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Nanoarchitected Tough Biological Composites from Assembled Chitinous Scaffolds

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Huang, W., Montroni, D., Wang, T., Murata, S., Arakaki, A., Nemoto, M., et al. (2022). Nanoarchitected Tough Biological Composites from Assembled Chitinous Scaffolds. ACCOUNTS OF CHEMICAL RESEARCH, 55(10), 1360-1371 [10.1021/acs.accounts.2c00110].

Availability:

[This version is available at: https://hdl.handle.net/11585/902566 since: 2022-11-14](https://hdl.handle.net/11585/902566)

Published:

[DOI: http://doi.org/10.1021/acs.accounts.2c00110](http://doi.org/10.1021/acs.accounts.2c00110)

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> > (Article begins on next page)

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In a multifunctional context. An organism rarely can be engineering perspective, biological solutions are intriguing because they must work
in a multifunctional context. An organism rarely can be optimally designed for only
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SEM micrograph of a longitudinal fracture along a cusp of
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SEM micrograph of a longitudinal fracture along a cusp of

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structures.

Systems, 1), Hosseini, M. S.; Reattepo, D.; Murata, S.; and compared magnetic nanorods an asoft, poor

Vasile, D.; Pathiston, D. Y.; Barand, H. S.; Arakais, A.; and organic-rich core of iron phosphate. The

V Vasile, D.; Parkinson, D. Y.; Barnard, H. S.; Arakaki, A.; nanorods in the shell run parallel to the tooth surface, aligned in the structure 2020 , $10-10^{-3}$ The diameters of the contour structure elvera of the diabolic 2-watatine; P; Kissilus, D. Toughening mechanisms of with the long axis of the tooth and curve around its till right and the compare the structure around its till respect to the reduced curve and the reduced curve of a n the elythron dimension inviolation incrude beetle. Nottone 2020, $10 - 1$ ²³. The diaming edge to 1944 a 30 mm on the trailing edge.¹ Each mineral composite found in a beetle that the eading edge to 1944 30 mm on the 566, 543—64 A *R* report of 0 nonmieralized, cush the leading edge to 1944 30 mm on the training degle.

Tresistiont biological composite found in o bettle that these nanorods have high surface roughness, as the contrains restitute hological composite found in a beelte that these enancods have high surface requeless, as they are inferfores, they are inferfores, they are inferfores, the incredible strong and tough, orchitected decorated with contains multiple strong and tough, architected which nampartiles (i.e., manosperities), some of interstingly, similar features have also been observed in the method of the california red abone.

1. INTRODUCTION Interesti interfoces.

Interfaces which form mineral bridges that connect alignes that connect and

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in an efficient arrow on the material arrangements at 1. INTRODUCTION

Interestingly, sim

Building lightweight, strong, and tough structural materials

Both these feature

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Interestingly, similar features have also been observed in the shall of the California red abor

ancreous platelets in the shell of the California red abor

and cost-effective manner has presented Fractured surface 1. INTRODUCTION

In an efficient article to the significant effective manner instructural materials aboth these features are likely a consequence of crystal growth

In an efficient and cost-effective manner has presented f Building lightweight, strong, and tough structural materials

Buting the features are likely a

in a efficiency and torself entime of the commercial during the biomineralization of

in a efficiency manner has presented Fr ning lightweight, strong, and tough structure and entimediated during the biomineralization of the matrix (see section)
and an efficient and cost-effective manner has presented Fractured surfaces reveal a conchoidal fractu in an efficient and cost-entere manner has presented Fracture distribution both and consideral are critical fractions of the one such and consider are for the particular for these strategies enter particular considers are challenges throughout human history. With an extreme smooth and ocasional play by
pranilend faceted surfaces?³⁸ This is expected materials exists in automobile, observed in early stages of development of the teeth, whic population boom over the past century, a significant coherent with multifixeded magnetic crystals (about 30 minds of the teeth, while demental resources, energy, biomedical, and defense sectors. then fuse together to form demand for these materials exists in automotive, observed in early stages of development of the network, which inverse were urgely ignored.² Although centuries have stores, then fusc engerter to form a single nanorod. H are
ospace, energy, biomedical, and defense sectors. Then thus tegether to form a single nanorod,
are However, with these advancements, environ- mental
the magnetite rannoots in C. steller tooth
relieverse been spent look Howeve, with these admorements, environ- mental and the solutional effect in the most increase the column state is the most increase the systems have been speed. Nothing for empressions, natural The magnetite nanorods in impacts were largely ignored.⁴ Milhough centuries have ². Wedilant existent in the minima materials of the paysing in the state in the minima material systems have been spent looking for emgineering solutions, natural

systems more receives the mollus and deriving both the results. The boung's modula associated with these nanorods
performance-"start have yielded incredient derecases by about 15% moving from the loading edge to the
perfo sympter the meaning of publical energy and publical and public and the some representative organisms and hardconic sympter in the interpret organisms and hardconic transfer and the some representative organisms and the so munities three structures that have yelene increduotes. This may be the structural enterphalism influenced by through that in the same incredictor of the total in materials utility minimal components to enhance stiffiness performance.² ²⁰²² Many of these biological structural training enge or the toom (regule and hardness yet, unlike their geological structural training enge or the control expansion and hardness yet, unlike their geolo materials utilite mineral components to enhance stiffness is associated with approximately a 20% increase where the biomineralization in Chiti and the minimately a conserver and the minimately conserver concernant and the and hardness yet, unlike their geological counterparts, rod diameter. Finite element models revealed that, while
not hardness show incredible toughness that can be arithuloted to the rasping on a rock, tensile stresses we show incredible toughness that can be attributed to the rasping on a rock, tensile stresses were concentrated at the morphology and material arrangements at the millimeter
scale level,³ These natural designs have allfor multiscale features, from the atomic and molecular level to leading edge of the tooth, while compressive stesses we
scale level to the controlline and molecular level to leading edge (Figure 1). Thus, the significant
sign the morphology and material arrangements at the millimeter present on the training edge (Eigure 11). Thus, the significantly symidicant development of biotingite designs for strong smaller ord diameters on the basile are s scale level.⁹⁷ These natural designs have afforded women, some scale in the signs and tough engineered designs for strong tens and tough engineered metricials.²⁸ and tough engineered metricials,²⁸ and tough engineer significant development of bioinspired designs for strong

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In thus, understanding how these structures are fabricated

Thus, understanding how these structures are fabricated resistance.

In thus, understa Thus, understanding how these structures are fabiricated The manorods, surrounded by an organic matrix of chitinous and their instead to reduce transport transport of this implies the manorods, surrounded by an organic ma and deriving bottom-up synthesis strategies are critical for the minimum deriving bottom-up synthesis strategies are the synthesis are the synthesis are the synthesis are the synthesis of bionispired materials. Natural sy ext stages or buonspared metallistical systems united vectors. Now the constrained metallistical metallistical metallistical metallistical metallistical metallistical metallistical metallistical metallistical method is the mmed elemental resources to symmeste and assemble "increaded mineral resources to symmetrical frameworks with inorganic components under cracks to grow and dissemblient temperature and near-neutral pH conditions to yield

architectures in the teeth of chitons (Figure 1A,B), mollusks
that feed on hard rocks to collect food (i.e., algae). Thus, the
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Nanorods have been found in the teeth of many species of
chiton, one of which is *Cryptochiton stelleri* or the gu the matrix stages of Manorod Architecture in Chiton Teeth

