

SEMICONDUCTOR NANOCRYSTALS

Shape matters

It is well known that quantum effects become increasingly important as the size of structures is reduced. But the influence of shape on quantum confinement is less appreciated. New data show that shape matters as much as size.

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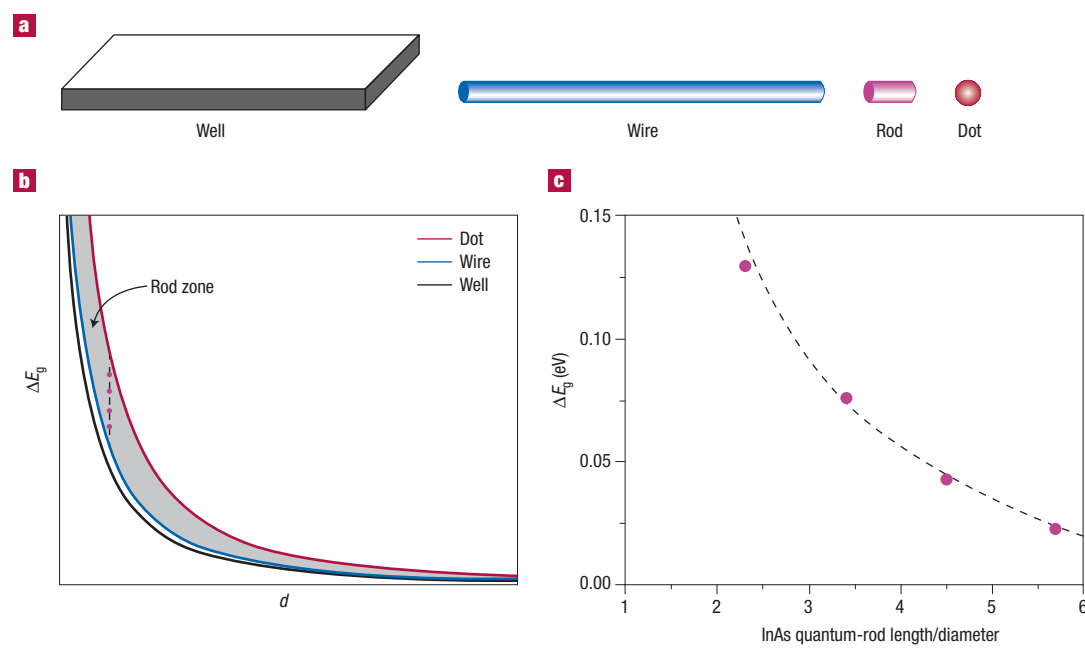
“Form ever follows function,” asserted architect Louis Henri Sullivan, providing a maxim for designers of all persuasions. His protégé, Frank Lloyd Wright, preferred “Form and function should be one.” Such adages express the widely held conviction that shape and utility or properties are inextricably linked. The experimental work by Kan *et al.* described on page 155 of this issue¹ provides a compelling demonstration of this principle. Kan and colleagues show that the electronic structure and optical properties (that is, the quantum confinement effects) of rod-like semiconductor nanocrystals depend sensitively on the ratio of their length and diameter. Thus, bodybuilders, distance runners,

architects and quantum mechanics agree: In function, performance and behaviour, shape matters.

Quantum confinement in semiconductors results from the geometric confinement of electrons and holes as independently acting ‘wave-particles’ or as bound pairs known as excitons². The normal size of an exciton in a large (bulk) crystal, expressed as an exciton Bohr radius, provides an approximate dimension for the onset of quantum-confinement effects. When an electron-hole pair is squeezed into a nanocrystal with one or more dimensions approaching the bulk exciton Bohr radius, the effective bandgap of the semiconductor increases. The smaller the nanocrystal, the larger the effective bandgap, and the greater the energy of optical emission resulting from electron-hole recombination. Typical exciton Bohr radii range from 2.2 nm (ZnS) to 7.5 nm (CdTe) in II–VI semiconductors, and from 11 nm (InP) to 60 nm (InSb) in III–V semiconductors². So the magnitude of quantum confinement is known to depend on nanocrystal size and composition. But what about the nanocrystal shape?

