped single carbyne chain (Shi *et al. Nat. Mater.* 2016, *15*, 634) suggests the possibility of carbyne's bulk production. Herein, we designed a type of carbon assembly that includes a possibly large array of carbyne chains confined within a single-walled nanotube sheath (nanotube wrapped carbynes, NTWCs), in which carbyne chains act as reinforcing building blocks, and the carbon nanotube sheath protects the multiple carbyne chains against chemical or topochemical reaction. We showed that NTWCs exhibit confinement-enhanced stabilities, even when they contain multiple neighboring carbyne chains. We developed a mechanics model for exploring the mechanical properties of NTWCs. On the basis of this model, the gravimetric modulus (and strength) of NTWCs was predicted to increase from 356.4 (50.25) to 977.2 $\mathrm{GPa{\cdot}g^{-1}{\cdot}cm^3}$ (71.20 $\mathrm{GPa{\cdot}g^{-1}{\cdot}cm^3}$) as the mass ratio of carbyne carbons to sheath carbons increases, which is supported by atomistic simulations. The highest calculated gravimetric modulus and strength of NTWCs are 174.2% and 41.7%, respectively, higher than those of either graphene or carbon nanotubes. The corresponding highest values of engineering modulus and strength of NTWCs with a density of 1.54 $\mathrm{g{\cdot}cm^{-3}}$ are 1505 and 109.6 GPa, respectively. Hence, NTWCs are promising for uses in high-modulus, high-strength, lightweight composites.

KEYWORDS: *carbyne, linear carbon, nanotube confinement, first-principles calculations, mechanical properties of carbon*

Carbon can be formed into a host of different allotropes having various hybridization of the electronic orbitals and coordination,[1] and considerable effort has been devoted to these allotropes and their assemblies during the past decades.[2−8] From carbon nanotube (CNT)[9] and graphene[10] to carbyne,[11] carbon nanostructures have promised exceptional stiffness and strength. Lee *et al.*[12] obtained a Young's modulus of about 1.0 TPa and a tensile strength of 130 GPa for graphene by using nanoindentation experiments, which agrees with predictions from first-principles calculations for defect-free graphene.[10] Although the strength of defect-free CNTs is predicted to be over 100 GPa,[9,13] the tensile strength measured from most experiments is only about 30 GPa. For example, Yu *et al.* measured the tensile strength of single-walled carbon nanotubes (SWNTs, 13−52 GPa)[14] and multiwalled carbon nanotubes (MWNTs, 11−63 GPa)[15] by stretching CNT bundles. Afterwards, tensile strengths of double-walled carbon nanotubes (DWNTs, 17−43 GPa),[16] triple-walled carbon nanotubes (TWNTs, 13−46 GPa),[16] and MWNTs (10−66 GPa)[17] were measured. It is worth mentioning that Peng *et al.*[18] measured a Young's modulus of 1049 GPa and a tensile strength of 110 GPa for a MWNT sample by *in situ* tensile tests, approaching the theoretical prediction for defect-free CNTs.[9]

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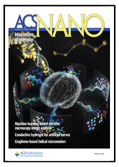

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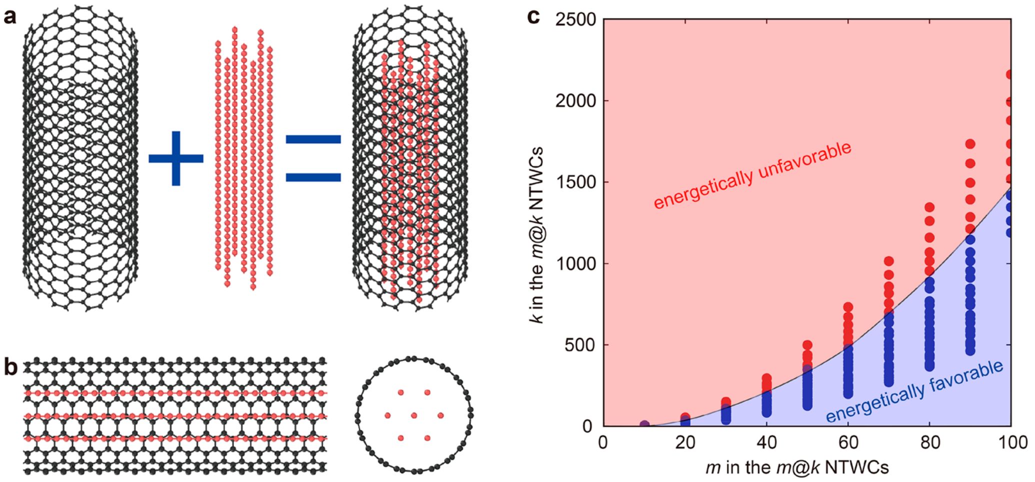

Figure 1. Illustration and energetic stability of NTWCs. (a) Illustration of a 10@7 NTWC and (b) longitudinal and cross-sectional views of this NTWC. (c) Energy map of NTWCs.

Notably, most experimentally measured stresses for MWNTs are calculated as the force per effective cross-sectional area of the outer shell, because of the observed "sword-in-sheath" fracture mode of MWNTs. If the engineering modulus and strength are calculated by using the cross-sectional area of the whole MWNT, these properties would be greatly reduced. For example, it can be expected that the modulus (1049 GPa) and strength (110 GPa) of a MWNT obtained in the previous work (calculated by normalizing the tensile force by the cross-sectional area of the outer shell of a MWNT)[18] would largely reduce to the engineering modulus and strength if the total cross-sectional area of the entire MWNT was used. More recently, Liu *et al.*[11] performed a computational study of the properties of a carbyne chain using first-principles calculations, and obtained a Young's modulus of 32.7 TPa and a tensile strength of 2501 GPa by adopting an effective mechanical diameter of 0.772 Å, which was derived from an equivalent continuum elasticity representation of carbyne. Similar to the case for CNTs, the cross-sectional area is diversely determined for carbynes, which primarily makes the reported high values of modulus and strength controversial. For example, when the cross-section area of a carbyne chain is adopted as 0.468, 3.14, and 11.22 Å^2, the reported values of the Young's modulus of carbyne in different literature become 32.7, 4.63, and 1.35 TPa, respectively.[19]

To exploit the mechanical properties of carbon nanostructures on the macroscopic scale, they must be assembled into bulk materials. For example, CNTs have been assembled into yarns having axial CNT orientation[5,20,21] and graphene platelets organized into bulk sheets having in-plane platelet orientation.[4,6] To achieve high-modulus and high-strength bulk carbons, two strategies have been developed: (1) Choosing high mechanical performance carbon nanostructures and improving the quality of these nanostructures, for example, modifying the chemical structures of graphene platelets;[22−24] (2) optimizing the assembly of carbon nanostructures, for example, increasing the alignment and density of CNTs.[25] Despite much progress made in the fabrication of high-modulus, high-strength carbon assemblies, the upper bounds on the modulus and strength of bulk carbon materials are still left unknown.

