

## INORGANIC MATERIALS

## Nanocrystals branch out

Inorganic colloids now come in many forms — spheres, discs and rods. With the addition of branched tetrapods to this list, the potential for creating materials with interesting mechanical, optical and electrical properties is even greater.

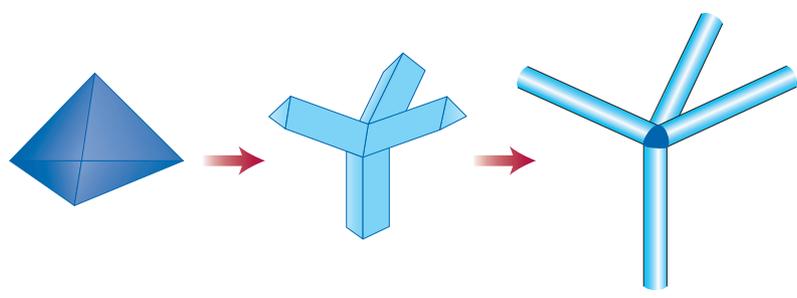
DELI WANG AND CHARLES M. LIEBER\*

are at the Department of Chemistry and Chemical Biology,  
Harvard University, Cambridge, Massachusetts 02138, USA.

\*e-mail: cml@cmliris.harvard.edu

**N**anostructures, such as nanocrystals and nanowires, represent key building blocks for nanoscale science and technology. They are needed to implement the 'bottom-up' approach to nanoscale fabrication, whereby well-defined nanostructures with unique physical properties are assembled into electronic and photonic devices and other functional materials. The building blocks are central to the success of this approach, and thus the more adept researchers are at controlling, for example, the size, morphology and composition of them through synthesis, the greater the potential will be for developing new nanotechnologies. The potential power gained by controlled synthesis of building blocks can perhaps be better appreciated through a biological analogy — in biology the bottom-up paradigm has a long and successful history, and building blocks, such as proteins and ribonucleic acids, yield diverse functions based on well-defined sequence/structure variations. On page 382 of this issue, Paul Alivisatos and colleagues<sup>1</sup> report a significant advance in the synthesis of nanocrystal building blocks — they have developed a general model for, and have demonstrated control over, both the length and diameter of the 'arms' of branched nanocrystals.

The synthesis of nanocrystals in solution has advanced greatly over the past decade. Today, it is possible to prepare semiconductor and metal nanocrystals with nearly monodisperse size distributions, to modify the structures with distinct shell coatings, and to have some degree of control over shape. For example, elongated nanorods can be made by controlling the birth of nanocrystals — the nucleation phase — and their subsequent growth<sup>2,3</sup>. Moreover, these advances in synthesis have enabled progress in understanding the intrinsic size-dependent properties of nanocrystal building blocks and their applications as bio-labels<sup>4</sup>, photovoltaics<sup>5</sup>, light-emitting diodes<sup>6</sup> and lasers<sup>7</sup>. Yet these building blocks are quite simple in

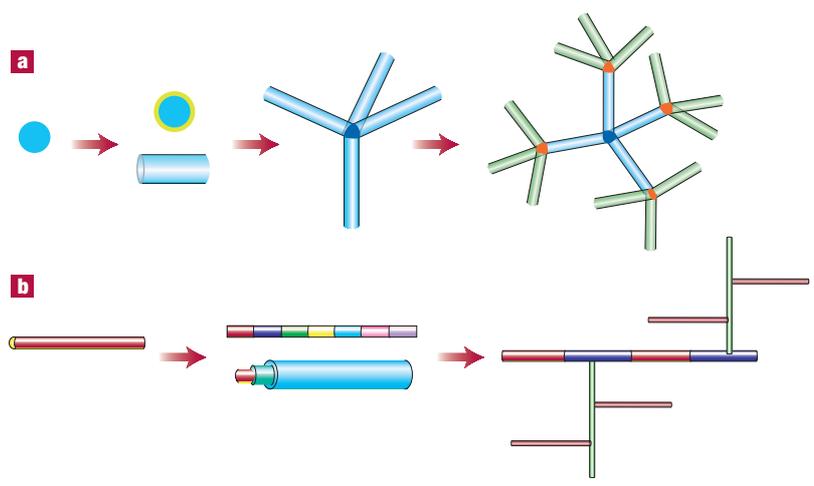


overall structure — single-crystal clusters or rods with controlled surfaces — and one can easily imagine many new directions were it possible to create more complex structural architectures.

Alivisatos and colleagues have done just this with the high-yield synthesis of tetrapod-shaped cadmium telluride (CdTe) nanostructures<sup>1</sup>. The concept underlying their work rests on controlling the relative stability and growth of two different crystal phases (Fig. 1). In CdTe and other tetrahedrally bonded compound semiconductors, cubic and hexagonal crystal phases are often sufficiently close in energy such that both can be accessed by simply varying the reaction conditions. These energetically similar structures are often detrimental to bulk crystal growth, leading, for example, to crystal defects. But they are turned into a big positive in the present study by recognizing the importance of surfaces — a large factor in all nanostructures — as a means for manipulating growth kinetics. Following initial nucleation of cubic nanocrystallites, the authors show that four hexagonal arms can be selectively grown in high yield from the tetrahedral cubic nuclei by using organic surfactants to inhibit growth at the sides of the arms but not at their ends, thereby resulting in selective elongation.

