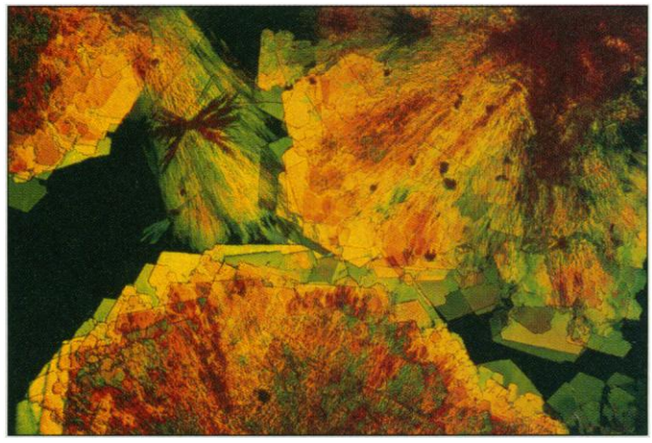
The Chemistry of Size and Order on the Nanometer Scale

James R. Heath

When given the task of altering some physical property of a particular material, a chemist will typically modify the structural or elemental composition of the material to achieve that change. However, for nanocrystalline materials, a modification of the size or shape of the crystallites may actually effect an equivalent change. Many fundamental properties of materials are characterized by length scales on the order of 10 to 200 Å. If a crystal is fabricated such that at least one of its dimensions is smaller than the length scale of some property, then that property is "confined" and becomes dependent on the size and shape of what is now called a "quantum crystal." In this issue, Murray, Kagan, and Bawendi (*1*) report a major step forward in achieving the self-assembly of such quantum structures into more complex arrangements.

In semiconductor nanocrystals, some of the most spectacular effects are observed in the case of three-dimensional exciton confinement. For direct-gap materials, exciton confinement leads to the development of discrete, excited electronic states with high oscillator strength and to band gaps that increase as an inverse function of crystallite size. In certain cases, finite-sized structures may exhibit fundamentally new properties. For example, although silicon is the dominant material of microelectronics, it is characterized by a dipole-forbidden $k = 0$ band-gap transition and is therefore not a useful optoelectronic light source. However, within sufficiently small (~20 Å) Si crystallites, the radiationless relaxation processes are all but eliminated and Si can become a very efficient photo- and electroluminescent material (*2*). The fact that a recent fundamental discovery could be made on a material as well studied as silicon serves to highlight the youth and potential of this field.

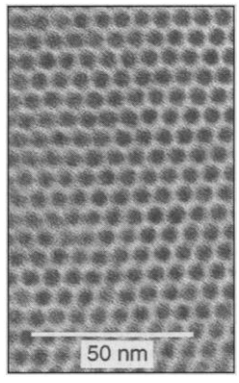
The development of general techniques for the fabrication of semiconductor quantum structures has been a major goal of materials chemistry and physics over the past decade. Two distinct approaches have been developed. The first, a "top-down" approach, uses lithographic and semiconductor processing technologies to fabricate low-dimensional structures. Such methods yield not only precise control over the size of the quantum structure, but also equally precise control over the absolute placement and the lateral and vertical environments of the structure. This approach is limited to the serial fabrication of structures near 500 Å in size, although technological advances may soon reduce this number to about 100 or 200 Å (*3*). For such "large" sizes, applied electrical fields, coupled with ultralow-temperature measurements, are necessary to observe confinement effects.



Colorful crystallites. Optical micrograph of cadmium selenide colloidal crystals. [Courtesy M. G. Bawendi; photo by F. Frankel.]