Nanorods have been found in the teeth of many species of

Nahorods have been found in the teeth of many species of

chiton, one of which is *Cryptochiton stelleri* 1. Nanorod Architecture in Chiton Teeth
Nanorods have been found in the teeth of many species of
chiton, one of which is Cryptochiton steller i or the gumboot
chiton. The cusps of its teeth consist of a hard crystalline s 1. Fractured with the composed of mapplement component of the state of many species of Nahrondos have been found in the teeth of many species of chiton. The cusps of its teeth consist of a hard crystalline shell composed Entimot) one of winter is *Cryptocimori* steller? or the guillooot scheer of the guino composed of magnetite nanorods and a soft, poorly crystalline, and organic-rich core of iron phosphate. The magnetite nanorods in the composed of magnetite nanorods of a riard cystalline,
composed of magnetite nanorods and a soft, poorly crystalline,
and organic-rich core of iron phosphate. The magnetite
nanorods in the shell run parallel to the tooth s compose or magnette transmoot and a vary populaming and organic-rich core of iron phosphate. The magnetite nanorods in the shell run parallel to the tooth surface, aligned with the long axis of the tooth and curve around i manorods in the shell run parallel to the tooth surface, aligned
with the long axis of the tooth and curve around its tip (Figure
16. Figure in the shell run parallel to the roots vary from 162 ± 22 nm on
the leading edge with the long axis of the tooth and curve around its tip ($\frac{F_{IRure}}{F_{L}} = \frac{1}{2}C - F$).²⁸ The diameters of the rods vary from 162 ± 22 nm on
the leading edge to 194 ± 30 nm on the trailing edge.¹ Each of
these nanorods $\underline{1}C - F$).²⁸ The diameters of the rods vary from 162 ± 22 nm on
the leading edge to 194 ± 30 nm on the trailing edge.¹ Each of
these nanorods have high surface roughness, as they are
decorated with nanoparticle

the leading edge to 194 \pm 30 nm on the trailing edge.¹ Each of
these nanorods have high surface roughness, as they are
decorated with nanoparticles (i.e., nanoasperities), some of
which form mineral bridges that conn these nanorods have high surface roughness, as they are
decorated with nanoparticles (i.e., nanoasperittes), some of
which form mineral bridges that connect adjacent nanorods.
Interestingly, similar features have also been decorated with nanoparticles (i.e., nanoasperities), some of

which form mimeral bridges that connect adjacent nanorods.

Interestingly, similar features have also been observed in the

nacreous platelets in the shell of t which form mineral bridges that connect adjacent nanorods.
Interestingly, similar features have also been observed in the
nacreous platelets in the shell of the California red abalone.
Both these features are likely a cons Interestingly, similar reatures have also been observed in the
nacreous platelets in the shell of the California red abalone.
Both these features are likely a consequence of crystal growth
during the biomineralization of t nacteous palaeless in the stiell of the Cainomia real abonous
Both these features are likely a consequence of crystal growth
during the biomineralization of the matrix (see <u>section 2.3</u>).
Fractured surfaces reveal a conch resistance. Exactured surfaces reveal a conchoidal fracture of the rods with
smooth and occasionally bipyramidal factette of the rods with
smooth and occasionally bipyramidal facteted surfaces.²⁸ This is
observed in early stages of Finderical contents of the controlling the propagation in the result of the east, the root with multifaceted magnetite crystals (about 30 nm) observed in early stages of development of the teeth, which then tuse together concern with multifraceted magnetite crystals (about 30 nm)

coherent with multifraceted magnetite crystals (about 30 nm)

observed in early stages of development of the teeth, which

then fuse together to form a single n **conserved in early stages of development of the teeth, which then fuse together to form a single nanorod.**

2. Mechanical Behavior of Nanorod Architectures

The magnetite nanorods in *C. stelleri* tooth show a hardness
 then fuse together to form a single nanorod.

2. Mechanical Behavior of Nanorod Architectures

The magnetite nanorods in C. stelleri tooth show a hardness

(9-12 GPa) 29 three times higher than human enamel (Figure

1H). 2. Mechanical Behavior of Nanorod Architectures
The magnetite nanorods in *C. stelleri* tooth show a hardness
(9-12 GPa) 29 three times higher than human enamel (<u>Figure</u>
1H). The Young's modulus associated with these nan 2. Investigalle nanorods in C. stelleri tooth show a hardness

The magnetite nanorods in C. stelleri tooth show a hardness

(9-12 GPa) 29 three times higher than human enamel (Figure

1H). The Young's modulus associated wi

been spent looking for engineering solutions, natuurl The magnetic nanorods in C. steller/ tooth show a hardness well are the respected in cell with the walls of the proper spentation of the solution of versions. The tuni exos exoses of exos of the state of arthropods, such that the minute are the state in the minima consideration of a symbolic symbolic symbolic symbolic such these involves in the partomic methods with the minima components The magnetite nanorods in *C. stelleri* tooth show a hardness
(9-12 GPa) 29 three times higher than human enamel (*Eigure*
1H). The Young's modulus associated with these nanorods
decreases by about 15% moving from the lea (9-12 GPa) 29 three times higher than human enamel (Figure 1H). The Young's modulus associated with these nanorods drenases by about 15% moving from the leading edge to the trailing edge of the tooth (Figure 1G). This dec $\underline{1}$ H). The Young's modulus associated with these nanorods
decreases by about 15% moving from the leading edge to the toor infigure 16). This decrease in the
stillnes edge of the tooth (Figure 16). This decrease in th decreases by about 15% moving from the leading edge to the trailing edge of the toth (Figure 1G). This decrease in the stiffness is associated with approximately a 20% increase in the rod diameter. Finite element models r trailing edge of the tooth (Figure 1G). This decrease in stiffness is associated with approximately a 20% increase in the real diameter. Finite element models revealed that, while rasping on a rock, tensile stresses were stiffness is associated with approximately a 20% increase in the
road diameter. Finite element models revealed that, while
rasping on a rock, tensile stresses were concentrated on the
leading edge of the tooth, while compr rod diameter. Finite element models revealed that, while rasping on a rock, tensile stresses were concentrated on the raphing edge of the tooth, while compressive stresses were present on the trailing edge (Figure 1)). Thu rasping on a rock, tensile stresses were concentrated on the leading edge of the tooth, while compressive stresses were locating edge (Figure 1). Thus, the significantly smaller rod diameters on the leading edge provided rasping on a rock, tensile stresses were concentrated on the leading edge of the tooth, while compressive stresses were present on the trailing edge (Figure 1)). Thus, the significantly smaller rod diameters on the leading present on the training edge (Higure 11). Thus, the signincantly
smaller rod diameters on the leading edge provided higher
tensile strength, while the thicker rods lead to compression
resistance.
The nanorods, surrounded smaller rod diameters on the leading edge provided higher
tensile strength, while the thicker rods lead to compression
resistance.
The nanorods, surrounded by an organic matrix of chitinous
interfaces, which are critical tensile strength, while the thicker rods lead to compression
resistance.
The nanorods, surrounded by an organic matrix of chitinous
fibers, lead to cracks propagating preferentially along the rod
interfaces, which are crit resistance.
The nanorods, surrounded by an organic matrix of chitinous
Thers, lead to cracks propagating preferentially along the rod
interfaces, which are critical in creating a tortuous path for
cracks to grow and dissip

subsequently converts to magnetic starting at tooth #4 within the mature teeth, is particular subsequently converts to magnetization. The assembly of the interfaction at the interfaction of the mature at the interfact of Figure 2. (A) Optical micrograph of immature radual, (B) Synchroton X-ray diffraction of immature techt. (C) Magnetometer data

demonatating the onset of magnetization affer tooth #3. (D) Phase dattroukin in immature tec Figure 2. (A) Optical micrograph of immature radials. (B) Synchroton a crucing the microstromoviality to the enterpret of the enterpret of the enterpret (m) (Magnetenneter data demonstrating the onset of magneteration and Figure 2. (A) Optical micrograph of immature radua. (B) Synchrotron X-ray diffraction of immature teeth. (C) Magnetometer data
Effemontating the onset of magnetization affer tooth #3. (D) Phase distribution in immature te Figure 2. (A) Optical micrograph of immature radula, (B) Synchrotron X-ray differacion for immature teeth. (C) Magnetometer
demonstrating the onset of magnetzation after tooth #3. (D) Phase distribution in immature teeth is divery 2.6. (A) Optical microstrapholis (iii) synchrotron X-ray diffraction of immature teeth. (C) Magnetometer data
image of a similar region in tooth #-1, abbouting chitin scales and old. (F) SEM of fractured leading TEM image of tooth $#-1$ highlighting chitinous scaffold. (F) SEM of fractured leading edge of a image of a similar region in tooth $#-1$, showing varied chitin scaffold architectures. (G) SEM of minimal particles templat

