Nanoparticles: Uses and Relationships to Molecular Cluster Compounds

By Norman Herron* and David L. Thorn

1. Introduction

More than a thousand articles on various aspects of nanoparticles and nanoscale chemistry have appeared in the last year.[1] Nanoparticles have attracted so much attention because they are both important and interesting. Important, as nanoparticles can have useful properties not exhibited by either smaller molecular systems or larger particulate matter; interesting, as working on supramolecular scales raises exciting synthetic challenges and allows intimate exploration of the relationships among atoms, molecules, and extended systems. In the first part of this article we briefly discuss a selected few of the useful properties exhibited by nanoparticles and/or nanostructured materials. In the second part of this article we examine a subset of the relationships between molecular and extended systems, especially between binary and ternary inorganic molecular cluster compounds and the smallest nanometer-sized particles, and consider some implications for the synthesis and chemistry of “nanoclusters”. In neither part of this article do we attempt a systematic review of the nanoparticle literature, but rather we focus on a few examples from research conducted at DuPont and from the literature. And, while we rely heavily upon experience with inorganic molecular cluster compounds—where chemistry and detailed structures are often much better understood than they are in larger particles—we caution that overly relying upon cluster experience would be misleading, as there are fundamental differences between molecular-sized clusters and nanometer-sized particles.

2. A Few Uses of Nanoparticles

2.1. Semiconductor Nanoparticles and Their Polymer Composites

During the past decade, tremendous progress has been made in the fabrication and understanding of three-dimensional confined semiconductor clusters (i.e., quantum dots, nanoclusters).[2] Our own efforts have evolved from work using a zeolite to template clusters of CdS,[3] through a range of sol-gel encapsulated clusters,[4] to free-standing, organically capped clusters[5] or layers[6] of a wide variety of semiconductors. Most of our own studies, and those of others, have focused on the spectroscopic, photochemical, photocatalytic, and nonlinear optical (NLO) properties of these materials.[7] For example, single- and bilayered perovskite materials derived from PbI2 and alkylammonium ions were prepared and characterized in an attempt to generate isolated layers of the PbI2 semiconductor as 2-dimensional nanosheets and to explore their remarkable excitonic properties and implied strong resonant third-order NLO behavior.[8]

Interest in the spectroscopic, photochemical, photocatalytic, and NLO properties of nanoclustered materials should be contrasted with studies involving bulk 3-dimensional semiconductors and 1- or 2-dimensionally confined semiconductor nanostructures (quantum wells, etc.) where transport properties are of great interest and importance for many technological applications. The most obvious reason for the difference is that clusters have tended to be embedded in insulating matrices such as polymers and glasses, where the transport of carriers is usually not feasible. In order to overcome this limitation and explore transport-related applications involving semiconductor nanocrystals, a matrix that is capable of both transporting carriers and interacting with the semiconductor clusters is needed. We have identified[9] just such a polymer, N-polyvinylcarbazole (PVK). 1

By synthesizing small tetrahedral CdS clusters (such as those to be described) inside PVK, we demonstrated, for the first time, that the resultant composite was capable of generating and conducting charges efficiently upon irradiation by light (see Fig. 1), and reported the field and wavelength dependence of the photoconductivity and a theoretical analysis in the framework of the Onsager charge recombination model.[8]
Such nanocrystal and nanocomposite semiconductor research exemplifies an important emerging area in modern materials science. The synergistic combination of inorganics and organics in a nanocomposite can lead to not only improvement in the existing materials properties but also to creation of new functionalities that do not exist for either material alone. Another example from our laboratories is an X-ray photoconductive nanocomposite consisting of BiI₃ nanoclusters dispersed in nylon-11, \([-\text{NH–CO–(CH}_2\text{)}_{11}\text{]}\). A more detailed consideration of this example illustrates several important points about the benefits of the nanocomposite approach. Note that neither BiI₃ nor nylon-11 alone shows significant X-ray photoconductivity, a technology that is key to the development of digital radiography.

Radiography is one of the remaining major diagnostic tools in health care that is still in analog format (e.g., magnetic resonance imaging (MRI) and computer aided tomography (CAT) scans are both “all-digital” techniques), thus the development of digital radiography is highly desired and actively pursued. One embodiment requires X-ray sensitive photoconductors. A useful X-ray photoconductive material a) has to be a good insulator in the dark and capable of sustaining a high electric field \((10^5–10^6 \text{ V/cm})\), b) must have a large X-ray absorption cross section and high charge generation efficiency, and c) must allow the generated carriers to move through the film without significant trapping. In spite of many years of research, selenium was the only useful X-ray photoconductive material that could meet these challenging requirements, but still not without some drawbacks.