The second approach to fabricating quantum structures is to build them from molecular or atomic precursors. This approach includes such exotic techniques as the use of the scanning tunneling microscope to fabricate structures atom by atom (*4*). More general, however, are chemical schemes for preparing colloidal solutions of various semiconductor nanocrystals (quantum dots), from the II-VI compounds (*5*) such as CdSe and CdS, to the III-V materials (*6*) such as GaAs and InP, to the group IV materials (*7*) Si and Ge. A formidable challenge with these syntheses is to achieve chemical control over the average size and size distribution of the product nanocrystals. Over 40 years ago Reiss showed that for any scheme in which particles are nucleated and grown by means of diffusion-controlled growth, the average particle size and the width of the size distribution are both functions of the temporal discreteness of the nucleation event and the growth time (*8*). Although this concept is readily understood, it is very difficult to put into practice. In 1993, Murray and co-workers reported a synthesis for the production of very narrow size distributions of II-VI quantum dots, which was an almost perfect demonstration of Reiss's model (*9*). Previous generations of synthetic schemes had already made the II-VI nanocrystal colloids the prototypes for the study of quantum size effects. Their paper raised the standard for such studies.

The nanocrystal colloid preparations have unique advantages: Nanocrystal size can be controlled within the range of 20 to 150 Å and so confinement effects can be directly investigated, even under ambient conditions. The particles are monodisperse, soluble, and obtainable in macroscopic quantities. The major catch is that these particles, whether in powder or colloid form, are randomly dispersed. These nanocrystals are fantastic entities, but they only make up half of a story. The other half involves finding ways to place the nanocrystals into chemically and structurally complex environments that take advantage of their unique properties, and therein lies the advance Murray *et al.* have made.



Nano order. Transmission electron micrograph of a face-centered cubic array of dots, each 48 Å in diameter [adapted from (*1*)].

Murray, Kagan, and Bawendi describe chemical techniques for directing the self-assembly of CdSe nanocrystals into three-dimensional ordered arrays (superlattices), and they demonstrate order control on several length scales (*1*). First, the individual quantum dots are crystallized into a close-packed lattice, which can extend over several micrometers. Second, the lattice spacings of the array are readily modified either by changing the size of the constituent nanocrystals or by altering the size of the organic passivants on the nanocrystal surfaces. Third, by forming the arrays at an interface, the nanocrystals assemble with their crystallographic axis at least partially

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aligned (see electron micrograph).

Crystals of nanocrystals are not new. Indeed, it has been known for some time that, under appropriate conditions, narrow size distributions of particles will self-assemble into ordered structures. What is new about this work is the level of control demonstrated, and the implications are many. For example, if the particles are in sufficient proximity that their electronic wave functions overlap, then the array will develop a unique electronic structure. In solid-state terminology, controlling this interaction is analogous to manipulating the width and shape of the energy bands of the extended solid. Such control is relatively commonplace for one-dimensional superlattices but is unheard of for the three-dimensional case.

The authors point out that their techniques should be applicable to nearly any particle system, provided that techniques for producing sufficiently narrow size distributions can be found. For the special case of metal nanocrystals, recent work indicates that narrow size distributions may not even be necessary (*10*). The dispersional attractions between metal particles are relatively strong and scale geometrically with particle size. This leads directly to size-dependent phase separations followed by superlattice formation, all within a single step.

The superlattice structures discussed in this issue represent only a first step toward putting quantum crystals into complex environments. Many applications envisioned for quantum dots are device-oriented, single-particle tasks that have various wiring, geometry, and insulation requirements. The development of techniques for the parallel construction of such devices remains a major challenge.

References

1. C. B. Murray, C. R. Kagan, M. G. Bawendi, *Science* **270**, 1335 (1995).
2. L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990); L. E. Brus, *J. Phys. Chem.* **98**, 3575 (1994); P. M. Bressers, J. W. Knapen, E. A. Meulenkamp, J. J. Kelley, *Appl. Phys. Lett.* **61**, 108 (1992).
3. A. J. Rimberg, T. R. Ho, J. Clarke, *Phys. Rev. Lett.* **74**, 4714 (1995).
4. M. F. Crommie, C. P. Lutz, D. M. Eigler, *Science* **262**, 218 (1993).
5. L. E. Brus, *J. Phys. Chem.* **90**, 255 (1986).
6. O. I. Micic, C. J. Curtis, K. M. Jones, J. R. Sprague, A. J. Nozik, *ibid.* **98**, 4966 (1994).
7. J. R. Heath, J. J. Shiang, A. P. Alivisatos, *J. Chem. Phys.* **101**, 1607 (1994).
8. H. Reiss, *ibid.* **19**, 482 (1951).
9. C. B. Murray, D. J. Norris, M. G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993).
10. P. Ohara, D. V. Leff, W. M. Gelbart, J. R. Heath, *Phys. Rev. Lett.* **75**, 3466 (1995).

