Nanostructures in Nature

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Introduction:

A nanostructure can be defined as a system in the order of 1-100 nm in size. A nanostructured material can be defined as a material with atoms/molecules arranged in nano-sized clusters which become the constituent grains or building blocks of the material.

All natural structures are created from their molecular precursors and are thus hierarchical. Every natural structure is built up from sub-structures that are of the nano-sized range. We are thus surrounded by nano-materials. Our own body is a perfect example of a nano-structured material. Every single part of the body is built up from nanostructures which have completely different structural arrangements that decide their functionality. The DNA structure that exists within the nucleus of a cell is one such nanostructure whose sole objective is to store and replicate information. Even the energy in the system cell is stored in the form of easy-to-manipulate bonds within nanostructures formed by Adenosine Tri – Phosphate (ATP) and Adenosine Di-Phosphate molecules (ADP). A Nano-structured membrane that forms the cytoskeleton of a cell performs yet another type of function: regulation of ion and molecular transport across the cell boundary.

The role of nanostructures is hence extremely significant and extensive research is being conducted in this field to gain greater understanding of the functionality of specific structures. Several methods such as X-ray Spectroscopy, Diffraction and Microscopy are being used for these experiments and the increasing necessity for better identification techniques has stimulated rapid advances in this field. Attempts are also being made to replicate these structures to exploit the properties that they show. This report discusses a few such nanostructures and gives a detailed explanation of the bone nanostructure.

Lotus leaf

Central strategy of science has been to try and mimic nature. Manufactured water-repellent and self-cleaning surface have potential uses in daily life, agriculture, and industry. Lotus leaf is the natural nanostructure which shows the above water repelling property.

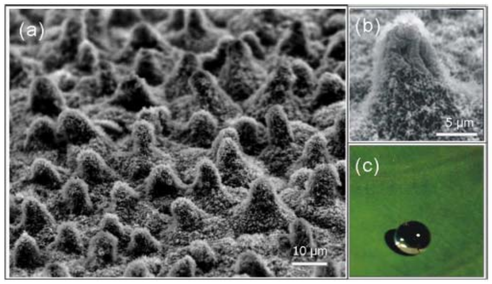

Figure 1: SEM image of protrusion on a lotus leaf [Stratakis et al; 2009]

SEM images have revealed the lotus leaf surface is covered with micrometer-sized papillae decorated with nanometre branch like protrusions. The roughness of the hydrophobic papillae reduces the contact area between the surface and a liquid drop, with droplets residing only on the tips of the epicuticular wax crystals on the tops of papillose epidermal cells.

Researchers were able to develop special technique to produce artificial material which mimic the lotus leaf. They are prepared with a simple one-step production process using ultrafast (femtosecond) laser irradiation of a silicon surface under a reactive gas atmosphere, followed by a chloroalkyl silane monolayer deposition. This consists of micro scale conical pyramidal asperities decorated with nano protrusions of up to a few hundred nanometers.

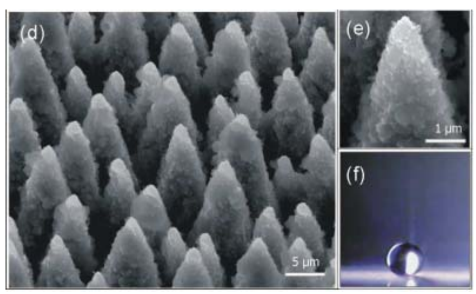

Figure 1: SEM image of the artificially prepared silicon surface [Stratakis et al; 2009]

Coefficient of restitution of the same is measured using special imaging techniques and is found to be nearly same. [1]

Gecko's Feet

Till now we have seen a nano structure which is resulting in repelling of water. Gecko's feet are another example of nano structures in nature.

According to [2], Geckos are able to perform many things that were never understood until their feet's nano structure was understood:

- Attach and detach their toes in milliseconds to nearly every material.
- Run on vertical and inverted, rough and smooth surfaces.

- Gecko toes don't degrade, foul, or attach accidentally to the wrong spot→ like a pressure sensitive adhesive.
- They are self-cleaning and don't stick to each other.
- Flatten their palm down and then unroll their toes; remove without any measurable force.