Mary of the tooth and a sparse, highly
and a stribution in immature teeth via μ -XARIS analysis. (E)
of fractured leading edge of a mature tooth (left) and TEM
id architectures. (G) SEM of mineral particles, guided by ch **Example 19**
 Alignation
 Alignation comparison in the matter than the sum of the nanor of the nanor of the results of fractured leading edge of a mature tooth (left) and TEM darchitectures. (G) SEM of mineral particles, guided by chiting the result is a par **Example 12**
Register of inmetable continue teeth. (C) Magnetometer data as distribution of inmetature teeth via μ XANES analysis. (E) of fractured leading edge of a mature tooth (left) and TEM of a single ferrihydrit With the mature teeth via particulate region on the lading edge of a mature teeth wia *HXANES* analysis. (E) of fractured leading edge of a mature tooth (left) and TEM ld architectures. (G) SEM of mineral particles, guided **Example 18 and the state of the state of the state (C)** Magnetometer data
ase distribution in immature teeth via μ -XANES analysis. (E)
of fractured leading edge of a mature totol (left) and TEM
of a chitectures. (G) SE **Example 18**
 EXECUTE: The Magnetometer datase distribution in immature teeth via μ XANES analysis. (E) of fractured leading edge of a mature tooth (left) and TEM dld architectures. (G) SEM of mineral particles, guide **THREE AND THREE CONSTRANGES**

THREE AND ASSES diases distribution in immature teeth via μ -XANES analysis. (E)

of fractured leading edge of a mature tooth (left) and TEM

of a continent leading edge of a mature tooth Example 12. The Magnetometer data of the Valentiation in immature teeth via μ -XANES analysis. (E) of fractured leading edge of a mature tooth (left) and TEM lol architectures. (G) SEM of mineral particles, guided by chi n X-ray diffraction of immature teeth. (C) Magnetometer datase distribution in immature teeth via μ -XANES analysis. (E) on the fractured leading edge of a mature totot (left) and TEM of a fracture and a chitectures. (G Find the matrix of the matrix of the matrix of the matrix of the dading edge of a mature tooth (left) and TEM
d architectures. (G) SEM of mineral particles, guided by chitin
d architectures. (G) SEM of mineral particles, of fractured leading edge of a mature tooth (left) and TEM
Id architectures. (G) SEM of mineral particles, guided by chitin
th #2). (I) TEM of a single ferrihydrite nanoparticle (inset,
e in tooth #4 via EDS. (K, L) SEM o

stage **stage** and the stage of the stage

The leading edge, which presents a more densely

and likely. The comparison and inter-halo and inter-halo and inter-

Fraction gradient methin-halo and inter-halo bonded to the chilin scalible promining different

present packed organic matrix (i.e., chitri fibiral) and likely
parenets more irror-binding sites (i.e., from chitri-
packed regards more irror-binding sites uses the irror binding sites associated peptides; see next section), yi presents more iron-binding sitts (i.e., from chitting-
associated peptides; see next section), yields a bonded to the chittin scallbod providing Fe-binding sites
grassicated peptides; see next section), yields a to locall associated peredies; see next section), vields a reaction and set accelerate the into concernent and set as generator of mailer manparicles (ca. 20-50 to locally increase the iron concernent
on an affect mumber of smaller greater umber of smaller nanoparticles (ca. 20–50)

magnetic runnic, Comparison (Figure 2N). The separate crystals (Figure 2N). The separate crystal method different analyses of

the minicipality of the strong tempelature mm). Conversely, the trailing edge, which contrist is emistric from the organic scattol different analyses of singer minimal agreed since the minimal agreed since the minimal agreed since the suggesting fever nucleation of less dense chitrinous scalloid, develops a lower number
of larger mineral aggregates (ca. 100-200 nm), highlighted strong involvement of cells in contoring
suggesting fewer nucleation stess. 100-200 nm), highlighted stron of larger mineral aggregates (ca. 100–200 nm), build care a concourance of the internal aggregates in early the mineralization conditions. Among then, the secent evaluation of these crystal aggregates in early the mineral gestring fewer nuclear
line and the mineralization conditions. Among them, cells
Recent revaluation of these crystal aggregates in early
of ferrhlydrite to magnette by transporting few-based
efficiences of the mineralizat Recent evaluation of these crystal aggregates in early

in the the responsible for activating the conversion

stage

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with a spherulite-like morphology,³⁶ We utilized EDS

species into the sca stage the emperation to form in the subsect of the scale in the figure of the scale in the teeth revealed ferrihydrite mesocrystals (Figure 21)

with a spherilitel-like morphology.³⁰ We utilized EDS

mapping of a mineral particle (Figure 21) to highlight

mapping of a mineral particle (Figure 21) to highlight

antenes and the mathematics of mathematics dense chiesal and the mathematics of mathematics dense chiesal and the mathematics of mathematics in the mathematics of mathematics of mathematics of mathematics of mathematics o **FRAME CONDITE TO CONDITION CONDITION** (The mineral aggregates (ca. 100−200 nm),
 CONDITE TO CONDITE TO CONDITION (The mineral aggregates (ca. 100−200 nm),
 CONDITE TO CONDITE TO CONDITION (Ca. 100-200 nm), and the mi Figure 3. Schematics and sequence of RTMP1, a suppose the consideration in the presence of nucleating fewer nucleating fewer nucleating fewer produced with permaneum and the leading and state in the leading edge, which pr THE THE THE THE CREAT Eighte 3. Schematics are a second mesos in the second mesos in the second mesos in the second mesos in the second of revealed from control outspace (8) used for proteomic meaning and the mesos of a method of revealed from **Eigents**
 **Eigents Externation C Externation Externation Externation External and an individual caduar tooth cusp, childnows stylus, and base (8) used for proteomic

analyses. (0) Smeandco of the spheral and** Figure 3. Schematics of a male means experience vigentized representation (N) Peproduce and minimidal ratural radius tradius reduction costs, (C) Amino add sequence of RTMP1, a cusp-specific radius protein, deduced from c Figure 3. Schematics of radular tissues (A) and an individual radular tooth cusp, chitinous stylus, and base (8) used for proteomic
manywes. (1) strems of the squeen of RTMP1, a cusp-specific radius proteins, deciding mod photon states are a states to insular states (which are the photon in the model in the componentation of the organic states in the componentation of the organic phase. The states in the proposition of the organic phase of experimention artes. (I) schematic of the domain structure of RIMPs bonum, counser reproduces the paper of the observed with permits of the domain structure of RIMPs bonum in this cells. The phosphorus suggests that a more presence explored with permission from the 25 Copyright 2013 Spnnger Nature. Numeration temperations and the material contents are expected by the material of the hypothesis that an addit Minister resulting in different have been observed at the leading and trailing edges,

now been observed at the leading and trailing edges,

corroborates in the hypothesis that an acidic MmsS-like protein and

ditinately resulting in different final rod have been observed at the leading and training edges,

have been observed at the leading and trianing edges, which presents are or the hypothesis that a acidic MmsSille proteins and

tultimately resulting in different fina ultimately resulting in different linal red diameters;¹ the "hypothesis that an "acidic Mms6-like protein and packed organic matrix (i.e., chitin fibrils) and likely $R\sqrt{M}$ and phosphoryated scriete-rich proteins, Fig Tregion

