

NANOPARTICLE ASSEMBLY

DNA provides control

Solution-based syntheses of nanoclusters typically produce a broad range of species. A step-by-step process using DNA-encoded nanoparticles assembled on a solid support aids in the design and production of specific self-assembled nanoclusters in high yields.

Vivek M. Prabhu and Steven D. Hudson

Enormous opportunities are available for the development of new functional materials from nanoparticles such as gold nanocrystals, quantum dots and carbon nanotubes. It would be particularly advantageous if these nanoscale components could be organized into structures through self-assembly processes without the need for expensive fabrication equipment. However, robust routes to assemble these nanoparticles are not yet available or practical. On page 388 of this issue, Oleg Gang and colleagues outline a method of controlled self-assembly that brings us one step closer to this vision¹. Their approach to the rapid manufacture of well-defined chemically and structurally anisotropic nanoparticles uses the information encoded in the sequence of oligonucleotides (DNA).

Existing models of molecular construction from polymer synthesis and

biochemistry can be used to guide new strategies to self-assemble nanoparticles. In polymer synthesis, the selection of the monomer unit determines whether the polymer will be a semiconductor or insulator. Exceptional control over basic polymerization and processing allows the function and properties of materials to be tailored for specific uses; similar starting materials can be formed into a disposable bag or into fibres for a bullet-proof vest. Analogously, in nature, multiple proteins assemble into a ribosome to guide protein synthesis. This hierarchy of structure (Fig. 1) is now emerging for nanoparticles, as exemplified by recent developments of assemblies of nanoparticles with unusual thermoelectric and optical properties. Nevertheless, we are still at the early stages of learning how to link nanoparticles in a predictable and reproducible manner. An important advance has been the new

field of DNA-based self-assembly, whereby complex shapes and structures are held in place through hydrogen bonding of complementary DNA strands^{2,3}. Guided by these approaches, gold nanoparticles have been functionalized with DNA to direct the solution-phase self-assembly of the particles into three-dimensional crystals^{4,5}.

But there is still a need for control over assembly of small clusters of nanoparticles. The Mirkin group pioneered the use of magnetic colloidal particles to serve as a substrate to functionalize and purify a uniformly DNA-encoded nanoparticle with oligonucleotides⁶. With this approach, they formed well-defined anisotropic gold nanoparticles and larger satellite and dendrimer structures through solution-based self-assembly.

The strategy adopted by the Gang group¹ has generated a modular route that incorporates two different oligonucleotide

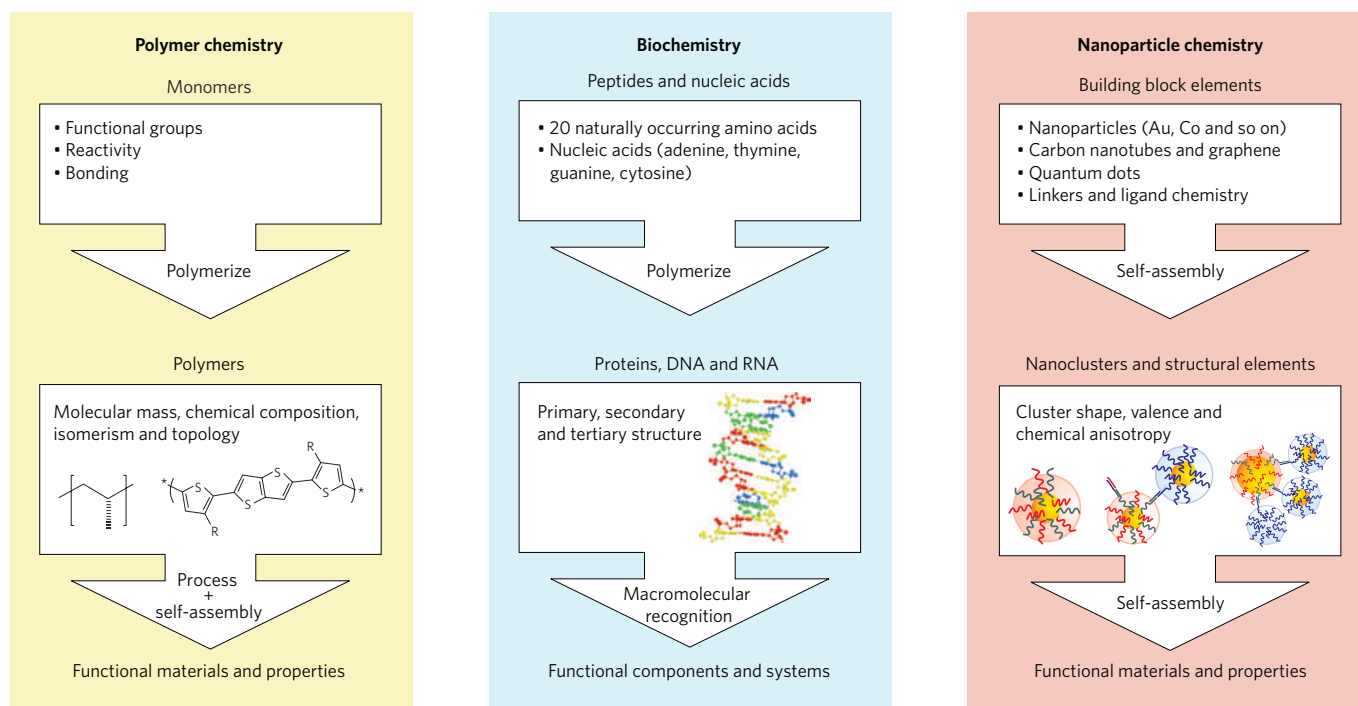


Figure 1 | Examples of the hierarchy of structure formation.

