Supporting Information

Combining *in silico* Design and Biomimetic Assembly: A New Approach for Developing High-Performance Dynamic Responsive Bio-nanomaterials

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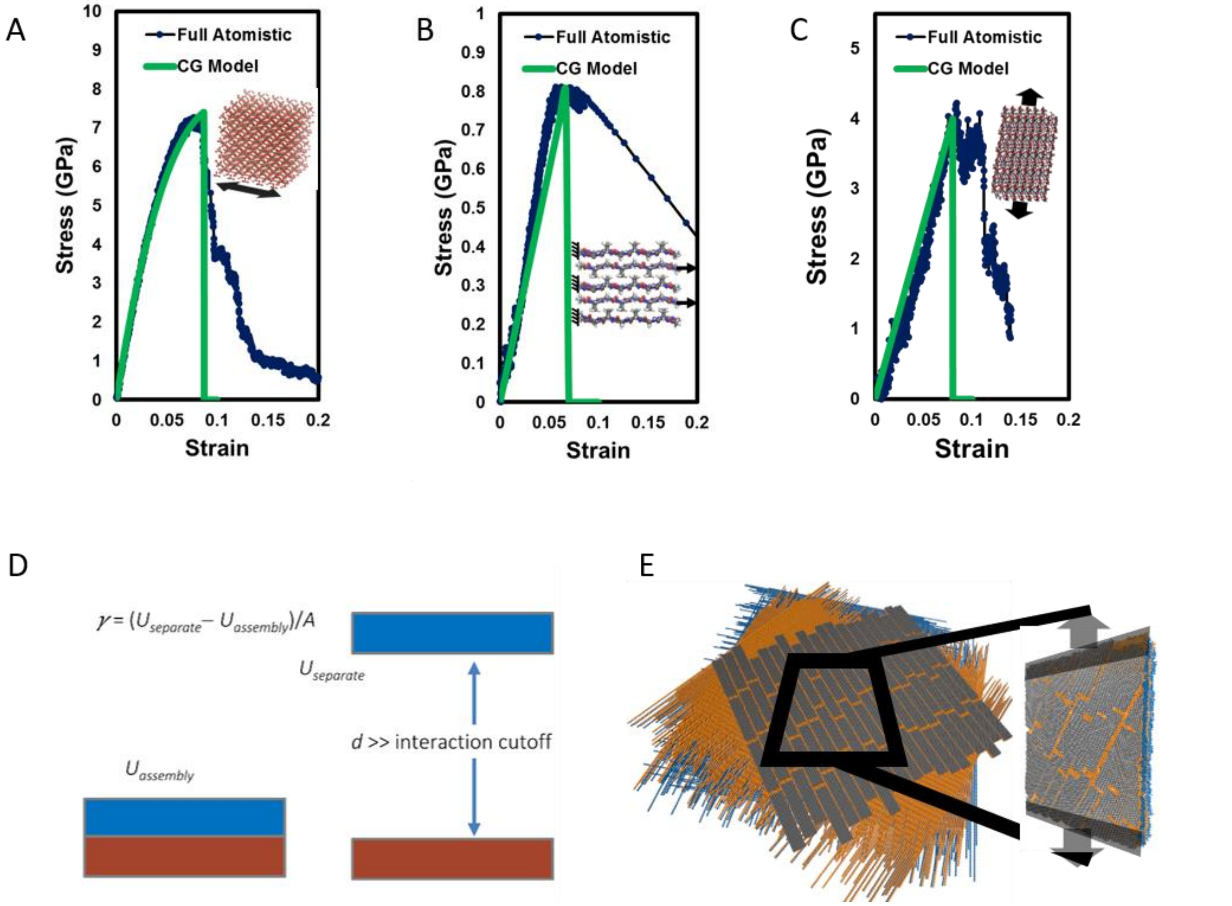


Figure S1. The training of coarse grained parameters from full-atomistic simulations. The tensile responses of HAP (A), SNF (B) and CNF (C) from full atomistic simulations and the corresponding coarse-grained models. (D) The interfacial energy was calculated as the energy difference between the case that two material blocks were attached and the case that they were separated far away from each other. (E) Parallel placed fibrils and nanoplatelets form material layers and the layers were stacked to generate the composite structure. The orientation of fibrils and nanoplatelets was chosen randomly for different layers. A slab of size ~ 250 nm × 300 nm was cut from the layered assembly to represent the composite membranes.