Carbyne's predicted modulus and strength are greater than any known material, including diamond, CNTs, and graphene,[11,26] and this encourages considering assemblies containing carbyne chains. However, because of sp^1 hybridization, carbyne has a much higher energy than graphitic carbons, and some materials containing carbyne chains even explode.[3,27,28] The high reactivity makes carbyne chains prefer to crosslink and degrade into more stable forms.[29−32] Hence, the existence of carbyne and bulk carbyne has long been questioned. Fortunately, a few methods for the synthesis of carbyne chains have been developed, including using end-capping groups for stabilization[33−35] and using CNTs as confining hosts.[36−38] By capping the carbyne chains with end-groups that separate different molecules to reduce the possibility of crosslinking, Tykwinski and Chalifoux have synthesized carbyne segments containing 44 carbon atoms.[33] Moreover, the longest carbyne chain (containing over 6000 atoms) has been recently synthesized inside a DWNT,[37] demonstrating that long carbyne chains can be produced in protected environments. In addition, atomistic simulations show that the carbyne chain within the core of a SWNT remains intact without dissociation up to 4200 K, while a free-standing carbyne chain curls upon itself and decomposes with several broken bonds at a temperature of 3000 K.[39] The improved thermodynamic stability is attributed to the confined geometry, in which van der Waals force between the carbyne chain and the nanotube sheath matters. Despite much progress made in the synthesis of carbyne chains, how to make use of the mechanical properties of carbyne chains on the macroscopic scale is an open issue.

In this work, we designed a type of carbon assembly that includes a possibly large array of carbyne chains within a SWNT sheath, that is, nanotube wrapped carbynes (NTWCs, as illustrated in Figure 1a and b). In this assembly, the SWNT is designed to densely wrap the carbyne chains. The CNT sheath can hinder the topochemical polymerization of carbyne chains and more generally protect these chains against chemical reactions. In this study, we first investigated the stabilities of NTWCs, which demonstrate the confinement-enhanced stabilities. Afterwards, we developed a mechanics model to predict the gravimetric stress-strain curves of NTWCs based on the mixture rule of composites. With an increasing number of carbyne chains within a SWNT, the gravimetric modulus and strength of NTWCs are predicted to increase from 356.4 and 50.25 to 977.2 and 71.20 GPa·g^{-1}·

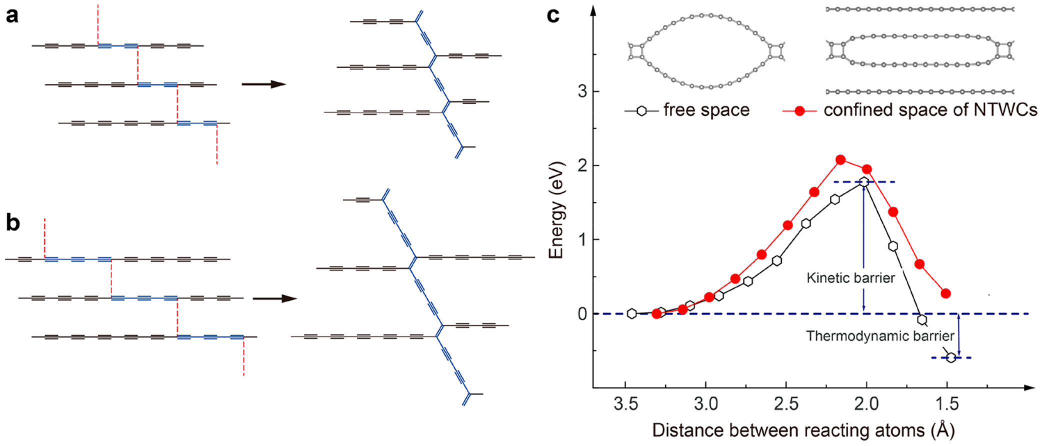

Figure 2. Possible inter-carbyne-chain reactions of NTWCs. Illustration of the solid-state reaction of neighboring carbyne chains by (a) 1,4-addition and (b) 1,6-addition polymerization. The dashed lines connect the reacting carbon atoms for these reactions. (c) Calculated dependence of free energy on the distance between reacting carbons in neighboring carbyne chains for the formation of four-membered rings between these chains in free space and in confined space between two immobile, parallel graphene sheets. This separation is sufficiently large to allow the parallel arrangement of two carbyne chains in the diameter direction. Insets are illustrations of four-membered crosslinks formed between free-stranding carbyne chains and that formed between carbyne chains that are confined between graphene sheets, respectively.

cm^3, respectively, which are supported by atomistic simulations. The engineering Young's modulus and tensile strength of NTWCs are also discussed and compared with those of other high mechanical performance carbons.

RESULTS AND DISCUSSION

Confinement-Enhanced Stabilities of NTWCs. Since material stability has great importance for applications, the stabilities of the NTWCs must be investigated. If too many carbyne chains are assembled into a particular diameter CNT, the interaction between carbyne chains, and the carbyne chains and the CNT sheath will become repulsive, which makes the NTWC less energetic preferable and thus more difficult to fabricate. Hence, these interaction energies should be made favorable by suitably selecting the number of carbyne chains that are incorporated within a given diameter SWNT.

Empirical atomistic simulations were used to determine the interaction energies resulting from confining different numbers of carbyne chains within a particular diameter CNT. The SWNT sheath for a NTWC is characterized by a chiral index of (m, n). In this work, $m = n$ because only armchair CNTs are considered. The number of carbyne chains within a NTWC is indicated by the index (k). Hence, a NTWC can be named $m@k$. NTWCs having different m and k were constructed and their structures were optimized. The calculated equilibrium structure of a 10@7 NTWC is illustrated in Figure 1a and b. In the atomistic simulations, the criteria for determining energetically preferable NTWCs is the binding energy, which is defined as the sum of the energy of noncollapsed SWNT and the energy of noninteracting carbyne chains minus the total energy of the assembled NTWC (normalized per atom). This binding energy must be higher than zero in order for the carbyne chains to infiltrate into a noncollapsed CNT sheath. The energy map for NTWCs is shown in Figure 1c, in which the isoline of 0 meV/atom for binding energy is here defined as the boundary between energetically unfavorable NTWCs and energetically favorable NTWCs. The energetically favorable NTWCs appear when the distance between carbyne chains, and the distance between carbyne chains and the SWNT sheath are larger than approximately 3.4 Å. For a particular (m, m) SWNT, the maximum number of carbyne chains that can be assembled into the SWNT (while providing a binding energy greater than zero) is defined as the maximum permissible number (k_{max}), and these assemblies are named $m@k_{max}$ NTWCs. Since k_{max} is approximately proportional to the cross-section area of a SWNT sheath, while the diameter of the sheath is proportional to m, it is expected that k_{max} is approximately proportional to m^2. However, some discontinuities appear in the simulations, since m and k_{max} must have integer values (Figure 1c).