There are clear reasons behind the difficulties involved in discovering new X-ray photoconductive materials. While many heavy element–containing inorganics such as BiI₃ absorb X-ray photons efficiently, it is difficult to fabricate them into good-quality, large-area thin films (for example, chest-sized X-ray plates). Furthermore, they usually have high dark conductivity at room temperature and cannot sustain a large electric field. On the other hand, polymers can

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be fabricated into good-quality thin films, have low dark conductivity and good dielectric properties, but are inefficient X-ray absorbers.

The composite approach we reported combines the advantages of both the organics and inorganics, and leads to a new class of X-ray photoconductive materials. The inorganics possess large X-ray absorption efficiency while the polymer matrix provides good dielectric properties and ease of thin-film preparation. A number of criteria need to be met for this approach to work; many of the criteria concern the ability to fabricate a nanophase/nanocomposite material.

1) The composite should be a nanocomposite. Simply pressing together large (micrometer-sized) inorganic particles and polymers is not effective. Extensive experience has shown that such composites cannot support large electric fields and they usually contain a large number of deep carrier traps.

2) Because of the dilution effect of the polymer, the volume fraction of the inorganic component has to be high enough so that the total X-ray absorption remains strong. For example, in the case of BiI$_3$/polymer, we calculate that ~65 wt.-% of BiI$_3$ is needed such that the X-ray absorption at 62 keV (tungsten radiation) of the composite is comparable to that of Se. Such a large amount of inorganic must be dispersed into the polymer, while maintaining the polymer’s mechanical and dielectric strength and yet avoiding the formation of carrier traps. Keeping the inorganic component as nanophase particles is the only practical method of doing this.

3) Finally, the composite has to be a good electron- and/or hole-transport material. This may be achieved by the use of a carrier-transporting polymer such as PVK or a polysilane. Alternatively, inorganic nanoparticles may together form a conducting percolation pathway at the typically high concentrations necessary to meet criterion 2.

The success of this approach can be seen in Figure 2, where preliminary X-ray induced discharge curves for the composite and a traditional Se film are compared.

### 2.2. Other Polymer/Inorganic Nanocomposites

In addition to the optically and electronically active composites described above, another aspect of polymer/inorganic composites is concerned with polymeric compositions where the polymer’s mechanical properties are markedly altered by small quantities of the inorganic nanophase. Two examples are 1) our work on polyamides with a fullerene component, and 2) the introduction of exfoliated inorganic clay materials into polymers of various sorts, which improve the stiffness and barrier properties of the resultant films. This latter aspect is dealt with in detail elsewhere in this issue.

Since the isolation of fullerenes by Krätschmer et al., the chemistry surrounding fullerenes has been the focus of intense research. Fullerenes have been studied per se and in combination with other substances with the goal of modifying the properties of the resulting compositions. These molecules are beautiful examples of objects exhibiting Gaussian curvature (a topic to which we will return in the second part of this article), and the interaction of these objects with the surrounding matrix can lead to interesting property modification by essentially crosslinking the polymer to the molecule surface. We have described the use of fullerenes to provide improved photoconductive compositions from both photoconductive and non-photoconductive polymers; in addition to these transport property enhancements we have also noted that fullerene/polymer composites produce aliphatic polyamides (nylons) having improved tensile strength, as measured by the maximum tenacity, and are less stretchable, as measured by the maximum elongation. From the optical and scanning electron microscopy (SEM) data we infer that the fullerenes are essentially dissolved as molecular entities in the polymer solvent.

Finally in the polymer/inorganic nanophase composite realm we should mention bulk inorganic materials containing a nanophase of polymer. Known examples include polyfluorosulfonate (Nafion) dispersed in a porous silica matrix, a particular material that is dealt with in detail in another article in this issue. But this relates to a wider area, that of using a porous support to template and disperse “nanoparticles of vacuum” into an active polymeric material, resulting in a highly accessible, high surface area/high activity composite. A manifestation of this is widely employed in immunoassay technologies that are based on nanoparticle aggregation and turbidity development. In this application, nanoparticles are typically treated with surface coupling agents, which allow attachment of a bioactive
molecule such as an antigen. Exposure of these derivatized particles to the desired analyte biomolecule causes the particles to aggregate around the analyte and increase turbidity. Currently, much of this technology is based on derivatized polymer nanospheres but the increased refractive index of inorganic oxide particles suggests that increased speed and sensitivity of the detection process could result if systems based on, for example, silane-derivatized oxides were developed. Of course this idea of dispersion of an active phase onto a support phase so as to maximize the “bang for the buck” performance is a traditional area of catalysis.