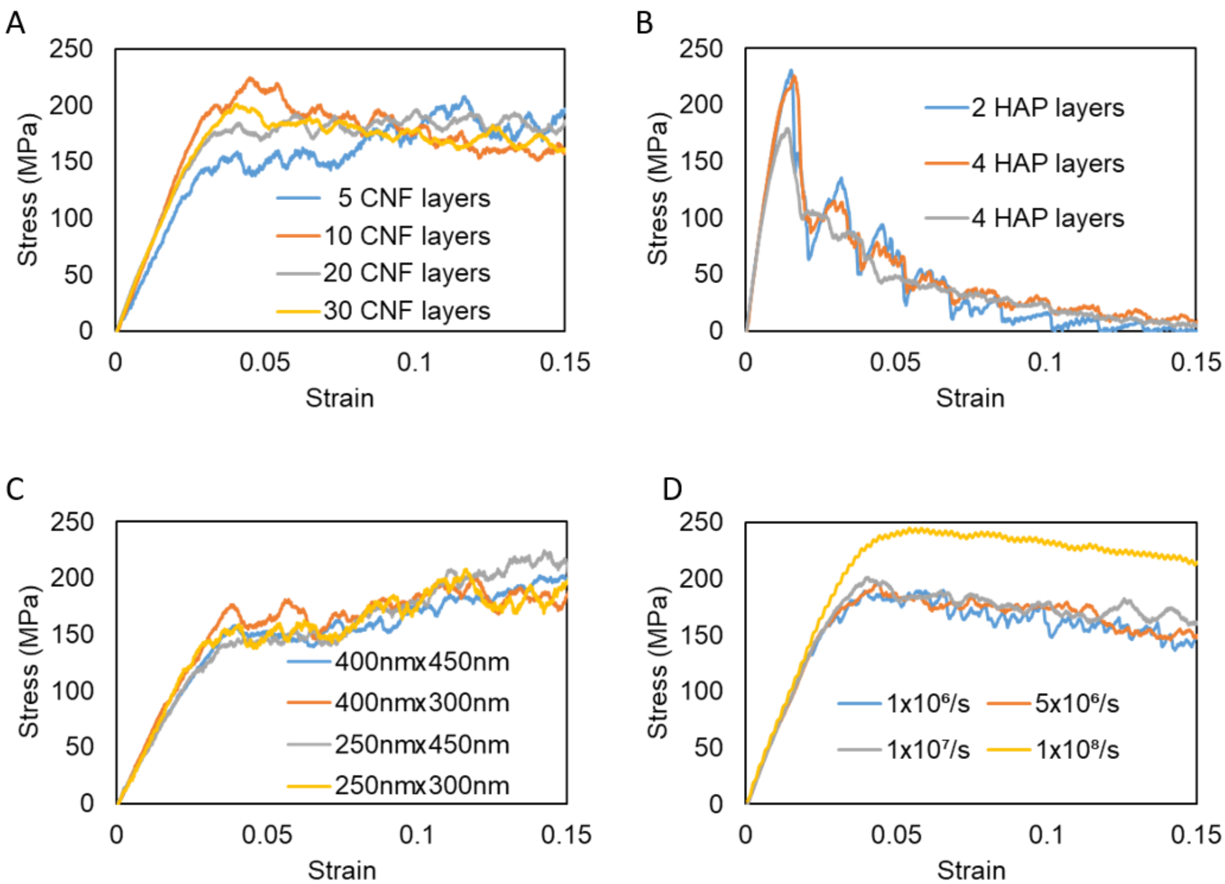


Figure S2. (A) The stress-strain responses of CNF membranes with various thicknesses (number of layers). (B) The stress strain responses of HAP/SNF membranes with various thicknesses. (C) The stress-strain responses of CNF membranes with various lateral dimensions. (D) The stress-strain responses of CNF membranes with various strain rates.

