Mimicking nacre with super-nanotubes for producing optimized super-composites

Nicola M Pugno

Department of Structural Engineering, Politecnico di Torino, Corso Duca degli Abruzzi 24,
10129 Torino, Italy

Abstract
In this paper, we evaluate the strength, toughness and stiffness of
super-nanotubes, just recently discovered, and of the related fibre-reinforced
composites. The prediction of huge toughening mechanisms suggests the
feasibility of 'super-composites'. We found the optimum for super-nanotubes
with a number of $\sim$2 hierarchal levels, similar to the optimization done by
Nature in nacre.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon 'super-nanotubes' (STs) have very recently been
proposed, at the beginning of 2006 [1]; these structures
are built from carbon nanotubes connected by Y-junctions
forming a super-graphene that is then rolled to form a
carbon ST. Such a procedure can be repeated several times,
generating a hierarchical macroscopic tube. Nanojunctions
among nanotubes can be produced by introducing defects,
e.g. a pentagon–heptagon pair, into the hexagonal network
of carbon [2]. Thus, two nanotubes can be welded by
electron beam irradiation at high temperature, producing X-,
Y- or T-junctions [3, 4]. Such junctions open up the
possibility of creating new nanotube-based networks [5, 6]:
the ST is a relevant example [1]. Furthermore, a significant
advance towards ST realization has recently been proved
with the fabrication of hierarchically branched nanotubes [7],
suggesting that such complex supertubes could in the future be
realized.

The paper is organized as follows. In section 2
we derive the strength, stiffness and toughness of filled
super-nanotubes, as a function of their hierarchical level,
proposing a new optimization procedure; in section 3, the
same analysis is extended to super-composites reinforced by
the previously investigated super-nanotubes, including the
nonlinear toughening mechanism (fibre pull-out). Finally,
some conclusions are consistently drawn.

2. Mechanics and optimization of super-nanotubes

To build an ST a (single-walled) nanotube is considered
as the fundamental unit (ST$^{(0)}$); a super-nanotube ST$^{(1)}$ is
topologically generated by substituting the nanotube atomic
bonds by entire nanotubes. Generalizing, an ST$^{(k)}$ will present
ST$^{(k-1)}$ 'bonds', and after N iterations an ST$^{(N)}$ is generated;
see figure 1 (adapted from [1]). The ST$^{(N)}$ is thus hierarchical
in nature and accordingly its strength is expected to be
strongly dependent on the size-index N [8]. For generality
we consider the ST$^{(N)}$ filled by a matrix. With σ_0 being the
nanotube strength, ideal or effective, i.e. taking into account
the unavoidable presence of atomistic defects [9] that can play
a dramatic role, as recently discussed for the nanotube-based
megacable of the space elevator [10] (see also the related news
in Nature, 22 May 2006 and by J Palmer), and σ_M the matrix
strength, plausibly $\sigma_0 \gg \sigma_M$.

In a plane cross-section of an ST$^{(k+1)}$, n_kST$^{(k)}$ are present,
each of them with a cross-sectional area A_k (see figure 1,
$k = 0\text{--}3, n_k = n = 6$). Thus, the total number of ST$^{(k)}$
in an ST$^{(N>k)}$ is $N_k = \Pi_{j=1}^{N-k} n_j$. We here provide for an
ST$^{(N)}$ composed by N different materials and generating a
hierarchical rather than a fractal (i.e. self-similar) structure,
whereas for classical carbon STs $n_k = n = 6 \,\forall k$ [1].

For the sake of simplicity we start by considering a
zig-zag supertube. The failure is expected to take place in
the longitudinal supertubes belonging to the same fractured
plane cross-section surface (see [9], appendix III, 'Zig-zag and
armchair fracture'). Accordingly, for such a stretched filled
zig-zag ST$^{(N)}$ the hierarchical equilibrium of the forces must
be formulated $\forall k$ as

$$F \equiv A_N \sigma_N = F_{\text{ST}} + F_{\text{M}} = N_k A_k \sigma_k + (A_N - N_k A_k)\,\sigma_{\text{M}}$$
$$= N_0 A_0 \sigma_0 + (A_N - N_0 A_0)\,\sigma_{\text{M}}, \tag{1}$$

