Naval Research Reviews

CLUSTER SCIENCE

Optical Data Storage

Laser Write

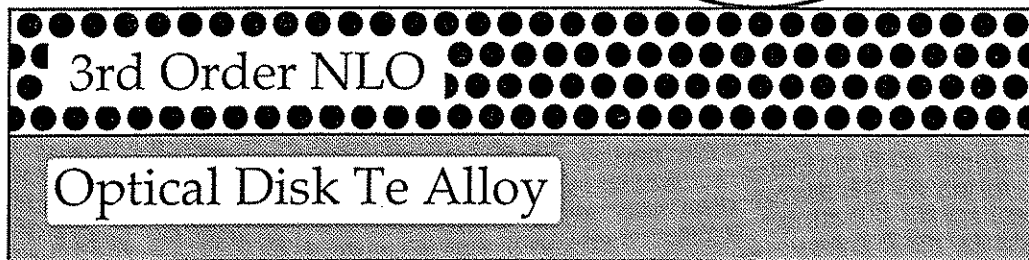|←——— Beam Width ———→|

Intensity

Write
Resolution

|←——→|

3rd Order NLO

Optical Disk Te Alloy

Research in Professor Galen Stucky's laboratory has yielded a new material and an improved method for optical disk storage. This figure is a schematic diagram of the process of laser "writing" on an optical disk storage medium. In order to get the highest resolution, the laser is focused as tightly as possible. However, the optical density will be limited by diffraction effects at small laser beam diameters and by the inhomogeneity of the laser intensity in its cross section, which also restricts the sharpness of reproduction. ONR-sponsored research contributed to the development of a new optical medium material that consists of quantum confined semiconductor clusters, which have nonlinear optical (NLO) properties. These properties include the variation of the refractive index and absorption edge with laser intensity, yielding an optical transistor. In essence, using a nonlinear optical material coating allows only the center portion of the laser beam, which has an intensity above a particular threshold, to be selected, which dramatically improves optical density, resolution and recording quality (see article by Stucky in this issue.)

Nanochemistry and Nanoclusters: The Beginning of Matter

Galen D. Stucky
Department of Chemistry
University of California, Santa Barbara

Introduction

Ultimately all materials and living organisms have their origins in the collective assembly of a small number of atoms or molecules. Whether it be the beginning of life, crystallization, or the natural formation of a complicated nanocomposite like a sea shell, this is a fascinating process because it is at this stage that the inherent future properties such as shape, mechanical strength, color, conductivity, etc. are established. It is also a time when the atoms or molecules are not certain as to whether they would prefer to be associated as an array or nano (a dimension on the order of atomic radii, 1 nanometer $= 10^{-7}$ cm) cluster or on their own in the surrounding environment. Physically this simply means that the intermolecular and interatomic interaction energies associated with the self assembly are of the same order of magnitude as the attractive energy that the atoms or molecules have for their surroundings. The chemistry of this nucleation process is therefore particularly sensitive to changes in composition and external effects such as temperature, electric fields, or anything that even slightly perturbs the dynamics and kinetics of the system.
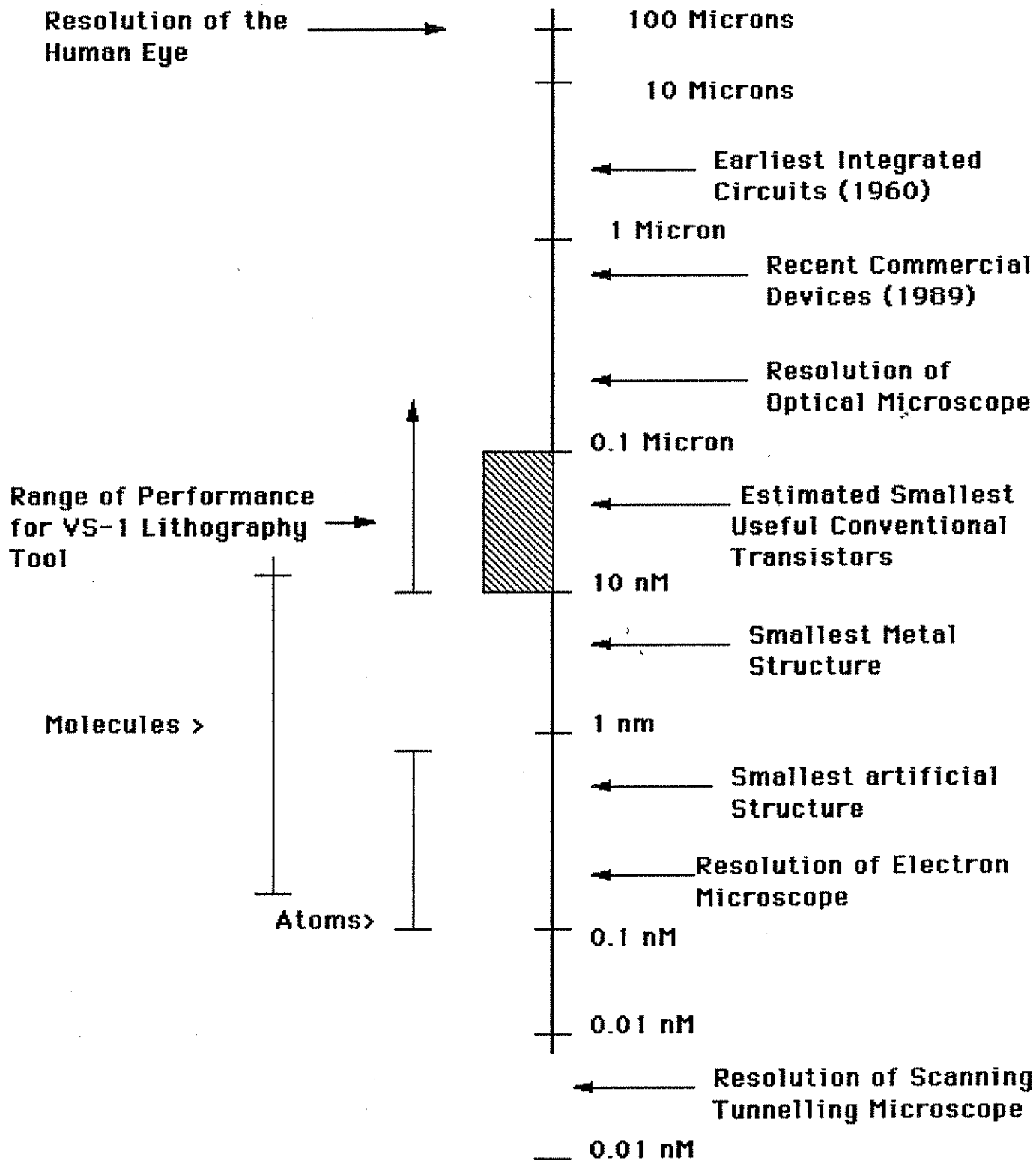
Why are arrays of atoms in this size regime important? In biological systems, for example, it means that the atoms that make up the cluster are readily accessible and can be efficiently used. The iron that our bodies need so badly is provided via an iron transport cluster entity called ferritin[1-3]. Ferritin consists of a shell of proteins which surround an iron core of up to 4500 iron atoms that is essentially spherical with a diameter of 80 Å. The composition approximates closely to $(FeOOH)_8$ $(FeO \cdot H_2PO_4)$. In fact, the iron core has a close structural resemblance to ferrihydrite, an iron oxide bulk solid $(5Fe_2O_3 \cdot 9H_2O)[4]$ that contains a close packed array of oxide and OH^- ions with iron atoms in octahedral interstices. Obviously it is not in the best interest of our bodies for the 4500 iron atom cluster to expand, i.e. to continue to crystallize, into several grams of ferrihydrite with $\sim 10^{23}$ atoms. Somehow nature provides a way to stop the growth at 4500 atom irons and to package these atoms in a useful way. In this case, phosphate $(PO_4)^-$ groups in ferritin cap and passivate the exterior surface.

