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# ASSEMBLY OF SUPRA NANOCLUSTERS WITHIN CRYSTALLINE AND AMORPHOUS 3-D SURFACES

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## 1. Introduction

Syntheses of nanoclusters can be carried out in a variety of ways to give unexpectedly different materials. These have varied structural, optical, and transport properties. Quantum confinement arises when a photon with energy equal to or greater than the energy gap ( $h\nu > E_g$ ) 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 ( $\sim 100 \text{ \AA}$ ). 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  $\text{\AA}$  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 motion of the weakly bound electron-hole pair becomes quantized. This gives unusual optical and electronic properties.

Less delocalization of the electrons in the conduction band means less kinetic energy. A reflection of this is that the absorption edge for direct transitions of nanosized semiconductor clusters is shifted to higher energies (blue shifted) than in the bulk parent materials. With nanosize (quantum confined) semiconductors as an optical medium, the refractive index and the absorption edge vary with the light intensity. As the intensity of the excitation light is increased, the absorption edge ( $\nu_1$ ) corresponding to the transition energy between the valence and conduction band at first changes slightly with filling of the lowest states in the first available energy band. This in itself is a nonlinear process with a change in the refractive indices which is

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proportional to the light intensity. Upon saturation of the transition, when the rate of filling is equal to the rate of depletion of the lowest energy band, any additional photons absorbed must have higher energy ( $\nu_2$ ) in order to promote electrons into the next available band. Photons with lower energy are then transmitted so that the nanosized semiconductor particle is transparent to light.

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. Unfortunately, at or near-resonant frequencies, photons are no 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.

Considerable effort has gone into the synthesis of quantum confined semiconductors. This can be done from colloidal solution and by molecular beam or atomic layer epitaxy. The structures formed include quantum wells, dots, or wires as discussed below. The approach discussed in this chapter differs from the above, rather taking advantage of the vast internal 3-dimensional surface of molecular sieves and porous glasses. This allows controls not generally available in solution chemistry or epitaxy. First, we will briefly review current methods employed to synthesize nanoclusters. Following that we outline the chemistry involved in preparing host/guest compounds of semiconductors in zeolites and porous silica glasses, and we will describe their unique physical properties. Finally, the use of solid state NMR to follow the reaction chemistry involved, which adds a dimension not previously available in this area, will be discussed.

## 2. Current Synthetic Methodologies

### 2.1 Chemical Approaches

The initial work in the area of small particle semiconductors was described by Brus<sup>1</sup>. It deals with the formation of size quantized particles in colloidal solution, their characterization, and the interpretation of this data using both classical theory and some quantum mechanics. Drawbacks to colloidal methods include lack of good control of cluster size, instability of clusters

toward aggregation, and difficulty in differentiating cluster - cluster interactions from surface or other effects.

Recently, chemists have confronted the problem of controlling cluster size by a molecular approach which involves using solution chemistry with arrested precipitation to form the semiconductor clusters, and then kinetically capping these clusters with covalently bound organic groups.<sup>2,3,4,5</sup> Figure 1. illustrates such a cluster<sup>2</sup> for  $[S_4Cd_{10}(SPh)_{16}]^{4-}$ . This structure forms tetrahedrally coordinated Cd and S atoms as does bulk CdS. However each Cd atom is also bonded to a surface S atom which is part of the thiophenol group. This manner of covalent bonding at the surface forms a method for control of cluster aggregation, and results in a monodisperse size distribution. This compound, hereafter referred to as the "Dance compound", can be isolated as single crystals, so that precise bond lengths and cluster geometry are known. The ratio of Cd:S in this material is not 1:1 as in the bulk but 1:2. This inconsistency with bulk composition is common among small particle semiconductors since in this size range we must account for surface atoms and their coordination. Another example is GaP included in zeolites which is discussed in the next section.

Other workers<sup>6</sup> have used variations on the idea of forming covalent bonds at the surface of clusters to stop their growth. The chemistry requires control of kinetic parameters at a level which is at the cutting edge of what has been previously achieved in solid state synthesis from solution chemistry.<sup>7</sup> The reaction is thermodynamically programmed to generate the bulk semiconductor given sufficient starting materials. The size of the cluster is determined by controlling the competitive reaction chemistry of surface capping and core 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<sup>8,9,10</sup>.

