



NANOYOU Teachers Training Kit in Nanotechnologies

# Chapter 2- Nanoscience in Nature

MODULE 1- Fundamental concepts in nanoscience and nanotechnologies

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## Chapter 2: Nanoscience in Nature

This Chapter introduces the concept of “natural nanomaterial” and illustrates with some detail few examples that can be introduced in class.

### What is a natural nanomaterial?

All materials can in principle be described at the nanoscale. By natural nanomaterials here we mean materials that belong to the natural world (animal and mineral), without human modification or processing, and that have **remarkable properties because of their inherent nanostructure**.

The chemical identity and properties of a substance depend upon its molecular structure. The nanostructure of a biological material is due to its supramolecular organization: arrangement of tens to hundreds of molecules into shapes and forms in the nanoscale range. The interaction of light, water and other materials with these nanostructures give the natural materials **sticking properties which can be appreciated at the macro scale**.

Natural nanomaterials provide an **inspiring way of bringing nanoscience in class**. Many natural materials that students will be very familiar with ought their properties to nanostructures in their composition. It can be really enlightening to realize that common natural materials, such as feathers and spider silk, or materials that we use every day, such as paper and clay, have properties that depend not only on their chemistry but also on their nanostructure.

### Overview of natural nanomaterials

We have hundreds of examples of nanoscience under our eyes daily, from geckos that walk up side down on a ceiling, apparently against gravity, to butterflies with iridescent colours, to fireflies that glow at night. In Nature we encounter some **outstanding solutions to complex problems in the form of fine nanostructures** to which precise functions are associated.

Here is a short list of some natural nanomaterials; it is not exhaustive, but the interest teacher can find more information in the Bibliography at the end of this Module.

- **Nanoparticles from natural erosion and volcanic activity**. Nanoparticles are part of our mineral world since they are naturally produced during erosion and volcanic explosions.

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- **Minerals**, such as **clays**, are nanostructured. Clays are a type of *layered silicates* that are characterized by a fine 2D crystal structure; among these, **mica** has been the most studied. Mica is made up of large sheets of silicate held together by relatively strong bonds. Smectic clays, such as montmorillonite, have relatively weak bonds between layers. Each layer consists of two sheets of silica held together by cations such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ . The presence of the cations is necessary for compensating the overall negative charge of the single layers. The layers are 20-200 nm in diameter laterally and come into aggregates called tactoids, which can be about 1 nm or more thick. Naturally occurring clays include montmorillonite (MMT) and hecrite. The fine nanostructure of clays determines their properties. when water is added, the clay swells, but the volume change is rather unusual, it is several times the original volume due to the “opening” of the layered structure by the water molecules that replace the cations. Clays swelling is a significant factor in soil stability and must to be taken into account in building roads etc.

- **Natural colloids**, such as milk, blood (liquid colloids), fog (aerosol type), gelatine (gel-type). In these materials nanoparticles are dispersed in the medium (liquid or gas) but do not form a solution, rather a colloid. All these materials have the characteristic of scattering light and often their colour (such in the case of blood and milk) are due to the scattering of light by the nanoparticles that make them up.



The **EXPERIMENT A in the NANOYOU Experiment module** investigates natural colloids (milk and gelatine) and how their properties are connected to their nanostructure. A **gold colloid** is the subject of **EXPERIMENT C in the NANOYOU Experiment module**.

- **Mineralized natural materials**, such as shells, corals and bones. Many of these materials are formed by calcium carbonate crystals that self-assemble together with other natural materials, such as polymers, to form fascinating three-dimensional architectures. For instance a **shell** is grown by a layer of cells that first lays down a coating of protein supported by a polysaccharide polymer like chitin. The proteins act like a nano-assembly mechanism to control the growth of carbon carbonate crystals. Around each crystal remains a honeycomb-like matrix of protein and chitin. This relatively “flexible envelope” is fundamental for the mechanical properties of the shell and mitigate cracking. The size of each crystal is around 100 nm. The result is that the nacre of mollusc shells has extraordinary physical properties (strength, resistance to compression etc.)