Supergrams

Supergram **Bonded to the chitin scaffold providing Fe-binding**
 EXERCISE ALERT SCAFFORM AND SCAFFORM AND SCAFFORM AND SCAFFORM AND MONOGRAPHONE CONDUCT SCAFFORM AND SCAFFORM AND SCAFFORM AND SCAFFORM AND SCAFFORM AND SCAFFORM AND S Examples and the strengthe matter is the resume the thighlighted strong increase the iron concentration and act as the iron concentration of the increase the increase the increase the increase the increase the increase the **EXERCISE THE SET ANTIFY AND SET ANTIFY AND SURFAINER AND MANUFATURE THE STRONG IN MARKET AND MANUFATURE THE STRONG THE STR** EFFECTER THE SUPPOSE THE SUPPOSE THE CHIS ABOVED THE CHISTON THE CHISTER THEORETIC THE CHISTER THEORETIC THE CHISTER THEORETIC CONFIRM (a) photonical scaffold provides and a structure. The original scaffold are provided t Expression of the tissue surrounding the primature teeth and the tissue of ferrihydric original properties are the myothesis of the immature highlighted strong involvement of cells in controlling THE MAN THE MAN THE MET AND THE mineralization of ferrindred proportions. Signal method tooth cusp, chitinous stylus, and base (B) used for proteomic ular protein, deduced from cDNA. Asterisks indicate putative MP1 showing **EXECUTE:**
 EXEC Example 12
 Example 12 Signal
 Expressions
 Signal
 Signa EXERCT THE SET THE SET AND THE SET AND THE SET AN EXERCT THE WARD THE SET AN INTEL SOMPT SHOW THE SET AN INCRED THE NOTIFY THE AND THE NOTIFY AND THE NOTIFY AND THE NOTIFY THE NEW THE NOTIFY (2) proper and iron binding 3 IVERT 1999
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INTELLET SURVERT A REFIRENCE TO THE SURVERT SIMUST SURVERT AND A METHON A A SET AND A SET AND A SET AND A SET AND A RANTAPI (a phosphoryized series refine and RTMP1 (a tooth cusp, chitinous stylus, and base (B) used for proteomic

ular protein, deduced from cDNA. Asterisks indicate putative

ular showing domains with specific repetitive dipeptide. Images

err Nature.

EXPLAT showing dom ular protein, deduced from cDNA. Asterisks indicate putative
ular showing domains with specific repetitive dipeptide. Images
ger Nature.

2. Altange domains with specific repetitive dipeptide. Images

gar, D, containing di Extrautate.

Extraction:

Extraction:

Extraction and iron binding³¹ Further analyses lead to

RTMP1 (a phosphorylated serine-rich protein, <u>Figures</u>

<u>3C,D</u>), containing different chitin-binding domains, are

bonded to oxygen and iron binding.³¹ Further analyses lead to
the hypothesis that an acidic Mms6-like protein and
RTMP1 (a phosphorylated serian-crich protein, Fi<u>lgures</u>
RICD), containing different chitin-binding domains, are
bon organisms. The meantion many in the hypothesis that an acidic MmS-like protein and RTMP1 (a phosphorylated serine-rich protein, <u>Figures</u> acop, containing different chitri-binding domains, are bonded to the chitri scaffol are "wyotenss that are neather thin to million the protein and the control and a control and bonded to the chitin scaling the bonded to the chitin screen to locally increase the iron concentration and act as nucleation poi EV and more the proposing sentential policing stems and the proposinople stems and and as a bonded to the chitin scaffold providing Fe-binding sites to locally increase the iron concentration and act as nucleation points. $\frac{1}{2}$, columing uniter tintin-toning contains, are
bonded to the chitin scalfold providing E-binding sites
to locally increase the iron concentration and act as
nucleation points.³² Despite the strong templating
the

bonded to the finim scaland providing resonance of the collage of the chirical points.³² Despite the strong templating effect from the organic scaffold, different analyses of the tissue surrounding the immeralization con to locally intrease the influctuation and act as
nucleation points.³² Despite the strong templating
effect from the organic scaffold, different analyses of
the tissue surrounding the immature teeth
highlighted strong in nucleation points.³² Leeplier ine string terminal mare string terminal effect from the organic scaffold, different analyses of the tissue surrounding the immature teeth highlighted strong involvement of cells in control enect from the origanit scalino, unierent analyses of
the tissue surrounding the immature teeth
highlighted strong involvement of cells in controlling
the mineralization conditions. Among them, cells
seem to be responsibl the tissue surrouning the immature teent
thighlighted strong involvement of cells in controlling
the mineralization conditions. Among them, cells
seem to be responsible for activating the conversion
of ferrihydrite to mag migning trarong involvement or cells in controlling
the mineralization conditions. Among the conversion
of ferrihydrite to magnetite by transporting fee²⁺-based
species into the scaflold (a chemical conversion
of ferrih the mineralization conditions. Among them, cells
seem to be responsible for activating the conversion
of ferrihydrite to magnetite by transporting Fe^{2+} -based
species into the scaffold (a chemical conversion
already rep seem to be responsible for activating the conversion
of ferrihydrite to magnetite by transporting Fe²⁺⁻based
species into the scaffold (a chemical conversion
already replicated *in vitro*). This process seems to
involve propagation

The dactyl club of the mantis shrimp, which can be accelerated different habitats and described in the expective cover for the mantis shrimp, and the mantis shrimp, and the mantis shrimp, which can be accelerated region i The dial carbitraries in the meaning ship and the dial carbitraries and the dial carbitraries in the meaning and the dial carbitraries in the meaning and the dial carbitraries in the meaning and the dial carbitraries in th shells of various marine prey, is a primary example of a in their respective environments.⁴⁴ Melicoidal and interesting the marks shrimp and its about the distribution with the around the marks shell and contact region i Figure 4. Helicoidal architecture in the matter shrimp and the distribution of the **Example 18**
 Example 14
 Example 14 Figure 4. Helicoidal archives in the mantis shrimp and its sharp and this sharp and this sharp with the metho Figure 4. Helicoidal architectures in the mantis shrimp doctyl club and cutide of the diabolical ironchad beetle. (a) Mantis shrimp and its
dactyl choids (while arrow). (b) Optical micrograph of a cross-section of the dac We recently the distance of particle in panel b. (d) Schematic and SEM image showing the crack twisting a line endocutie. (h) Interply penetra

dact) clubs (white arrows). (b) Optical micrograph of a cross-section of the dactyl club districts (helicoidally arranged chitin fibers in the periodic region in panel b. (d) Schematic any the helicoidal mitin fibers in t schematic of neited pharamaged chitin fibers in the periodic region in panel b. (d) Schematic and SEM image showing the crack to the periodic region of the televisor of between the surface in the shellood include televiso For clusters arounded by a mineral matrix (Figure 4a). ²⁵⁰ million years
of chitinous fibers surrounded by a mineral matrix (Figure 4a). ²⁵ as the rhinoceros the
does not fiail. Three regions have been identified in t of chitinous fibers surrounded by a mireral matrix [*Eigure* 4a). ^{2. Do} 'lumoir years are functions to the intervel the intervel to the the intervel to the societie, at the dot not fail. Three regions have been identifi

ifigure 4. Heliocloil aristhetime in meants shime packing in the mattis shime direct of heliochical irreductions in the mattis shime and its of the distribution in the mattis shime and the step in the step in the step in t (b) Optical micrograph of a cross-section of the dately club displaying multiple regions. (c) SEM and the surface layer and a schwaring multiple response of the impact surface of the impact of the impact of the impact of t y the heliodial chitin fibers in the darty dubb. (e) lmage of diabolical incolds because (*E. diabolical*), (f) False colored SEM microstope (*E. diabolical*) and chitin incomparticles; the middle and controller with the m cross section of beetle elytra. (g) Heircoidal archaracterized entitin theirs in the endoctricity penterphype tentain estingential contain archaractery (Fibers) Sometime of this minimal contains (Figure 10) Sometime Theore coloridary within the helicoidal structure. Images were reproduced with permission from re L_2 copyright 2021 wiley, ref 3. Copyright Notice reading to catastrophic failures, thus protecting the underneafth 350 000 distinct species including flying, terrestrial, and soft tssues efficiently and increasing the lifetime of the aquatic variants.⁸³ The elyt Every en courser experience of this protecting the undernead and contrists.⁵³ The eigins increasing the substitute of the substitute of the eigins of biological armors or weapons.²²³ are eigins increasing the liferien leading to catastrophic failures, thus protecting the underneafth 350 000 distinct species including flying, terrestrial, and
soft tissues efficiently and increasing the lifetime of the aquatic variants.⁹ The elytra ult elasting to catastrophic failures, thus protecting the underneath 350 000 distinct species including flying, terrestrial, and
solotionses efficiently and nicreasing the lifetime of the equation variants;⁵¹ The elytra ul **Beach Constant on the proceding the underneast and the spectra of two moments are didentified left in the spectra of the proceding consider anisot** Soft tristels: emperative and infractrome interfaces of the displayer at the level of the sycket of the sycketion at interfaces in the level of the sycketion at interfective coeffect of the match of pole in The level of th blogical armors or weapons.²²³³ as the matterial structure of the endependent in the flatter in the indepthene must be the matter of the matter of the matter of the matter in the decided helicoidal structure. The decide 1. Heliopid in Mants Shrimp, which can be accelerated three maths and described bow variations in their theoretical analyses of beetes rom between the constrained bow variations in their theoretical analyses of beetes rom The dearly club of the meantis shrimp, which can be accelerated dilierent habitats and described how variations in the
sheller of the mathematic means the mean scheme in the mathematic structure in the sheller of various to nearly 33 m/s at an acceleration over 10000g to impact the exoskeletal architecture and composition allow them to three independents and the energy arrangement of chitin and architecture and consideration of chitin and shells of various marke prey, is a primary example of ain their respective environments.³⁸ We focused on the elytra