2.3. Nanophase Materials as Catalysts

Bulk inorganic/organometallic catalyst materials can become nanophase materials by being “supported” onto what are typically oxide matrices. Often, the very act of supporting the active phase causes a large increase in surface area, which translates into higher activity. This is far from the only effect, however, and, in many cases, completely different reactivity begins to become manifest as the particles of the catalyst phase extend down to the nanoparticle regime. This has been well known in the noble metals catalysis arena where highly dispersed Ru, Pd, Pt, Rh, etc. can all perform catalytic transformations that the more bulk-like metals cannot. This is often interpreted in terms of the particular structure of the nanoparticles of the metals, which tend to expose surface steps and edges in concentrations much increased over their presence in the bulk phases and the catalytic chemistry is in turn attributed to these surface discontinuities.

While deposition of surface nanoparticles of noble metals is a long-practiced art, the deposition of more complex two or more component materials has been less thoroughly explored. In our own work we have tried to build upon lessons from the area of metal–organic chemical vapor deposition (MOCVD) and to design single-molecule precursors to complex fluorides and oxides, in order to allow ready processibility for eventual deposition from solution and subsequent thermal conversion into nanophase-supported materials. We give two examples of this idea from our own work.

AlF₃ is an important CFC-alternatives catalyst. We have explored alternate routes to AlF₃, starting from a number of organic cation salts of the AlF₆⁻ anion, which were prepared as organic solvent soluble species. These salts were then used to produce a variety of new and known AlF₃ phases by thermal elimination of the organic cation fluoride equivalent. This allowed us to not only prepare novel bulk phases of AlF₃ but also to deposit the normally refractory AlF₃ as a nanophas onto other supports (e.g. alumina or in the pores of zeolites) with precise control of the stoichiometry of the final nanocomposite.

A similar approach using discrete clusters of vanadophosphates has allowed us entry to highly desirable supported butane oxidation catalysts such as vanadium pyrophosphate and vanadium phosphite. The idea of using discrete molecular precursors to complex catalyst or electronic materials phases appears simple yet provides a powerful approach to generation of supported nanophase versions of those phases. In addition, the approach may also provide superior synthetic routes to the normal bulk phase material, or novel processing options for that phase that are unavailable by traditional techniques.

2.4. “Nanoparticles of Vacuum”—Zeolites and the MCM-41 Family

In the areas of catalysis, separations, and sorption phenomena the role of porous inorganic oxide matrices has long been recognized. In particular, the role of zeolites in improved gasoline yields alone accounts for billions of dollars in increased GDP. Viewed from the perspective we take in this article, such porous media could be thought of as nanoparticles of vacuum entrapped within a “dense” oxide phase. An old and powerful theme in the zeolite literature concerns organic molecules that act as “templates” for the various pore network structures. Lobo et al. have described the ongoing quest for a rational method of preselecting the appropriate shape for a template in order to define the ultimate zeolitic architecture. Interestingly, there is a strong correlation of the ability of a particular organic template molecule to direct the crystallization of a unique zeolite type with the increasing size of the template. We can interpret this as an example of the ability of the inorganic’s network structure to “sense” the shape and curvature of the template. If the template is too small relative to the atomic connectivity of the host network, the network may accommodate the template in any of a variety of possible ways all with essentially equivalent energy. This leads to multiple pore structures from a single spherical template (e.g., at least ten structure types are templated by tetramethylammonium ions). As the template becomes larger and more rigid in shape and curvature, the network has fewer and fewer options for accommodating it within a crystalline structure, and the number of templated networks is reduced dramatically until unique structures become the norm. As an extreme example of this kind of templating phenomenon, one can consider the use of surfactant micelles or liquid crystals as the equivalent of very large template molecules for the MCM-41 class of materials. Cylindrical rods of hexagonal close-packed micelles essentially segregate the synthesis phase space and dictate the assembly of the inorganic network. By doing so, these templates define a hexagonal close-packed network of linear pores having very uniform diameters. The micelle geometry has such an enormous templating effect on the inorganic network that in order to accommodate the template, the network must remain amorphous and resist crystallizing. Is it possible to extend this idea to very large molecular assemblies, for
example, nanoparticles of polymers or inorganic materials with very uniform size, shape, and charge that self-assemble into clusters of clusters? These could act as either relatively passive templates for unique nanoparticles of vacuum in inorganic or other polymeric networks or else create novel active pseudocrystals of ordered nanoclusters with fascinating optical and electronic properties. Experience and evidence suggest this ought to be possible, and very interesting.