- **Materials like skin, claws, beaks, feathers, horns, hair**. These materials are made largely by very flexible proteins like keratin, elastin and collagen. Keratins have a large content of glycine and alanine. This leads to  $\beta$ -sheets that can bond strongly one with another in an aligned fashion. Fibrous keratin molecules can twist around each other to form helical intermediate filaments. Similarly collagen (not related to keratin in term of primary structure) has a high percentage of glycine, and forms flexible triple-helix structures. In addition to intra and intermolecular bonds, keratins have numerous cysteins that can form stable di-sulphide bonds. The amount of cysteins in the protein

determines the strength and rigidity of the material; keratin in human hair for instance contains about 14% of cysteins. Materials like nails, hooves and claws have higher percentage of cysteins.

- **Paper and cotton.** Both are made mainly of cellulose. The high strength, durability and absorbency of cotton are due to the nanoscale arrangement of the fibres.

- **Insect wings and opals.** The colours seen in opals and butterflies is directly connected to their fine structure, which reveals packed nanostructures that act like a diffraction grating and induces iridescence. In the case of opals this is due to packed silica spheres in the nanometre range, uniform in size and arranged in layers. Butterflies owe the colour of their wings often to pigments that absorb specific colours; in some species, like the beautiful *Morpho rhetenor*, colours are due to the presence in the wings of nanostructures which are photonic crystals. This example is discussed in more details in the next session of this Chapter.

- **Spider silk.** Silk is the material with the highest known strength, about five times that of steel of the same weight. The extraordinary properties of spider silk are due to the proteins that make up the silk (mainly fibroin) and its supramolecular organization which is at the nanoscale level.

- **Lotus leaf and similar (Nasturtium).** The nanostructure of the leaf in these plants is responsible for their extraordinary surface properties and the ability to “self-clean”. This example is discussed in more details in the next session of this Chapter.

- **Gecko feet.** The structure of the Gecko feet is an amazing example of relationship between function and nanostructure. The ability of geckos to walk upside-down, against gravity, even on wet or dirty surfaces is intimately connected to its feet nanostructure. This example is also discussed in more details in the next session of this Chapter.

### Learning from Nature

Natural nanomaterials are of interest not only for understanding (and appreciating) the amazing properties of biological materials but also to gather **inspiration for the design and engineering of new materials with advanced properties.**

The physical origins of the remarkable properties of many biological materials are due to complex, often **hierarchical structure**<sup>1</sup>. They are characterized by a surprising level of adaptability and multifunctionality. These materials can provide a **model for designing radically improved artificial materials** for many applications, such as solar cells, fuel cells, textiles, drug delivery systems etc.

<sup>1</sup> *Hierarchical structures are those structures that are synthesized at different levels of complexity by alternating growth conditions.*

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What is even more inspiring is the notion that in Nature some very simple laws apply:

1. Nature runs on sunlight and uses only the energy it needs. Natural nanomaterials are extremely energy efficient!
2. Nature fits form to function and recycles everything-waste products are minimized in Nature!
3. Nature rewards cooperation although it encourages diversity and local expertise.

The field of material engineering that is devoted at trying to fabricate artificial materials that mimic natural ones is conventionally called **biomimetics**. Nanoscience is a fundamental component of biomimetics.



Natural nanomaterials are inspirational for the engineering of new materials with advanced functionalities. In **Chapter 5 “Overview of nanomaterials”** we will see some examples. Below is a short list of biomimetic materials inspired from natural ones.

Biomimetic material.....	...inspired from
Polymers	Sub-structure of nacre
Structural elements	Wood, ligaments and bone
Electrical conduction	Eels and nervous system
Photoemission	Deep-sea fish and glow worms
Photonic crystals	Butterfly and bird wings
Hydrophobic surfaces	Lotus leaf and human skin
Adhesives	Gecko’s feet
High tensile strength fibre	Spider silk
Artificial intelligence and computing	Human brain

### Detailed description of some natural nanomaterials

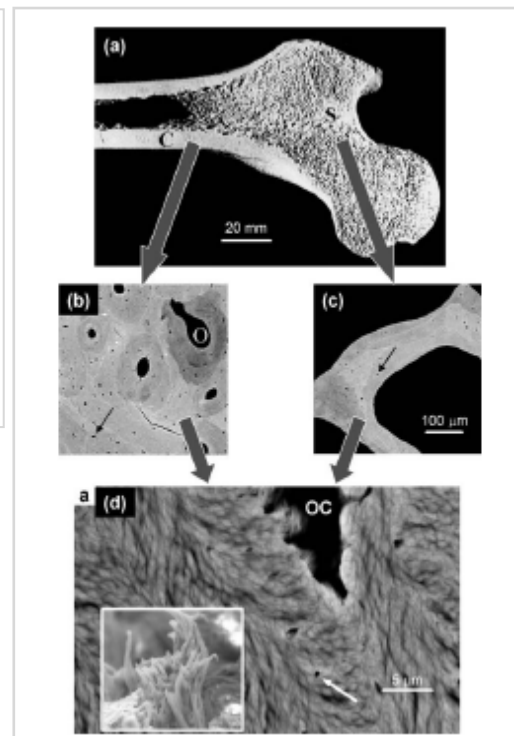
We will now describe in some detail some fascinating natural nanostructures, and explain how their natural nanostructure is responsible for their properties (like adhesiveness, strength, flexibility, colour etc.)