The surfaces of nanosized clusters must either have considerable curvature or else abrupt changes in shape. During catalysis, this means that the atoms on nanosized clusters are more exposed than those in larger particles, making them much more reactive towards other chemical species. On the other hand, this exposed atom reactivity also means that the

Resolution of the ⟶   **100 Microns**
Human Eye

        10 Microns

⟵   **Earliest Integrated**
     Circuits (1960)

1 Micron

⟵   **Recent Commercial**
     Devices (1989)

⟵   **Resolution of**
     Optical Microscope

0.1 Micron

Range of Performance   **⟵**   **Estimated Smallest**
for VS-1 Lithography ⟶   **Useful Conventional**
Tool   **Transistors**

10 nM

⟵   **Smallest Metal**
     Structure

Molecules >   **1 nm**

⟵   **Smallest artificial**
     Structure

⟵   **Resolution of Electron**
     Microscope

Atoms>   **0.1 nM**

     0.01 nM

⟵   **Resolution of Scanning**
     Tunnelling Microscope

     0.01 nM

clusters are not very stable and can either join with neighboring clusters or be poisoned with respect to the catalytic process by other reactions.

A third area where nanocluster materials have a significance and impact is in photonic/electronic applications. The miniaturization of electronic and optic devices has revolutionized response times, energy loss, and transport efficiency (Figure 1). Additionally, the presence or absence of a few atoms and the geometrical disposition of each atom can significantly modify electronic and photonic properties as one approaches the nanosize regime. This control can be further supplemented by "packaging" assemblies of atoms or molecules into thin film or nanocomposite bulk materials to define surface states, cluster environment and geometry, intercluster interactions, and consequently, a wide tunable range of optical and charge carrier responses.

Utilizing nanoclusters in photo-optics has attracted considerable commercial interest (See inside cover figure). Collimation of a laser beam to get the highest possible optical density in writing on a optical disk is limited by diffraction effects if collimation is used to attain a small laser beam diameter. We also see that the intensity of the laser beam is not homogeneous in cross section which also restricts the resolution and sharpness of reproduction. Nanosized semiconductors display a peculiar nonlinear optic property: they will absorb light if it is not too intense, but will transmit light if the number of photons surpasses a certain threshold value. By using a thin film mask containing the semiconductor clusters, only the center portion of the beam, which has a photon flux above a certain intensity cutoff, is transmitted, dramatically (~50%) improving both optical density and recording quality. Using shorter wavelengths further improves the resolution. Fortunately, the optical absorption and emission bands of a semiconductor shift to shorter wavelengths if the semiconductor atoms are in an appropriately small cluster. If these effects are observed, the electrons in the semiconductor are said to be quantum confined, and the semiconductor is sometimes referred to as a quantum confined material.

Quantum confined materials are creating numerous opportunities to develop new science and technologies. Research on electro-optic (EO) and nonlinear optic (NLO) processes began in earnest in the early 1960's after the invention of the laser so that the topic of nonlinear optical materials is just beginning to reach the mainstream of chemistry. However, when one realizes the possibilities for decreasing computing times with optical computers, increasing our capabilities to manipulate and store visual images using thin panel optical display devices, forming optical neural networks involving "thought" processes similar to those of our own brains, and a host of other applications, the reason for excitement about this rapidly growing field becomes clear. Optical data transmission can be accomplished with less energy loss and device heating. In addition, optical signal transmission is much less vulnerable

Figure 2.

Variation of free energy of nucleation with cluster radius during synthesis. r_c is the kinetic critical radius and r_0 is the thermodynamic critical radius. For the solid line the surface and bulk free energy contributions are assumed to be the same, while for the dashed line the bulk free energy is assumed to be twice as large as the bulk free energy.
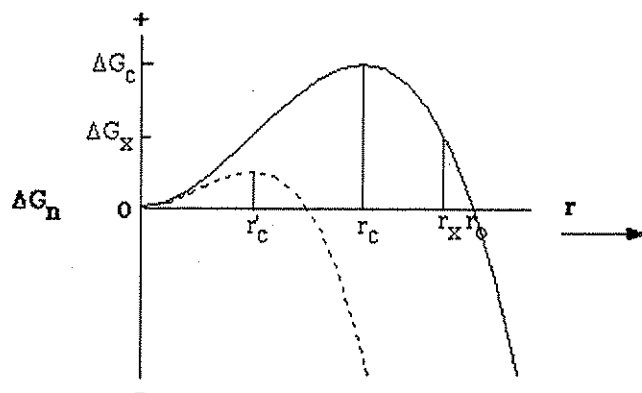
to disruption by external electromagnetic fields or other radiation sources. It has been suggested that the former of these effects will lead to desk top Cray computer capabilities within the next ten years.

Many other examples could be cited. A bottom line is that classical laws become unreliable as the dimensions become smaller and smaller. This applies not only to electro-optic phenomena, but also to mechanical concepts, such as friction, fatigue, and stress. Yet, IBM researchers have shown that near 0°K it is possible to arrange 35 xenon atoms into an array which spells out the IBM logo by manipulating individual atoms with a scanning tunneling microscope tip. It is a very exciting and unpredictable frontier between the classical and the quantum world.