3. Another Look at Nanoparticles: So Much Curvature, So Little Room

Nanoparticles characteristically have a high surface to volume ratio. Thus the chemist concerned with the rational, deliberate synthesis of nanoscale materials recognizes the challenge: “How does one stabilize the large surface area of a particle in the small cluster size regime?” Surface chemistry figures crucially in the syntheses and intrinsic properties of the nanoparticles themselves, and surface chemistry dictates how the nanoparticles, once made, will materially interact with their environment. To further explore the details of nanocluster surfaces, consider the discrete tetrahedral cluster/nanoparticle \( \text{Cd}_{10}S_4(SR)_{16}^{4–} \) sketched in Figure 3, one of several fascinating clusters/nanoparticles based on 12–16 semiconductors. Higher members of this particular family of all-sphalerite-like (“zinc-blende”) compounds are listed in Table 1. The second member of this family, \( \text{Cd}_{20}S_{13}(SR)_{22}^{8–} \) is about 12 Å (roughly 1 nm) in size, thus representing the transition from big clusters to small nanoparticles. Of the 35 S atoms of \( \text{Cd}_{20}S_{13}(SR)_{22}^{8–} \), 34 are “surface” and only one is “interior”. In Table 1 we see the large surface/interior ratios persisting for even larger cluster sizes. Perhaps the most extreme examples of a high surface/volume ratio are the fullerenes and carbon nanotubes, which—if single-walled—are comprised entirely of surface carbon atoms with no interior carbon atoms.

But surfaces of nanoparticles have another characteristic, besides being large relative to volume, that makes them different from the surfaces of much larger particles/bulk phases. In order to completely enclose a volume, any closed surface must exhibit mean and positive Gaussian curvature. For purposes of this discussion, the Gaussian curvature at a point on a surface is determined by the relative senses of the two primary arcs of curvature that intersect at that point. If both arcs curve in the same direction, as in Figure 4a, the Gaussian curvature at that point is positive. If the two primary arcs curve in opposing directions, as in Figure 4c, the Gaussian curvature is negative. And if there is curvature along only one arc, the other being essentially uncurved as in Figure 4b, the point has zero Gaussian curvature but non-zero mean curvature. Perhaps even simpler, a sphere has positive Gaussian curvature everywhere; a portion of a sphere, e.g., a bowl—whether pointed up or pointed down—likewise has positive Gaussian curvature (except at the rim); a ring or cylinder has zero Gaussian curvature but non-zero mean curvature; a saddle has negative Gaussian curvature.

By now the reader may be asking, So what? Why do we need this concept? After all, generations of chemists have...
appreciated the fundamental and intimate relationships among connectivity, topology, shape, valence, and reactivity, without resorting to the concepts or language of “curvature”.

An sp³-hybridized carbon center participates in chain or ring formation if it is a methylene group, in cluster or cage formation if it is a methine group, and in spiro or network compounds if it is a quaternary carbon. What is to be gained by calling this zero Gaussian curvature, positive Gaussian curvature, and negative Gaussian curvature, respectively?

We use “curvature” in the remainder of this article because the concepts and language allow us to articulate relationships and comparisons among different compounds having different metal centers perhaps with different coordination numbers. We will be looking at selected binary or ternary inorganic cluster compounds that are or approach nanoparticulate size, and “curvature” gives us a basis on which to make some qualitative generalizations about such clusters/nanoclusters/nanoparticles and their surfaces. We make no attempt to quantify “curvature” here and our usage of the concept is strictly descriptive.

A particle has a surface that is topologically closed, and as such must have regions of positive Gaussian curvature. If the particle is a simple polyhedral object, the regions having positive Gaussian curvature are the corners, and indeed positive Gaussian curvature is a necessary requirement for a surface region to be a corner. Surfaces of larger particles have the luxury of exhibiting the requisite curvature only at a relatively small fraction of the overall surface—zero Gaussian curvature (but non-zero mean curvature) at edges, positive Gaussian curvature at corners. But surfaces of small particles must achieve closure in less space and exhibit the requisite curvature with fewer atoms, and therein lies a fundamental uniqueness of nanoparticle surfaces: the nanoparticle surface bears a high fraction of “edge-like” and “corner-like” curved regions, and in some cases (most notably in very small nanoclusters having acute angles between faces, as in the tetrahedral objects of Fig. 3 and Table 1) nearly every atom of the entire particle is “edge-like” or “corner-like”. Edges and corners have long been recognized as having different properties than level surfaces; for example, growth of macroscopic crystals usually occurs at the edge-like sites of dislocations, and corner/edge-rich catalyst nanoparticles are often unusually reactive.