Figure 2. shows the reaction scheme for using inverse micelles as the microheterogeneous reaction media to "cap" clusters as they are growing. The micelle molecules (AOT) on the surface of the  $(CdSe)_n$  cluster on the left are long chain organic groups with polar head groups attached to the cadmium atoms on the cluster surface. In this example  $RSe^-$  (from the  $RSeSiMe_3$  molecule, where R = aromatic organic group and Me is  $CH_3$ ) then caps the cluster and terminates growth. An inorganic phosphate polymer, such as sodium hexametaphosphate<sup>11</sup> can also be used for growth termination and capping. Clusters prepared in this manner have a poly dispersity of  $\pm 10\%$  in particle diameter<sup>(1,2)</sup>. It is particularly interesting that even very small capped clusters, such as the Dance compound have a large nonresonant nonlinear optical response in solution.<sup>12</sup> In order

to utilize this large nonresonant nonlinearity for electro-optic applications, the clusters must be incorporated into a sample in high concentrations.

Nature in an elegant way also creates nanosized clusters of  $\text{Cd}_x\text{S}_y$  that are similar to the Dance compound. The clusters are formed using short chelating peptides in yeast as part of the biochemical mechanism of entrapping heavy metal atoms such as Cd.<sup>13</sup> At the time of their characterization, these clusters were found to be more monodisperse than those which had been prepared chemically.

Another approach<sup>[14]</sup> allows synthesis of small particle III-V semiconductors through what is essentially the hydrolysis of a monomeric arsinogallane. The reaction of one mole of  $(\text{C}_5(\text{CH}_3)_5\text{Ga}-\text{As}(\text{Si}(\text{CH}_3)_3)_2$  with two moles of t-butanol, shown in Figure 3, yields (over several hours) small  $\text{Ga}_x\text{As}_y$  particles (shown as GaAs in Figure 3). This is observed by the shift to longer wavelength in the absorption UV-Vis spectrum with time. This is the first example of a solution phase reaction which yields size quantized ( $< 100 \text{ \AA}$  for GaAs, see introduction) III-V semiconductors. This reaction is not controlled as in the capped clusters, but goes on to form bulk GaAs through the course of the reaction. Recently, Wells and Alivisatos have carried out arrested precipitation reactions to form capped GaAs clusters with a smaller distribution of cluster sizes.

Many of these solution methods for preparing small particle semiconductors have been recently reviewed.<sup>15</sup> Other methods to prepare size quantized semiconductors include the use of Langmuir-Blodgett films to make layers of CdS particles which are less than  $50 \text{ \AA}$  in diameter,<sup>16</sup> formation of PbS particles on ethylene-methacrylic acid copolymers,<sup>17</sup> and the formation of glass matrices around colloidal solutions of CdS.<sup>18</sup> In these nano-sized particle systems, quantum confinement is three dimensional and the structures are referred to as quantum dots or quantum boxes.

## 2.2 Epitaxial and Gas Phase Growth

Molecular beam epitaxy (MBE) and atomic layer epitaxy (ALE)<sup>19</sup> allow for the fabrication of ultra thin (monolayer) semiconductor layers. Figure 4 shows how carrier confinement is achieved by sandwiching the semiconductor layer between two wider-bandgap semiconductor epitaxial layers.<sup>20,21,22</sup> Also, epitaxial growth of GaAs on high surface silica has been used to produce size quantized GaAs particles.<sup>23</sup> Quantum wires, in which carriers and the electronic wave function have one degree of freedom, can be formed in the MBE approach by corrugation of quantum layers, or by lateral structuring.<sup>24,25</sup> A promising new development is the use of the scanning tunnel microscope (STM) as a lithographic tool to create barriers on the 10 to  $1000 \text{ \AA}$  scale.<sup>26</sup>

Recently, gas phase syntheses of  $Ga_xAs_y$ <sup>27</sup> and neutral indium phosphide clusters<sup>28</sup> have been reported. This is an important step to further understanding these small clusters since the particles can be selectively created using differing ratios of constituents and studied. A disadvantage to gas phase clusters is in making enough clusters to do the important spectroscopic experiments needed to fully understand how particle size dictates their behavior. Also, structural details critical to understanding their surface properties are not readily obtained.

### 3. Host - Guest Synthesis

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, each with a specific topography. In the MBE and AIE 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<sup>2</sup>/g. The idea is then to assemble clusters within these cages and channels, a process commonly called inclusion chemistry. In principal this could be at high concentrations to give useful optical densities.