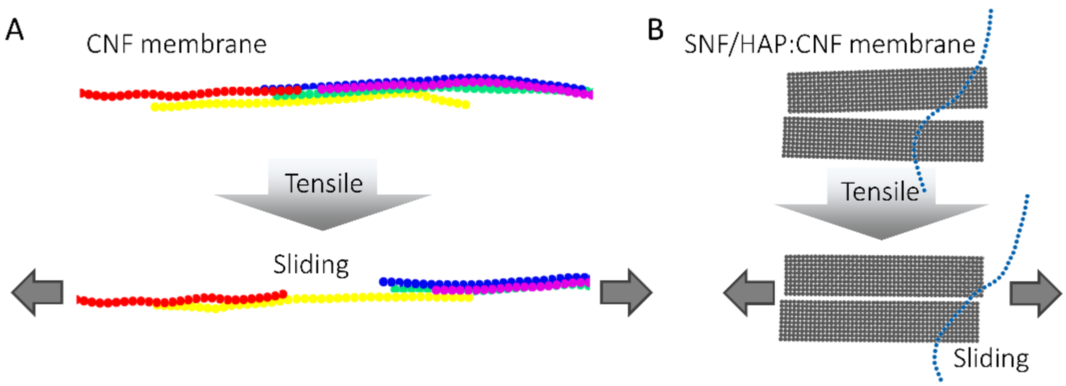


Figure S3. Sliding behavior of CNFs. (A) Inter-fibril sliding in CNF membrane during the *in silico* tension test. (b) Sliding between CNF and HAP nanoplates in SNF/HAP:CNF membrane during the *in silico* tension test.

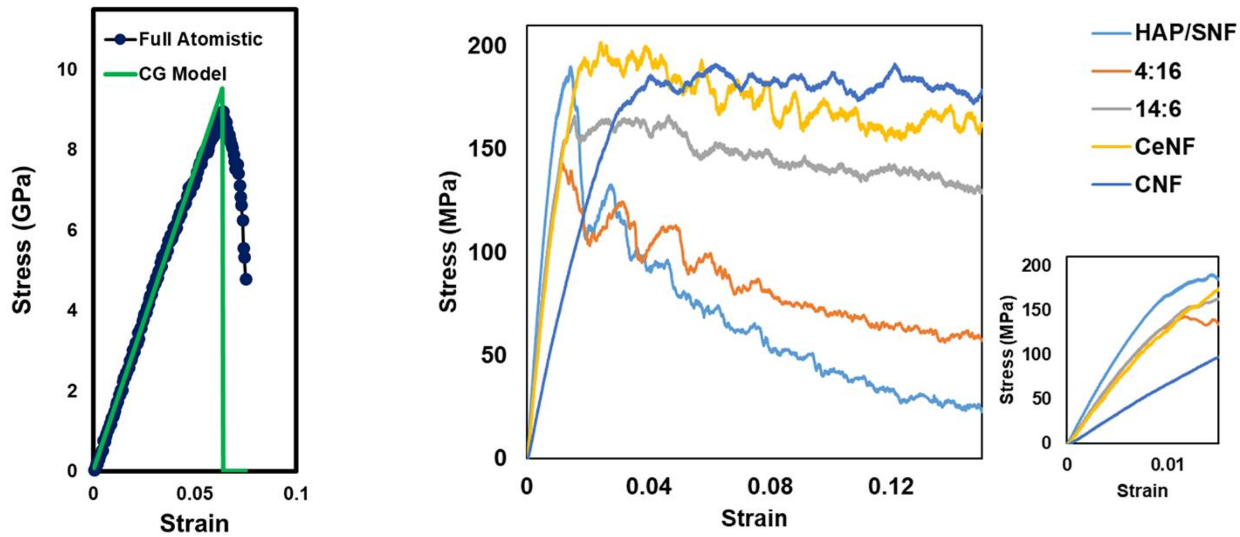
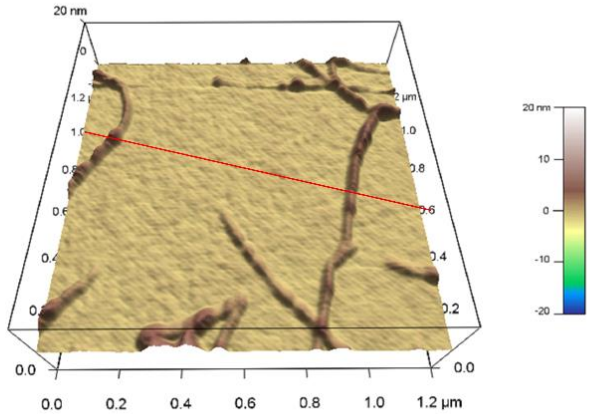