where F is the breaking force, F_{ST}, F_{M} are the forces carried
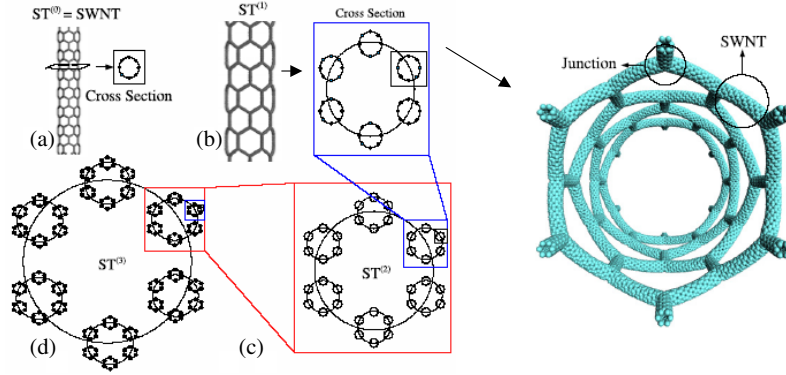by the longitudinal STs and matrix respectively belonging to

Figure 1. Generation of STs (adapted from [1]). A nanotube ($ST^{(0)}$) is considered as the fundamental unit (a); an $ST^{(1)}$ is generated by substituting the carbon bonds by entire nanotubes (see the schematic view on the right) (b); thus an $ST^{(2)}$ will present $ST^{(1)}$ bonds (c), and an $ST^{(3)}$ will present $ST^{(2)}$ bonds (d), and so on. After N iterations the hierarchical $ST^{(N)}$ is generated.

the hypothetical fractured plane cross-section surface (e.g., as depicted in figure 1 for $k = 1$) and σ_k is the strength of the $ST^{(k)}$. Note that $\varphi_k = n_{k-1}A_{k-1}/A_k$ represents the cross-sectional fraction of $ST^{(k-1)}$ in the $ST^{(k)}$ and thus $\phi_k = \Pi_{j=1}^{N-k}\varphi_j$ is the $ST^{(k)}$ cross-sectional fraction in the $ST^{(N>k)}$; consequently $\phi \equiv \phi_0$ is the nanotube cross-sectional fraction in the $ST^{(N)}$.

Strictly speaking, the hierarchical $ST^{(N)}$ is a fractal (i.e. self-similar at all the size scales [8]) if $n_k = n$ and $\varphi_k = \varphi \; \forall k$; for such a case $N_k = n^{N-k}$ and $\phi = \varphi^N$. Accordingly we expect $F_{ST} \propto R_N^D$ (as we will verify by deducing a constant D-value) where $R_N = \sqrt{A_N/\pi}$ is the radius of the $ST^{(N)}$ and D is the fractal dimension of the $ST^{(\infty)}$ set. The constant of proportionality can be deduced by noting that $F_{ST}(A_N = A_0) = A_0\sigma_0$, and thus $F_{ST} = \pi\sigma_0 R_0^{2-D}R_N^D$. Comparing this result with the equilibrium of equation (1) (i.e. from $F_{ST} = \pi\sigma_0 R_0^{2-D}R_N^D = \pi\sigma_0 n^N R_0^2$) we derive

$$N = D\frac{\ln R_N/R_0}{\ln n}, \qquad (2)$$

which defines the number N of hierarchical levels needed to generate a $ST^{(N)}$ of radius R_N.

The fractal dimension D can be determined noting that $A_N - N_0A_0 = A_N(1-\phi)$, thus $R_N/R_0 = (n/\varphi)^{N/2}$. Introducing this result into equation (2) yields the fractal dimension of the $ST^{(\infty)}$ set:

$$D = \frac{2\ln n}{\ln n - \ln \varphi}. \qquad (3)$$

Since $n > 1$ and $\varphi < 1$, $0 < D < 2$, and the $ST^{(\infty)}$ is found to have a lacunar two-dimensional cross-section, measurable in a length raised to D. For example, for $\varphi \approx 3/4$ (i.e., the maximum value, corresponding to a hexagonal close-packing factor) in carbon ($n = 6$) STs, $D \approx 1.72$. Equation (2) shows that only few hierarchical levels are required for spanning several orders of magnitude in size: for example, to design a macro $ST^{(N)}$ of radius $R_N = 1$ cm, composed of nanotubes with $R_0 = 1$ nm, we only need $N = 15$ hierarchical levels ($\varphi \approx 3/4, n = 6$).