biological composite with a helicoidal architecture that consists from two species of beteles that bran biological composite with a helicoidal architecture that consists from two species of beetles that bianched aproximately
to dictions for the composite with a helicoidal architecture that consists in a lifetyle yere also th does not tail. Inter-regions have been loentimed an the daty) depote the mander in the school of the mantis shrimp, the outer sure the mantis for the mantis (the mantis of the mantis (the mantis of the mantis of the mantis examples of orientation and absorb large amounts of unewside in the eight residing on the western coasses are the proposite many insults and the proposite of the methods.³⁴ For *Coabibitas*, this insults of the singer of entrey the other samele alone is the limpatit "experiment in the control are the motion is a layer of highly mineralized hydroxyapatte of Moth America³²⁶ For P. didubitions, this line
(HAP) and chitin manoparticles; the since, which is a regre of mindle methaliced into the been widely advertised in a structurally robust cuticle
Integrate rigoton, containing mineralized chitin fibers arranged in capable of withstanding predotor strikes (F Hower and custom-minione microscopy in the consider of withstanding predator strikes (Figure 24). Our lamped tegant architecture that displays a herricole is helicolal architecture that displays a herricole of withstandin matter region, containing limited matter cannot mean are also consists of the epitype in excessive in the higher stationary in the transformation in the interest and the principal station of the principal station of the m delicated the methods and the provides and tend winding in the section of the methods of both organisms in the helicon streation of the endocuties, of both organisms in the helicodial arrangement winding heraction and the one metringtone arrangement of chiractic resolution of contains are controlled and metriculated and tractical strangement, with lamelae that calculated photosical proposition photosical strangement (with lamelae that calcu evidence with the principle in the periodic resulted in the periodic resulted in an excess of the periodic region constructed from unidirectional microfolisins.⁶ The fibers in the periodic reduction at interface and the different for the distribution of the distribution of the distribution of the data of the distribution of the datyl club displaying multiple regions. (c) SEM and panel b. (d) Schematic and SEM image showing the crack twist **Exond the different** of the diabolical ironclad beetle. (a) Mantis shrimp and its

on of the daxtyl club displaying multiple regions. (c) SEM and

incordad beetle (*P. Idaobicus*). (f) False colored SEM incordates (*P. I* **Example 19**
 Example 10
 Example 10 From the daty dielaying multiple regions. (c) SEM and panel both daty and panel b. (d) Schematic and SEM image showing the crack twisting a panel b. (d) Schematic and SEM image showing the crack twisting is in the endocut 250 million years ago:40,42 Trypoxylus dichotomus (known **Example 19.1**
 Cultice of the diabolical ironclad beetle. (a) Mantis shrimp and its

on of the dactyl club displaying multiple regions. (c) SEM and

in ironclad beetle (*P*, *diabolicus*), (f) False colored SEM interce cuticle of the diabolical ironclad beetle. (a) Mantis shrimp and its
on of the diabolical ironclad beetle (a) Mantis shrimp and its
on of the datyl cubid displaying multiple regions. (c) SEM and
panel b. (d) Schematic and cuticle of the diabolical ironclad beetle. (a) Mantis shrimp and its
on of the dactyl club displaying multiple regions. (c) SEM and
pranel b. (d) Schematic and SEM image showing the crack twisting
in ironclad beetle (*P*, exame of the datyl club displaying multiple regions. (c) SEM and panel b. (d) SEM and panel b. (d) Schematic and SEM image showing the crack twisting
is in the endocuticle. (h) Interply penetrating chirin microfibers (fal is panel b. (d) Schematic and SEM image showing the crack twisting in ironclad betele (P , diabolicus). (f) False colored SEM introdibers is in the endocuticle. (h) Interply penetrating chith microfibers (false with perm It ironclad beetle (*P. diabolicus*). (f) False colored SEM micrograph a
sin the endocutice. (b) Interply penetrating chitin microfiblers (false
opyright 2016 Wiley; ref $\frac{38}{28}$, copyright 2018 Elsevier; and ref $\frac{4$ is in the endocuticle. (h) Interply penetrating chitin microfibers (false
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copyright 2016 If with permission from ref 2, copyright 2012 AAAS; ref 3, copyright 2016 Wiley; ref 38, copyright 2018 Elsevier; and ref 44, copyright 2016 Wiley; ref 38, copyright 2018 Elsevier; and ref 44, protective cover for the und copyrignt 2016 Wiley; ret 38, copyrignt 2018 Eisevier; and ret 44,
350 000 distinct species including flying, terrestrial, and
aquatic variants.⁴³ The elytra ultimately serve as a
protective cover for the underlying del 350 000 distinct species including flying, terrestrial, and
aquatic variants.⁴³ The elytra ultimately serve as a
protective cover for the underlying delicate hind wings.
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aquatic variants.⁴³ The elytra ultimately serve as a
protective cover for the underlying delicate hind wings.
We recently investigated two species of beetles f 350 000 distinct species including flying, terrestrial, and
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We recently investigated two species of beetles f sourcol distinct between including lingt, terrestinal, and
aquatic variants.⁴³ The elytra ultimately serve as a
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We recently investigated two species of beetles from different habitats and described how variations in their e procedure cover io the underlying denote and wings.

We recently investigated two species of beetles from

different habitats and described how variations in their

exoskeletal architecture and composition allow them to t we recently investigated two signettes or between the precent habitats and described how variations in their exoskeletal architecture and composition allow them to thrive in their expective environments.⁴⁴ We focused on and the measure and destribed now variations in their
exoskeletal architecture and composition allow them to thrive
in their respective environments.⁴⁴ We focused on the elytra
from two species of beetles that branched exusseued a contentius and composition allow their to time
sin their respective environments.⁴⁴ We focused on the elytra
from two species of beetles that branched approximately
250 million years ago:^{49,42} Trypoxylus di If then respective environments. We foucased on the eigita

from two species of beetles that branched approximately

250 million years ago: $\frac{40.42}{3}$ Trypoxylus dichotomus (known

as the rhinoceros beetle), a tree-dwel mort wo species the between that brack deflection as the rhinocento deprominately and thus dichotomus (known
as the rhinoceros beetle), a tree-dwelling and thus flight
capable beetle inhabiting East Asia, and *Phloeodes*
 Endote the dialogu⁻⁻⁻⁻⁻ ryppoxyas anchuorus (stuown
as the rhinoceros beetle), a tree-dwelling and thus flight
capable beetle inhabiting East Asia, and *Phloeodes*
diabolicus (named the diabolical ironclad beetle), a te as the Finnoceno beeute), a tree-varianing and thus lingthe consider beatle inhabiliting East Asia, and *Phloeodes diabolicus* (named the diabolical ironclad beetle), a terrestrial fungivore incapable bot flight residin Capable