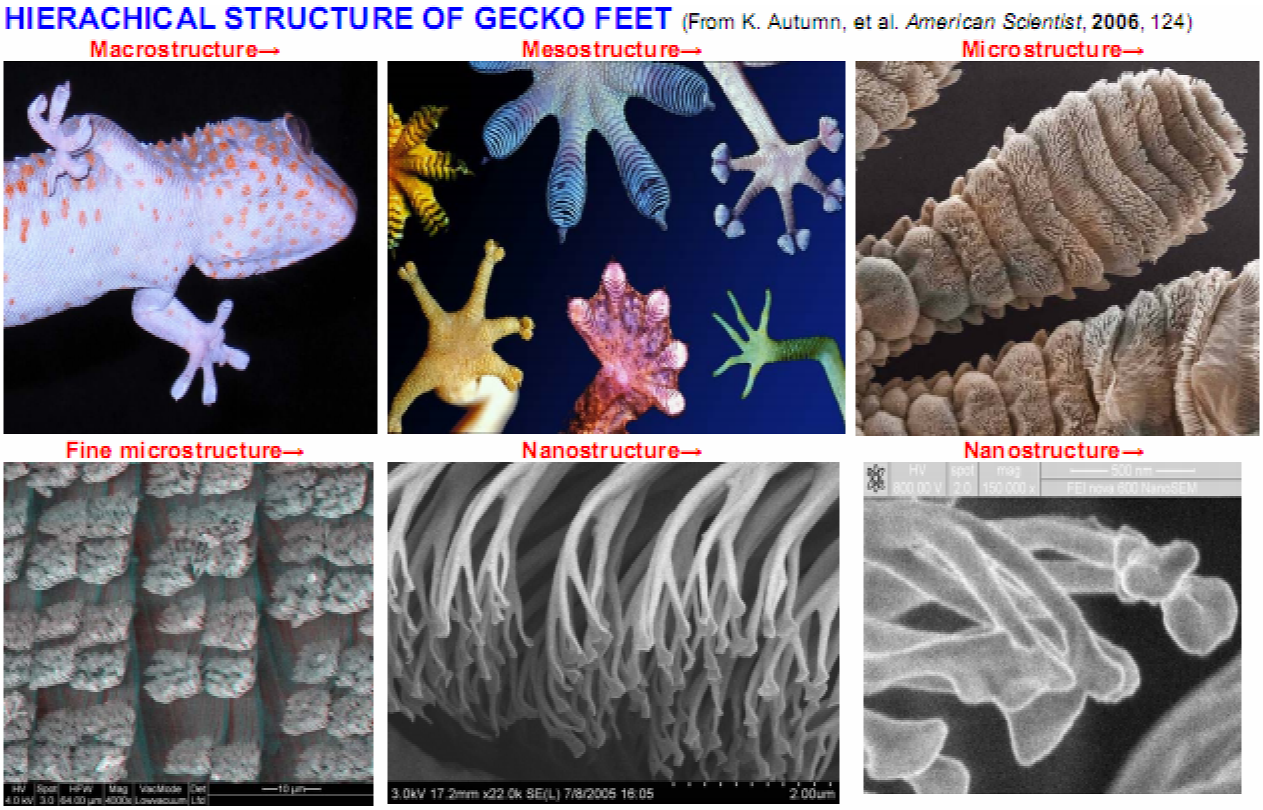

Figure 2: Figure showing the hierarchical nature of the Gecko's feet [Autumn et al; 2006]

Butterfly

Replication is a method of using biotemplates for achieving nanostructures made of more stable, harder, and high-temperature-tolerable inorganic materials that may have some designed functionalities for practical applications.

Butterfly is one of the typical template used for building photonic related replications. The beautiful colors exhibited by butterfly wings are usually contributed by two sources: pigments and periodical submicrometer structures, which are also referred to as "chemical" and "physical" colors, respectively.

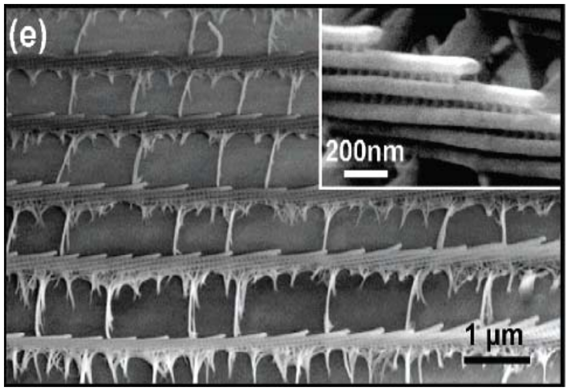

Figure 3: SEM image of the butterfly wings showing nano scale

The above image shows the high resolution SEM image of the butterfly wing. It clearly shows how the lamellae are arranged in the butterfly wing. Atomic layer deposition (ALD) technique was used to replicate the wing structure by Al_2O_3, which was carried out at 100°C. The color can be controlled by the thickness of the replica. With the coating of Al_2O_3 layer, the color of the butterfly wing was also changed. By increasing the coating thickness from 10 to 40 nm with a 10 nm interval, the reflected color shifted from original blue to green, yellow, orange, and eventually pink.