Furthermore, the thermodynamic stabilities were investigated as follows. Possible chemical instabilities of NTWCs may arise (1) from reactions between NTWC and surrounding molecules, (2) from reactions between the carbyne chains and the SWNT sheath, and (3) from inter-carbyne-chain reactions (Figure S1). First, considering that defect-free CNTs are almost chemically inert, the reactions between NTWC and surrounding molecules can be inhibited by the SWNT sheath. Regarding stability with respect to reactions between the carbyne chains and the SWNT sheath, the absence of experimentally observed reactions of a single carbyne chain with a surrounding SWNT for temperatures up to 1460 °C[37] suggests that such reactions will not occur for bundles of carbyne chains enclosed in a SWNT sheath, as long as the carbyne chains are not so densely packed that they are subjected to high pressures. Additionally, Wang *et al.*[39] used atomistic simulations to find that a single carbyne chain in the core of a CNT remains intact without dissociation up to 4200 K, while a free-standing carbyne chain curls upon itself and decomposes by bond breaking at a temperature of 3000 K.

The stability of NTWCs with respect to inter-carbyne-chain reactions is of special interest, since such reactions can make polyynes explosive.[27,28] Depending on the packing of diacetylene groups, triacetylene groups, or longer polyyne groups in neighboring carbyne chains, 1,4-addition, 1,6-addition, or higher-addition polymerization (Figure 2a and b) potentially occur.[40] In fact, 1,4-addition polymerization commonly occurs for conjugated diynes, triynes, and tetraynes, and 1,6-addition polymerization has been observed for a specially engineered triyne crystal.[41,42] These polymerizations

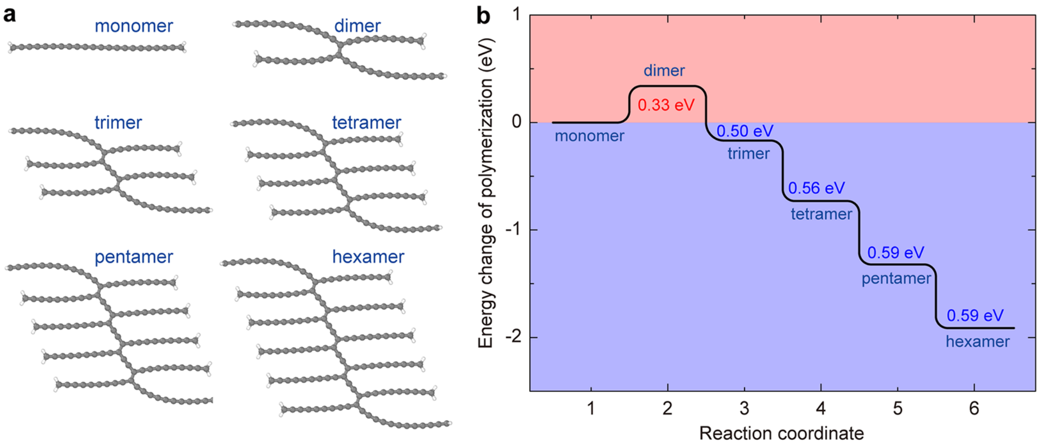

Figure 3. Reaction diagram for solid-state polymerization of diacetylene groups in finite-length carbyne chains terminated by hydrogen atoms. (a) Calculated configurations of carbyne chains after 1,4-addition polymerization of diacetylene groups in different numbers of carbyne chains. (b) Energy change on 1,4-addition reaction of diacetylene groups in 2 (for the dimer) to 6 (for the hexamer) finite-length carbyne chains.

can occur rapidly, and the corresponding heat release can be sufficient to cause an explosion.[3] For example, this heat of polymerization of PTS crystals is −36.5 kcal/mol.[43] Also, the reaction of neighboring acetylene groups by forming four-membered rings is known.[40] Similarly, the formation of crosslinks between carbyne chains was observed in experiments[31] because the *sp* carbon atoms tend to react and crosslink to form sp^2 or sp^3 carbon structures.[44] However, inter-carbyne-chain reactions in the confined space of NTWCs have not yet been investigated.

The bond angle changes associated with these reactions will cause local curvature of carbyne chains in free space.[11] However, there is little room for such configuration changes when densely packed carbyne chains are confined within NTWCs. Hence, we expected that confining carbyne chains inside SWNTs would provide additional barriers for these reactions. To verify this expectation, we performed density functional theory (DFT) calculations to quantify the energy barriers for inter-carbyne-chain crosslinking reactions in confined space and free space. Guided by the evidence for the formation of four-membered rings,[45] we modeled formation of such rings as a representative inter-carbyne-chain crosslinking reaction (Figure 2c). To minimize computational cost, a model of carbyne chains confined between two immobile graphene sheets was constructed for calculating the energy barrier during the crosslinking reaction. For comparison, inter-carbyne-chain crosslinking reactions in free space were also modeled (Figure 2c, inset). The inter-carbyne-chain crosslinking reactions in free and confined spaces are shown in Movies S1 and S2, respectively. The energy profiles for four-membered-ring formation by crosslinking inter-carbyne-chains in both free and confined spaces, calculated by DFT, are shown in Figure 2c. First, the free energy after inter-carbyne-chain reactions decreases by 0.59 eV in free space, while the free energy increases by 0.27 eV after inter-carbyne-chain reactions in confined space, indicating the confinement-induced transition of crosslinking reactions from thermodynamically favorable to unfavorable. Second, the kinetic energy barrier for inter-carbyne-chain reactions in confined space (2.08 eV) is slightly higher than that in free space (1.78 eV). This is because spatial confinement reduces the room for the crosslinking reaction (Figure 2c) and thus raises the system energy for the reaction, resulting in the increased barriers for the crosslinking reaction in a confined space.