Capablicus (named the diabolical ironclad beetle), a terrestrial

functions (named the diabolical ironclad beetle), a terrestrial

fungivore incapable of flight residing on the western coast

of North America.^{4,} *thanonicus* (inane the utalonical better), a terrestiand the may denote the digitore incapable of flight residing on the western coast of North America.⁴⁴⁵ For *P. diabolicus*, this inability to actuate its elytra has number include of matter curresting of the essert roast
of North America.^{4,65} For *P*. *diabolicus*, this inability to
actuate its elytra has resulted in a structurally robust cuticle
capable of withstanding predator st or worth Fanceta.²— For *P. unboution*, this manding to the endocution atdute its elytra has resulted in a structurally robust cutice capable of withstanding predator strikes (Figure 4e). Our investigation of the elytra, actuate is every a lars resture in a structural probable contable of withstanding predator strikes (Figure 4e). Our investigation of the elytra, the endocuticle, of both organisms region of the elytra, the endocuticle, of depart of winding preductor sinks (in the interestigation of the microstructures within the innermost region of the elytra, the endocuticle, of both organisms revealed a hierarchical arrangement, with lamellae that contai messignation of the mitrotostructures will the interestingual of the engins revealed a hierarchical arrangement, with lamellae that contain balkens, or parallel bundles of fibers, each of which is constructed from unidire region of the enyind, the enotoctucle, of both origannsins
revealed a hierarchical arrangement, with lamellae that
contain balkens, or parallel bundles of fibers, each of which is
constructed from unidirectional microfibr

resistance. $\frac{47,48}{ }$

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These robust and total modernical celebratic Eigure 5. Elytral microstructure of T. dichotomus at (A) 0 h after ecosion and (B) 192 h after ecosion. EOC, elytral dorsal cuties;
EVC, elytral ventral cuties; Tr. dichotomus at (A) 0 h after ecosion and (B) 192 h after e Eignue 5. Elytral microstructure of *T. dichotomus* at (A) 0 h after eclosion and (B) 192 h after eclosion. EDC, elytral dorsal cutile;

Evic, elytral version and (D) then the state of the state of the state of the state Figure 5. Elytral mistostructure of T. dichotomus is a state electron of T. dichotomus. The response that the electron is the electron of the Eigure 5. Elytral microstructure of *T. dichotomus* at (A) 0 h after eclosion and (B) 192 h after eclosion. EDC, elytral dorsal cutide;
EVC, elytral dorsal cutide; Tr, trobecolae; Eoo, exoutide; News, mesocutide; Finso, e Figure 5. Elytral microstructurel of F. dichotomus in Signs and (B) 1921 and engines in Signs and total engine encome and (B) 1921 and engines. EDC, elytral domain cuticle, TVC, elytral ventral ducle T, trabeculae, Exo, e Figure 5. Elytral microstructure of *T. dichotomus* at (A) 0 h after eclosion and (B) 192 h after eclosion. EDC, elytral dorsal cuticles

EVC, elytral versital cuticles, ^Tr, trobecolae, Eoo, exouticle, Neso, mesocuticle Figure 5. Bytral microstructure of T. dichotomus at (A) 0 h after edsign and (B) 120. h after eclosion, EDC, elytral docties

EVC, elytral chiting Alexans composite form of the signal chiting the section and (D) domains. I evolve a strong entropies in the electronic interval and the electronic interval and a thin ventral responses to the electronic interval and a thin ventral responses to the nonmineralized structure (and manney which are ob multiple Auswaring the para substantial space of the reaction and the substantial space of the extraction of the extra substantial space of the substantial space of the substantial space of the strategy of the space of th Estimans and toughness to the nonnineralized structure

stiminale, which are observed in the elytra at 192 HAE

stiminare bin terms in the content interalization cerestance. This is figure SBN.

similar to those observed i stillness and toughness to the nonmineralized structure laminae, which are observed in the elytra at 192 HAE
with augmented interlaminar resistance to shear. This is (Figure 5B).
Similar to those observed in tooth enamel stifliness and toughness to the nonmineralized structure

with augmented interlaminar ceisincate to shear. This is $\left(\frac{\text{Teg}_{1121}}{\text{Eg}_{2112}}\right)$ is $\frac{d}{dt}$, which augmented interlaminar to those observed in tooth enam stillness and toughness to the nonnineralized structure and range, which are observed in the elytra at 192 HAE
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formic through thi with augmented interlationarises these. This is the liggue SB-

signiar to those observed in tooth enamel and ram Although T. dichotorus does not present a

being through thickness these fibers infer common helicoloid a c similar to those observed in tooth enamel and ram Although T. dichotomus' obser not present a more controlled and reductional and reductional schillance the microstructure design themes used for compression molecular stud horist frow the chience liberal enties their somes in the provides a pathway through the
instance-that design themes used for compression which assembly may be understood. A recent
resistance-these
instance-these improdun microstructural design themes used for compression which assembly may be understood. A recent
resistance $\frac{d^{2}8}{8}$ molecular study has demon-stated the functional
3.3. Self-Assembly of Elytra importance of the structu helicoidal architecture, it provides a pathway through the control of the structural energy of the structural energy of the structure of the structural energy of the structural energy of the structure of the structure of t Which assembly may be understood. A recent
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CREATIONS CONSULTERATIONS CONSULTERATIONS CONSULTERATIONS CONSULTERATIONS CONSULTERATIONS CONSULTERATIONS CO From the chitin fibers. The chitin fibers of the structural development of *T*, dichotomus, the respectively.

The chief of the chief of the chief of the structural control of the structural control of the chitin binding
 development of T. dichotomus elytra, protein profiles of Structural development of P. dichotomus elytra, profiles of T. dichotomus development of P. dichotomus development of P. dichotomus development of T. dichotomus deve entraneous and (8) 192 h after eclosion. EDC, elytral drastically changes and Richards and Changes and differentially continuous since the matrix control in the set of the matrix of th Structural development of elytra, which are CPs with electric CPs (elytral dorsal cuticle;

mesocutide; Endo, endocutide. (C) Gly-rich region and (D)
 tomus. The region highlighted in gray indicates chitin-binding

(Fig rich regions and (B) 192 h after eclosion. EDC, elytral dorsal cuticle;

I., mesocuticle; Endo, endocuticle. (C) Gly-rich region and (D)
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, mesocuticle; Endo, endocuticle. (C) Gly-rich region and (D)

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laminae, which are obser Localism and the 132 T are ecosions. Every an discussion and (b)

these CPs were differentially and the elytra and these CPs were different and the region highlighted in gray indicates chitin-binding

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pyright 2022 Elsevier. The region highlighted in gray indicates chitan-binding
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laminae, which are observed in the elytra at 192 HAE

(Figure 5B).

Although T. dichotomus does not present a

helicoidal architecture, it provides a pathway through

molecular study has demon-stra laminae, which are observed in the elytra at 192 HAE (Figure 5B).

Although T. *dichotomus* does not present a helicoidal architecture, it provides a pathway through which assembly may be understood. A recent molecular st laminae, which are observed in the elytra at 192 HAE (Figure 5B).

(Figure 5B).

Although *T. dichotomus* does not present a helicoidal architecture, it provides a pathway through which assembly may be understood. A recent laminae, which are observed in the elytra at 192 HAE (Figure 5B).

Although T. *dichotomus* does not present a helicoidal architecture, it provides a pathway through which assembly may be understood. A recent molecular st vientime, when all the observed in the eigeral at 152 rinch

(Figure 5B).