This clearly shows that the diffraction of light is responsible for the color of a butterfly wing.

Bone

We will deal in detail about human bone and nano structural nature attached to it.

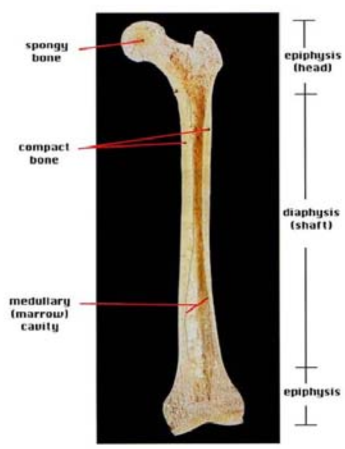

Figure 4: Image of the macroscopic structure of a bone [Wikipedia]

Bones are rigid organs that form part of the endoskeleton of vertebrates. They function to move, support, and protect the various organs of the body, produce red and white blood cells and store minerals. Bone tissue is a type of dense connective tissue. Because bones come in a variety of shapes and have a complex internal and external structure they are lightweight, yet strong and hard, in addition to fulfilling their many other functions. One of the types of tissue that makes up bone is the mineralized osseous tissue, also called bone tissue that gives it rigidity and a honeycomb-like three-dimensional internal structure. Other types of tissue found in bones include marrow, endosteum and periosteum, nerves, blood vessels and cartilage.

Bone is not a uniformly solid material, but rather has some spaces between its hard elements.

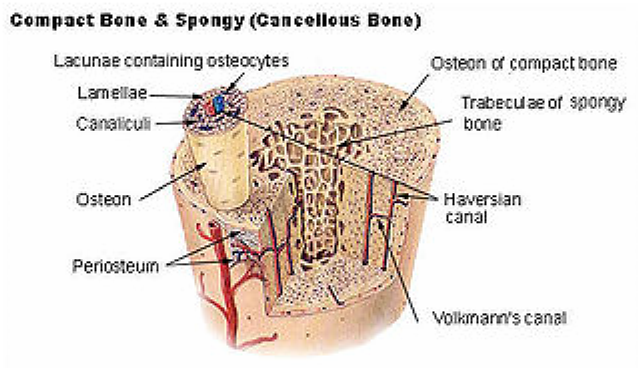

Figure 5: figure showing compact and spongy bone [Wikipedia]

Compact bone or (Cortical bone)

The hard outer layer of bones is composed of compact bone tissue, so-called due to its minimal gaps and spaces. This tissue gives bones their smooth, white, and solid appearance, and accounts for 80% of the total bone mass of an adult skeleton. Compact bone may also be referred to as dense bone.

Trabecular bone

Filling the interior of the organ is the trabecular bone tissue (an open cell porous network also called cancellous or spongy bone), which is composed of a network of rod- and plate-like elements that make the overall organ lighter and allowing room for blood vessels and marrow. Trabecular bone accounts for the remaining 20% of total bone mass but has nearly ten times the surface area of compact bone.

Proteins are the key molecular building blocks of such biological matter and they play a vital role in making these materials lightweight, yet strong, elastic and tough.

One of the most intriguing protein materials found in nature is bone, a material composed out of assemblies of tropocollagen molecules and tiny hydroxyapatite crystals, forming an extremely tough, yet lightweight material.

The figure below depicts the geometry of the nanostructure of bone, showing several hierarchical features from atomic scale to micro scale.

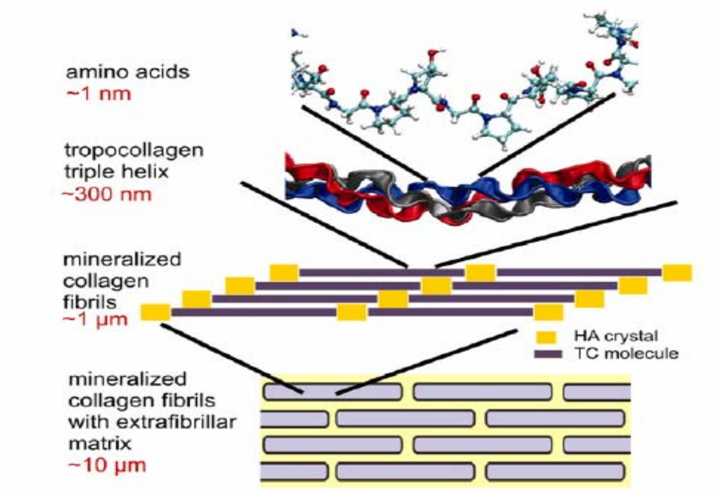

Figure 6: Figure showing the hierarchical structure of the bone formation [Buehler 2007; Nanotechnology]