Because of the importance of nanocluster chemistry to a wide variety of fields, ranging from atom and electron transport in biological systems, heterogeneous catalysis, photo-catalysis, to the development of new electro-optic devices based on quantum confinement, there has been an explosion of interest in this area by scientists from many areas. Nanocluster syntheses have been carried out in numerous ways to give unexpectedly different materials with varied structural, optical, and transport properties. Molecular inorganic, physical, and biochemists have generated nanoclusters by building up arrays from solution or gas phases atom by atom.[5-7] From the other directions, solid-state physicists and engineers have focused on increasingly smaller and smaller dimensions with engineering based directly on a solid-state atomic lattice substrates.[8,9] *The materials chemistry at this molecular and solid-state interface requires a precise definition of the number of*

atoms, their siting (e.g. bulk versus surface), and ultimately the manner in which they are assembled on the surface and within the cluster to form a nanocomposite array. It is for these reasons that while the convergence of molecular and solid-state chemistry is near, the somewhat diffuse materials synthesis interface between isolated clusters and the infinite solid array is only beginning to be resolved.

This article is concerned primarily with nanocluster packaging. In order to demonstrate why packaging is important, we will first briefly review the thermodynamics associated with cluster synthesis by the assembly of atoms through nucleation.

Nucleation and Critical Radii

Nucleation means change. The system of interest has been perturbed in some fashion so that thermodynamically it is no longer at equilibrium. In order to induce nucleation we may lower the temperature to decrease solubility or increase the concentration of the particle that we wish to nucleate. We also can change the solvent medium so that the solvation energies are decreased, which will in turn result in interparticle interactions becoming dominant.

For any process to proceed spontaneously, the free energy for the change, ΔG_n, where n refers to the nucleation, must be < 0. Assume that the species are randomly ordered at the beginning, which is usually the case. Since the disorder of the system decreases during nucleation, the entropy contribution to the free energy change will be unfavorable (< 0) and becomes increasingly so with increasing temperature.

The driving force for the nucleation is the attraction of the atoms or molecules for each other. Ordinarily this attraction is three dimensional, and is accompanied with a decrease in free energy per unit volume, $-\Delta G_v$. Therefore, for a spherical cluster of radius r, the gain in free energy is $-(4/3)\pi r^3 \Delta G_v$. Assuming that we have adjusted the temperature, solvation effects, and other factors that would favor the isolated nuclei, what prevents nucleation from occurring? Clusters have surfaces, and associated with these surfaces is a surface energy which makes a positive contribution to the nucleation. One way to view this effect is that the atoms at the surface interact more strongly with their neighbors than do the atoms in the bulk. In a sense the surface must be weakened and possibly rearranged in order to continue the cluster growth. Denoting the surface free energy change per unit area of the cluster as ΔG_s, the net change in free energy during nucleation is:

$$\Delta G_n = 4\pi r^2 \Delta G_s - (4/3)\pi r^3 \Delta G_v \qquad (1)$$

This relationship is plotted in Figure 2 and reveals several key points. The most important point for our purposes is the critical role that the surface plays in the process of forming a cluster. Initially the overall free energy for the nucleation is positive, but with increasing radius of the hypothetical spher-

ical cluster, ΔG_n passes through a maximum ΔG_c when the cluster has a radius r_c. As the radius increases, ΔG_n decreases to zero and first becomes negative for $r > r_o$. The significance of this can best be seen by considering the fate of a small cluster with radius r_x. Thermodynamically this cluster is unstable since $\Delta G_x > 0$. However, if it were to start to dissolve, its radius would decrease and the free energy would become even greater so that it is <u>kinetically stable.</u> We conclude that clusters with a radius $r \geq r_c$ are going to continue to grow. Nuclei with radii $r_c < r_x < r_o$ are called metastable since they require an activation energy ($\Delta G_c - \Delta G_x$) for their dissolution. Clusters with radii $r < r_c$ are unstable since there is no barrier to their dissolution. Clusters with radii $r > r_o$ are over the hill, i.e. stable, since growth to larger clusters is then both kinetically and thermodynamically favored.

So how can we stabilize smaller clusters or possibly intercept clusters with an arbitrary radius? One way is shown by the dashed line in Figure 2. Here $\Delta G_v = 2\Delta G_s$ while for the solid curve it is assumed that $\Delta G_v = \Delta G_s$. Clearly if we can increase the binding energy between our atoms in the bulk relative to the surface energy, smaller clusters will be more stable. Another alternative is to "package" the clusters. Chemically this means that as a cluster is forming the atoms on the surface of the cluster will be capped and passivated with respect to further growth. This could be done either by simply adding a passivating reactant to the nucleation media or by growing the clusters within a protein or inorganic cavity, the walls of which contain the passivating groups. Both of these approaches are described below. We begin with molecular or polymeric packaging.

Growing and Packaging Molecular Clusters

Unreactive and Reactive Cluster Surfaces

As described in this issue's accompanying articles by Smalley and Weaver, it is now possible to synthesize a variety of clusters of specific size and shape by high-vacuum vapor phase techniques. In a few cases, such as for the remarkable C_{60} Buckyball, it has been possible to develop macroscopic synthesis techniques to create relatively large quantities of solid-state materials which contain the same carbon cluster. This is possible because of the stability of the closed electronic shell structure obtained by the carbon atoms on the surface of the Buckyball. Their arrangement is similar to that in graphite with aromatic delocalized bonding through alternating C-C and C=C bonds with no "dangling" bonds, i.e. the Lewis octet rule is satisfied for all the carbon atoms. In terms of the thermodynamic model described above, ΔG_v is defined by the formation of a closed surface with anisotropic bonds within the surface. The alternative of a fragment of a graphite sheet with dangling radical bonds is less favorable.

Metal Clusters

Apparently metals also can form resonance bonding of this type, but not to the extent of being able to exclude reaction at the metal cluster surface. For example, Schmid has reported a family of clusters based on the closest packing of heavy Au and Pd atoms to give "magic" numbers of 13, 55, etc. with the nth shell containing $10n^2 + 2$ atoms. These include $Au_{55}(P(Ph)_3)_{12}Cl_6$ (Ph = C_6H_5) and $Pd_{561}(phen)_{36}O_{190-120}$ (~26 Å in diameter with 5 spherical shells, and phen = phenanthroline).[10] Isolation and characterization of a pure phase of the latter has not yet been reported. The largest metal-metal bonded nanocluster which has been synthesized and structurally characterized by single crystal diffraction measurements is $[HNi_{38}Pt_6(CO)_{48}]^{5-}$.[11] These are excellent examples of the "passivating reactant" approach described above used for the stabilization of clusters. More graphically, they can be viewed as small chunks of metal which are solubilized by a coating of ligands (phenanthroline, CO, $P(Ph)_3$).

