COMPOSITE MATERIALS

Taking a leaf from nature's book

Amyloid protein fibrils and graphene sheets can be combined to make a material that is biodegradable and has useful shape-memory and enzyme-sensing properties.

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Most biological materials are constructed from simple building blocks, yet they exhibit extraordinary properties. High-performance organic protein materials such as silk or collagen, for example, are usually composed of only a few distinct amino acids, but they combine to form structures that display a very wide range of material properties and perform many different biological functions[1–5]. And the addition of other types of building blocks leads to even better performance: for example, bone is strong and tough because the collagen matrix also contains hydroxyapatite mineral platelets. What's intriguing is that the macroscopic properties of the final material are much more than the sum of the parts, and that these properties can change in response to the demands being placed on them (a property referred to as tunability)[2–5]. These exciting features are known to derive from the peculiar structural make-up of natural materials, which contain geometric details over a vast range of length scales, merging the common concepts of 'structure' and 'material'.

Today it is possible to routinely synthesize nanoscale building blocks with many excellent material properties, such as carbon nanotubes or graphene sheets, but there has been relatively little progress in exploiting these properties in large-scale materials and devices. We lack the ability to map the excellent properties of these tiny material building blocks towards larger scales, where the performance of resulting materials doesn't live up to our expectations. It seems natural, therefore, to look to nature for inspiration when seeking to make new materials that can harness the potential of these synthetic building blocks[4,6]. Indeed, by starting with building blocks that are superior to those used by nature, it should be possible to develop new materials with properties that greatly surpass the natural ones. In addition to enhanced strength, for example, such a material could display an exquisite responsiveness to external cues, which could be used to tune its properties on demand or be exploited in sensing applications.

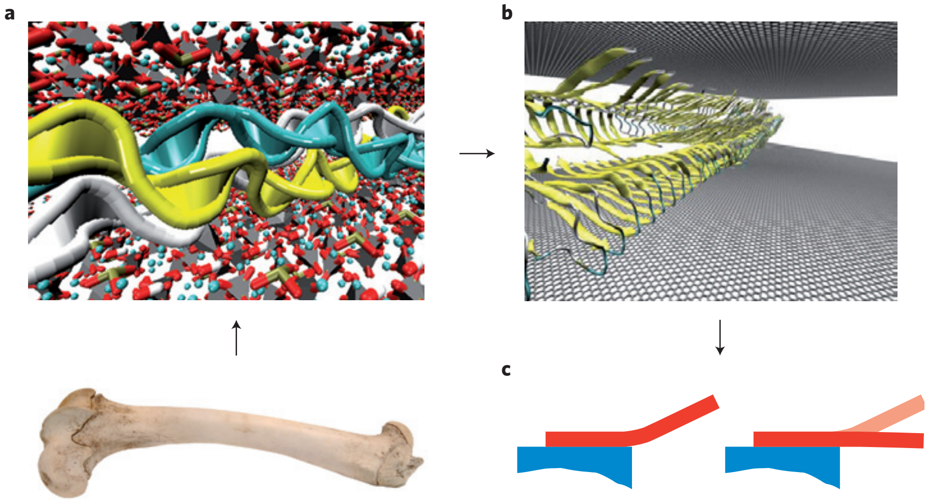

Figure 1 | Bioinspired nanocomposites. **a**–**c**, The nanostructure of bone provided the inspiration for the amyloid–graphene nanocomposites developed by Mezzenga and co-workers[7]. The natural building blocks of bone, collagen (triple helices) and hydroxyapatite mineral platelets (**a**), were replaced with amyloid protein fibrils and sheets of graphene, which are significantly stronger and stiffer than their natural counterparts. The new nanocomposite (**b**) has many useful properties: its mechanical properties can be tuned by varying the proportions of amyloid and graphene, and also by changing the level of humidity; it has shape-memory properties (**c**); and it is responsive to enzyme activity, which makes it biodegradable. It is also possible to make a sensor that can detect enzyme activity by connecting the nanocomposite to a simple electronic circuit and measuring changes in electrical response. Panel **a**: (top) courtesy of A. Nair, MIT; (bottom) © Ingram publishing/Alamy.

