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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Published online: 20 May 2012

SELF-ASSEMBLY

Judging a nanocube by its cover

One-dimensional strings of metal nanocubes can be precisely self-assembled with the help of polymer chemistry.

Oded Rabin

Bottom-up approaches to nanotechnology, in which individual nanoparticles or other nanoscale components are assembled into artificial structures and devices, are often inspired by the way biological systems create complex architectures from simple building blocks. State-of-the-art nanomanipulation systems, such as those based on scanning probe microscopy hardware, can be used to precisely position individual nanoscale objects on surfaces. However, to arrange nanoscale building blocks into large-scale assemblies cheaply and in a parallel fashion, researchers often rely on self-assembly. In this approach, forces that act on the building blocks as they are mixed together (such as electrostatic or van der Waals interactions) are used to drive assembly processes that, when properly tuned, can give rise to periodic structures.

The ordered structures that self-assembly methods can create have been of particular value in plasmonics[1]. Plasmonic structures can be used to enhance, focus and manipulate light with extraordinary control. To optimize their interactions with visible and infrared light, the plasmonic structures should be constructed from nano-objects (typically made of noble metals) positioned in a custom-designed dielectric environment. The optical response of the plasmonic structures can be tuned by adjusting the size and shape of the nano-objects, as well as the relative alignment between them in an assembly. Assemblies of anisotropically shaped nano-objects, such as nanocubes, offer the most complex and versatile plasmonic structures, but their optical properties cannot be utilized