Molecules containing diacetylene groups or longer groups of directly connected acetylene groups (like for triynes, tetraynes, and carbyne) are well known to polymerize in the solid state by addition polymerization if these groups in parallel molecules are optimally packed in the solid state.[40−43] Hence, this reaction must be considered when examining the stability of an array of parallel carbyne chains within a NTWC. As shown in Figure 2a, 1,4-addition polymerization of diacetylene groups in neighboring carbyne chains causes such a large increase in interchain separation that these reactions will be energetically unfavorable for densely packed carbyne chains within NTWCs. To be specific, since the separation between neighboring carbyne chains is about 3.7 Å (reasonably close to the van der Waals diameter of carbon, 3.4 Å) and the separation of the carbyne chains near to the polymerization site is about 4.9 Å, polymerization will increase volume (or increase pressure if the carbyne chains are laterally constrained with respect to volume increase). Similarly, 1,6- and higher addition polymerizations are likewise energetically more unfavorable within NTWCs because they necessitate even larger volume increases. Furthermore, more than two parallel carbyne chains must react before the reaction product (with associated radicals) has a lower energy than the reacting chains (Figure 3), even when such carbyne chains are free to separate without a substantial energy penalty.[43] In summary, solid-state reactions are predicted to be limited for NTWCs because of the confinement of carbyne chains, which improves their stability.

Extraordinary Mechanical Performance of NTWCs. To obtain the intrinsic mechanical properties, and avoid controversies regarding the cross-sectional area, gravimetric stress (σ_g) can be used, which is defined as the tensile stress of a material (σ) divided by the original mass density (ρ). By neglecting the small contribution of intermolecular nonbond interactions on the stress in the chain orientation direction, the gravimetric stress of NTWCs as a function of the nominal strain (ε) can be theoretically derived as the sum of contributions from the SWNT sheath and the wrapped carbyne chains:

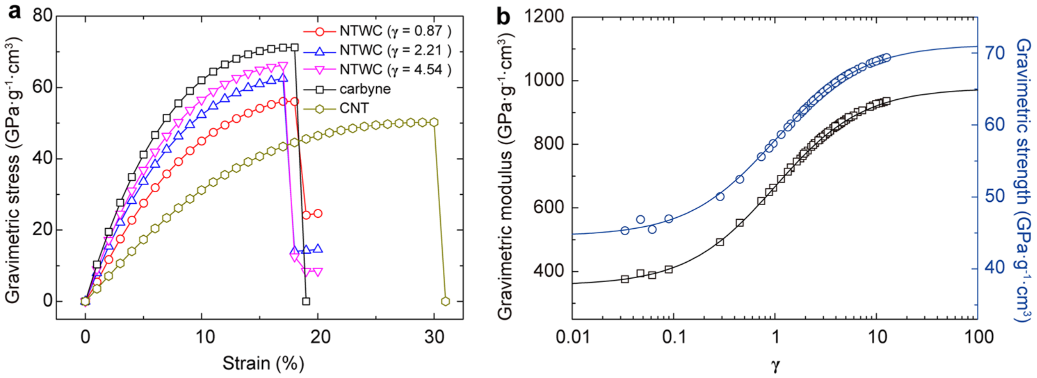

Figure 4. Gravimetric mechanical properties of NTWCs. (a) Gravimetric stress-strain curves of typical NTWCs, as compared with a carbyne chain and CNT sheath. (b) Gravimetric modulus and strength of NTWCs as a function of the mass ratio of carbyne carbons to sheath carbons. The lines are the theoretical predictions from eq 1 and the dots are from direct atomistic simulations.

$$\sigma_{\mathrm{g}}(\varepsilon) = \sigma(\varepsilon)/\rho = \frac{k\lambda_{\mathrm{carbyne}}\sigma_{\mathrm{g}}^{\mathrm{carbyne}}(\varepsilon) + m\lambda_{\mathrm{cnt}}\sigma_{\mathrm{g}}^{\mathrm{cnt}}(\varepsilon)}{k\lambda_{\mathrm{carbyne}} + m\lambda_{\mathrm{cnt}}} = \frac{\gamma\sigma_{\mathrm{g}}^{\mathrm{carbyne}}(\varepsilon) + \sigma_{\mathrm{g}}^{\mathrm{cnt}}(\varepsilon)}{\gamma + 1} \quad (1)$$

where $\sigma_{\mathrm{g}}^{\mathrm{carbyne}}(\varepsilon)$, $\sigma_{\mathrm{g}}^{\mathrm{cnt}}(\varepsilon)$, and $\sigma_{\mathrm{g}}(\varepsilon)$ are the gravimetric stresses of elastically deformed carbyne, CNT, and NTWC under a tensile strain of ε, respectively. The mass ratio of carbyne carbons to sheath carbons for a *m*@*k* NTWC is $\gamma = k\lambda_{\mathrm{carbyne}}/m\lambda_{\mathrm{cnt}}$, where $m\lambda_{\mathrm{cnt}}$ and $k\lambda_{\mathrm{carbyne}}$ are the linear mass densities of CNT sheath and the core of carbyne chains, respectively. This equation will degenerate into $\sigma_{\mathrm{g}}(\varepsilon) = \sigma_{\mathrm{g}}^{\mathrm{cnt}}(\varepsilon)$ and $\sigma_{\mathrm{g}}(\varepsilon) = \sigma_{\mathrm{g}}^{\mathrm{carbyne}}(\varepsilon)$ as the sheath of CNT and the core of carbyne chains dominate the gravimetric stress-strain curves, that is, $\gamma \to 0$ and $\gamma \to \infty$, respectively. On the basis of this equation, the gravimetric stress−strain curve, gravimetric modulus ($E_{\mathrm{g}} = \partial\sigma_{\mathrm{g}}(\varepsilon)/\partial\varepsilon|_{\varepsilon\to 0}$) and gravimetric strength ($\sigma_{\mathrm{g}}^{\mathrm{s}} = \max_{\varepsilon}[\sigma_{\mathrm{g}}(\varepsilon)]$) for an arbitrary NTWC can be predicted from $\sigma_{\mathrm{g}}^{\mathrm{carbyne}}(\varepsilon)$, $\sigma_{\mathrm{g}}^{\mathrm{cnt}}(\varepsilon)$, and γ. Figure 4a provides the calculated $\sigma_{\mathrm{g}}^{\mathrm{carbyne}}(\varepsilon)$, $\sigma_{\mathrm{g}}^{\mathrm{cnt}}(\varepsilon)$, and $\sigma_{\mathrm{g}}(\varepsilon)$ for a carbyne chain, a CNT sheath, and *m*@*k* NTWCs having different γ, respectively. Figure 4a indicates that the gravimetric stress-strain curve of NTWCs evolves from that of CNT to that of carbyne chains as γ increases. To further quantify the mechanical performance, we derived the gravimetric modulus and strength from the gravimetric stress-strain curves of NTWCs having different mass ratios (γ) of carbyne carbons to sheath carbons. Equation 1 predicts the convergences of gravimetric modulus and strength of NTWCs to that of carbyne or the SWNT sheath as γ increases or decreases, respectively, which is supported by atomistic simulations of NTWCs (Figure 4b). The maximum values of gravimetric modulus and strength of NTWCs at zero temperature are 935.9 and 69.38 GPa·g^{-1}·cm^3 from atomistic simulations, which approach the theoretical upper bounds of 977.2 and 71.20 GPa·g^{-1}·cm^3 for carbyne chains, respectively (Figure 4b). These extraordinary high upper limits for gravimetric modulus and strength of NTWCs are 174.2% and 41.7% higher than that of graphene (356.4 and 50.25 GPa·g^{-1}·cm^3, respectively, when stretched along the zigzag direction that is the tensile strain direction for the used (*m*, *m*) SWNT sheaths).