Studies of these metal nanoclusters have beautifully demonstrated the fact that the bonding at the exterior surface of the cluster can energetically dominate the ultimate cluster geom-

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Figure 3.

Isolated capped metal atom clusters. Note the hexagonal closest packing (hcp) and cubic closest packing (ccp) arrangements even for clusters of this size.

Metals

$M(CO)_n$

$[Pt_{15}(CO)_{30}]^{2-}$ $[Rh_{13}(CO)_{24}H_2]^{3-}$ + $[Pt_{26}(CO)_{32}]^{2-}$

(hcp)

$[Pt_{19}(CO)_{22}]^{4-}$ $[Pt_{38}(CO)_{44}H_{12}]^{2-}$ + $[HNi_{38}Pt_6(CO)_{48}]^{5-}$

(ccp)

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etry. The dimensions of these fragments are large enough so that one observes both hexagonal and cubic close packed arrangement of metal atoms in $[Pt_{26}(CO)_{32}]^{2-}$ and $[Pt_{38}(CO)_{44}H_x]^{2-}$ clusters respectively.[12] However, in $[Pt_{15}(CO)_{30}]^{2-}$, the platinum metal atoms arrange themselves in a helical array of triangular Pt_3 units and in $[Pt_{19}(CO)_{30}]^{2-}$ the metal cluster is a bicapped pentagonal-prism similar to the geometry reported for certain microcrystalline materials such as metal dendrites and whiskers.[13] These geometries are still an unresolved challenge to theoretical chemistry as well as to the development of useful predictive theories for nucleation phenomena.
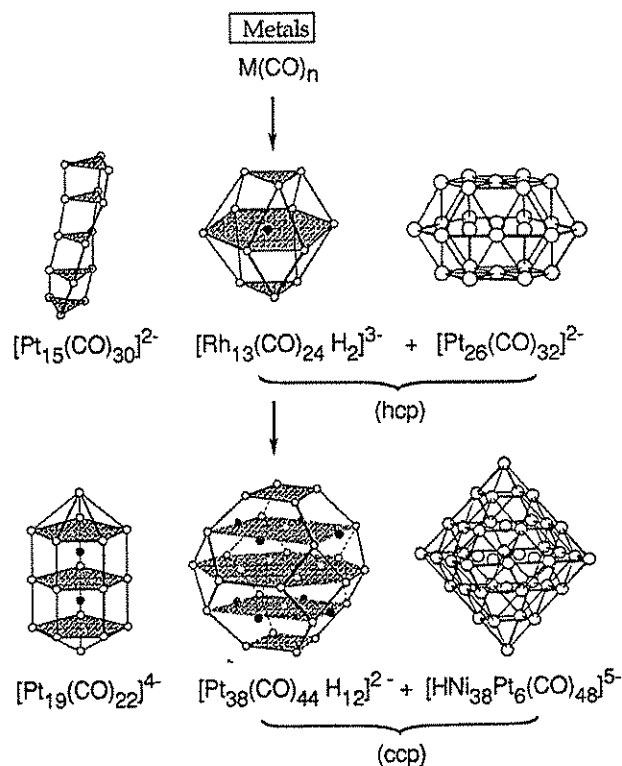
Semiconductor Clusters

Approach and Background

Even more so than for metal clusters, resonance and delocalized bonding are not available to stabilize the cluster surface for inorganic materials such as semiconductors or the ferritin clusters described above. The atoms on the surface of the cluster for these classes of materials are highly reactive and without exception need to be stabilized, either by coordinating molecules which block the surface or by atoms which provide the necessary electrons for an inert gas configuration. In practice this means that given the opportunity the cluster will either continue to add more of the same atoms to give further cluster growth or will react with the atoms and molecules in the immediate environment. The size of the cluster that is synthesized is, therefore, determined by (1) the strength of interaction of the capping ligand to the surface relative to the bulk atom-atom interactions and (2) the kinetics associated with the competition between cluster growth and capping. For example, if the growth media is saturated with the capping ligand, the probability of cluster growth is minimized even though it may be thermodynamically favored.

The chemistry needed to generate nanoclusters is indeed state-of-the-art, requiring control of kinetic parameters beyond the limits of that which have been previously achieved in solution chemistry.[14] The goal is essentially to arrest a runaway reaction, which if given sufficient starting materials will result in the generation of a bulk material. The appropriate cluster size is achieved by competitive reaction chemistry between core cluster growth and surface capping which terminates the cluster growth. This kinetic control is obtained by adjusting the reactant concentrations, diffusion rates, temperature of reaction, choice of solvent, time of reaction, and the use of microheterogeneous reaction media. Cluster growth is then terminated by the use of strong coordinating ligands.[15-17] For small clusters (8-15 Å), which are soluble in organic solvents, a single size can be obtained either during synthesis or by separation after synthesis. For larger clusters the kinetics of the nucleation and passivation processes are fast and in
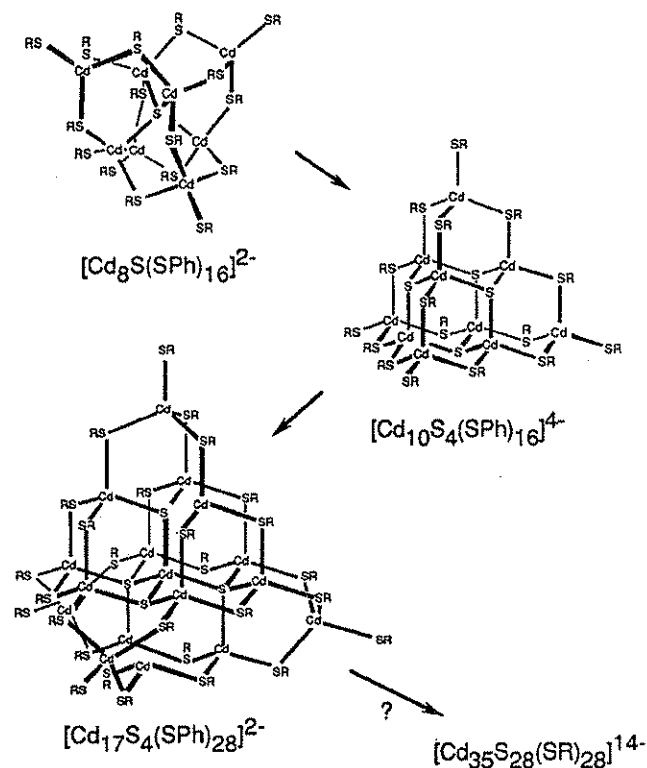
$[Cd_8S(SPh)_{16}]^{2-}$

$[Cd_{10}S_4(SPh)_{16}]^{4-}$

$[Cd_{17}S_4(SPh)_{28}]^{2-}$

?