Ensemble Activity and Behavior: What's the Code?

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The brain processes enormous streams of temporally and spatially varying information within anatomically precise networks, by reading a poorly defined spatiotemporal code (*1*). Single-electrode recordings can determine both the firing rate of individual neurons and the correlation of this rate with sensory and behavioral events, but such perievent histograms reveal only small bits of the activity in the brain. This approach to understanding the neural basis of cognition and behavior is like trying to decipher a video image one pixel at a time while the video image constantly changes: Only as one views many pixels does the image become apparent. For this reason, large-scale neuronal recordings are necessary to examine activity in ensembles of neurons (*2*) and to understand how the brain processes behaviorally relevant information.

Much of our thinking about networks and ensembles in the mammalian brain has come from studies of single-electrode recordings of neurons obtained serially, in moderate to large numbers, within the same experimental context. The recordings are then combined and analyzed, post hoc (*3*). Such reconstructed ensembles reveal recurring temporal firing patterns associated with specific sensory stimuli. This approach is analogous to restarting the video (one hopes at exactly the same place) over and over again and observing a different pixel each time, eventually reconstructing the video image after a sufficient number of pixels have been serially processed. Such studies show that ensembles of 50 to 100 neurons can uniquely encode a finite number of input features (*3*). Because such analyses are by necessity reconstructed, they provide only indirect evidence that the neural activity driving behavior is distributed among coherent neurons (*4*). Nevertheless, most models of decision-making by neural networks assume such a distribution (*5*).

Although problematic, this approach has been productive. Georgopoulos (*6*) provided the initial evidence that populations of neurons in the motor cortex of the monkey encode information better than single neurons. In ensembles that code the direction of limb movement, a derived intention vector predicted limb movements more accurately than individual neurons. Studies by Schultz *et al.* (*7*) showed temporally distinct firing of different types of neurons in the monkey striatum during a task, such that the combined ensemble suggested that the triggering of one cell by another could temporally link the different phases of the task.

Technical developments now allow direct recording of ensemble activity in behaving animals: These include (i) multielectrode fabrication techniques (*8*), (ii) multichannel (10 or more) recording of extracellular neural spike data in awake behaving animals (*9*), and (iii) appropriate statistical analysis (*10*). Although implementation of this new technology is in its infancy, several new findings have emerged. Wilson and McNaughton (*11*) recorded from 100 neurons in rats that were exploring a novel environment. They observed a tight correspondence between place-field firing and movement trajectories (*6*), although the pattern of firing in these neurons could have reflected the animal's presence in, rather than a movement toward, a particular location (*12*).

It is essential to use appropriate statistical analyses to identify what kind of information is actually encoded by ensembles during behavioral events (*13*). Nicolelis *et al.* (*14*), recording from large ensembles of neurons, demonstrated that interaction between sensory receptive fields for whisker movement is widespread and is likely to involve most of the whisker-projection area of the cortex and thalamus. Using principal components and factor analysis of ensemble firing, they found that sensory receptive fields consisted of both temporally and spatially distributed firing patterns and that particular subsets of neurons functionally combined to provide parallel, distributed encoding of tactile stimuli within ensembles. In addition, they demonstrated a 7- to 12-Hz rhythm initiated in the cortex that eventually synchronized neurons in the thalamus and trigeminal nucleus and modulated tactile encoding as a function of exploratory movements. Thus, there is an association among sensory input, ensemble encoding, and processing of that information during behavior.

Correct computation and appropriate

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