#### Bone

If you think about it, the unique properties of bone are a list of apparent contradictions: rigid, but flexible; lightweight, but solid enough to support tissue growth; mechanically strong, but porous. Bone can withstand weight without breaking. Its compressive strength is about twice its tensional strength. These outstanding properties are the result of bone's complex hierarchical structure and composition: bone material is made of a composite of collagen (mainly type I) fibrils reinforced with calcium phosphate particles (hydroxiapatite<sup>2</sup>).

From a mechanical point of view many bones such as the femoral head can be described as a “sandwich” structure with a dense external shell (cortical bone) and a spongy interior (cancellous bone). In cancellous bone, only about 20% of the volume is filled with bone material, the rest is made of bone marrow. Cortical bone is made of **fibrils regularly arranged** (see **Figure 1**).

**Figure 1.** (a) Section through a femoral head showing the shell of cortical bone (C) and the spongy bone (S) inside. (b) Enlargement of the cortical bone region revealing several osteons (O) corresponding to blood vessels surrounded by concentric layers of bone material. (c) picture of a single trabeculum from the spongy bone region. (d) Further enlargement showing the lamellar and fibrillar material texture around an osteocyte lacuna (OC) as visible in scanning electron microscopy (see white arrow). The lamellae are formed by bundles of mineralized collagen fibrils (insert). (Reprinted from: Fratzel et al., *Journal of Material Chemistry* (2004) 14, 2115-2123. Reproduced by permission of the Royal Society of Chemistry).

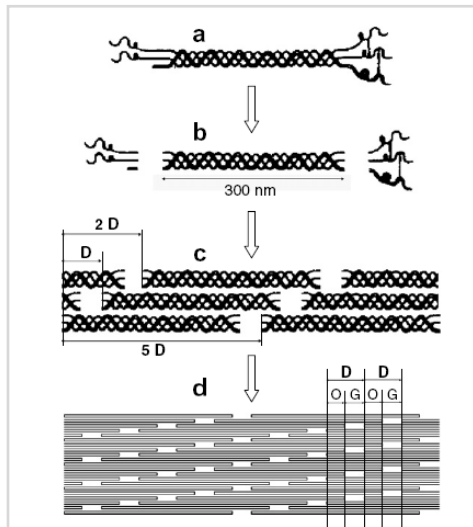


The fibrils consist of an **assembly of 300 nm long and 1.5 nm thick collagen molecules** which are deposited by the osteoblasts (bone-forming cells) into the extracellular space and the self-assemble into fibrils. Adjacent fibrils molecules are staggered along the axial direction by about  $D = 67\text{nm}$  (see **Figure 2**),

<sup>2</sup> Hydroxiapatite:  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$

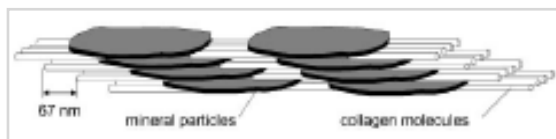
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generating a characteristic pattern of gap zones with 35 nm length and overlap zones with 32 nm length within the fibril.



**Figure 2.** Self-assembly of collagen fibrils. (a) Procollagen molecule after excretion from the cell. (b) Collagen after cleavage of the propeptide ends. (c) Parallel self-assembly with a staggering period of  $D$ . (d) Periodic density variation along the fibril axis, resulting from the staggering. In the stripes labeled O, there is an overlap of all molecules. In the stripes labeled G (gap region), one molecule out of five is missing and the density is accordingly smaller. (Reprinted from: Fratz et al., *progress in Materials Science* (2007) 52 (8), 1263-1334, with permission from Elsevier).