$[Cd_{35}S_{28}(SR)_{28}]^{14-}$

general a typical preparation gives a poly dispersity of $\pm 10\%$ in particle diameter.

What Size?

The first question that needs to be addressed in nanoclusters is obviously the desired size of the cluster. In principal, such size can be arbitrarily adjusted. Because of the many potential applications, semiconductor clusters in which the electrons are quantum confined are highly desirable. A brief definition of quantum confinement is, therefore, in order.

Quantum confinement arises when a photon with energy equal to or greater than the energy gap ($h\upsilon > E_g$) of a semiconductor induces an electronic transition from the valence to the conduction band. Spatially the electron moves from an atomic site through the lattice via the conduction band orbitals. The positive charge left behind is appropriately called a hole and is weakly bound to the electron over relatively large distances (~ 100 Å). This bound electron-hole pair is called an exciton. It is easier for the electron to delocalize through the lattice if the valence and conduction bands are close in energy since thermodynamically there is not as much to be gained for the electron to recombine with another hole. For this reason the

distance of the electron from the hole is inversely proportional to the band gap, E_g.

To a first approximation the exciton can be viewed as the analog of a simple Bohr hydrogen atom. The electron orbits around the positive charge in the lattice at distances on the order of 20-300 Å depending on the band gap. Quantum confinement occurs when the individual clusters of the semiconductor are the same size or smaller than the exciton radius. The electron finds that it is not free to move as far away from the hole as it would like and the motion of the weakly bound electron-hole pair becomes quantized. The size of the cluster required for quantum confinement in a small bandgap semiconductor such as InP ($E_g = 1.27$eV) is on the order of 400 Å since the exciton electron-hole separation is about this large, while that for a large band gap semiconductor like CuCl ($E_g = 3.1$ eV) is only ~ 14Å. In general, unusual optical and electronic properties will be evident at or below these respective radii for these materials.

An Example - Group II-VI Atoms

A good example of the application of this approach to molecular cluster packaging is provided by recent studies of cadmium sulfide. Dance has created soluble molecular clusters such as $[C_{10}S_4(SPh)_{16}]^{4-}$ (Fig. 4, Ph is a phenyl group, C_6H_5) which can be considered as fragments of the bulk semiconductor lattice.[18-20] As molecular entities these are soluble in organic solvents so that they can be isolated and structurally characterized, with the largest structurally characterized cluster reported to date being $[Cd_{17}S_4(SPh)_{28}]$.[8, 21] This structure contains tetrahedrally coordinated Cd and S atoms as does bulk CdS, however, each Cd atom also is bonded to a surface S atom which is part of the -SPh thiophenol group. This manner of covalent bonding at the surface provides the passivation necessary to control cluster aggregation and gives a monodisperse size. Notice that the ratio of Cd:S in this material is not 1:1 but approximately 1:2. This nonstoichiometry is common among small particle semiconductors as will be discussed for GaP included in zeolites in the next section. As illustrated in Figure 4, a variety of nanocluster geometries are possible.

Although this review is directed primarily towards nanocluster chemistry, it is useful to ask whether these very small semiconductor atom fragments have any potential in optical applications. The optical disk storage example in the introduction has a substantial 3rd order non-linear optic response, which in turn implies a high degree of polarizability of the atoms. The strongest nonlinear response to incident light occurs at _resonant_ frequencies; natural frequencies for transitions between quantum states. At these frequencies, transitions to higher energy rotational, vibrational, or electronic states lead to large charge displacements. This has meant that in the search for large optical responses, resonant or near resonant optical frequencies have been used for the light signal carrier. Unfortunately, at or near-resonant frequencies, photons are no

Figure 5.

Nonresonant 3rd order nonlinearity of quantum confined CdS clusters.
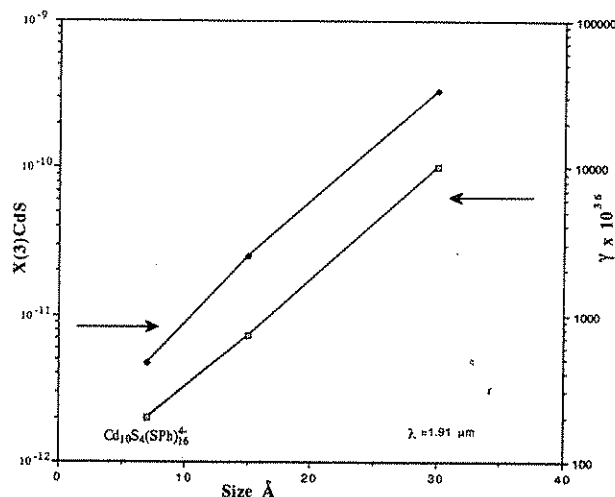
longer weakly perturbed as they travel through the optical medium; non-radiative decay from the high-energy or excited states to the ground state can result in sample heating and loss of photon efficiency. If the photons are being used as optical signal carriers, these loss factors can be disastrous. Ideally, one would like to create optical materials for electro-optic device applications which could be used at non-resonant frequencies with no photon dispersion.

Cheng, Herron and Wang[22] have demonstrated that the very small clusters, shown in Figure 5, have large nonresonant nonlinearities (Figure 5). In fact, the Dance compound has a nonresonant nonlinearity comparable to that of conjugated organic dye molecules and bigger clusters have even larger nonlinearities. This strongly suggests the possibility of using semiconductor nanoclusters in relatively loss-free data transmission or electro-optic photonic devices.

Packaging The Clusters In Solids – Nanocomposites

With very few exceptions, the isolated molecular nanocluster is only part of the story. For most practical applications, the nanoclusters must be incorporated into a processable matrix. We will call this combination of a host matrix and the guest nanocluster a *nanocomposite*, indicating a material consisting of two or more phases with different physical properties that are interfaced at nanoscale dimensions. The

nanocomposite can be constructed (1) directly by synthesis, (2) by first creating the host and then carrying out nanocluster synthesis within the host, or (3) by creating both host and guest and then diffusing the guest into the host. For frequency conversion or optical bistable devices, such as the optical disk example above, a high-optical density is required with the nanoclusters closely packed. The nanoclusters will then be separated at distances comparable to their own dimensions. The figure of merit parameters that might be used to optimize a nanocomposite are defined by the intended application.

