Supporting Information

Carbon Nanoscroll- Silk Crystallite Hybrid Structure with Controllable Hydration and Mechanical Properties

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S1. Detailed description of potential energy function and parameters for graphene simulation

The potential energy of carbon atoms on graphene is described by a Morse bond, a harmonic cosine term for the bond angle, a cosine term for torsion and a Lennard-Jones (L-J) term for the van der Waals (vdW) interaction $as^{1,2}$

$$\begin{split} U(r_{ij},\theta_{ijk},\phi_{ijkl}) &= K_{Cr} \Big[e^{-K_C (r_{ij}-r_C)} - 1 \Big]^2 + \frac{1}{2} K_{C\theta} (\cos\theta_{ijk} - \cos\theta_C)^2 \\ &+ \frac{1}{2} K_{C\phi} (1 - \cos 2\phi_{ijkl}) + 4\lambda \varepsilon_{CC} \Bigg[\left(\frac{\sigma_{CC}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{CC}}{r_{ij}} \right)^6 \Bigg] \quad , \end{split}$$

where, ${}^{K_{c}}$ denotes the steepness of Morse potential well, ${}^{r_{ij}}$ is the distance between two bonded atoms, ${}^{\theta_{ijk}}$ is the bending and torsional angle, and ${}^{K_{Cr}}$, ${}^{K_{C\theta}}$, ${}^{K_{c\theta}}$ are the force constants of stretching, bending and torsion, respectively. The values of the parameters are provided in Table S1 below.^{1,2}

| $K_{cr} = 47890 \ kJmol^{-1}nm^{-2}$ | $r_c = 0.142 \text{ nm}$ | $K_c = 21.867 \text{ nm}^{-1}$ |
|--|--------------------------|--------------------------------|
| $K_{C\theta}$ = 5622 kJmol ⁻¹ | $\theta_{c=120^0}$ | |
| $K_{C\phi} = 25.12 \text{ kJmol}^{-1}$ | $\phi_{c=180^0}$ | |

Table S1 Interaction potential parameters.^{2,3}

A vdW interaction with a cross-section of $\sigma_{cc} = 3.400$ Å, a potential well depth of $\varepsilon_{cc} = 0.3601 k Jmol^{-1}$, and the tuning parameter λ is used to control the vdW interaction

between layers of carbon nanoscroll (CNS), and applied only to carbon-carbon interactions on CNS.²

The accuracy of the potential of graphene sheet adopted in the current study has been checked by a series of earlier studies, for example, on the interlayer energy and bending stiffness of the graphene and nanoscrolls⁴, and the oscillation mode of the scroll.³

The van der Waals parameters between different types of atoms in graphene and other molecules are calculated from the parameters of the pure atoms using combination rules.⁵ The graphene-water/biomolecule interaction potentials adopted here are well-accepted and have been validated by many studies, including the investigations of carbon nanotubes in water,⁶ and the interactions between carbon nanotube/graphene and biomolecules.^{2,7,8}

S2 Formation of a CNS in molecular dynamics simulations

A CNS is formed by rolling up a flat graphene sheet using a type (20, 20) single-walled carbon nanotube as a template, as shown in Figure S1. After the CNS is formed, the nanotube was removed and the CNS was subjected to molecular dynamics simulations for at least 2 ns to obtain its equilibrated structure. The molecular simulation was carried out using NVT ensemble and temperature of 300K. The self-folding process of forming the CNS is driven by the van der Waals interaction.



Figure S1 Illustration of formation of a carbon nanoscroll in molecular dynamics simulations.

S3. Description of Electric field introduced dipole-dipole interactions

It has been previously shown that the polarizability of single-walled carbon nanotubes (SWCNTs) in the axial direction is one order of magnitude higher than that perpendicular to the axis.⁹ In current study, we only consider the axial polarizability of carbon atoms in the CNS. The electric field will cause the carbon atoms to be polarized with the following dipole–dipole interactions.⁹

$$V(\vec{r}_{ij}) = \frac{1}{4\pi\varepsilon_0 |\vec{r}_{ij}|^3} \left[|\vec{p}_i| |\vec{p}_j| - \frac{3(\vec{r}_{ij} \cdot \vec{p}_i)(\vec{r}_{ij} \cdot \vec{p}_j)}{|\vec{r}_{ij}|^2} \right]$$

Where \vec{r}_{ij} is the distance between dipole i and dipole j, $\vec{p}_i = 4\pi\varepsilon_0 \alpha_i \vec{E}$ is the induced dipole moment, \vec{E} being the applied electric field, ε_0 is the vacuum permittivity, and α_i is the polarizability of atom i. The dipole–dipole interaction leads to the interlayer interaction change.

Representative values of λ and corresponding electric fields have been studied before and are shown in Table S2.² The corresponding core sizes of the CNS at equilibrium are also provided. $\lambda = 1$ implies no electric field applied and $\lambda = 0.3$ corresponds to a strength of electric field of ~0.42 V nm⁻¹. Although the applied electric field tends to reduce the effective surface energy, which corresponds to $\lambda < 1$, we have also considered the cases of $\lambda > 1$, implying a stronger interlayer interaction energy, which may be realized by other approaches, e.g., by choosing different types of two-dimensional materials with different strengths of interlayer binding energy,¹⁰ or to tune the interlayer interaction by doping and functionalization of the materials.¹¹ The corresponding core size of the CNS at equilibrium was also provided. There exists a critical value of $\lambda cr=1.6$, beyond which, the core size keeps unchanged.

| λ | 0.4 | 0.8 | 1.0 | 1.6 |
|-------------------------|------|------|------|------|
| r [nm] | 0.99 | 0.67 | 0.48 | 0.18 |
| E [V nm ⁻¹] | 0.39 | 0.23 | 0 | - |

Table S2. The equilibrated core size of the CNS at representative tuning parameter λ and the corresponding electric fields.²

S4 Supporting information for crystallite structure and CNS-silk interactions

| | Control (without CNS) | Α | В | С |
|--|-----------------------------|-------------------|-------------------|-------------------|
| Vdw tuning parameter (λ) | N/A | 0.3 | 1 | 1.6 |
| Water content inside the scroll | N/A | 1332 | 92 | 83 |
| UTF (Rupture force)- Surface layer middle chain | 3551.64 | 3469.56 | 4464.67 | 4727.70 |
| Crystalline hydrogen bond number | 226.86 ± 4.3 | 231.67 ± 4.1 | 190.53 ± 5.2 | 190.02 ± 5.66 |
| Crystalline-water hydrogen bond number | 200.56 ± 8.22 | 156.85 ± 7.26 | 169.36 ± 7.56 | 155.95 ± 7.11 |

Table S3. Different interlayer interaction energy determines the different water content, and rupture force, as well as the hydrogen bond number on the silk crystalline.

We have repeated the pull-out tests for both control case and Case B (without electric field) for 5 times, and calculated the mean value and the standard deviations of UTF as control: 3557.83 ± 7.04 pN and case B: 4487.13 ± 15.81 pN. Based on the results of multiple runs, we see that the UTF only fluctuates within a small range. Thus our results can reasonably represent the trend of influence of CNS on the mechanical properties of the crystallite.



Figure S2. Normalized interaction energy of silk-water as a function of simulation time, where N_W denotes for water molecules in the vicinal layer of the protein (distance within 3 Å from the silk), showing the cases for λ =0.3 and 1.



Figure S3. Configuration of the crystallite at λ =0.3 and 1 after equilibration. CNS and water molecules not shown for clarity.

References in Supporting Information

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