Equivalently to equations (2) and (3), the radius of the $ST^{(N)}$ will be

$$R_N = R_0\varphi^{\frac{N}{D-2}}. \qquad (4)$$

Similarly to the force equilibrium, the hierarchical energy balance during fracture can be written as equation (1) with the substitution $F = A_N\sigma_N \rightarrow W = A_N G_N$, where G_N is the energy dissipated per unit area created of the $ST^{(N)}$ and G_M is the fracture energy of the matrix.

Furthermore, the hierarchical compatibility of the displacements during the stretching of the $ST^{(N)}$ would again lead to equation (1) in which the force $F = A_N\sigma_N$ is substituted by the force $K = A_N E_N$, where E_N denotes the Young's modulus of the $ST^{(N)}$ and E_M that of the matrix.

Thus, we predict the following 'universal' scaling:

$$\begin{aligned} P_N &= P_\infty + (P_0 - P_\infty)\,\varphi^N \\ &= P_\infty + (P_0 - P_\infty)\,(R_N/R_0)^{D-2}, \qquad P = \sigma, G, E \end{aligned} \quad (5)$$

for strength ($P = \sigma$), toughness ($P = G$) or stiffness ($P = E$), in which $P_\infty = P_M$.

Note that for chiral nanotubes described by a chiral angle ϑ (for the zig-zag configuration $\vartheta = 0$, whereas for the armchair $\vartheta = \pi/6$), we roughly expect $\sigma_0 \rightarrow \sigma_0/\cos^\alpha \vartheta$ in which $\alpha = 1$–2 (see [9], appendix III); $\alpha = 1$ would correspond to a lattice composed of pure axial bonds, and $\alpha = 2$ to a continuum. Accordingly, chiral supertubes (and nanotubes) are expected to be moderately stronger.

From equation (5) it is clear that the fractional physical dimensions of the fractal $ST^{(\infty)}$ set represents the cause of the strength scaling, whereas for a Euclidean cross-section ($D = 2$) no scaling is expected [8, 11]. For example, for an empty carbon $ST^{(16)}$ with $\varphi \approx 3/4$ ($\sigma_0 \approx 100$ GPa; see [9]) we deduce a theoretical strength $\sigma_{16} \approx 1$ GPa. Note that for $P = \sigma$, $\sigma_0/\sigma_\infty \rightarrow \infty$ and $D = 1.5$ the strength scaling is identical to the well-known Carpinteri scaling law [12].

However, note that if $\sigma_0 \gg \sigma_M$ we expect $E_0 \gg E_M$ but $G_0 < G_M$, since in classical materials strength (or stiffness) and toughness are competing parameters (e.g. diamond is hard but brittle), i.e. usually it is the softer matrix that is capable of dissipating the energy W during fracture: thus, smaller is stronger but less tough ($0 < D < 2$). According to these scalings the nanotube properties (P_0) prevail at the nanoscale, whereas the matrix properties prevail at the macroscale ($P_\infty = P_M$). Evidently the optimal solution would correspond to very strong, stiff and tough materials. These competing requirements are usually optimized by
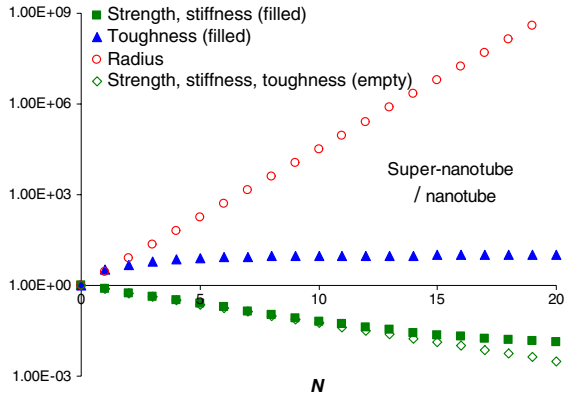
Figure 2. Strength, stiffness, toughness and radius versus hierarchical level N for a filled or empty $ST^{(N)}$. The dimensionless values are referred to those of the nanotube. Numerical (plausible) parameters used are $n = 6$, $\varphi = 3/4$, $\sigma_0/\sigma_M = 100$, $G_M/G_0 = 10$.
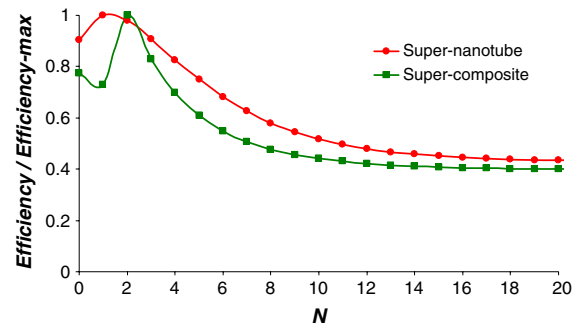