In order to take maximum advantage of the unique properties associated with nanoclusters, the packaging must maintain a precise definition of the number of atoms, their siting (e.g. bulk versus surface), and the manner in which they are assembled to form a nanocomposite array. A compromise will sometimes be commercially necessary for processability or materials cost advantage, and for some applications the figure of merit criteria could be met with this in mind. The following discussion briefly reviews the types of host matrices that have been used for amorphous host and layer (1-d) packaging, and then continues along the lines indicated above, namely with the intent of seeking the most precise ways of packaging quantum confined semiconductor clusters *in a 3-d array*. Ideally this packaging would result in a nanocomposite that would include:

- size and topographical uniformity of nanoclusters
- 3-d periodicity
- tunability with respect to atomic modification of
  – topography
  – cluster dimensions
  – surface states defined by the cluster/packaging
    interface
  – intercluster coupling
- thermal and optical stability
- optical transparency

Amorphous Hosts

Porous glasses[23], polymers[24], micelles[25], and colloids[26] have been used as host matrices. Specific examples include the formation of PbS particles on ethylene-methacrylic acid copolymers[27], and glass matrices around colloidal solutions of CdS.[28] In all of these systems, however, the crystallinities, pore sizes, and ultimate cluster geometry are not well defined. Nevertheless, porous glasses are promising in that they offer the advantages of having a large range of pore sizes, ease of optical characterization, and the potential for use as thin monoliths in optical devices. Photo and thermal stability are crucial if the nancomposites are to be used in laser device applications. For example, in optical computer or optical switching applications, the nanocomposite should be able to perform trillions of switching operations/sec for years at a time. As inorganic hosts, porous glasses have been demonstrated to greatly increase the lifetime of organic dye lasers

which have been built into their pores.[29] This is an important property of the inorganic host/organic guest combination that will undoubtedly be pursued further. Several types of sol-gel derived glass have been used in attempts to vary the size of the particles which are produced. In addition to the sol-gel derived glasses, commercial Vycor (Corning Glass) has been used. Vycor is significantly stronger than the sol-gel derived glass since it is synthesized via a high-temperature acid leaching process of borosilicates. The high temperature imparts mechanical strength to the glass.

Layered Synthesis and 1-d Confinement – Ordered Arrays

Sophisticated techniques currently are available to obtain 1-d confinement of atomic or molecular monolayers (~5Å) by molecular beam epitaxy (MBE), electrochemical, atomic layer epitaxy (ALE)[30] and Langmuir Blodgett film synthesis.[31,32] Molecular beam epitaxy (MBE) and atomic layer epitaxy (ALE) allow for the fabrication of ultrathin- (monolayer) semiconductor layers, and have lead to the design and creation

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Figure 6.

Molecular beam epitaxy derived quantum superlattice.

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of 1-d quantum confined materials. Figure 6 shows how carrier confinement is achieved by sandwiching a GaAs semiconductor layer between two wider-bandgap semiconductor epitaxial layers.[33-35]

The superlattice layered structure approach is an important step towards achieving the degree of sophistication required to obtain a periodic array of quantum confined planes of atoms. However, the development of photonic transistors or other electronic device analogs requires 2-d (quantum wires) and 3d (quantum dots) confined structures. Some ingenious approaches to this problem using tilted superlattices have been partially successful but are challenged by the difficulty in obtaining the necessary precision to create lateral surfaces for boxes or walls with dimensions less than ~100Å.

# 3-d Surfaces and Periodic Packaging

The above discussion describes the generation of isolated clusters and the formation of superlattices with confinement in one dimension (perpendicular to the epitaxial grown layers). The ideal extension of these concepts would be to create a three-dimensional periodic array of nanoclusters. In the MBE and ALE synthesis of nanostructures, a two-dimensional layered substrate is used. Molecular sieves and zeolites are examples of possible three-dimensional substrates consisting of periodic crystalline porous frameworks with open channels and cages. They have extremely high-internal surface areas, as much as 800 cm^2/g and as high as 50% void space, so that high concentrations of nanoclusters and optical densities are possible. Clusters and molecules can be incorporated within these cages and channels either directly during synthesis, by "ship in the bottle" synthesis within the host, or by gas phase or melt inclusion into an empty host. The thermal stability of these frameworks depends on the framework composition, but in some cases it is over 1000° C.

A schematic illustrating the structural chemistry of some zeolites is shown in Figure 7. M in the empirical formula at the top of Figure 7 refers to a monovalent organic or inorganic cation. The framework is made up of AlO_2- and SiO_2 units which are connected so that the Al and Si atoms are tetrahedrally coordinated. By using organic molecules or inorganic cations as templates when these connections are made during synthesis, a large variety of channels and cages can be constructed. Figure 7 shows an example of condensation of the AlO_2^- and SiO_2 units into a 60 atom (silicon, aluminum, and oxygen atoms) sodalite cage which geometrically is a truncated octahedron. The upper right hand part of Figure 7 shows only the 24 metal atoms which make up the sodalite cage. The 36 connecting oxygen atoms connecting these metal atoms (middle figure, top of Figure 7) make up the remainder of the 60 atoms in the polyhedron.