The smallest scale hierarchical features of bone include the protein phase composed of tropocollagen (TC) molecules and collagen fibrils (CFs) as well as mineralized collagen fibrils (MCFs) .Tropocollagen molecules assemble into collagen fibrils in a hydrated environment, which mineralize by formation of hydroxyapatite (HA) crystals in the gap regions that exist due to the quarter staggered geometry. MCFs arrange together with an extrafibrillar matrix (EFM) to form the next hierarchical layer of bone.

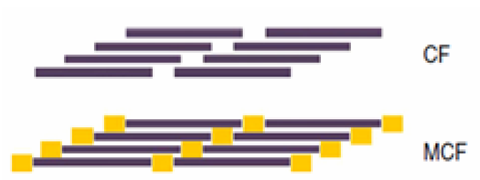

Figure 7: Representation of collagen fibrils (CF) and mineralized collagen fibrils (MCF) [Buehler 2007; Nanotechnology]

While the structures at scales larger then MCFs vary for different bone types, mineralized collagen fibrils are highly conserved, nanostructural primary building blocks of bone that are found universally. Each MCF consists of TC molecules with approximately 300 nm lengths, arranged in a characteristic staggered pattern. Gap regions in this arrangement are filled with tiny hydroxyapatite (HA) crystals. We here mainly focus on the scale of mineralized fibrils, with the objective of providing insight into the most fundamental scale of bone and its mechanical properties.

Mechanism of bone support

The Bone as you have seen is a composite of Hydroxyapatite crystals and Tropocollagen molecules.

When a tensile load is applied on the composite, the mineral crystals bear most of the load and the areas where there is a crack, i.e, a discontinuation in the crystals; the force is transmitted from one crystal to the other through the collagen via shear. The shear modulus of the protein is reasonably high because of the innumerable number of hydrogen bonds that exist within the collagen fibres. Thus the Young's modulus of the bone is a function of the shear modulus of the collagen fibre and the Young's modulus of the mineral platelets. A simple model for the Young's modulus of the bone arrived at by Huajian Gao [5] is explained below.

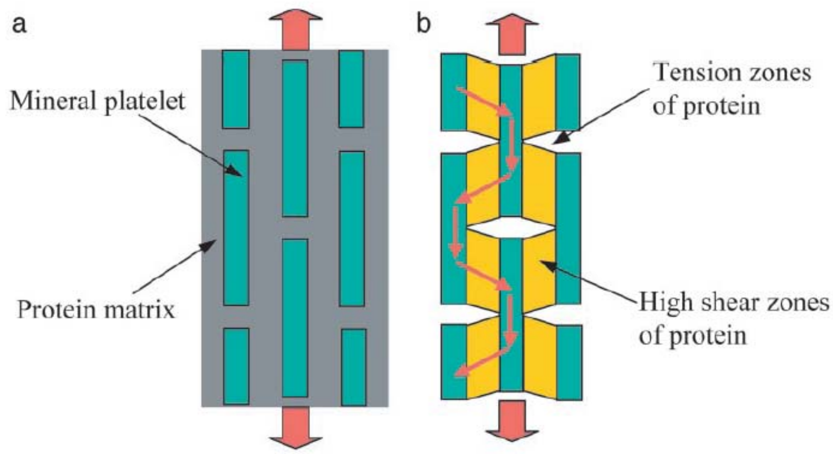

Figure 8: Tensile load bearing mechanism of a bone [Gao et al., Appl. Phy. Sciences, Vol. 100, No.10]

Young's modulus of bone

The model for the Young's modulus of the bone is:

$$\frac{1}{E} = \frac{4(1-\emptyset)}{G_p \emptyset^2 \rho^2} + \frac{1}{E_m}$$

Where, where Em is the Young's modulus of mineral, Gp is the shear modulus of protein, Φ is the volume concentration of mineral, and ρ is the aspect ratio of the mineral platelets. Since the aspect ratio is reasonably high, we find that the Young's modulus of the composite is high and is influenced highly by the Young's modulus of the mineral crystal.
The experimental setup used to validate the model is shown:

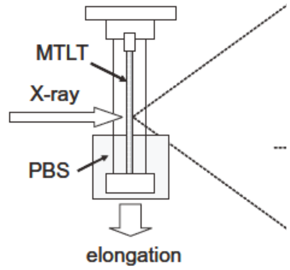

Figure 9: Experimental setup [H.S. Gupta et al., Physical Review Letters, Vol.93, No.15]

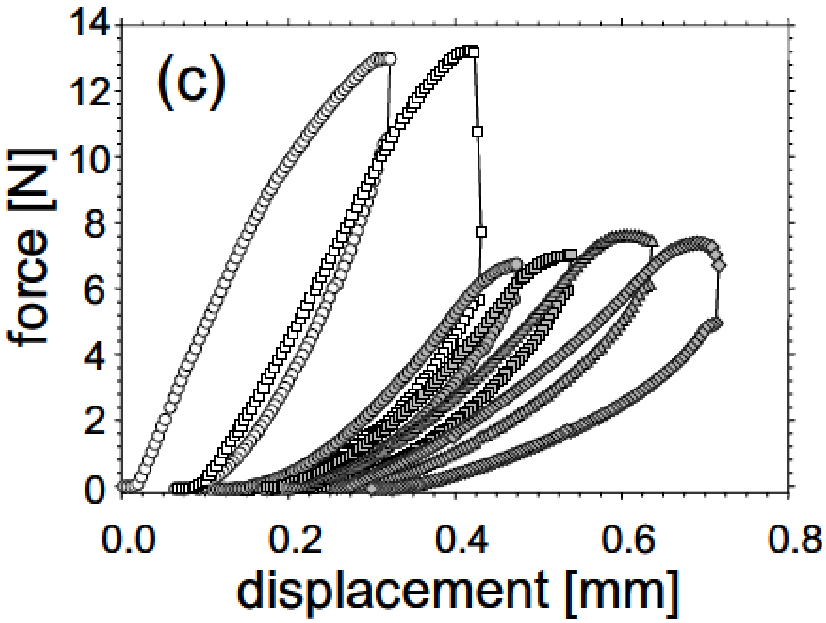

Figure 10: Force-displacement graphs for consecutive cycles showing more collagen like behavior as number of the cycle increases [H.S. Gupta et al., Physical Review Letters, Vol.93, No.15]

The measurements are carried out using the instrument shown. It is a specially designed instrument with a clamp on one end and the other moved with a motorized translation stage. A synchrotron X ray diffraction instrument is used to measure the strain on the bone. The experiment was carried out in several cycles where each cycle begins at the unstrained state of the bone and ends when the fracture strain is reached. As the cycles continue, we realize that the load is being borne more by the yielding collagen fibers when compared to the mineral crystals that were cracking at the end of each cycle. Thus we see a clear transition from bonelike behavior in the initial cycles to the unmineralized tendon like behavior in the later stages. This experiment proves that the model is right.

A synchrotron X ray source is used because we are trying to collect the diffracted light that passes through reasonably soft bone tissue which absorbs a large amount of the incident light. Also, we need to measure the local strain experienced by the bone at different values of force applied quickly. Hence, synchrotron diffraction measurements which can be taken at extremely short intervals of time (Billionths of a second) are used.

Significance of the bone nanostructure:

Also for robustness of the design we must consider the possibility that a mineral might actually contain flaws. The crack-like flaws are the protein molecules that may have been present within the mineral crystals and are equivalent to micro cracks because of their low load bearing capacity. The fracture strength of a cracked mineral crystal is usually much lower than that of a perfect crystal by virtue of the crack present.

However there exists a critical thickness below which the crack present in the crystal does not affect the load bearing capacity of the crystal. This is typically about 30nm for the material of the bone and thus, mineral crystals of less than 30 nm thickness when embedded in the bone give it its characteristic load bearing ability by acting as perfect crystals.

Therefore, the nano-scale in bio-composites is selected for ensuring maximum tolerance of flaws and optimum tensile strength. Thus, we have seen that the bone exhibits exceptional properties by virtue of its structure. Similarly there are several other nanostructures in nature that show exceptional properties and have redefined the means to achieve specific properties. These properties of nano-structures are being researched extensively and attempts are being made to create materials that mimic them.

It is clear that there is still a huge amount of potential for research in this field and there are still a large number of nanostructures whose properties can be identified and utilized for preparing sophisticated materials. What Dr. Richard Feynman had said during his lecture several decades ago still holds true: There's plenty of room at the bottom.

References

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