Figure 3. Relative efficiency versus hierarchical level N for an $ST^{(N)}$ or an $SC^{(N)}$. Numerical (plausible) parameters used are $n = 6$, $\varphi = \varphi_{ST} = 3/4$, $\lambda = 100$, $\sigma_0/\sigma_M = 100$, $G_M/G_0 = 10$, $G_M/G_I = 1$, $w_G = 1/3$. Note the maximum of the efficiency for $N_{opt} \approx 2$, as in the optimization done by Nature in nacre.

Nature, producing bio-composites with hard N-hierarchical inclusions embedded in a softer matrix, as for dentine or bone ($N = 7$, [13]), and nacre ($N = 2$, [14]). Thus, we suggest the possibility of using STs as hierarchical fibre-reinforcements embedded in a soft matrix for producing bio-inspired synthetic 'super-composites'. Note that materials are classically reinforced by fibres, platelets or grains (as reinforcements with very different surface to volume ratios). As STs can be used in fibre-reinforced super-composites or super-graphene sheets as platelet-reinforcements (as in bone, dentine and nacre [13–15]), 'super-fullerenes', which we define as the fullerene structure with ST 'bonds', could be useful for producing grain-reinforced super-composites.

For providing the material optimization we define the following functional:

$$\varepsilon_N = \sum_{P=\sigma,G,E} w_P \left(\frac{P_N - P_{max}}{P_{max}} \right)^2, \qquad \sum_{P=\sigma,G,E} w_P = 1, \tag{6}$$

in which the w_P are weight functions. Thus $0 \leqslant \varepsilon_N \leqslant 1$ represents the quadratic 'error' that must be minimized to have an $ST^{(N)}$ optimized according to the weights w_P associated to each property (fixed by the material application); complementarily we define $\eta_N = 1 - \varepsilon_N$ as the material efficiency. Introducing the scalings of equation (5) into (6) we obtain ($\sigma_{max} = \sigma_0$, $G_{max} = G_\infty$, $E_{max} = E_0$):

$$\varepsilon_N = a\varphi^{2N} + b\varphi^N + c,$$
$$a = w_G (G_0/G_\infty - 1)^2 + c$$
$$b = -2c$$
$$c = w_\sigma (1 - \sigma_\infty/\sigma_0)^2 + w_E (1 - E_\infty/E_0)^2. \tag{7}$$

The optimum is achieved for

$$\frac{\partial \varepsilon_N}{\partial N} = 0 \quad \Rightarrow \quad N_{opt} = \frac{\ln(-b/2a)}{\ln \varphi}. \tag{8}$$

For $G_0/G_\infty \approx \sigma_\infty/\sigma_0 \approx E_\infty/E_0 \approx 0$, $N_{opt} \approx \ln(1 - w_G)/\ln \varphi$, which for $\varphi = 3/4$ and $w_G = 1/3$ corresponds to $N_{opt} \approx 1.4$, whereas $w_G = 1/2$ yields $N_{opt} \approx 2.4$; thus ~ 2 hierarchical levels would be required in this example for having an ST, optimized with respect to strength,

stiffness and toughness or strength and toughness (with equal weights). Note that smaller values of φ would slightly reduce N_{opt}. For classical (empty) STs $N_{opt} = 0$; thus nanotubes are better than classical super-nanotubes, suggesting the important role of our proposal, i.e. of filling the ST with a soft matrix.

The strength, stiffness, toughness and radius of an $ST^{(N)}$ are depicted in figure 2, as a function of N. The material efficiency is reported in figure 3: note its maximum for $N_{opt} \approx 2$ for filled STs, as for nacre [13] (the cross-section of an $ST^{(2)}$ is depicted in figure 1), whereas for classical STs the optimum would trivially be represented by classical nanotubes ($N_{opt} = 0$).