Collagen fibrils are filled and coated by tiny **mineral crystals of hydroxiapatite**. These are mainly flat plates mostly arranged parallel to each other and parallel to the fibril main axis. Crystals occur at regular intervals along the fibrils, with an approximately repeat distance of 67 nm. In mammalian species bone mineral crystals have a thickness of 2-4 nm (**Figure 3**).



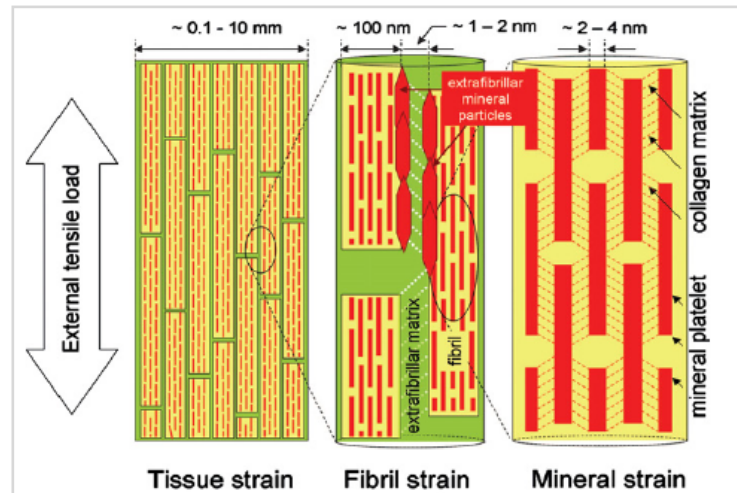
**Figure 3.** Sketch of the arrangement of mineral particles in collagen fibrils. Mineral particles are typically very thin objects (2–4 nm) and aligned with the collagen matrix. (Image credit: Fratzel et al., *Journal of Material Chemistry* (2004) 14, 2115-2123. Reproduced by permission of the Royal Society of Chemistry).

To summarize, bone is formed of a soft organic matrix (collagen) reinforced by an anisotropic stiff inorganic component (crystals of hydroxiapatite). These two components are assembled in a hierarchic structure which is organized at the nanoscale level. It is this nanoscale hierarchic organization that allows bone to tolerate small microfractures that arise from normal activity and dissipate deformation energy without propagation of the crack. Hydroxiapatite is a rigid material which is not capable of dissipating much energy; therefore collagen is believed to have a major role in the structural properties of bone (elastic and plastic deformation). **Figure 4** illustrate the **role**



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of collagen during bone deformation. Older bone, which is more mineralized and thus has a larger percentage of hydroxiapatite, is stiffer and breaks more easily.



**Figure 4.** Schematic model for bone deformation in response to external tensile load at three levels in the structural hierarchy: at the tissue level (left), fibril array level (center), and mineralized collagen fibrils (right). The stiff mineralized fibrils deform in tension and transfer the stress between adjacent fibrils by shearing in the thin layers of extrafibrillar matrix (white dotted lines in the center plot show direction of shear in the extrafibrillar matrix). The fibrils are covered with extrafibrillar mineral particles, shown only over a selected part of the fibrils (red hexagons) so as not to obscure the internal structure of the mineralized fibril. Right: within each mineralized fibril, the stiff mineral platelets deform in tension and transfer the stress between adjacent platelets through shear in the interparticle collagen matrix (red dashed lines indicate shearing qualitatively and do not imply homogeneous deformation). (Reprinted from: Fratz et al., progress in Materials Science (2007) 52 (8), 1263-1334, with permission from Elsevier).



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Bone is a “perfect” nanocomposite which is used as a model for **polymer composites reinforced for instance with nanomaterials** such as carbon nanotubes. Polymer composites and their applications are covered in **Chapter 5 of Module 1 (“Overview of nanomaterials”)**.

## Lotus leaf

The Lotus plant (*Nelumbo Nucifera*) is a native Asian plant which has the distinct property of having its leaves particularly clean even if its natural habitat is muddy. For this reason this plant is considered sacred in some cultures and a sign of purity. The leaves of the Lotus plant have the outstanding characteristic of totally repelling water because they are superhydrophobic (**Figure 5**). The consequence is that water droplets roll off the leaf surface and in doing so it to drag dirt away from it, as in the illustration (**Figure 7**). This effect, called “self-cleaning” renders the Lotus leaf clean and resistant to dirt. The same effect is found in other leaves such as those of *Tropeolum- Nasturtium* and some Canas, and in some animals such as the water strider.