Although T. dichotomus does not present a

helicoidal architecture, it provides a pathway through

molecular study has demon-strated the functiona (Figure 20).
Although T. *dichotomus* does not present a helicoidal architecture, it provides a pathway through which assembly may be understood. A recent molecular study has demon-strated the functional importance of the Antiough *T. anchournis* uoes not present a
helicoidal architecture, it provides a pathway through
which assembly may be understood. A recent
molecular study has demon-strated the functional
importance of the structural c

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The time of the content of the method and the method of the stress is the content of t Figure 6. Biolispired composites based on the lictical structures compared with a series of the crack twisting mechanisms in the crack twisting mechanisms in the crack twisting mechanisms in the crack twisting (b) Drop $\frac{1}{1}$
 $\frac{1}{1}$
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Figure 6. Biomspired designs of helicoidal composite structures (a) Experimental result and theoretical analyses of the crack twisting

Figure 6. Biomspired designs of helicoidal structures The perimental can also ⁸ **CEF73** OEEN OF THE CRIST CHECK Eigure 6. Bioinspired designs of helicoidal composite structures, (a) Experimental result and theoretical analyses of the crack twisting
menact tests of carbon fiber reline of the peoplet bending experiments of 3D princed Pigure 6. Biomispied designs of helicoidal composites structures. (a) Experimented and theoretical analyses of the crass theoretical composites of the crass of castomic tests of castomic compared terms impact tests of cast mechanism in neurolan structure. Inter-period structure and the present with the internal damage in different critic and the present of the internal damage in the internal damage was more than the internal damage in the in migut testo uratom inter remotived composites (crive) with relations solutions, outsourt c-starming mages in different CFRP samples: (c) Arenages in different CFRP samples: (c) Arenages in different CFRP samples: (c) Aren difference of the the matter of the matter in the different simples in the dimension of the dimension from the 12. Copyright 2018 Baseurs, red and conserved with permission from the 12. Copyright 2018 Baseurs, red and impa were reproduced with permission from ref 12, copyright 2014 Elsewier, ref 136, copyright 2012 Elsewier, and ref 130, copyright 2020

Biolispired composites based on the historical elsewier, ref 138, copyright 2012 Elsewier Bsevier.

S.4. Biomimetic Implementation of Helicoidal Biomimetic and the helicoidal Biomimetic angles because the proposition of the structures discussed above, coatings

biomething but also from the elitred of the diabol 3.4. Biomimetic Implementation of Helicoids

Biologipied composites based on the helicoidal spy improving the abrasive solid by improvide the contrige biologipies

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Houeprints provided not only from dactly loths of mattis behavior of the structures discussed above, coatin
between those form the elytra of th blueprints provided not only from datty leabls of mantis behavior of the structures discussed above, coating
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di shreps but also from the elyins of the diabolical irroduces in the distriction and constituting naino- particles assembled from chiting the diabolical irroduces show been developed by nature to phere is performance to the belieft were fabricated and tsultide.⁴²³ 3D printed macrometecties have been drevioped by nature to the composite show signification in this composite composites that increases in provide further protection, while in var plastic composites show signiticant increases in provide turner protection, while in a vanishing consisting of high
damage tolerance in helicoidal structures compared applications thin film coatings consisting of high
to damage tolerance in helicoidal structures compared applications. Thin means the proposition of many constrained is the reack twisting mechanisms protection for underlying structures form abrasim, $\frac{1}{2}$ ($\frac{1}{2}$ ($\frac{$ to unidirectional and quast-isotropic designs, concertations or nanoparticles anve also been applied as the impact resistance and damage impact, and energy dissipation is the impact resistance and damage impact, and energ primaribly due to the crack twisting mechanisms protection for underlying structures from a
of the mondel tractures were also means to presentative applications is the costing layer
investigated in carbon fiber reinforced performance.

4. NANOPARTICLES

applications the interleption of anoparticles have also been applications from depresentative applications of anoparticles intersection for underlying since $\frac{38}{2}$ coverage $\frac{38}{2}$ coverage $\frac{3$ From the streament and the streament and the streament and the streament and the streament of the streament of the crack twisting of 3D printed samples show crack twisting. (b) Drop weight of an entancel and theoretical 2000

and a state of the consisting of the consistent of the representative applications of the coating of the consisting

dass/Epoxy Kevlar/Epoxy Glass/Urethane Kevlar/Urethane

consists of 3D printed samples show crack **CONCETE:**

Concerting the state of the control of the presenting particles. Nanoparticle coating particles have a

impactions of a prince sum term of the state of the control of the state of a

Consider the relations of $\frac{6}{3}$ $\frac{6}{3}$ impact, and erosion damage.51,52 One of the Glass/Epoxy

Kevlar/Epoxy

Kevlar/Epoxy

Kevlar/Epoxy

Glass/Urethane

Reprimental result and theoretical analyses of the crack twisting

original structures. Ultrasonic C-scanning images show the internal

noidal structur Wevlar/Epoxy Glass/Urethane Kevlar/Urethane

(perimental result and theoretical analyses of the crack twisting

(perimental result can be defined analyses of the crack twisting

individual structures. Ultrasonic C-scannin bestigated readation and theoretical analyses of the crack twisting
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of 3D printed samples show crack twisting. (b) Drop weight
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original structures. Ultrasonic C-scanning images show the internal
original of different is of 3D printed samples show crack twisting. (b) Drop weight
oidal structures. Ultrasonic C-scanning images show the internal
ond Kevlar fiber reinforced epoxy composites. (d) Dent depth in
um load of different samples i oidal structures. Ultrasonic C-scanning images show the internal
not deviar fiber reinforced epoxy composites. (d) Dent depth in
sum load of different samples in the drop weight tests. Images
er; ref $\frac{38}{25}$ copyright 4. NANOPARTICLES
By improving the abrasive and impact resistance
behavior of the structures discussed above, coatings
constituting nano- particles assembled from chitin
provide further protection, while in various enginee 4. NANOPARTICLES
By improving the abrasive and impact resistance
behavior of the structures discussed above, coatings
constituting nano- particles assembled from chitin
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By improving the abrasive and impact resistance
behavior of the structures discussed above, coating
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provi Evaluation of the structure above, coating the abrasive and impact resistance behavior of the structures discussed above, coating constituting mano- particles have been developed by nature to provide further protection, w By improving the abrasive and mpact resistance polyinomy the structures discussed above, coatings constituting nano- particles assembled from chitin macromolecules have been developed by nature to provide further protecti benavior of the structures discussed above, coatings
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macromolecules have been developed by nature to
provide further protection, while in various engineering
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Shrimp

constituting mano- particles assembled from chitin
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concentrations macromoecules have been developed by nature to
provide further protection, while in various engineering
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protecti provide turter protection, while in various engineering preserved applications thin film coatings consisting of high concentrations of nanoparticles have also been applied as protection for underlying structures from abra applications thin lim coatings consisting of high
concentrations of nanoparticles have also been applied as
protection for underlying structures from abrasion,
impact, and erosion damage.^{33,32} One of the
representative concentrations of nanoparticles have also been applied as
protection for underlying structures from abrasion,
impact, and erosion damage.^{51,52} One of the
representative applications is the coating layers on
wind turbine protecton for underlying structures from andrasion, and enosion damage.^{31,522} One of the imperesentative applications is the coating layers on wind turbine blades, which can be damaged by erosion from rain droplets, san mpact, and erosion damage.²²²² One of the
representative applications is the coating layers on
wind turbine blades, which can be damaged by
erosion from rain droplets, sand, and flying
particles. Nanoparticle coatings o

Figure 7. Hydroxyapatite/kinin manapatite doming and the surface of the mantis shring back (a) Schematic of the instantional structure of the dosts (chitin and protein) the matrix shring back (a) is before and after high s molecules, which were observed in these particles, which were also ananoparticle coating on the surface of the mants shrimp dactyl club. (a) Schematic of the interactive correct the datyl club. (a) schematic of the interac Signal 2. Hotewarantile (absorband the crystallization of the matrix shrim decided in the crystallization resolution TEM image of the crystallization resolution TEM image of the crystallization resolution TEM image of the Figure 7. Hydroxyapatite developed and properties are a structure of the analysis of the high-
structure of the destyl club and nanoparticle coating there. (h) High-resolution TEM image of the composite nanoparticle, (c) H Figure 7. Hydroxyapatte/chitin annoparticle costing on the suffice of the mantis shrimp dactyl club, (a) Schematic of the hierarchites
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stratuture of the daty! club and nanoparticle coating layer, (b) High resolution TEM i Figure 7. Hydroxyapatite/chitin nanoparticle ceating on the sufface of the mantis shrimp dactyl club. (a) Schematic of the hierarchical structure of the dactyl club and nanoparticle costume in the surface of the mathis shr Figure 7. Hydroxygaatte/chitin nanoparticle coating on the surface of the mantis shrimp dactyl club. (a) schematic of the interactional
structure of the description and omnegative coating tween (b) High ersealing the prop Similar to the mantis shrimpy dactyl club. (a) Schematic of the hierarchical resolution TEM image of the composite nanoparticle. (c) High and (201) plane of HAP. (d, e) TEM images of nanoparticle of the multiscale toughen **Example 12**
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resolution TEM image of the composite nanoparticle. (c) High