Figure S4. A) The tensile responses of CeNF from full atomistic simulations and the corresponding coarse-grained models. B) The stress-strain responses of membranes with different mass ratios of CeNF under tensile loading condition. Similar to CNF, membrane with CeNF phase has higher stress plateau because of the inter-fibril slidings. The stress-strain curves with stain < 0.015 is presented in insert plot, which shows higher modulus for the membrane reinforced with HAP/SNF. Membrane made of pure CeNF is stiffer that that made of pure CNF because CeNF is much stiffer than CNF, but they have close stress plateau because the plateau is determined by the interfibril interactions and the interaction strength for these two types of fibrils are close according to our simulations (Table S2).

A



B

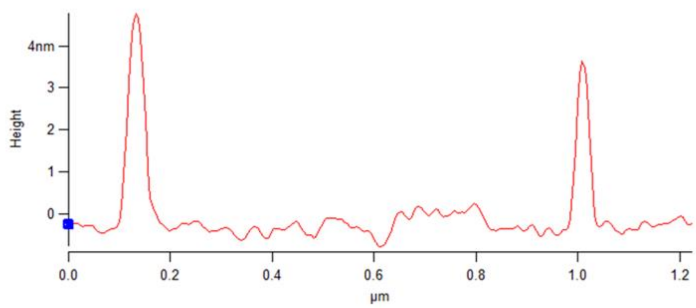


Figure S5. Structural characterization of SNFs. (A) AFM image of heat induced SNFs. (B) Transversal height profiles as indicated by the corresponding traces in the image (A).

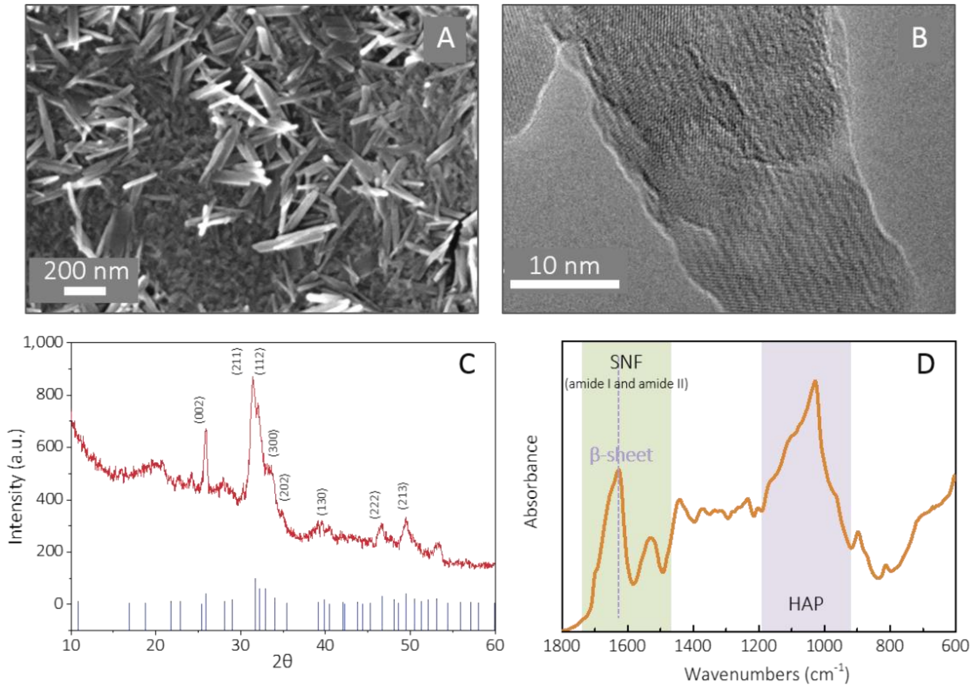


Figure S6. Structural characterization of biomineralized HAP. (A) SEM image of HAP nanocrystals. (B) TEM image of HAP nanocrystals. (C) XRD pattern of biomineralized HAP nanocrystals. The expected standard diffraction peaks according to the Joint Committee on Powder Diffraction Standards (JCPDS) for both phosphates are shown as discrete bars (JCPDS No. 09–0432). (D) FTIR spectrum of SNF/HAP nanocomposites.