The results of this study are remarkable for several reasons, beyond the physical beauty of these new building blocks. First, the authors have found that the lengths of the arms of individual tetrapods are the same to within a few percent, suggesting that the four facets of the initial cubic crystallites have nearly identical

**Figure 1** Synthesis of branched nanocrystal structures by manipulating the stability of two crystal phases<sup>1</sup>. Initial nucleation produces a cubic nanocrystal (dark blue) with tetrahedral morphology and four (111) crystal facets. Subsequent growth of the hexagonal phase (light blue), which has (0001) facets that are identical to the (111) facets of the cubic phase, produces four arms. The rate of axial elongation versus radial thickening of the arms can be independently controlled through variations in the reactant and surfactant concentrations.



**Figure 2** Emerging diversity in nanocrystal and nanowire building blocks. **a**, Progression of nanocrystal structures from homogeneous clusters, to core-shell and elongated structures, to branched tetrapod and multi-branched materials. **b**, Progression of nanowire structures from uniform wires, to structures modulated in the axial and radial directions, and finally to multi-branched materials. In both sequences, distinct colours are shown to indicate variations in material composition and/or doping.

reactivity when the hexagonal phase starts to grow. Second, they show convincingly that the length and diameter of these tetrapod structures can be varied independently through well-defined changes in the Cd/Te and Cd/surfactant ratios, as is consistent with kinetically controlled growth of the arms<sup>3</sup>. Together, these results offer a new level of control over the synthesis of nanocrystal building blocks and provide new structural diversity for possible applications. For example, these or similar branched structures might serve as attractive additives for structural composites or for nanocrystal-based solar cells<sup>5</sup>.

Looking to the future, it is worth considering adding further structural complexity to the nanocrystal family of building blocks, as well as their relationship to related nanowire structures (Fig. 2). In the case of nanocrystals, these building blocks have evolved from homogeneous, roughly spherical clusters to core-shell, and now to the present tetrapods. As Alivisatos and co-workers suggest, it is natural to consider further branching — that is, nucleation of a cubic phase after initial arm elongation followed by another period of arm growth — analogous to organic dendrimers (Fig. 2a). A similar progression has

occurred in the structures of nanowire building blocks, which typically have higher length/diameter ratios than elongated nanocrystals. In just the past year, nanowires have developed from uniform structures, to ones with composition and/or doping modulated along the axial<sup>8</sup> and radial<sup>9</sup> directions, and even towards the first signs of branched structures<sup>10</sup> (Fig. 2b), albeit lacking the control of this new nanocrystal work. It is interesting to see that the branched structures of both nanocrystals and nanowires are converging to a very similar point, and we also recognize that enhanced knowledge of fundamental factors controlling growth has been crucial to the advances in structural complexity in these two areas.

Are such branched nanostructures the limit we can achieve by rational synthesis? We think the future holds the potential for much greater complexity and that this may drive some of the most unique and exciting applications possible from the bottom-up approach to nanotechnology. For example, consider further the case of multi-branched nanocrystal and nanowire structures (Fig. 2). If researchers can extend the work of Alivisatos and co-workers<sup>1</sup> to enable sequential branching with variations in the composition and/or doping, it will be possible to introduce novel electronic and photonic functionality into these building blocks. Returning to the analogy with biology, such multi-branched structures might serve as building blocks for three-dimensionally interconnected computing structures, not unlike the neural connections found in the brain.

#### References

- Manna, L., Milliron, D. J., Meisel, A., Scher, E. C. & Alivisatos, A. P. *Nature Mater.* **2**, 382–385 (2003).
- Murray, C. B., Kagan, C. R. & Bawendi, M. G. *Annu. Rev. Mater. Sci.* **30**, 545–610 (2000).
- Manna, L., Scher, E. C. & Alivisatos, A. P. *J. Cluster Sci.* **13**, 521–532 (2002).
- Jovin, T. M. *Nature Biotech.* **21**, 32–33 (2003).
- Huynh, W. U., Dittmer, J. J. & Alivisatos, A. P. *Science* **295**, 2425–2427 (2002).
- Tessler, N., Medvedev, V., Kazes, M., Kan, S. H. & Banin U. *Science* **295**, 1506–1508 (2002).
- Klimov, V. I. *et al. Science* **290**, 314–317 (2000).
- Gudiksen, M. S., Lauhon, L. J., Wang, J., Smith, D. & Lieber, C. M. *Nature* **415**, 617–620 (2002).
- Lauhon, L. J., Gudiksen, M. S., Wang, D. & Lieber, C. M. *Nature* **420**, 57–61 (2002).
- Gao, P. & Wang, Z. L. *J. Phys. Chem. B* **106**, 12653–12658 (2002).

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