3.1. Capping, Gaussian Curvature, and the Preferences of Sulfur Centers

Consider first the relationship between “capping” and Gaussian curvature. In “inorganic” objects of cluster/nanoparticulate size the sites of positive Gaussian curvature, the corners, are often single atomic sites. Chemically, atoms at these corner sites typically have three (or, less commonly, four) valence orbitals bonding to the neighboring atoms of the particle, and direct one (less commonly, two or three) valence orbitals outward from the mean particle surface. For a tetrahedral atomic center, the very fact that one of its valence orbitals points outward from the surface while the remaining three bonds point toward the rest of the particle prejudices it toward having positive Gaussian curvature, see Figure 4a. A tetrahedral atomic center using all four of its valence orbitals in bonding to the rest of the particle must either be part of the interior network or bulk (in which case “curvature” in the present context is not applicable) or it defines a negatively Gaussian-curved surface region (Fig. 4c).

In order for the resulting particle to be stable, outward-pointing orbitals of surface atoms must be filled, whether by non-bonding electrons, adduct formation with Lewis bases, or covalent bond formation with organic groups. (Surfaces that might be electron acceptors/Lewis acids spontaneously tend to bind donors/Lewis bases, thereby becoming a modified surface that is less Lewis acidic.) Filling these outward-pointing orbitals amounts to capping the so-called dangling valences. The phenylthiolates in the cadmium-sulfide clusters alluded to above are excellent examples of “capping agents” by virtue of the phenyl groups and, indeed, the very existence of these particular clusters depends on capping agents. Without them there is no reason for the “CdS” particles to stop growing at nanosize, unless the surrounding medium intervenes by physically prohibiting further growth or by inhibiting reagent diffusion, thus starving the growing particles.

The positive Gaussian curvature of each corner region of Cd₂₅S₄(SR)₄₆⁻ (Fig. 3) and the higher members of this family (Table 1) is provided by a cadmium center, (phenyl)thiolato-capped, as in Figure 5. The particle edges are defined by bridging (phenyl)thiolato groups, where their sulfur centers exhibit zero Gaussian curvature. This dual role of (phenyl)thiolato groups reflects their well-known structural versatility. Thiolates can be non-bridging or can bridge two or more metal centers, depending on the particular environment in which they participate (and how many Lewis
acid sites are nearby), owing to the fact that thiolato sulfur centers are Lewis bases with filled valence orbitals. The metal centers tend to be Lewis acids and seek higher coordination numbers (typically four or more), and therefore surface metal centers generally emerge at sites of Gaussian curvature — either positive, at corners, or negative, at points of fusion. And since, as described above, positive Gaussian curvature requires an outwardly directed valence orbital, there will be an opportunity for surface chemistry at the metal-occupied corner sites. In one interesting example, cadmium centers that occur at the corners of a quasitetrahedral nanocluster have lost their terminal phenylthiolates and bind instead to dimethylformamide molecules. In a second set of examples, an adamantanoid (PhS)_6Cd_4 cluster framework binds counterions (ClO_4^-) or soft ligands (PPh_3) at the corner Cd centers.

In principle the sulfur center of a (phenyl)thiolato group could bridge three metal centers, exhibit positive Gaussian curvature, and serve itself as a particle corner. Such a role for thiolato groups is sketched in Figure 6a, yet we have found no examples of discrete clusters having this structure type. All the crystallographically characterized examples of discrete “adamantanoid” clusters involving metal and chalcogenide centers in the cage put the metal center at the sites of positive Gaussian curvature (corner, bridgehead) and the chalcogenide center at sites of zero Gaussian curvature (edges), as in Figures 5 and 6b. There are indeed examples of clusters where sulfur centers bridge three or more metal centers and exhibit positive Gaussian curvature at corner regions, but in most of these examples the cluster is “cubane”-like as in Figure 6c, with several examples of “cuboctahedral” clusters, Figures 6d and 6e. And it is the cubane/cuboctahedral model that underscores an interesting trend: yes, sulfur centers can exhibit positive Gaussian curvature and serve as corners, but if the adjacent metal centers follow their natural tendency and exhibit non-zero Gaussian curvature, the resulting entity will be a small cluster, e.g., Figures 6c–e, or perhaps not even a recognizable closed object. The paucity of structures such as that in Figure 6a, then, results from the difficulty in forcing metal centers to exhibit zero Gaussian curvature and assume edge positions. This raises an aspect of nanoparticles we will allude to again: in order for an assembly to grow beyond the molecular cluster regime and become a many-atom particle with well-defined edges on the order of nanometers, there must be an adequate supply of zero-Gaussian-curved atomic centers that command, or at least tolerate, positions on nanometer-long edges.