A schematic illustrating the structural chemistry of some zeolites is shown in Figure 5. M in the empirical formula at the top of the page 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 5 shows an example of condensation 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 5 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 5) 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 in the upper right hand corner of Figure 5. 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 5 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 inclusion chemistry of I-VII<sup>29,30,31</sup>, II-VI<sup>32,33,34,35</sup> and III-V semiconductors<sup>36</sup> has been investigated concentrating on the structural, optical, and photochemical<sup>37,38</sup> 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 5). 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<sub>2</sub>S or H<sub>2</sub>Se. 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<sub>2</sub>S or H<sub>2</sub>Se in order to obtain materials which can be consistently reproduced and which contain monosize clusters.

Structural studies have been carried out using powder Rietveld X-ray diffraction methods.<sup>39</sup> These have established cubane like clusters of (CdS)<sub>4</sub> located in the sodalite cages of the structure. The coordination sphere of Cd in the structure was examined by extended X-ray absorption fine structure (EXAFS) spectroscopy and confirmed that each cadmium atom is 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 as a cluster templating agent which stabilizes the cubane like geometry. However, the clusters produced in this way are very small compared to the area available for formation of clusters in the supercages.

For this reason, and also to study III-V semiconductors, a new approach to the synthesis was developed.

Past attempts to use aqueous solution ion exchange as a route to the formation of III-V semiconductors in zeolite frameworks resulted in the loss of crystallinity of the aluminosilicate framework due to the very low pH required to solubilize group III cations. Alternate methods using anhydrous nitrate and halide melts also failed to give the desired inclusion products, as did methylene chloride solutions of group III halides as precursors. The approach which succeeded in synthesizing GaP inside the pore structure of zeolite Y involves a metal organic chemical vapor deposition (MOCVD) approach.<sup>28</sup> The interior surface of the zeolite can be modified by ion exchange, for example M (empirical formula at the top of Figure 5) can be Na<sup>+</sup> (designated as NaY) or H<sup>+</sup> (designated as HY) which is formed by first ion exchange with NH<sub>4</sub><sup>+</sup>, and then deammoniation. The reaction of (CH<sub>3</sub>)<sub>3</sub>Ga with PH<sub>3</sub> is carried out within the pores of zeolite HY or NaY at a series of temperatures. This gives small GaP particles which show blue shifts in the UV-Vis spectra and upfield shifts in the solid state NMR. Both these shifts are indicative of size quantization effects. 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 7). Either a Ga atom or P atom at the center of the cluster is consistent with the spectroscopic data. In the case of a P atom at the center, the charge on the cluster must be balanced by connection to the anionic framework or residual methyl groups. However, with a Ga atom at the center, the charge could be accounted for by excess protons remaining on the P atoms due to incomplete phosphine dissociation. 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 of about the size of the diameter of the supercage.

Porous glasses offer less control than zeolites over the size, shape and cluster - cluster interactions of semiconductor particles within their pores. Yet, the glasses offer the advantages of having larger pore sizes, ease of optical characterization and the potential for use as thin monoliths in optical devices. The approach to the synthesis is similar to that of GaP in zeolite Y. In fact, metal alkyl reactions with phosphine and arsine have formed size quantized III-V semiconductor particles in porous glasses, and these composites have large resonant nonlinearities.<sup>40</sup>

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.

It is highly desirable in organometallic based methods of nanocluster synthesis in porous materials to obtain as clean elimination of the organic groups at as low temperatures as possible. The approach is to choose an organometallic precursor whose ligands are extremely stable as free entities, ie. CpH and Cp\*H. Furthermore, glass pores can be made much larger (~100 Å) than zeolite cages or channels, so that more complicated and larger organometallic precursors can be used. Pentamethylcyclopentadienylindium(I) (Cp\*In) and cyclopentadienylindium (I) (CpIn) can be used as molecular precursors to reproducibly make size quantized InP within the pores of the sol gel glass. Both organometallic complexes can be sublimed readily and other substituted Cp ligands (eg. methyl and ethyl cyclopentadiene) are viable precursors for making single crystal thin films via an MOCVD process.<sup>41</sup>