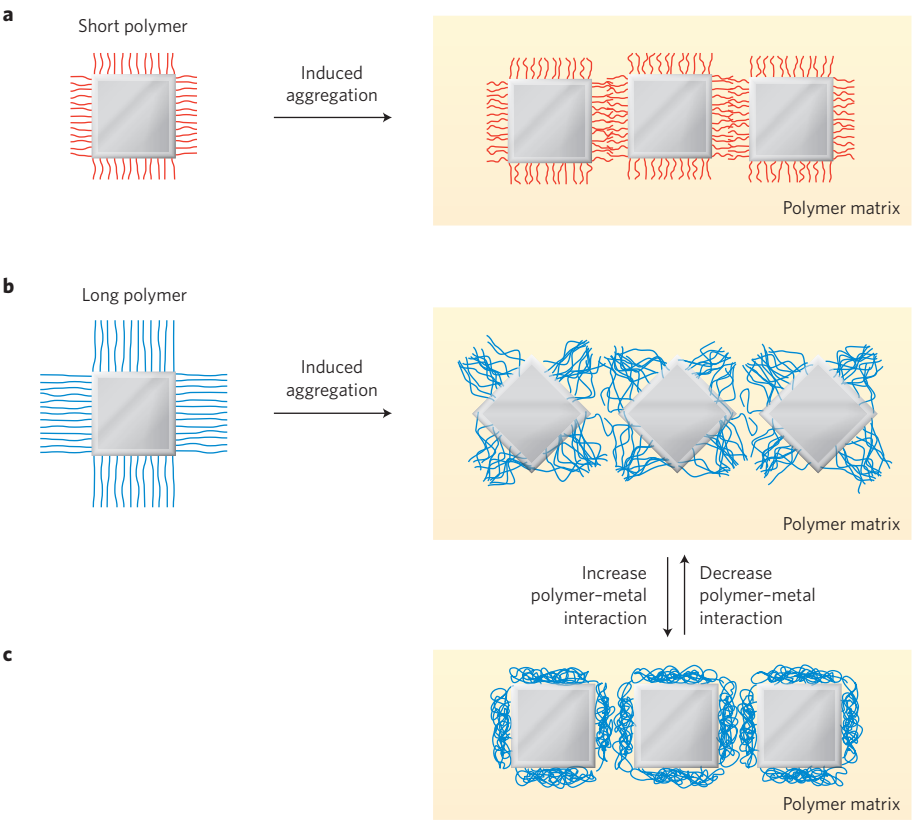

Figure 1 | Modes of assembly of polymer-coated nanocubes. **a**,**b**, The silver nanocubes are coated with hydrophilic polymer chains and embedded into a polystyrene thin film. During annealing, the system can undergo phase segregation and form one-dimensional strings of nanocubes. By attaching short polymer chains to the nanocubes, assemblies with face-to-face configurations are created (**a**). By attaching long polymer chains, edge-to-edge configurations are created (**b**). **c**, Computational analysis also suggests that by adjusting the polymer–metal surface interaction energy, different configurations of assemblies can be formed. This feature could be of particular use in developing functional plasmonic devices. For example, changes in the configuration of the strings of nanocubes could be used to change their optical response, such as switching between resonant absorbers and broadband absorbers.

unless they are fabricated reproducibly and economically[2]. So far, studies of the plasmonic properties of metal nanocubes have used only random assemblies or close-packed structures[3–6]. Writing in *Nature Nanotechnology*, Andrea Tao and colleagues at the University of California, San Diego have now shown that non-close-packed assemblies of plasmonic nanocubes can be created deterministically using self-assembly[7].

To control the assembly of the nanocubes, Tao and colleagues used the phase behaviour of mixtures of polymers placed around the nanocubes (Fig. 1). Immiscible mixtures of polymers can generate a variety of compositional patterns through a type of self-assembly known as microphase segregation[8]. In this latest work, silver nanocubes with an edge length of 80 nm were coated with hydrophilic polymeric surfactants and embedded in a thin film of hydrophobic polystyrene (the matrix). The repulsion between the two types of polymers leads to spatial segregation of the nanocubes, which is assisted by the long-range attractive interactions between nanocubes. However, the low mobility, two-dimensional diffusion of the nanocubes in the matrix, and steric repulsion between surfactants on adjacent nanocubes, prevent the formation of closed-packed assemblies. Instead, linear and branched strings of nanocubes are obtained.

Using computational modelling, the Californian team determined that the hydrophilic polymer chain length and the polymer–metal surface interactions can alter the minimum energy configuration of the one-dimensional nanocube assemblies: short polymer chains and strong polymer–metal surface interactions favour face-to-face alignment of neighbouring nanocubes; longer polymer chains and weaker polymer–metal surface interactions favour edge-to-edge alignment of neighbouring nanocubes. Notably, with short polymer chains the edge-to-edge configuration was predicted to be a local minimum-energy state (a metastable state). These results were corroborated by experiment. The nanocubes with short polymer surfactants were kinetically trapped in the edge-to-edge configuration, and switched to the face-to-face configuration on subsequent annealing. The nanocubes with long polymer surfactants favoured the edge-to-edge configuration even with prolonged annealing.

Because of the plasmonic qualities of the silver nanocube assemblies, the frequency dependence of the extinction and scattering of light by the films is an indicator of the interparticle distance and the alignment of neighbouring nanocubes. In particular, the films were found to change colour as the nanocubes rotate by 45 degrees when switching from one configuration to the other. Moreover, the face-to-face nanocube strings act as broadband absorbers in the visible and infrared regions, whilst the edge-to-edge nanocube strings preserve a resonant mode at ~900 nm associated with hot spots at the narrow junctions.

Researchers have only just begun to explore the structural diversity that mixed systems of polymers and inorganic nanoparticles can provide. For example, combinations of bottom-up and top-down approaches could potentially offer greater control and reproducibility of the nanoparticle assembly process[9]. Alternatively, by using responsive polymers, whose properties can be reversibly tuned by external stimuli, functional plasmonic architectures could be self-assembled and used, for example, in biosensing[10]. The more we understand about the non-specific interactions in such systems, and how they can be used to balance attractive and repulsive forces on multiple length scales, the more deterministic and technologically relevant the self-assembly process will become. ❐

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