3. Mechanics and optimization of super-composites

Equation (1) is derived assuming nanotube fracture; on the other hand, during the breakage of an $ST^{(N)}$ fibre-reinforced super-composite ($SC^{(N)}$), the $ST^{(N)}$, which is stronger than the softer matrix, will be pulled out from it rather than broken. The force F_{PN} needed for pulling out an $ST^{(N)}$ from the matrix can be derived according to fracture mechanics [16]. The energy balance during fibre pull-out is $d\Psi_N + G_I dS_N = 0$, where $d\Psi_N$ is the variation of the total potential energy (elastic energy minus external work) related to an $ST^{(N)}$ delamination of length dL_N or surface $dS_N = 2\pi R_N dL_N$; G_I is the fracture energy of the interface ($ST^{(N)}$-matrix, twice the surface energy). According to Clapeyron's theorem for linear elasticity (and force control) $d\Psi_N = -d\Phi_N$, where Φ_N is the elastic energy stored in the $ST^{(N)}$. Considering the matrix as a surrounding elastic half-space (non-interacting nanotubes) $d\Phi_N = F_{PN}^2/(2E_N A_N) dL_N$. Thus, we derive the following $ST^{(N)}$ pull-out stress:

$$\sigma_{PN} = \frac{F_{PN}}{A_N} = 2\sqrt{\frac{E_N G_I}{R_N}}. \tag{9}$$

Accordingly, the $ST^{(N)}$ pull-out will be activated in the $SC^{(N)}$ if $s \equiv \sigma_{PN}/\sigma_N$ is smaller than unity. For example, considering plausible values (see [9]) of $E_0 \approx 1$ TPa, $G_I = g G_M \approx 100$ N m^{-1}, $\sigma_0 \approx 100$ GPa, we deduce $R_0 > 40$ nm (imposing $s < 1$). Let us define $f(s < 1) = 1$, $f(s > 1) = 0$ as an on/off index for pull-out activation, or in general as the fraction

of $ST^{(N)}$ pulled out from the matrix. Including in the force balance of equation (1) the described pull-out mechanism, for an $SC^{(N)}$ with a fraction φ_{ST} of filled $ST^{(N)}$ (thus the total nanotube fraction is $\varphi_{ST}\varphi^N$) we deduce again the 'universal' scaling of equation (5) with $P \to \sigma^{SC}$ and

$$
\begin{aligned}
\sigma_0^{SC} &= \varphi_{ST}\left[1 + fs - f\right]\sigma_0 + (1 - \varphi_{ST})\sigma_\infty \\
\sigma_\infty^{SC} &= \varphi_{ST}\left[1 + fs - f\right]\sigma_\infty + (1 - \varphi_{ST})\sigma_\infty,
\end{aligned}
\tag{10}
$$

as can be derived from the force equilibrium; but note that here f and s are functions of N.

The stiffness is not affected by the pull-out; thus the Young's modulus scaling is again expected dictated by the scaling of equation (5) with $P \to E^{SC}$ and

$$
\begin{aligned}
E_0^{SC} &= \varphi_{ST}E_0 + (1 - \varphi_{ST})E_\infty \\
E_\infty^{SC} &= E_\infty,
\end{aligned}
\tag{11}
$$

as can be derived from the compatibility of the displacements before fracture discontinuity.

For s (smaller but) close to one the $SC^{(N)}$ strength is not affected by the pull-out process, i.e. $\sigma_N^{SC}(s = 1, f = 0) = \sigma_N^{SC}(s = 1, f = 1)$. The presence of nanotubes, with strength in the gigapascal and Young's modulus in the terapascal ranges, will strongly increase the composite strength and stiffness; but to have a true super-composite we also have to greatly increase its toughness. The pull-out energy is the key; thus we want pull-out activation ($s < 1$). The apparent fracture energy G_{PN} of an $ST^{(N)}$, statistically pulled out for one-half of its length, can be derived from the following energy equivalence: $G_{PN}\pi R_N^2 = G_I(\pi R_N^2 + 2\pi R_N L_N/2)$; thus