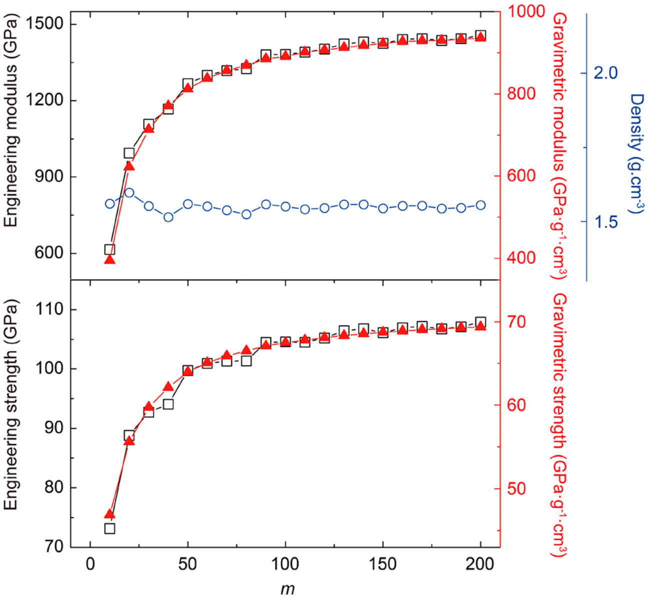

Figure 5. Mechanical properties and densities of NTWCs. Engineering modulus and strength, gravimetric modulus and strength, and density of *m*@k_{max} NTWCs as a function of *m*.

For further comparing the mechanical performance of NTWCs with other materials, we also calculated the engineering stress−strain curves of NTWCs. As is the case for compared materials, these stresses are normalized with respect to the entire cross-sectional area of non-stretched NTWCs. Assuming that the carbyne chains are sufficiently long that they deform uniformly with the surrounding SWNT, the engineering stress of a NTWC is obtained (Figure 5), where the cross-sectional diameter of the NTWC is the diameter of the original SWNT plus the van der Waals diameter of carbon (3.4 Å). As *m* increases, the gravimetric modulus and strength of *m*@k_{max} NTWCs increase, while the density of NTWCs is nearly constant. Finally, the overall densities and gravimetric modulus and strength converge to constant values of 1.54 g·cm^{-3}, 977.2 GPa·g^{-1}·cm^3, and 71.20 GPa·g^{-1}·cm^3 (gravimetric modulus and strength for carbyne chains from empirical atomistic simulations), respectively, as *m* and k_{max} increase. The engineering modulus and strength converge to 1.54 g·cm^{-3} × 977.2 GPa·g^{-1}·cm^3 = 1505 GPa and 1.54 g.cm^{-3} × 71.20 GPa·g^{-1}·cm^3 = 109.6 GPa, respectively, which correspond to the predicted upper limits for the engineering mechanical properties of NTWCs. This high engineering modulus (1505 GPa), high engineering strength

(109.6 GPa), and light weight (1.54 g/cm^3) make the NTWCs attractive for possible advanced engineering applications.

Potential Applications of NTWCs. The above results show that lightweight NTWCs have extraordinarily high modulus and strength. Hence, a few suggestions for NTWC applications are made, including reinforcing high modulus and high strength composites, tips for scanning tunneling microscopes, and cables for a space elevator (Figure 6). When used for reinforcement, NTWCs are expected to enhance the modulus and strength of the composites. When used as probe tips for a scanning tunneling microscope, the carbyne chains are expected to enhance the bending stiffness of the tips, which helps to prevent the commonly observed buckling failure of the tips. For example, the bending stiffness of a 10@7 NTWC tip (2.04 keV·nm) is 18% greater than that for the same diameter SWNT tip (1.72 keV·nm). Herein, the bending stiffnesses were obtained by calculating the energy required to form 70 nm-radius circular rings from the straight NTWC and SWNT, in which the radius of the circular rings is large enough to avoid the nonlinearity at high curvatures (Figure S2), as done in previous work.[11]

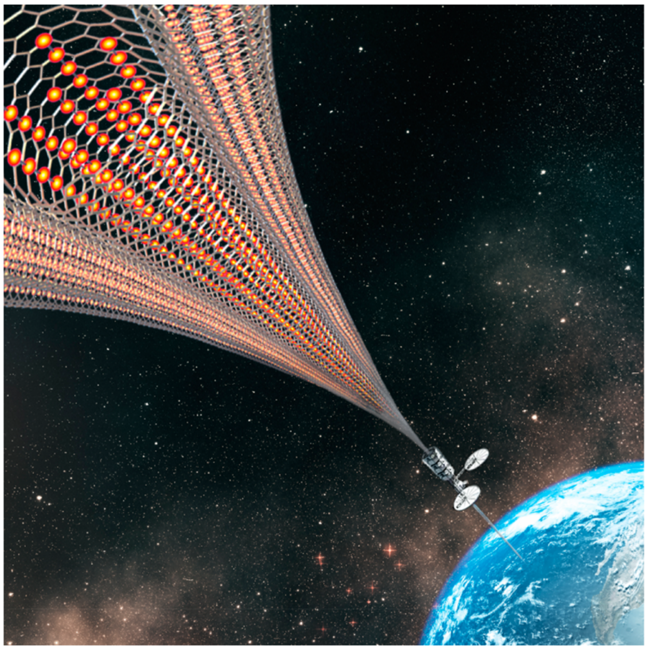

Figure 6. Potential applications of NTWCs. A space elevator using the NTWCs as the cable.