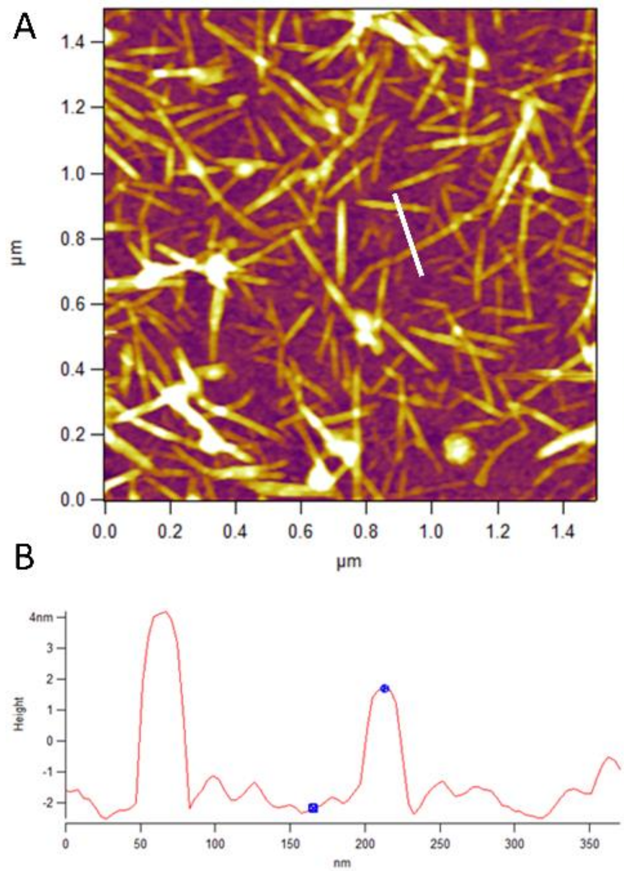


Figure S7. Structural characterization of TEMPO-CNFs. (A) AFM image of heat TEMPO-CNFs. (B) Transversal height profiles as indicated by the corresponding traces in the image (A).

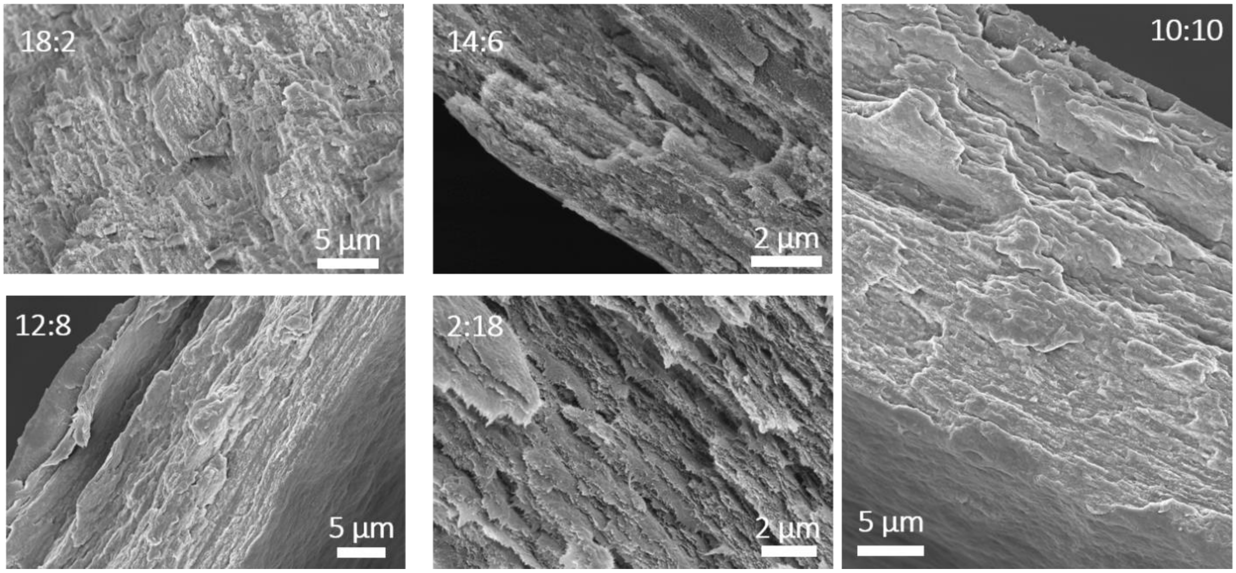


Figure S8. Cross-sectional SEM image of SNF/HAP:CNF nanocomposites with different SNF/HAP and CNF ratios.