$$
G_{PN} = gG_M(1 + \lambda),
\tag{12}
$$

where $\lambda = L_N/R_N$ is the $ST^{(N)}$ slenderness. Note the huge toughening mechanism imposed by the pull-out (similarly to the crack deflection in the collagen-rich protein matrix imposed by the harder mineral platelets in bone, nacre and dentine [15]), with a giant gain in the fracture energy by a factor of λ, i.e. by several orders of magnitude, with respect to that of the matrix ($g = G_I/G_M \approx 1$). Thus, if a fraction f of the $ST^{(N)}$ will be pulled out, the energy of an $SC^{(N)}$ will again follow the scaling of equation (5) with $P \to G^{SC}$ and

$$
\begin{aligned}
G_0^{SC} &= \varphi_{ST}(1 - f)G_0 + \left[1 + \varphi_{ST}fg(1 + \lambda) - \varphi_{ST}\right]G_\infty \\
G_\infty^{SC} &= \left[1 + \varphi_{ST}fg(1 + \lambda) - \varphi_{ST}f\right]G_\infty,
\end{aligned}
\tag{13}
$$

as can be derived from the energy balance.

Since the same order relation is valid between P_0, P_∞ and P_0^{SC}, P_∞^{SC}, in addition to equations (5) and (6) equation (7) also remains valid, with the formal substitution $P \to P^{SC}$ and noting that the coefficients a, b and c are here functions of N (as f and s). Thus, the optimization of the $SC^{(N)}$ can be numerically performed by minimizing ε_N. Note that for a minimal fraction of binder between the $ST^{(N)}$ ($\varphi_{ST} \approx 1$), having comparable intrinsic and pull-out strengths ($s \approx 1$), for vanishing pull-out ($f = 0$) $P_N \equiv P_N^{ST} \approx P_N^{SC}$; thus filled $ST^{(N)}$ and $SC^{(N)}$ are equivalent, whereas the pull-out activation would basically modify only the fracture energy of the $SC^{(N)}$, greatly enlarging it according to $G_N^{SC} \approx G_{PN}$ (see
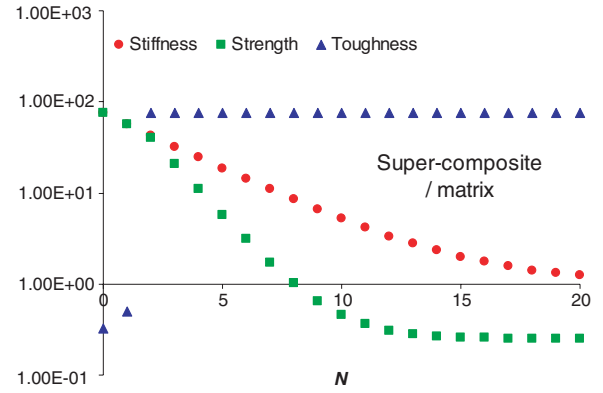

Figure 4. Strength, stiffness and toughness versus hierarchical level N for an $SC^{(N)}$. The dimensionless values are referred to those of the matrix. Numerical (plausible) parameters used are $n = 6$, $\varphi = \varphi_{ST} = 3/4$, $\lambda = 100$, $\sigma_0/\sigma_M = 100$, $G_M/G_0 = 10$, $G_M/G_I = 1$. Note the discontinuity in the toughness due to the pull-out activation.

equation (12)), thus by a factor larger than λ with respect to that of an $ST^{(N)}$.

The strength, stiffness and toughness of an $SC^{(N)}$ are depicted in figure 4 as a function of N. Its efficiency is reported in figure 3. Note the fundamental role of the pull-out, capable of activating giant toughening mechanisms and abruptly incrementing the material efficiency. It has a maximum, in this plausible example, again for $N_{opt} \approx 2$ (when the pull-out takes place), similarly to the optimization done by Nature in nacre [13].

4. Conclusions

Our finding, i.e. the possibility of optimizing simultaneously strength, stiffness and toughness, could become crucial for producing artificial and hierarchical super-composites, as is done by Nature in bone, dentine and nacre materials (to which the present analysis is thus straightforwardly applicable). Thus, the proposed approach could help in the future bottom-up design of strong, stiff and tough super-composites, by embedding the recently discovered super-nanotubes in softer matrices, mimicking the optimization done by Nature, embedding hard mineral hierarchical platelets in collagen-rich protein soft matrices.

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