The cuboctahedral compounds above raise another aspect of chalcogen chemistry. Four-coordinate sulfur centers in small molecules often are in +4 oxidation states and are not tetrahedral (e.g., SF_4). Such an intermediate-valence sulfur center is able to exhibit positive Gaussian curvature as in Figure 6d. Sulfur(+6) in sulfate and sulfonate can exhibit Gaussian curvature much like phosphates, which will be discussed below. But in many sulfur–metal compounds, especially sulfur compounds with group 12 metals (Zn, Cd, Hg), the sulfur is in the +2 oxidation state; if four-coordinate it is tetrahedral, and if unadorned by organic groups it is prejudiced to exhibit negative Gaussian curvature. Such tetrahedral sulfur centers of course comprise the network “core” of the 12–16 semiconductor nanoparticles, but could also be imagined in a surface, where they serve as sites of fusion of polyhedra.

Spelled out in this manner, we see that the ingredients for a nanoparticle include: unsubstituted atomic centers that can comprise the core/interior of the particle, atomic centers (substituted or electronically saturated) that can stabilize planar surface regions, substituted centers that exhibit mean curvature and can serve as edge sites, and other substituted centers that exhibit positive Gaussian curvature and serve as corner sites, all in the right ratio. A deliberate, rational synthesis of such an object clearly becomes a multicomponent challenge, seldom undertaken. Fortunately, experience has shown that some fascinating nanomaterials can be obtained using less deliberate control. The ability of phenylthiolates to participate in both corners and edges contributes to the remarkable capacity for the family of Cd/S/SR clusters/particles to dissociate, reassemble, and merge into higher nanosized clusters. Were one interested in more strict control of cluster/particle size, one approach is to use different capping agents that are more “predictable” and less “versatile”. For instance, if there were a thiolato group SR’ that only terminally bonds with a Cd center and thus with its bound Cd center reliably caps only corners of CdS clusters, and a second thiolato group SR” that reliably caps only edges,
and a mixture was prepared in the ratio \( R'S'/R'S'/Cd^{2+}/S^2- = 4:12:10:4 \) the compound \( \text{Cd}_{10}S_4(SR')_4(SR')_2 \) (essentially the first entry in Table 1) would be expected.

From the discussion above, one might conclude that corner-capping need not be of overriding concern to the nanoparticle chemist. The chemist who emphasizes corner capping, that is, positively Gaussian-curved synthetic building blocks, risks biasing his/her reaction mixtures toward making entities rich in corners, i.e., molecular clusters. What may be more important for the preparation and subsequent chemistry of nanoparticles is that there be ample groups that prefer zero Gaussian curvature and serve as edge sites. There is precedent for metal-centered corner sites to cap themselves with Lewis bases, e.g., solvent[31] and require no special attention from the chemist. One can imagine devising polydentate ligands that would help define a nanoparticulate edge, as sketched in Figure 7a against the \( \text{Cd}_{10}S_4(SR')_2 \) cluster. Such an edge-definer would need a S–S separation of 4.0 Å to fit the CdS-based sphalerite nanoclusters (Fig. 7a, b).

In a set of examples from the cluster literature, 1,2-dithiolates, 1,3-dithiolates, and 1,4-dithiolates[38,39] all serve as sulfur centers (edges) in adamantanoloid \( \text{Cu}_4(S–R–S)_4 \) clusters. Here the spanned S–S separation is on the order of 3.7 Å owing to distortion of the adamantanoloid cage (Fig. 7c), as occurs even in unchelated \( \text{Cu}_4(SPh)_6 \)[40] thus it is unlikely that such dithiolates would serve to define the edges of CdS-based sphalerite nanoclusters as in Figure 7a. There is a family of “wurtzite-capped” CdS clusters/nanoclusters[31,41] where the particle edges are actually clefts; the S–S separation across these clefts is on the order of 3.7 Å, so the dithiolates could conceivably serve to define these edges, as in Figure 7d.