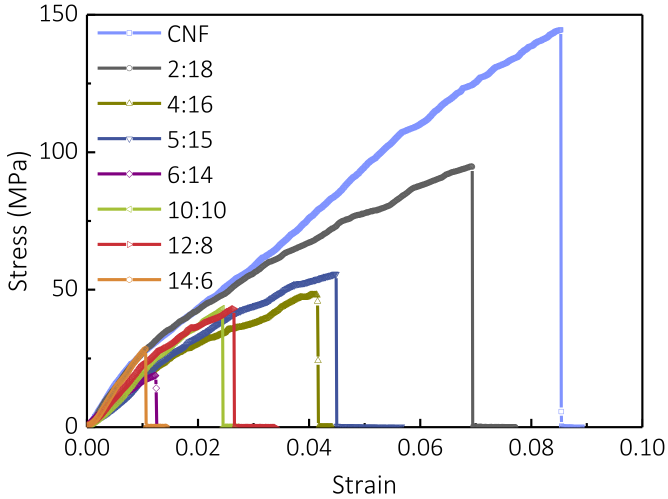


Figure S9. Stress-strain curves of SNF/HAP:CNF prepared from solution casting.

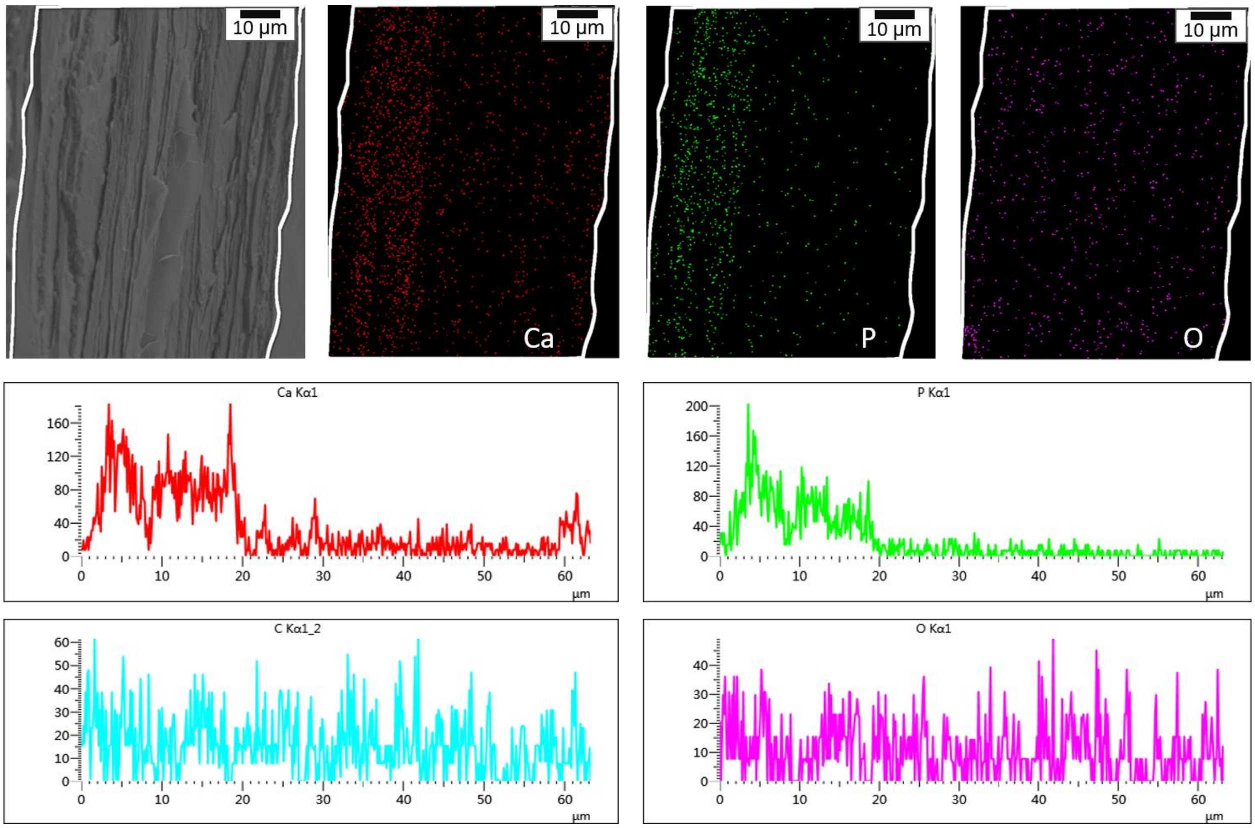


Figure S10. EDX image of the 10:10 SNF/HAP:CNF nanocomposites prepared from vacuum filtration.

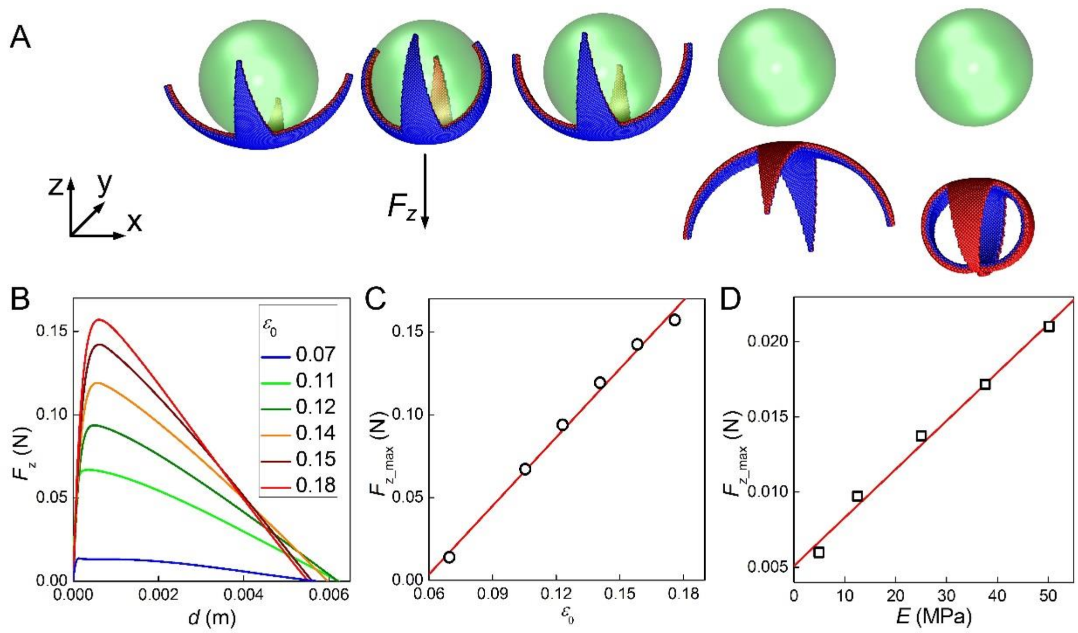


Figure S11. The modeling of SNF/HAP:CNF nanocomposites self-folding. (A) The modeling snapshots of the SNF/HAP:CNF nanocomposites in responding to water absorption (left) and "grab and release" design (right). (B) The total force on the spherical object as a function of the displacement of the nanocomposite. Each individual curve is the result tested for different mismatching strain ε_0 and the peak value corresponds to the maximum grabbing force. (C and D) The peak grabbing force recorded as a function of ε_0 in (C) and material stiffness E in (D).

Table S1. The parameters associated with the coarse-grained model.

	HAP		SNF		Chitin	
Bonded interactions	D = 4839 kcal/mol α = 0.31 Å^{-1}		K_b = 20 kcal/(mol·Å^2) K_a = 2288 kcal/mol		K_b = 85 kcal/(mol·Å^2) K_a = 9535 kcal/mol	
Non-bonded interactions	HAP-HAP	SNF-SNF	CNF-CNF	HAP-SNF	HAP-CNF	SNF-CNF
ε (kcal/mol)	723.6	123.5	174.8	269.5	277.7	114.1
σ(Å)	26.63					
r_c (Å)	51.96					

Table S2. The parameters associated with CeNF.