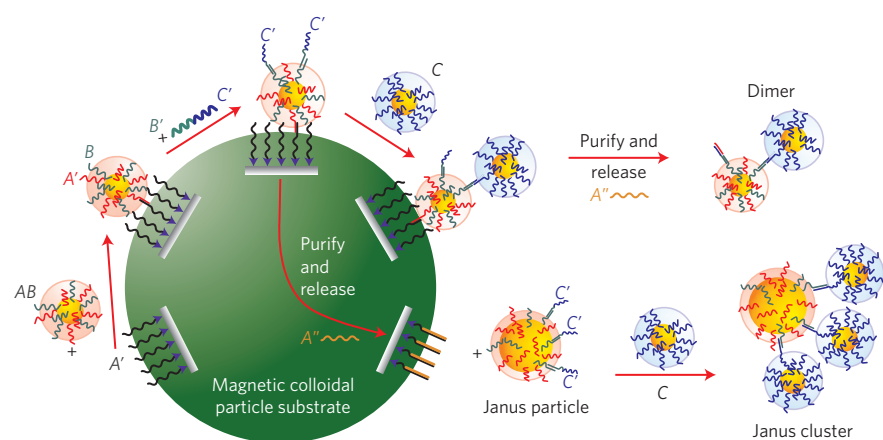


Figure 2 | Stepwise self-assembly on a functionalized magnetic colloidal particle surface. One self-assembly path leads to dimer nanoclusters, the other to Janus particles and clusters. In each case, the DNA encoding of both the substrate and nanoparticles allows the specific self-assembly of nanoclusters and release from the supporting colloid.

strands on a single nanoparticle: one oligonucleotide, A, recognizes the magnetic colloidal particle substrate and the other (oligonucleotide B) serves as a handle for the next step (Fig. 2). Strand A attaches to the magnetic supporting particle by means of complementary strand A'; subsequently, strand B is functionalized with a linker, B'C', that provides a handle for further self-assembly. Two different step-wise growth processes then produce either well-defined dimer nanoclusters or multivalent Janus nanoclusters (Janus particles, named for the two-faced god, are particles in which the hemispheres have different properties). The dimers are produced on the support and then released by a thermodynamically favourable single-stranded DNA, A'',

rather than the DNA melting approach used by Mirkin⁶. The solid-supported assembly shows remarkable control over dimer distributions and purity. This is particularly advantageous because the purity of DNA-functionalized nanoparticles is critical to preparing hierarchical structures and nanoclusters with solution-based assembly⁷. To assemble the Janus clusters, the oligonucleotides on the supported nanoparticle are functionalized with linker strands B'C' and released as Janus particles. These can subsequently be assembled into Janus clusters (Fig. 2).

The considerable achievement of Gang *et al.* is a modular process that produces a 73% yield of dimers from the successive bio-encoding and nanoparticle

recognition of the next element. The Janus particles and clusters provide a basic structural element that can be used to produce different topologies. Further, this strategy has the potential to recycle and reuse the reagents; a promising step that conserves valuable materials while maintaining the high purity needed to produce useful nanoparticle clusters through self-assembly. Akin to polymer chemistry, approaches like this can greatly expand the diversity in materials properties and nanoparticle configurations through the design of specific functions in the nanoparticle, linker chemistry, substrates and processing conditions. As general routes to predictable, reliable fabrication of nanostructures become available, perhaps we will find new memory and electronic components, and biomolecular sensors and markers in the marketplace. □

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NANOCAPACITORS

Undead layers breathe new life

Theoretical advances demonstrating an improved dielectric response in nanocapacitor structures will lead to advanced electronics with greatly increased memory densities.

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Since the beginning of quantum mechanics, physicists have dreamed of designing materials using fundamental physics at the atomic scale. That dream has slowly been realized, starting with understanding simple metals, semiconductors and more and more complex active materials, with parallel advances in chemistry that led to an understanding of even more complex

molecular systems. On page 392 of this issue, Stengel *et al.* move this undertaking forward one more important notch by suggesting a pathway to improved nanocapacitors¹ — electronic devices that consist of a thin layer of a ferroelectric with metallic electrodes.

Nanocapacitors are the largest elements in integrated circuits, and reducing their size and increasing their speed is

an important step in the advancement of electronics. When used as memory, ferroelectric nanocapacitors are as quick as the fastest flash memory, can be packed more densely than dynamic random access memory, and have the permanent retention power of static random access memory. Memory densities of up to a terabit per square inch have already been attained in the laboratory^{2,3}. One thing that has held