Yet, edges and corners do, to some extent, control each other, and it would be a mistake to ignore corners completely. An interesting approach taken by Raymond and co-workers[42] is to employ ligands that span a considerable distance and command particular interligand angles, thereby establishing metal centers at distances several angstroms from each other in symmetrical polyhedral arrangements (see Fig. 8). The metal centers thus established could conceivably become corners of genuine nanoparticles, once the chemistry is found that will fill in edges and bulk/interior. Another fascinating approach is taken by Seeman et al.,[43] who introduce branches into synthetic DNA molecules. These branches become corners that assemble the DNA strands into beautiful 3-dimensional cages.

3.2. Phosphato- and Related Oxygen-Containing Compounds

Some attempts at semirationally controlled cluster synthesis are found for phosphonato/phosphato compounds. Ordinarily, tetrahedral phosphate \( \text{PO}_4^{3–} \) in inorganic compounds is bound by each oxygen to a metal center and is part of the bulk lattice or, if it appears on a surface, a local site of negative Gaussian curvature, Figure 4c.[30] By “capping” one corner of the phosphorus tetrahedron with a robust organic substituent the phosphonato/phosphato group can exhibit positive Gaussian curvature and prefer, even command, corner sites of clusters. A number of transition-metal phosphonato/phosphato cluster compounds have been described,[44] all using \( \text{RPO}_3, \text{ROPO}_3 \), or analogous arsenate groups to serve as positively Gaussian-curved corners; an example from our work is sketched in Figure 9.[30]

With two robust organic substituents, the phosphorus tetrahedron no longer exhibits positive Gaussian curvature and cannot (by itself) command a corner site, but it does exhibit mean curvature. As such it could cap or serve as an edge site of a cluster. Examples include “lantern dimers” such as in Figure 10a[45] and the trivanadyl cluster sketched in Figure 10b[39] (additional examples can be found in the...
literature\cite{44}). This last structure is the dialkylphosphato analog of the “basic acetate” compounds (Fig. 10c), which are well-known for many of the transition metals\cite{46}. The “basic acetate” structure is especially instructive to the nanoparticle chemist: by our simplistic analysis it is not really a closed polyhedral object, but rather a ring, which—like a cylinder—has no Gaussian curvature. This is the counterpoint to the lesson drawn above: when the chemist emphasizes synthetic building blocks that have no Gaussian curvature, the resulting products are biased towards chains or rings, which have no corners, and hence no polyhedral structures!

Here we must examine the “edge” with closer scrutiny. So far the emphasis has been on centers that have positive Gaussian curvature (corners) or zero Gaussian curvature (not corners). Edges of polyhedral objects are extended regions of zero Gaussian curvature but non-zero mean curvature, as in Figure 11a where the extended direction (x-axis) is essentially uncurved across many angstroms and the curvature is in the yz-plane. In the metal-sulfur compounds the yz curvature at edges is actually provided by metal centers, and the uncurved x-axis is established by the bridging (phenyl)thiolato group, as in Figure 11b. This bridging (phenyl)thiolato group can be viewed as having mean (but not Gaussian) curvature of its own but it does not, by itself, comprise the polyhedral edge. Similarly, carboxylato and dialkylphosphato groups have mean curvature, but when we try to build an edge using this mean curvature our constructions look like Figure 11c. These have no direct bonding along the extended direction and look unpromising for robust stable nanoobjects. Small rings, or compact molecular clusters, as in Figure 10, seem to be the more natural expression of the mean curvature of carboxylates and dialkylphosphates (although, we respect nature’s ability to use groups in ways we have not anticipated). Note, this postulated tendency of disubstituted phosphato centers to avoid edges of nanoclusters is a property of phosphato centers (–O–PR$_2$–O–). If one is working with phosphido centers in the context of nanoparticulate metal phosphide compounds M$_x$P$_y$, then disubstituted phosphido centers (–PR$_2$–) could well serve as edge sites, similar to thiolates in metal-sulfur compounds.

With three robust substituents the phosphorus center can no longer by itself offer curvature to a cluster/particle surface but it can serve as a monodentate Lewis site. As such it can modify/protect Lewis acid sites of the surface. In some instances, its adduct with the Lewis acid site can be a modestly robust entity and this joint adduct can function as a capping agent (Fig. 7). Trialkylphosphine oxide and trialklyphosphine chalcogenides have often been used in this manner\cite{47}.