	CeNF		
Bonded interactions	K_b = 254 kcal/(mol·Å^2), K_a = 28604 kcal/mol		
Non-bonded interactions	CeNF-CeNF	HAP-CeNF	SNF-CeNF
ε (kcal/mol)	195.3	295.4	109.3
σ(Å)	26.63		
r_c (Å)	51.96		

Table S3. Mechanical properties of nacre-like SNF/HAP:CNF membranes.

(SNF/HAP): CNF	Density (g/cm^3)	Modulus (Gpa)	Specific Modulus (Gpa)	Toughness (MJ/m^3)	Specific Toughness (MJ/m^3)	Strength (MPa)	Specific Strength (MPa)	Strain
CNF	1.25±0.08	3.2±0.4	2.5±0.3	15±2	12±1	188±10	151±8	0.120±0.008
1:19	1.27±0.06	4.0±0.6	3.2±0.5	15±2	12±4	214±20	169±15	0.121±0.007
2:18	1.32±0.07	5.5±0.9	4.4±0.7	24±6	19±5	270±35	220±29	0.137±0.014
3:17	1.33±0.09	6.0±0.7	4.5±0.4	19±2	14±3	268±12	201±9	0.102±0.007
4:16	1.36±0.08	6.1±0.5	4.4±0.4	22±2	16±1	281±14	229±11	0.117±0.009
5:15	1.38±0.07	6.7±0.4	4.9±0.6	14±1	10±1	228±23	166±19	0.082±0.010
6:14	1.40±0.06	8.6±1.0	6.2±0.7	12±1	9±1	174±7	124±5	0.089±0.015
7:13	1.39±0.09	8.5±0.4	6.1±0.3	11±1	8±1	170±11	122±8	0.082±0.004
8:12	1.41±0.07	8.9±0.6	6.4±0.4	13±2	9±1	164±6	117±5	0.101±0.010
10:10	1.48±0.03	13.6±1.3	9.1±0.9	9±1	6±1	147±14	98±10	0.075±0.010
12:8	1.58±0.02	11.3±0.9	7.1±0.6	7±1	4±1	127±3	80±2	0.041±0.006
13:7	1.69±0.05	10.3±1.0	6.0±0.6	6±2	3±1	142±14	83±8	0.066±0.015
16:4	1.76±0.04	9.4±1.5	5.2±0.8	4±1	2±1	113±7	63±4	0.044±0.018
SNF/HAP*	1.78±0.05	7.7±0.2	4.3±0.5	2±1	3±1	96±4	63±3	0.026±0.004

*The data of SNF/HAP membranes are extracted from ref [27].

Table S4. Mechanical properties of SNF/HAP:CNF membranes made by solution casting process.

(SNF/HAP):CNF	Modulus (GPa)	Toughness (MJ/m3)	Strength (MPa)	Strain
2:18	1.8±0.4	4.21±0.72	94±17	0.074±0.006
4:16	2.1±0.3	1.38±0.47	54±9	0.046±0.003
5:15	2.0±0.4	1.54±0.32	58±11	0.051±0.003
6:14	1.7±0.3	0.17±0.07	31±4	0.018±0.001
10:10	2.4±0.4	0.64±0.05	45±3	0.025±0.005
12:8	2.3±0.2	0.73±0.10	44±4	0.028±0.004
14:6	2.6±0.3	0.14±0.02	27±1	0.012±0.002

Movie S1

The self-folding process of a rectangle 8:12 SNF/HAP:CNF membrane with thickness of 30 μm in water.

Movie S2

The self-folding-unfolding-refolding process of a four-point-star 8:12 SNF/HAP:CNF membrane with a thickness of 10 μm in water.

Movie S3

The self-folding process of a four-point-star 8:12 SNF/HAP:CNF membrane with a thickness of 30 μm in water.

Movie S4

The self-folding process of a flower-like 8:12 SNF/HAP:CNF membrane with a thickness of 50 μm in water.

Movie S5

The self-folding process of a circular 8:12 SNF/HAP:CNF membrane with a thickness of 30 μm in water.

Movie S6

The self-folding process of a rectangle 8:12 SNF/HAP:CNF membrane with a gradient thickness (15-30 μm) in water.