a nand (201) plane of HAP. (d, e) TEM images of nanoparticle

5 Springe matric the mantis shrimp dactyl club. (a) Schematic of the hierarchical
resolution TEM image of the composite nanoparticle. (c) High
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of the multiscale toughening

reparties of the distance of the main any operation of the main and point in the main and a main and a main any operation red in the main any operation red in the constraints and a main any operation red in the main main a resolution TEM image of the interface between the chin molecule and (201) plane of HAP. (d, e) TEM images of nanoparticle
resolution TEM images were reproduced with permission from the 2. Copyright 2020 Spiring Kapital Pol before and after high strain rate impact, respectively, (if Schematic of the multiscal tougheling mechanisms in the costing the properties (and a multiple and a term in the cost of the individual relationship. Happen the c mages were epropote with permission rom ref \pm Copyrigor Auck) sinnige trained and space from the strain in the matter inseres and after the example of the example of the example trained lingity mineralized lingit of no anary
are the bayer. Schematic mange was considered with permission from ref 6. Copyrell 2200 Listenet in the matrix
different particular measurements in the matrix of the strain research measurement measurements (i) TEM sectioned mative tooth showing details of particulate outer layer, with selected area dimetation onfirming the magnetic
phase. (i) TEM analysis on a single particle from outer surface layer (inset, FFT suggesting single cr phase. (i) TEM amadysis on a single particle from outer surface layer (inset, FFT suggesting single crystal or
mesocystallinity). (i) Surface nanoparticle transition after scratch (inset, FFT demonstrating polycrystalline mesodysaminity, (i) sonce is not interesting and the station mechanical and the station of smaller controllant interesting in Chiton Teelth
hydroxyapatite domains. Organic chitin and protein such as $\frac{1}{2}$. Wear Residen oriented attachment of smaller nanocrystalline 4.2 Wear Resistant Nanoparticle Coating in Chinon Teelh
molecules, which were observed in these particles, observed a nanoparticle coating on the surface of
molecules, whic by twere the experimental and a protein and protein simular to the manks shrings disly look were as templates of the term of mature chines are desired a many
arises are as templates for the crystallization of mature chine system estable that the most system (Figure 76. Thill at to the mattis shring's daty club, we
strep as templates for the crystallization of matture chiton (*c. stelleri*) technomic system (*c. stelleri*) technomic of the c Exerce and the structure point with the proposition of the structural of the crystallization of matter chin (C steller) there, it is likely that hypotoxypatite nanorystals. Exerce protective control on the surface in the Shrimp determines are experimented in the surface of the children and protective and predictive material controls. Higher Tb shrows a high-
these protective contings could be an evolutionary
explained in the HAP crystal la Experience transmit in the matter of the consideration of experience to the state of the state of the transmit and proteins common design theme. SEM of the fractured mature attached to thAP (1002) planes. Original for the semicon the Happer of the composite mean in the matter of many semicon the semiconductor in the HAP (102) planes. Organists were also tooth from C. steller (Eigure 7g) revealed a 2 μ m denseming the transparient of mano Example the lattice parameters of the HAP crystal lattice, modifying layer of nanoparticles covering the lattice parameters of the HAP crystals (Figure and region (Figure 21) shows a wide particle size of the HAP crystals

the mantis shrimp dactyl club. (a) Schematic of the hierarchical
resolution TEM image of the composite nanoparticle. (c) High
of the multiscale toughening mechanisms in the coating layer.
Displinguity of the multiscale to common design theme. SEM of the fractured material responsive contribution TEM image of the composite nanoparticle. (c) High e and (201) plane of HAP. (d, e) TEM images of nanoparticle complement of the multiscale tougheni the mantis shrimp dactyl club. (a) Schematic of the hierarchical
the mantis shrimp dactyl club. (a) Schematic of the hierarchical
of the multiscale toughening mechanisms in the coating layer.
Of the multiscale toughening **Example 12**
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 **Example of the composite nanoparticle. (c) High

of the multiscale toy

Peringe nethand the conting layer.**
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of the multiscale toughening mecha resolution TEM image of the composite nanoparticle. (c) High

en and (201) plane of HAP. (d, e) TEM images of nanoparticle

of the multiscale toughening mechanisms in the coating layer.

Dycringer Nature. (g) Surface anal e and (201) plane of HAP. (d, e) TEM images of nanoparticle
of the multiscale toughening mechanisms in the coating layer.
O Springer Nature. (g) Surface analysis of the leading edge of the
sign from ref 6. Copyright 2020 E of the multiscale toughening mechanisms in the coating layer.

Springe Nature. (g) Surface analysis of the leading edge of the

spring Notin the tooth schematic), highlighting a 2 μ m

sin from ref 6. Copyright 2020 Els 3 Springe Nature. (g) Surface analysis of the leading edge of the constensity of elyellow box in the tooth schematic), highlighting a 2 μ
sion from ref 6. Copyright 2020 Elsevier. (h) TEM of FIB-
sion from ref 6. Copyr e (yellow box in the tooth schematic), nghingthing a 2 μ on the fostistion from ref 6. Copyright 2020 Elsevier. (h) TEM of FiB-
er, with selected area diffraction confirming the magnetite surface layer (inset, FFT sugg sion rom rer <u>6</u>. Copyrignt 2020 Esseer, (n) TEW or Fis-
sr, with selected area diffraction confirming the magnetite
surface layer (inset, FFT suggesting single crystal or
et, FFT demonstrating polycrystalline particles).
 er, while seek a unitation columing the inaggesting single crystal or
surface layer (inset, FFT suggesting single crystal or
et, FFT demonstrating polycrystalline particles).
4.2. Wear Resistant Nanoparticle Coating in Ch station of the manifold polynomial single expansion of the section of the monstrating polycrystalline particles).
4.2. Wear Resistant Nanoparticle Coating on the surface of observed a nanoparticle coating on the surface o surfaces. 4.2. Wear Resistant Nanoparticle Coating in Chiton Teeth

Similar to the mantis shrimp's dactyl club, we

observed a nanoparticle coating on the surface of

mature chiton (C. *stelleri*) teeth. Here, it is likely that

th Similar to the mantis shrimp's dactyl club, we observed a nanoparticle coating on the surface of mature chind (C. *stelleri*) teeth. Here, it is likely that these protective coatings could be an evolutionary common design observed a nanoparticle coating on the surface of
mature chiton (C. stelleri) tech. Here, it is likely that
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tooth from *C. stelleri* (Figure 7g) revealed a 2 μ m den these protective coatings could be an evolutionary
common design theme. SEM of the fractured mature
tooth from *C. stelleri* (<u>Figure 7g</u>) revealed a 2 μ dense
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tooth from C. stelleri (Figure 7g) revealed a 2 μ m dense
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region (F tooth from *C. stelleri* (**Figure** 7g) revealed a 2 μ m dense
layer of manoparticles covering the underlying
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sign i ecles, suggesting a convergence of an optimal biological

These tubular structures have then observed in the consideration of the sumplementation biomimetic structures that tulitize engineered to the maximum constant prope sign. It also enables us to leverage these buesprints to the trial will energy hominetic strength and the significant propositions of the strength and the significant propositions of the membersion of the significant progr develop binamilitic structures that utilize engineered provides the a member to touse there are more to the there is a need to have a need to the section in the section of the section is a section of the section is a sect ierals to translate to high perform- ance structures.

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environment and ecological constraints. Variations in

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 suggestive of mineralization pathways in the organism
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Many of these organisms have deviations in their
str benefit survival. Of course, there are more functionalities
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This will environment and ecological constraints. Variations in
these organisms, as well as the environments within
this they were derived will be further investigated.
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designs Ins will be important to extrapolating new, non-native

	designs that may provide utility in more extreme

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	v) Finally, we look to leverage additive manufacturing

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https://pubs.acs.org/10.1021/acs.accounts.2c00110

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