Now, writing in *Nature Nanotechnology*, Chaoxu Li, Jozef Adamcik and Raffaele Mezzenga of ETH Zürich report that they have combined graphene sheets with amyloid protein fibrils to create a nanocomposite with useful chemical, mechanical and sensing properties[7] (Fig. 1). Mezzenga and co-workers emulate the molecular structure of bone, with graphene sheets replacing the rigid hydroxyapatite mineral platelets found in bone, and amyloid protein fibrils replacing the softer collagen protein fibres. They start by simply combining amyloid protein fibrils and sheets of graphene oxide in water. The amyloid fibrils adhere to the graphene oxide sheets, and after stirring this suspension with hydrazine at 80 °C for 20 h to reduce the graphene oxide to graphene, the fibrils act as surfactants to stabilize the suspension of the graphene sheets in solution. Robust, free-standing films of the amyloid–graphene nanocomposites with centimetre-scale dimensions and thicknesses in excess of 50 μm can then be formed by vacuum filtering the solution.

The two building blocks in the new nanocomposite are both exciting materials in their own right. Graphene is well known for its excellent electronic properties[8] and for being the strongest and stiffest material known, with a Young modulus of almost ~1,000 GPa (ref. 9). Amyloid protein fibrils are best known for their role in diseases such as Alzheimer's and Parkinson's, but they are also among the stiffest protein fibres known (with a Young modulus of ~20 GPa), and are increasingly being used as functional nanomaterials[3,10].

The ETH team discovered that its nanocomposite has properties that are not found in either amyloid or graphene alone. For example, when exposed to high levels of humidity, films of the nanocomposites became less stiff and much more ductile, allowing the mechanical properties of the material to be tuned via simple post-processing. The films also display a fully reversible shape-memory response when the humidity level is cycled between high and low values. Because these responses are due to the protein content in the film, the sensitivity to humidity changes can be tuned *a priori* by simply varying the relative amounts of graphene oxide and amyloid protein fibrils in the solution before the films are created or, potentially, by altering the sequence of amino acids in the protein. The presence of proteins in the nanocomposites means that it can bind enzymes, which makes it biodegradable and allows it to measure enzyme activity. This combination of tunable mechanical properties, shape-memory behaviour and responsiveness to enzyme activity could prove useful in a variety of applications including biocompatible actuators and sensors and, possibly, drug delivery.

However, much work is needed to improve the methods by which biological concepts are translated into synthetic materials. Natural materials can be extremely complex, the key structural motifs that lead to their extraordinary properties typically span multiple length scales, and it is often not clear which of them are critical to achieve certain properties. Spider webs, for example, are remarkably robust because a specific combination of ordered and disordered protein domains on the nanoscale results in the silk fibres that make up the web having nonlinear elastic properties[5], but at present it is challenging to fabricate new materials with such controlled complexity across so many length scales.

One solution is to directly incorporate natural or biological components into new materials, as Mezzenga and co-workers have with their amyloid–graphene nanocomposites, but this leads to new challenges in terms of materials selection and optimization. For example, there are countless proteins that form amyloid structures, and it is unclear how the use of different proteins would change the properties of an amyloid–graphene nanocomposite. Some researchers are looking to a branch of mathematics called category theory for inspiration, and critical mechanistic insights could also come from less obvious fields of research where function emerges from hierarchical structures, such as language and music[11].

Although the structure of the amyloid–graphene nanocomposite made by the ETH team is not as complex as the bone structure on which it is based, it still represents an impressive new material with a unique combination of properties. Moreover, it confirms that combining natural and synthetic components is a method with seemingly limitless potential for the development of a new generation of novel bioinspired nanomaterials. ❐

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