Semiconductor quantum confinement was discovered almost 40 years ago³ in layer-like nanocrystals of MoS₂, and shortly thereafter in similarly shaped GaAs

Figure 1 Comparisons of quantum wells, wires, rods and dots. **a**, Geometries of the different structures. **b**, Plots of ΔE_g (the increase in the bandgap over the bulk value) against d (the thickness or diameter) for rectangular quantum wells, cylindrical quantum wires and spherical quantum dots obtained from particle-in-a-box approximations. The grey area between the dot and wire curves is the intermediate zone corresponding to quantum rods. The vertical dotted line and points qualitatively represent the expected variation in the bandgap for InAs quantum rods of varying length/diameter ratio, as studied by Kan *et al.*¹. **c**, A plot of ΔE_g against length/diameter ratio for the InAs quantum rods synthesized by Kan *et al.*, showing the dependence of the bandgap on the shape of the quantum rods. The dotted line represents the variation expected from a particle-in-a-box approximation¹.



quantum wells⁴. These quantum nanostructures are large in two geometric dimensions, and confined only in the third dimension (1D quantum confinement; Fig. 1a). Quantum dots, which are confined in all three dimensions (3D confinement), have also been extensively studied². Least studied are 2D-confined quantum wires, primarily because of difficulties in fabrication. Molecular beam epitaxy growth is challenging, and catalysed-growth methods generally produce nanowires with diameters larger than the bulk exciton Bohr radii. Attempts to produce quantum wires by adapting the colloidal synthesis methods used to produce quantum dots have so far produced only comparatively short quantum rods (Fig. 1a). One may reasonably wonder which shape — wells, wires, rods or dots — will show the inherently strongest quantum-confinement effects.

The answer, which has long been known theoretically and is arrived at by simple considerations, is shown in Fig. 1b. Particle-in-a-box approximations find that 3D confinement is stronger than 2D confinement, which in turn is stronger than 1D confinement. These conclusions, also supported by higher-level theoretical approximations⁵, predict that the change in the bandgap energies (ΔE_g) in quantum nanostructures of a given composition and thickness (or diameter) should be the greatest in dots, followed by rods, wires and finally wells. But experimental confirmation of this prediction is largely lacking. So far no systematic experimental comparison has been made of the relationships between bandgap energies and size in systems that differ only in the geometric dimensionality of confinement: that is, 1D against 2D, 2D against 3D, or 1D against 3D. The work of Kan *et al.* makes an important step in that direction by exploring the transition from 3D to 2D confinement in InAs quantum rods¹.

The authors prepare InAs quantum rods with uniform 4-nm diameters and a mixture of lengths, which were separated into various length fractions having length/diameter ratios ranging from 2.3 to 5.7. The bandgaps of the rods were found to decrease with increasing length/diameter ratio (the points in Fig. 1c), as predicted by Fig. 1b. As the rod length increases, the bandgap decreases towards the value expected of true quantum wires. A similar length dependence was previously demonstrated in CdSe quantum rods by Alivisatos and co-workers⁶. So both II–VI and III–V semiconductor nanostructures have now been shown to have shape-sensitive bandgaps.

The excited-state dynamics in quantum rods are apparently quite distinctive. The results of Kan *et al.* indicate that the luminescence quantum yield decreases as the quantum rods lengthen, which is probably because of an increasing spatial separation of electron and hole wavefunctions¹. Reducing the wavefunction overlap should decrease the probability of electrons and holes recombining radiatively, and thus reduce photoluminescence efficiency. Finally, the authors report that, unlike isotropic InAs quantum dots, the InAs quantum rods show polarized luminescence (along their long axes). This phenomenon has been previously demonstrated in semiconductor quantum rods⁷ and nanowires⁸. The work of Kan *et al.* and others convincingly establishes that both the magnitude and character of quantum confinement in semiconductor nanostructures are highly shape-dependent.

Potential applications are now emerging that exploit the anisotropic shapes of quantum rods and wires. The pseudo-1D morphologies of rods and wires increase carrier transport in light-harvesting cells⁹, and aid their assembly into complex crossed-nanowire devices¹⁰. Polarized emission supports applications such as orientation-sensitive fluorescence labels, and allows linearly polarized lasing¹¹. Ensembles of rods or wires could have collective properties, such as the efficiency of interparticle energy transfer, that are different from and perhaps better than those of close-packed dots. We expect continued improvements in quantum-wire syntheses, and completion of the missing systematic comparisons of true 1D, 2D and 3D confinement systems. Much is to be gained by recognizing that quantum confinement in semiconductors is a matter of shape.

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