When used as the cable for a space elevator, the materials should be super-strong and ultra-lightweight, enabling them to connect to a space station far away from earth, without being fractured by the load generated by their own weight.[46,47] Various cable materials have been previously proposed for space elevators, such as CNTs[47] and prestressed CNTs.[48] In theory, CNTs have the potential to be 100 times as strong as steel, at one-sixth the density, which endow CNTs with a gravimetric strength that is presently predicted to be about 50 GPa·cm^3·g^{-1}. Xu *et al.*[48] proposed prestressed CNTs with a tensile strength about 20% higher than normal CNTs. By comparison, the maximum gravimetric strength of NTWCs is as high as 71.2 GPa·g^{-1}·cm^3, about 1.4- and 4-fold, respectively, that of CNTs and what is needed for the space elevator. Hence, NTWCs are attractive for such application.

Additional Remarks on the Fabrication of NTWCs and the Grip Effect. The fabrication of ultralong NTWCs, especially those containing many parallel carbyne chains, provides an enormous challenge. We believe that the most attractive approach is to synthesize the NTWCs by the polymerization of the carbyne chains within double wall or more wall nanotubes. This approach, where the carbons in one or more inner walls provide the carbons for the carbyne chains, has already been used by Shi *et al.*[36] to synthesize NTWCs that contain a single carbyne chain. Centimeter-long few-walled nanotubes having a tensile strength of 118.9 GPa have already been produced by Wei's team,[49] and we suspect that these long nanotubes might be convertible to NTWCs containing multiple carbyne chains by a high temperature thermal process, like used to make NTWCs containing a single carbyne chain. In fact, Toma *et al.*[50] have already made in low yield NTWCs that contain two or three parallel carbyne chains. The number of carbyne chains inside a CNT sheath is predicted to be determined by energetics, since there is an optimal number of carbyne chains inside a CNT sheath with a particular diameter that minimizes the system energy. Also, the number of interior carbyne chains could be limited by restricting the number of interior walls in the nanotube.

The next challenge would be how to assemble these NTWCs into extremely long yarns. Guidance here is provided by previous work on yarn spinning from CNT forests,[5,20] yarn spinning from floating catalyst synthesized CNTs,[51] and solution spinning of relatively short CNTs from superacidic solutions.[52] These yarns could be produced before converting the CNT fibers to NTWCs by high temperature thermal annealing, or possibly after such thermal conversion. Since nanotubes draw from a CNT forest can be used to make highly oriented CNT sheets,[20] application of the analogous thermal annealing method might be used to make NTWC forests from CNT forests or to convert transparent forest-drawn CNT sheets into transparent NTWC sheets.

For the finite-length NTWCs used in practical applications, when tensile loads are applied by gripping the outer CNT sheath, the loads need be transferred into the core of carbyne chains through interfacial stress transfer. If the grip length is too short to transfer the stress, the overall mechanical properties of NTWCs will be reduced, which is called the grip effect. On the basis of the shear-lag model,[53] atomistic simulations of pull-out tests were conducted to determine the critical grip length for stress transfer. In the simulations, an innermost carbyne chain was pull-out from gripped 10@7 NTWCs with grip length of 0.87, 2.18, and 4.36 μm. The interfacial force per grip length between the carbyne chain and the NTWC host is determined as 0.32 nN/μm (Figure 7a). Combining the above-calculated intrinsic strength of carbyne chains (11.1 nN), the grip length that balances tensile and shear stress transfer is about 11.1 nN/(0.32 nN/μm) = 34.7 μm. When the grip length is significantly larger than this critical length, the Young's modulus and tensile strength is expected to converge to the modulus and strength of infinite-length NTWCs. For example, for a cable for a space elevator, the NTWC can be buried in a binding polymer matrix that is held by the grips that are longer than the critical stress transfer length. Additionally, a circular belt of a continuous NTWC (*i.e.*, an endless NTWC) can reinforce a circular cylinder and be everywhere strong.

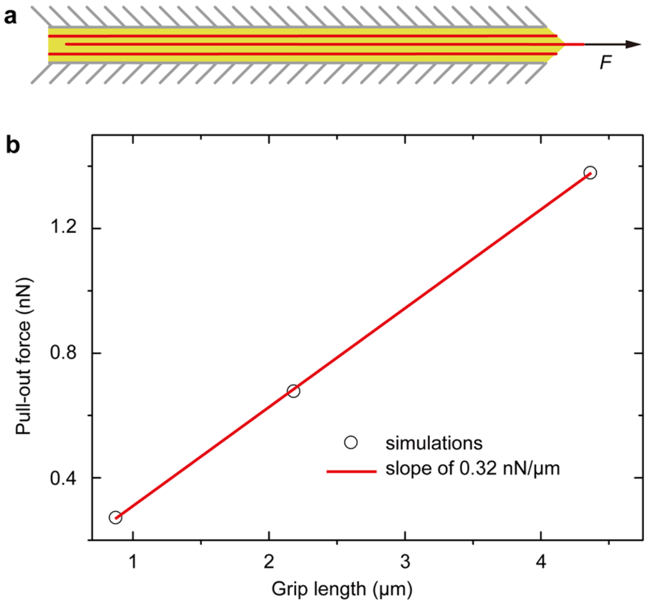

Figure 7. Grip effect for NTWCs. (a) For the simulations of pull-out tests, the innermost carbyne chain was pulled out of the NTWC, while the rest of the NTWC was fixed along the axial direction. (b) The pull-out force for the central carbyne chain as a function of the grip length.

CONCLUSIONS

In summary, we explored a type of carbon assembly that contains an array of carbyne chains wrapped by a SWNT sheath. We first investigated the stabilities of the NTWCs and showed that chemical reactions and topochemical polymerization of carbyne chains can be limited by the SWNT sheath. Afterwards, a mechanics model was proposed for exploring the gravimetric mechanical properties of NTWCs. This model predicts that the gravimetric modulus (and strength) of NTWCs increases from 356.4 (50.25) to 977.2 GPa·g^{-1}·cm^3 (71.20 GPa·g^{-1}·cm^3) as the mass ratio of carbyne carbons to sheath carbons increases, which are supported by atomistic simulations. The highest calculated gravimetric modulus and strength of NTWCs are 174.2% and 41.7%, respectively, higher than those of either graphene or CNTs, and the corresponding highest values of engineering modulus and strength of NTWCs with a density of 1.54 g·cm^{-3} are 1505 and 109.6 GPa, respectively. Possible applications of NTWCs are considered, as is mitigation of the grip effect.

METHODS

First-Principles Calculations. To investigate the stabilities of NTWCs and to benchmark the empirical potential for carbyne chains used in molecular simulations, first-principles calculations based on the DFT framework were performed by using the Vienna *Ab Initio* Simulation Package (VASP).[54] In the DFT calculations, the Perdew−Burke−Ernzerhof parameterization[55] of the generalized gradient approximation was used for the exchange-correlation functional. Projector augmented wave potentials were used to treat ion-electron interactions.[56] An energy cut-off of 400 eV was used, and *k*-point mesh with the density of about 40 Å (the product of each lattice constant and the corresponding number of *k*-points) was used for the Brillouin zone sampling.[57] The conjugated gradient algorithm was adopted for geometry relaxation, in which the force on atoms is converged below 0.01 eV/Å. A vacuum layer of 40 Å was used in the aperiodic directions and held constant through modifying the VASP code to minimize the interaction between periodic images.