The usual convention is to designate the pore openings by the metal atoms only. Thus, the term "6 ring" is used to describe the hexagonal faces shown for the sodalite cage in the
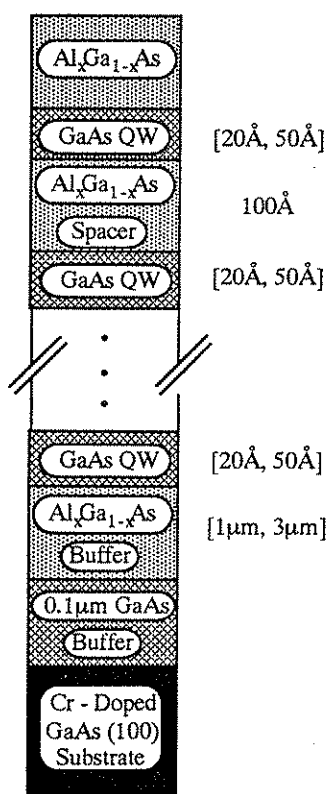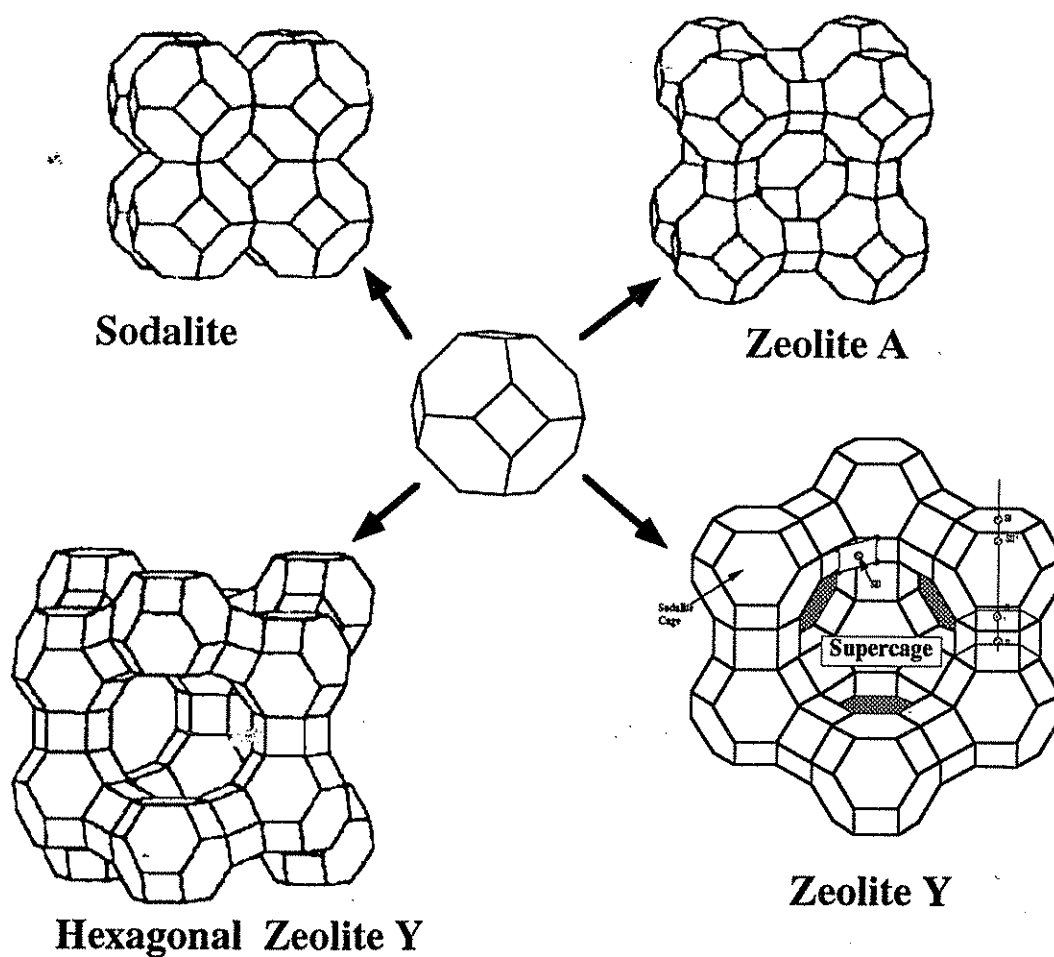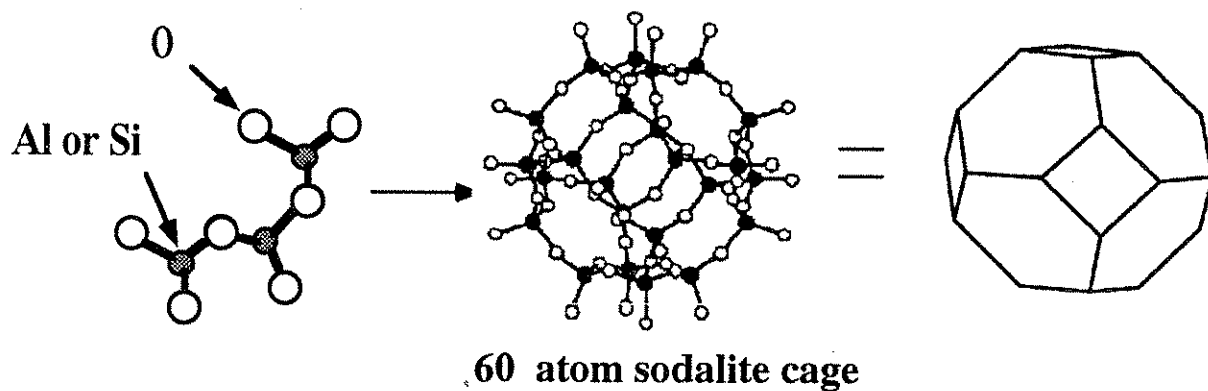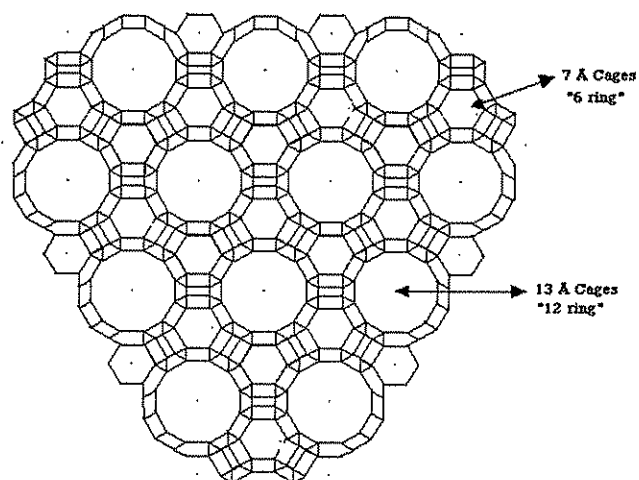
Figure 7.

Illustration of zeolite composition and synthesis. The 60 atom sodalite cage can be used to form "clusters of cages" in different ways to give the indicated zeolite structures.

0

Al or Si

60 atom sodalite cage

Sodalite

Zeolite A

Hexagonal Zeolite Y

Supercage

Zeolite Y

Figure 8.

Section of periodic 3-d lattice of zeolite Y.

7 Å Cages
"6 ring"

13 Å Cages
"12 ring"

upper right hand corner of Figure 7. The reader should be aware that these are in fact 12 atom ring openings with alternating metal and oxygen atoms. Similarly, the "4 rings" define 8 atom (metal + oxygen atoms) ring openings. In the remainder of this paper we will retain the usual zeolite molecular sieve convention of denoting these pores by the metal atoms only (i.e. as 6 rings and 4 rings).

This simple cage structure is an important fundamental building block and can be used to generate different porous zeolite structures by structural architecture based on putting together "clusters of cages" as shown in Figure 7 for sodalite, zeolite A, zeolite Y, and the hexagonal form of zeolite Y. In these structures, the oxygen atoms coordinated perpendicular to the surface of the truncated octahedron can be part of another cage (sodalite) or serve as connections to other cages (zeolite A and Y structures). The net result is a periodic, 3-dimensional crystalline lattice of cages and channels (Figure 8).