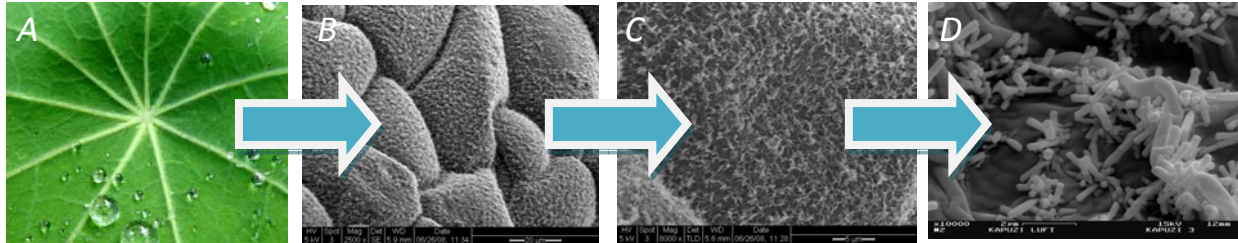


**Figure 5.** /Left to right): A Lotus leaf (iNANO, Aarhus University, Creative Commons ShareAlike 3.0), *Tropeolum-Nasturtium* leaves (Wiki Commons, Creative Commons ShareAlike 3.0), and a water droplet resting on the surface of a nasturtium leaf (A. Otten and S. Herminghaus, Göttingen, Germany, NISE Network, reprinted under NISE network terms and conditions).

### HOW IS THIS NANO?

The surface properties of the Lotus leaf were first investigated by Wilhelm Barthlott. In 1997 he published an important paper where he described for the first time the “Lotus effect” (a term that he later copyrighted) responsible for the self-cleaning properties of the Lotus leaves. In his original paper Barthlott showed that the self-cleaning properties of the Lotus plant is the **combination of the micro-structure of the leaves, and of the epidermal cells on its rough surface, which are covered with wax-crystals (Figure 6)**. These crystals provide a **water-repellent layer**, which is enhanced by the roughness of the surface, making it a superhydrophobic surface, with a contact angle of about 150. The consequence is that water droplets on the surface tend to minimize the contact between the surface and the drop, forming a nearly-spherical droplet. **Figure 6** shows the progressive magnification of a Nasturtium leaf. In the last image on the right **nanocrystals few tens of nanometres** in size are shown.

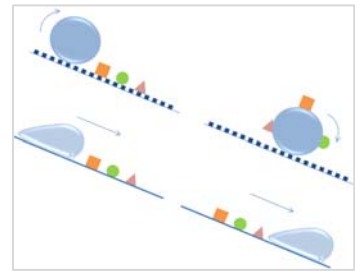
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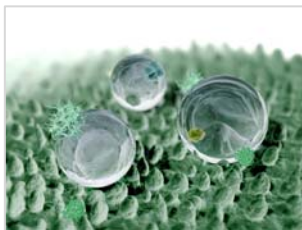
**Figure 6.** Close- up views at progressive magnification of a Nasturtium leaf revealing the presence of surface nanocrystals (image on the far right). (Image credit (A): A.Snyder, Exploratorium; (B, C): A.Marshall, Stanford University, (D): A. Otten and S. Herminghaus, Göttingen, Germany, all images are material of the NISE Network, reprinted under NISE network terms and conditions).

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Contaminants on the surface (generally larger than the cellular structure of the leaves) rest on the tips of the rough surface. When a water droplet rolls over the contaminant, the droplet removes the particle from the surface of the leaf



(**Figure 8**).



**Figure 8.** From left to right: graphic representation of water droplets on a Lotus leaf, actual SEM image of a droplet of mercury dragging dirt away on a lotus leaf. (Image credit: by William Thielicke, Creative Commons Attribution ShareAlike 3.0).

**Figure 7.** Diagram summarizing the connection between roughening and self-cleaning. While on smooth surfaces the particles are mainly redistributed by water (bottom), they adhere to the droplets surfaces on rough surfaces and are removed from the leaves when the droplets roll off (right)



The Lotus effect® has been an **inspiration for several innovative materials**, mainly with the aim of inferring them self-cleaning properties to reduce the amount of cleaning needed, with an obvious environment benefit. This includes also textiles. This is covered in **Chapter 2 of Module 2 (“Application of Nanotechnologies: Environment”)**. The Lotus effect® is also used in new solar-cells covers to increase their efficiency; this is explored in **Chapter 3 of Module 2 (Application of Nanotechnologies: Energy”)**.