Empirical Atomistic Simulations. First-principles calculations generally reliably predict the reactivities and mechanical properties of carbon nanostructures, but at the expense of high computational costs. While we use the first-principles calculations for investigating possible reactions of NTWCs, we will use empirical potentials for mechanical property calculations for NTWCs. Adaptive intermolecular reactive empirical bond-order (AIREBO) potentials[58] have been extensively and successfully used for predicting the mechanical properties of sp^2 carbon nanostructures (Table S2). However, first-principles calculations show that this potential cannot accurately capture the mechanical behavior of sp^1 carbyne chains (Figure S3 and Table S1). To address this issue, we developed an empirical potential for carbyne chains that provides results that agree with first-principles calculations. In this potential, the strain energy of carbynes is the sum of the bond stretching energy $[V_b = D[1 - e^{-\alpha(r-r_0)}]^2, r < r_c]$ and the angular bending energy $[V_a = k_a(\theta - \theta_0)^2]$, where r and θ are the bond length and angle, respectively, and the parameters with subscript "0" are their values at equilibrium. D and α are the depth and width of the Morse potential well, respectively; r_c is the bond breaking length, and k_a is the stiffness of the angular spring. On the basis of the tensile deformation and bending deformation on carbynes using first-principles calculations, the parameters of this potential were developed (Table S3). Figure S3 compares the gravimetric stress−strain curves of carbyne chains obtained by using the Morse-form potential with those obtained by using the AIREBO potential and first-principles calculations, which indicates the reliability of the developed empirical potential for the relevant strain range for carbynes. In addition, the tensile stiffness of 151.7 nN, tensile strength of 11.1 nN, and bending stiffness of 3.6 eV·Å for carbyne chains calculated from this force field agree with previous *ab initio* calculations (tensile stiffness of 153.1 nN, tensile strength of 11.7 nN, and bending stiffness of 3.6 eV Å).[11] Considering that this force field has successfully reproduced the tensile and bending properties of carbyne chains, it is reasonable to expect here that the neglect of bond alternation in this force field has little effect on the exploration of the modulus and strength for carbyne chains. On the basis of these considerations, AIREBO[58] and Morse-form potentials were adopted for CNTs and carbynes, respectively. To avoid the original overestimation of the strength of the C−C bonds, the potential cutoff was set to 2 Å for the AIREBO potential.[59−61] Additionally, a Lennard-Jones potential was adopted for non-bonding intermolecular interactions of NTWCs, that is

$$V_{ij}^{\mathrm{LJ}}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \quad (2)$$

where a σ of 3.4 Å corresponds to the distance between atoms when the potential energy equals 0 and a ε of 2.84 meV defines the potential well.[58] Considering the weak interaction, the possible difference of Lennard-Jones parameters between sp^1- and sp^2-hybridized carbon atoms was neglected.

To determine the binding energy, atomistic simulations with the empirical force field were conducted using the large-scale atomic/molecular massively parallel simulator (LAMMPS) computational package.[62] First, various structures involving carbyne chains, SWNT sheaths, and their combinations were constructed. Then, these structures were energy minimized using a conjugate gradient method. Periodic boundary conditions were used along the axial direction. A periodic length of approximately 4.4 nm was used to ensure lattice match between carbyne chains and the SWNT sheaths ($m = n$) used in this work. Finally, the binding energy was calculated as the sum of the energy of the noncollapsed SWNT and the energy of noninteracting carbyne chains minus the total energy of the assembled NTWC (normalized per atom).

Atomistic simulations were used for exploring the mechanical properties of NTWCs. The NTWC was modelled by assembling parallel carbyne chains within a SWNT sheath. To avoid the effects of strain rate, energy-minimized tensile simulations were used to explore the mechanical behaviors of NTWCs. Before any tensile deformation, all NTWC structures were fully energy minimized using a conjugate gradient algorithm. Afterwards, a tensile strain increment of 0.5% per step was applied by deforming the simulation box and applying affine displacements to the atomistic positions along the axial direction, while other freedoms of the structure were energy minimized using a conjugate gradient method. Finally, the stress and strain for each tensile step were recorded for obtaining the stress−strain curves of NTWCs.

To determine the critical grip length for stress transfer, we did static pull-out tests on 10@7 NTWC with length of 0.87, 2.18, and 4.36 μm using atomistic simulations. Before pull-out tests, the NTWC was fully energy minimized using a conjugate gradient algorithm. Afterwards, the innermost carbyne chain was pulled-out of the NTWC with an increment of 0.05 Å, while the rest of the NTWC was fixed along the axial direction. The total pull-out distance of the innermost carbyne chain was 10 Å, which ensures that the maximum pull-out force was recorded.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c06602.

Chemical stability of NTWCs, mechanical properties calculations, and the developed potentials for carbyne chains (PDF)

Inter-carbyne-chain crosslinking reactions in free space (MP4)

Inter-carbyne-chain crosslinking reactions in confined space (MP4)

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Notes

The authors declare no competing financial interest.

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Supporting Information for

Predicted Confinement-Enhanced Stability and Extraordinary Mechanical Properties for Carbon Nanotube Wrapped Chains of Linear Carbon

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The Supporting Information contains

- Figures S1-S3.
- Tables S1-S3.
- Movies S1-S2.