The synthesis of InP in the porous glass via Cp\*In can be optimized conveniently using infrared (IR) spectroscopy and <sup>1</sup>H solid state Magic Angle Spinning (MAS) NM, both of which differentiate well between the various hydrogen environments present. Before reaction with Cp\*In, a sharp resonance at 2.2 ppm and an IR band at 3750 cm<sup>-1</sup> are observed for the glass. Based on previous spectroscopic studies of hydrous glasses, these features are assigned to SiOH groups involved in weak hydrogen bonding.<sup>42</sup> After loading with Cp\*In, the spectra show multiple features due to several inequivalent CH<sub>3</sub> groups in the glass which then disappear upon treatment with PH<sub>3</sub>. <sup>1</sup>H spin counting establishes that for a 2 hour heating time in PH<sub>3</sub> to 300 °C, the residual carbon-bonded hydrogen content is less than 0.15 wt%. Formation of quantum sized InP is confirmed by <sup>31</sup>P dipolar spin-echo and MAS NMR of both <sup>31</sup>P and <sup>115</sup>In. In the spin-echo experiment, the echo amplitude is monitored as a function of evolution time, during which the spins dephase at a rate related to the second moment (M<sub>2</sub>) characterizing the homonuclear <sup>31</sup>P-<sup>31</sup>P interaction. The experimental result, M<sub>2</sub>(<sup>31</sup>P-<sup>31</sup>P) = 20.0 x 10<sup>6</sup> (rad/s)<sup>2</sup> is in excellent agreement with the value observed (21.0 x 10<sup>6</sup>(rad/s)<sup>2</sup>) and calculated (19.5 x 10<sup>6</sup> (rad/s)<sup>2</sup>) for bulk InP. The experiment also confirms that the bond lengths in the nanosized material are not substantially different from those in the bulk. The <sup>31</sup>P MAS spectrum of the quantum sized InP is somewhat broadened and shifted upfield with respect to bulk InP. In conjunction with the UV-Vis results, this shift can be interpreted in terms of a systematic change in the average excitation energy of Ramsey's paramagnetic chemical shielding contribution as a result of size quantization. This observation is in close analogy with the behavior of the <sup>77</sup>Se resonance in colloidal<sup>43</sup> CdSe and the <sup>31</sup>P resonance<sup>3</sup> of GaP in zeolite Y. Furthermore, it was

even possible to detect a  $^{115}\text{In}$  resonance. The excitation behavior of this signal indicates that - in contrast to bulk InP - only the central  $I = -1/2 \rightarrow 1/2$  transition is observed. The resonance is also substantially broadened with respect to that of bulk InP due to second-order quadrupole and chemical shift distribution effects. Due to the large electric quadrupole moment of  $^{115}\text{In}$  ( $I = 9/2$ ), only nuclei in highly symmetric environments are detectable. This indicates that the cluster particles are large enough to have a core of bulk-like InP.

X-ray powder diffraction of the InP/glass composite shows reflections indicative of InP, with an average particle size of  $\sim 80\text{\AA}$  determined from the peak broadening.<sup>44</sup> There are no peaks in the X-ray which corresponded to In metal. As the synthesis temperature is lowered from 300 to 100 °C, the presence of smaller InP molecular species are indicated by sharper features in the UV-Vis spectra. Composites prepared at 300°C showed blue shifted spectra with tails but no sharp excitons. Elemental Analysis of the glass semiconductor composite give an In:P ratio as 1.1:1, and <0.5wt% C. The material contains  $\sim 11\text{wt}\%$  In which is higher than (almost double) that found in materials prepared from Group III metal trialkyls.

#### 4. Conclusions

The use of a three dimensional crystalline superlattice as a host for cluster synthesis adds several important dimensions to the design of semiconductor quantum confined structures. Cluster geometry and size distribution are controlled by the topography of the three dimensional host surface, making it possible to create semiconductor quantum superlattices. Novel, normally very unstable, nanosized clusters can be synthesized via encapsulation and coordination to the host framework. The use of large three dimensional surface areas permits studies of cluster interactions over a wide range of concentrations and at relatively high optical densities. Cluster electronic properties can be altered by varying the dielectric and charge properties of the nanoporous host.

For optical studies, larger single crystals or thin films are needed. This shortcoming is currently being addressed.<sup>45,46</sup> The possible novel photonic and electronic properties of molecular sieve nanocomposites<sup>47</sup> is resulting in new approaches to the synthesis of molecular sieves themselves. Much of the past research in the synthesis of such hosts has been in conjunction with their use as high temperature (to 1000 °C) catalysts, so that the exploratory chemistry was limited by that goal. Low temperature routes to new open framework materials, which no longer contain only tetrahedral connecting atoms, are rapidly becoming available.

In addition to single crystals, the porous glasses discussed above add new possibilities for

following the chemistry involved in forming small semiconductor particles, as well as determining their photophysical properties. Study of these glass systems in conjunction with structural characterization of zeolitic systems should lead to a better understanding of this exciting new regime in solid state chemistry.

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