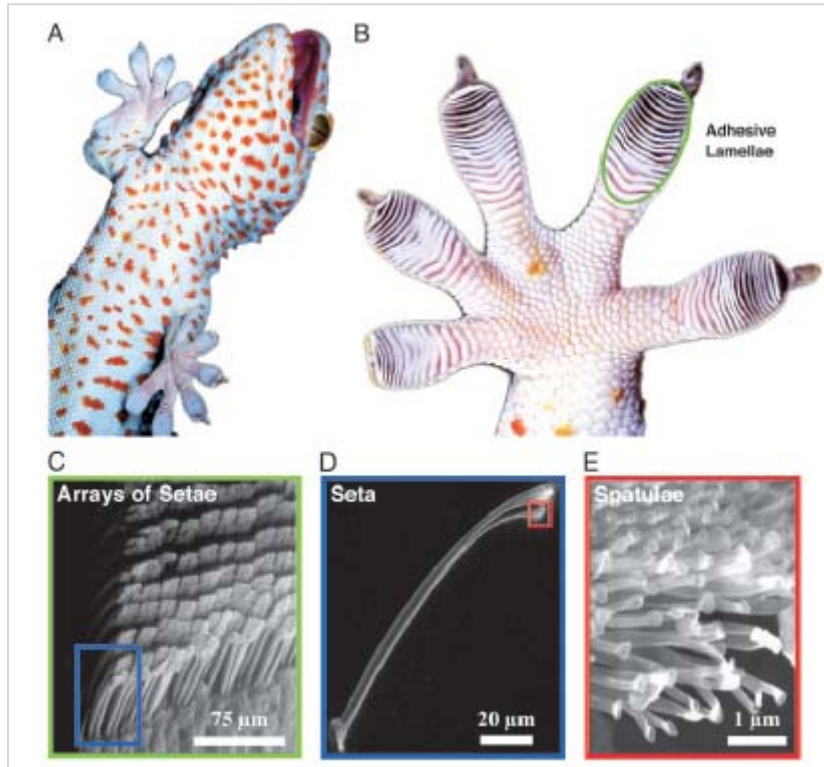
The **EXPERIMENT D in the NANOYOU Experiment module** investigates the Lotus effect in real plants and in innovative materials such as Nano-Tex® fabric and nanoporous silicon.

## Gecko

A gecko can cling virtually to any surface at any orientation; walk on smooth or rough surfaces, even upside down on a glass surface; and walk on dirt or wet surfaces maintaining full contact and adhesion to it. As he walks, a gecko **does not secrete any sticky substance**, and its feet do not have any suction-like features (even at microscopic sizes). The reason of the gecko’s amazing properties lies on the nanostructures that are present on his foot.

The gecko foot has a series of small ridges called scansors which contain numerous projections called setae. Each setae is about 100 µm long and has a diameter of about 5 µm. There are about half a million of these setae on the feet of a gecko. Each setae is further subdivided into about a thousand 200-nm wide projections called spatulae (**Figure 9**). **As a result, the total surface area of the gecko feet is enormous.** The gecko spatulae are very flexible so they essentially mould themselves into the molecular structure of any surface. The result is a strong adhesion which is entirely due to Wan der Waals forces. A single seta can resist 200 µN of force, or ~ 10 atmospheres of stress. **The gecko case is thus a very good example on the effect of large surface area on small forces.**

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**Figure 9.** Structural hierarchy of the gecko adhesive system. (A) Macrostructure: ventral view of a tokay gecko (*G. gecko*) climbing vertical glass. (B) Mesostructure: ventral view of the foot, with adhesive lamellae (scansors) visible as overlapping pads. Note the clean appearance of the adhesive surface. (C) Microstructure: roximal portion of a single lamella, with individual setae in an array visible. (D and E) Nanostructure: single seta with branched structure at upper right, terminating in hundreds of spatular tips. (Reprinted with permission from: Hansen et al., *Proceedings of the national Academy of Science* (2005), 102 (2), 386-389. Copyright (2005) National Academy of Science, USA)

Another very interesting property of geckos is that **their feet don't get dirty as they walk**, even if they walk on a surface covered with sand, dirt, water etc. Its feet stay clean even on dirty surfaces, and full adhesion is maintained. The issue was investigated and it was found that the feet remain clean because it is more energetically favourable for particles to be deposited on the surface rather than remain adhered to the gecko spatulae. If a gecko walks over a dirty surface, he just needs few steps to get his feet totally clean again, and adhesion is not compromised.