The inclusion chemistry of I-VII[36-38], II-VI[39-41] and III-V[42] semiconductors[43] has been investigated concentrating on the structural, optical, and photochemical[44,45] aspects of the clusters. The following discussion focuses on the formation of binary semiconductor systems in a superlattice host. Two roles of the superlattice host are emphasized: 1) the definition of the quantum confinement geometry, and 2) perhaps more importantly, the three- dimensional periodicity which directs the formation of a "supra-molecular" composition and the overall quantum lattice. Some examples of the use of selective siting and the use of host internal surface topology to define cluster geometry follow.

Zeolite Y, an aluminosilicate host, has two types of cages available for cluster formation, the smaller 6 Å sodalite units and the larger 13 Å alpha cages (Figure 7). For the purposes

of this discussion there are 5 sites (I,I',II, II', III) which are available for cation siting within the sodalite and supercages. II-VI and I-VII quantum confined clusters can be synthesized by well understood ion-exchange methods, followed in the II-VI case by treatment with H_2S or H_2Se. It is important to note that the ion exchange process can yield very different siting of cations depending on temperature, pH, solvent vs. melt ion inclusion, other extra-framework ions, calcination, and loading levels. Thus, this process must be systematically controlled, along with the conditions for treatment with H_2S or H_2Se in order to obtain materials which can be consistently reproduced and which contain monosize clusters.

Structural studies by X-ray diffraction and EXAFS methods[46] have established cubane like clusters of $(CdS)_4$ located in the sodalite cages of the structure with each cadmium atom coordinated to three framework oxygen atoms and three S atoms. The framework fills the role of capping ligands described for the molecular clusters above. The sodalite cage acts

Figure 9.

$Ga_{16}P_{13}$ cluster synthesized in zeolite Y.

Ga   P
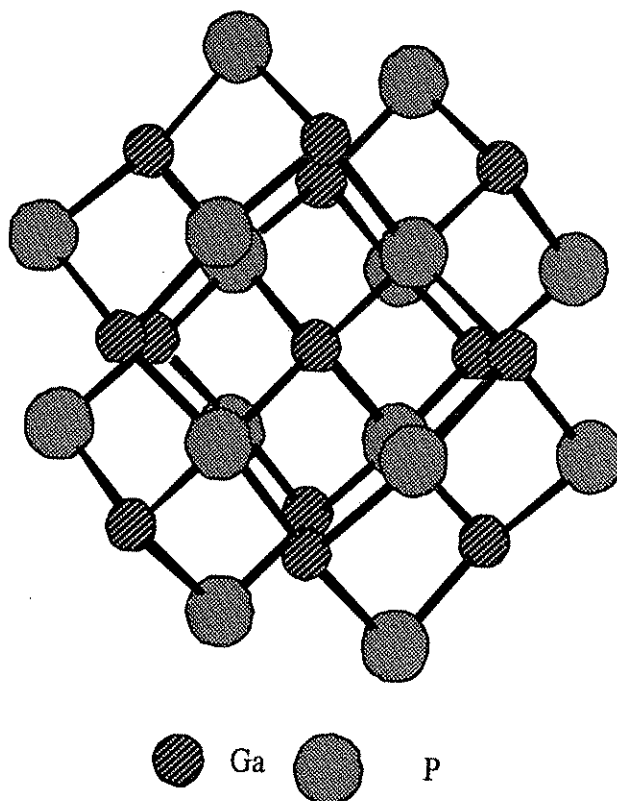
as a cluster templating agent which stabilizes the cubane like geometry. However, the clusters produced in this way are small compared to the volume available for formation of clusters in the supercages. For this reason, and also to study III-V semiconductors, a metal organic chemical vapor deposition (MOCVD) approach to the synthesis was used.

The reaction of $(CH_3)_3Ga$ with PH_3 carried out within the pores of the zeolite gives GaP_x particles which show blue shifts in the UV-V is spectra and upfield shifts in the solid-state NMR. Both these shifts are indicative of size quantization effects.[47] Extended X-ray absorption fine structure (EXAFS) spectroscopy has identified particles of ~11 Å in diameter, corresponding to 3 coordination spheres of the bulk structure (see Figure 8). X-ray diffraction data confirm long range ordering of the cluster electron density located in the supercages of the structure, but with different cluster orientations from cage to cage. This observation supports the EXAFS data for clusters which are close to the size of the diameter of the supercage.

The research in this area is rapidly gaining momentum.[47,48] Japanese scientists have systematically synthesized and studied semiconductor nanocomposites made up of selenium[49], tellurium and lead iodide clusters[50] within molecular sieve frameworks. The absorption band energies in these systems depend on the size of the cage or channels with energies which are considerably blue-shifted compared to the bulk exciton energies. Other researchers have studied tungsten oxide[51] and silver halide clusters and constructed supralattices of the semiconductor clusters by building them up from the isolated cluster and then gradually adding nearest neighbor cluster to determine intercluster effects.[52] Considerable exploratory work is still needed, however, in single crystal or thin film growth and in obtaining larger cages and channels. Considerable progress is being made in resolving both of these problems.

Summary

The understanding and new synthetic approaches to nanocluster synthesis have opened extensive new vistas for all areas of science. The incorporation of nanoclusters into composites will require the continued development of highly sophisticated new chemical techniques and molecular engineering. Much will depend on the ability to utilize and understand the exterior surface chemistry of the nanophsases. The health of the field has been demonstrated by rapid progress in optoelectronics and the recent isolation of large new polyhedral aromatic clusters, fullerenes. Control of cluster geometry and size distribution by the topography of three-dimensional host surfaces, makes it possible to create semiconductor quantum superlattices. The use of large three-dimensional surface areas permits concentration studies of cluster interactions over a wide range, and at relatively high-optical densities. It is to be expected that novel, normally very unstable, nanosized phases can be synthesized and stabilized via encapsulation and integration with the open polyhedral framework systems that are now being developed.

Biography

Galen Stucky received his Ph.D. in 1962 from Iowa State University in physical chemistry. After postdoctoral study at MIT in physics, he served as a faculty member in the Division of Inorganic Chemistry at the University of Illinois for 16 years (1964-1980). He has also held positions at Sandia National Laboratory (1979-1981) and DuPont Central Research and Development Department (1981-1985). He joined the UCSB chemistry faculty in 1985. Dr.Stucky has been particularly active in the American Chemical Society, serving as Editor of the Journal of Inorganic Chemistry for eight years, Chairman of the Solid State Subdivision, Chairman of the Inorganic Division and more recently a member of the Inorganic Division Executive Committee. He has served on the Advisory Boards of the Journals of *Inorganic Chemistry* and *Chemistry of Materials*. His recent research publications and interests cover a wide range of topics including the synthesis of new nonlinear optic materials, photoinduced superconductivity, 3-d packaging of electro-optic molecular and atomic arrays and low temperature materials synthesis.

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