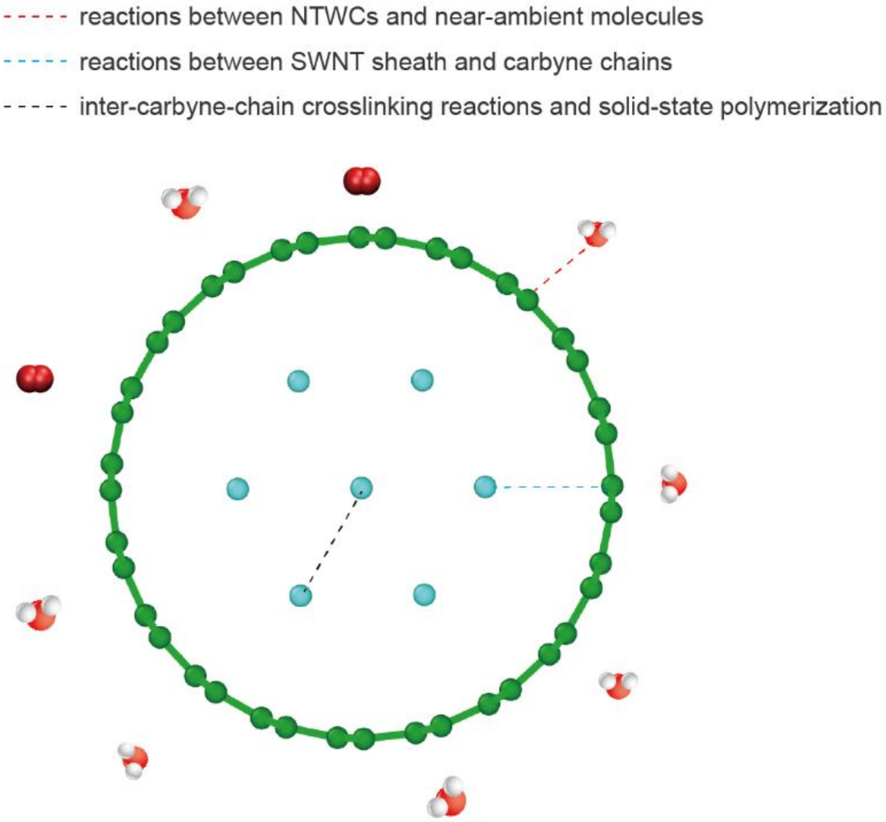

Figure S1. Possible chemical instabilities of NTWCs: (1) Reactions between NTWC and surrounding molecules, (2) reactions between the carbyne chains and the SWNT sheath, and (3) inter-carbyne-chain reactions.

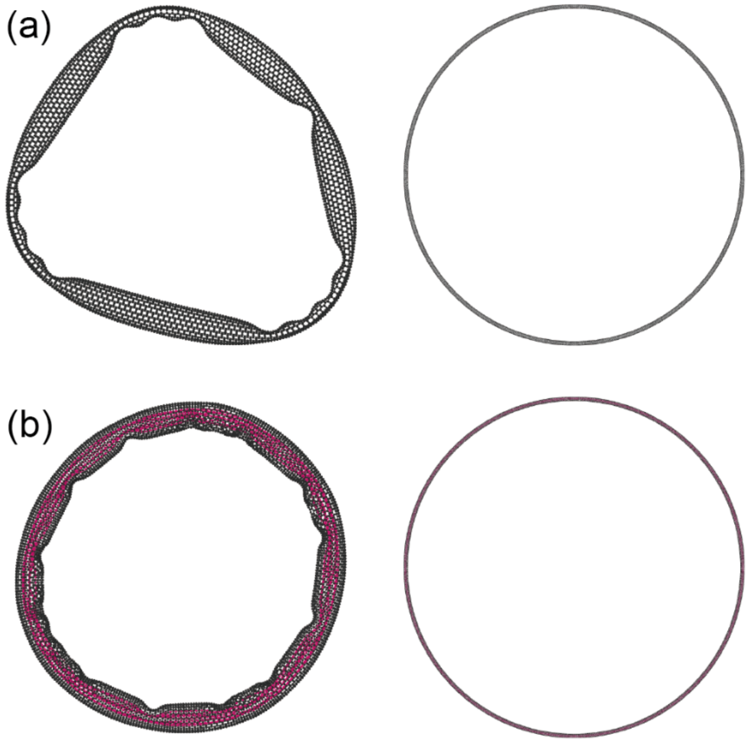

Figure S2. (a) Bending tests of (10,10) SWNT and (b) 10@7 NTWC with different radii.

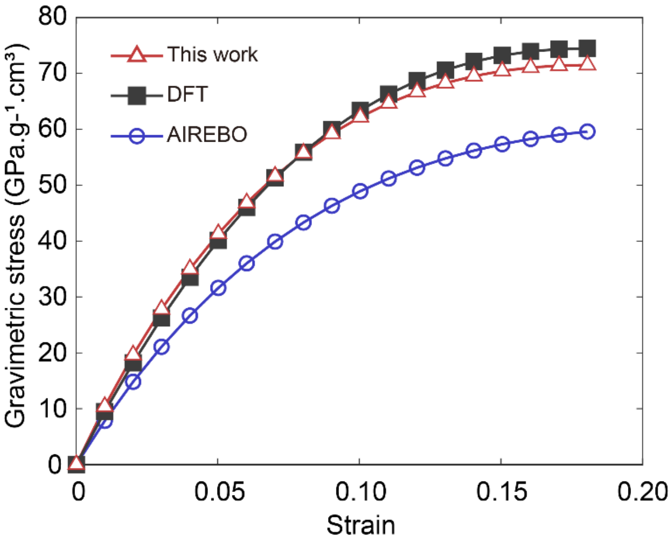

Figure S3. Gravimetric stress-strain curves of carbyne chains using the Morse potential, AIREBO potential, and DFT calculations.

Table S1. Mechanical properties of carbyne chains calculated using different methods.

	DFT	Morse	AIREBO
σ_{gs} (GPa·g^{-1}·cm^{3})	74.20	71.20	60.25
Y_g (GPa·g^{-1}·cm^{3})	906.8	977.2	738.4
ε_s (%)	18	18	22

[*] A unit cell of the carbyne chain containing 2 atoms with periodic boundary condition along the axial direction was adopted in DTF calculations.

Table S2. Mechanical properties of graphene calculated using different methods.

	AIREBO	DFT
σ_{gs} (GPa·g^{-1}·cm^3)	50.25	49.01
Y_g (GPa·g^{-1}·cm^3)	356.4	429.1
ε_s (%)	30	24

*Graphene was stretched along the zigzag direction, which is consistent with the stretching direction of the armchair SWNTs used in this work.

Table S3. Morse-form potential developed for carbyne chains.

Interaction terms	Functional forms	Parameters
Bond stretching	$V_b = D[1- e^{(-\alpha(r - r_0)}]^2$, with a cut off of bond length ($r < r_c$).	$D = 4.6$ eV; $\alpha = 3.0$ Å^{-1} $r_0 = 1.283$ Å; $r_c = 1.514$ Å
Angle bending	$V_a = k_a(\theta - \theta_0)^2$	$k_a = 1.39$ eV; $\theta_0 = 180$ °
Non-bond interaction	$V_{ij}^{LJ}(r_{ij}) = 4\epsilon[(\frac{\sigma_0}{r_{ij}})^{12} - (\frac{\sigma_0}{r_{ij}})^6]$	$\varepsilon = 0.00284$ eV; $\sigma_0 = 3.4$ Å

Movie S1: Inter-carbyne-chain crosslinking reactions in free space.

Movie S2: Inter-carbyne-chain crosslinking reactions in confined space.