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**This self-cleaning property of the gecko feet is now investigated to design new materials** that stay clean and/or can self-clean for instance as “bio-rubbers”. This is discussed in **Chapter 5 of Module 1 (“Overview of Nanomaterials”)**.

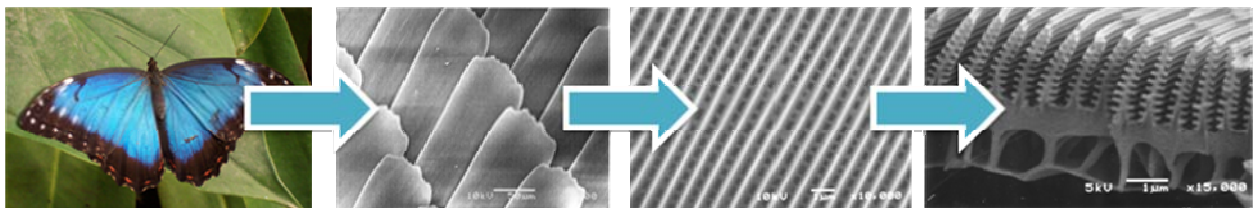
## Morpho rhetenor

The wings of butterflies often display extraordinary colours which are a consequence of the wing's surface and its interaction with light. The wings also exhibit iridescence, which is the shift in colour of an object when observed at different angles. The effect can easily be seen by observing a music CD.

**Iridescence** is a “physical colour” and it results from the interaction of light with the physical structure of the surface. To interact with visible light those structures must be nano-sized (visible light is between 380 and 750 nm). The interaction of light with this nano-rough surface can lead to **constructive or destructive interference**. The colour, intensity, and angles of iridescence depend on the thickness and refractive index of the substrate, and on the incident angle and frequency of the incident light.

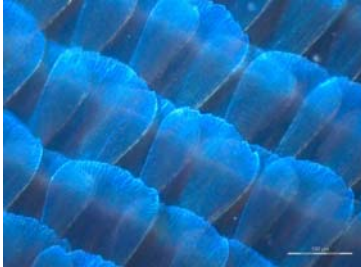
In materials like opals, natural iridescence is observed, due to packed silica spheres in the nanometre range, uniform in size and arranged in layers. This provides appropriate conditions for interference.

In the case of butterflies and moths, the iridescence is produced in a peculiar way. Scientist have studied the structure of the *Morpho rhetenor* in details and have found that these are formed of rows of **scales** arranged like tiles in a roof. Each scale is about 70x200  $\mu\text{m}$  and has a smaller structure on its surface, a very intricate and highly ordered nanometre organization of ridges. Each ridge is about 800 nm wide. The spaces between them form a **natural photonic crystal** that can generate constructive and destructive interference. The SEM analysis of the cross section of the ridges on the wings shows and even more intricate structure that look like evergreen trees (last image in **Figure 10**).



**Figure 10.** Close- up views at progressive magnification of the *Morpho rhetenor* showing the scales, which magnified show photonic crystal structure, which in turn show a cross section displaying satae that look like evergreen trees. (Images credit: (far left): Wiki Commons, Creative Commons Attribution ShareAlike 3.0; (all other images): S.Yoshioka, Osaka University, NISE Network, reprinted under NISE network terms and conditions)

These are called *satae*, are about 400 nm long, and are responsible for producing **constructive interference in the blue wavelengths** which generate the strong blue colour (**Figure 11**).



**Figure 11.** The blue colour of the wings are due to the constructive interference of light generated by the photonic crystal in the wings structure (Image credit: F. Nijhout, Duke University, NISE Network, reprinted under NISE network terms and conditions)



A photonic crystal is a periodic nanostructure that can modify the passage of light. The refractive indices of the materials that make up the crystal, and the presence of cavities or other defects determine which frequencies of light can propagate well.



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In **computing**, propagation of light (rather than electrons) is being investigated as an alternative to current integrated circuits. Photonics and photonic crystals in particular are described **Chapter 4 of Module 2 (“Application of Nanotechnologies: ICT”)**.