In phosphato chemistry as in metal-chalcogenide chemistry, deliberate rational syntheses of nanoclusters using the right ratio of appropriately curved building blocks may be possible, but a phosphate-based edge-preferring building block has not been identified. Despite our suspicion that dialkylphosphates are not suitable for bridging edges of larger clusters, we did try ourselves to make vanadyl compounds bearing both BuOPO$_2$\textsuperscript{2–} and (BuO)$_2$PO$_2$\textsuperscript{–} groups. But the compound that resulted incorporated only the BuOPO$_2$\textsuperscript{2–} groups (at the corners of a quasitetrahedral cluster) and the (BuO)$_2$PO$_2$\textsuperscript{–} groups were left untouched in the reaction solution\cite{50}.

Here we return briefly to the notion outlined above, that carboxylato and dialkylphosphato groups tend not to define nanocluster edges. Metal-oxide nanoparticles are technologically important, serving, for example, to impart useful properties to polymers in which they are imbedded\cite{49} or exhibiting novel photophysical effects\cite{49}. Looking for structurally characterized cluster compounds of early-metal oxides, we found a number of metal-oxo-alkoxo-carboxylato cluster compounds\cite{50} where carboxylato groups do serve as cluster edges. But these clusters are compact objects with short edges, consistent with the earlier discussion, and we do not see how they could be easily enlarged into nanoclusters.

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Fig. 9. Sketch of the cluster (VO)$_6$(O$_2$PO$_2$SiMe$_3$)$_8$Cl, see [30]. The chloride occupies the center of the cluster and is not shown. Each corner phosphorus center bears a terminal –OSiMe$_3$ substituent, omitted for clarity. The dashed lines indicate the cubic nature of the object and are not chemical bonds.

Fig. 10. Sketches of selected dialkylphosphato and carboxylato structures. a) From [45]. Trimethoxysilyloxy and t-butoxy substituents on the phosphato groups are omitted; R = Bu. b) From [18]. Ethoxy substituents on the phosphato groups are omitted; solv = CH$_3$CN. c) “Basic acetate” structure. See text.
Indeed, the carboxylato groups appear to serve explicitly to prevent formation of extended nanometer-sized arrays and force the formation of small, tractable, molecular cluster compounds. If nanoclusters of early-metal oxides are desired, a more promising approach may be to keep carboxylates away and use alkoxide groups\[^{[51]}\] for capping; terminally bound alkoxides support positively curved metal centers at cluster corners and bridging alkoxides define the cluster edges, as sketched in Figure 12. (In chloride-rich media\[^{[49]}\] chlorides could mimic alkoxides in their ability to define edges.) Viewed in this manner, early-metal oxides can be "capped" by alkoxides in ways that remind us of late-metal sulfides "capped" by phenylthiolato groups.

3.3. On Using Metal Centers to Define Nanocluster Edges

Earlier we noted that, at least in metal-chalcogenide clusters, metal centers are unlikely to exhibit zero Gaussian curvature. Thus while they can provide the mean curvature necessary for edge sites they do so only in cooperation with a capping, edge-defining thiolate, as in Figures 5 and 11. But the discussion on phosphato compounds suggests a simple means whereby a nanocluster chemist might alter the usual preferences of a metal center, at least a tetrahedral metal center, and enable it to appear directly on particle edges: provide the metal center with two robust substituents that themselves will not participate further in cluster bonding, as sketched in the hypothetical examples of Figure 13. This leaves the tetrahedral metal center with only two valence orbitals to use in bonding to a cluster, and forces it to exhibit zero Gaussian curvature. This represents a reversal of the usual role of the metal center in cluster compounds, and we have not yet found clear examples of such metal centers in binary or ternary inorganic cluster compounds.\[^{[52]}\] There are intriguing uses of phenanthroline (phen) to help stabilize very large palladium clusters,\[^{[53]}\] where the exact role played by phen is not known but perhaps phen-Pd centers (Fig. 13) help define particle edges. In at least two examples of molecular clusters containing tetrahedral phen-Pd or bipyridyl-Pd units, these metal centers approach edge-defining roles.\[^{[54]}\]
If we allow enlargement of the coordination number at the metal center to five- and six-coordinate, the possibilities become nearly endless. To begin thinking about these possibilities, we recall that the metal-carbonyl fragments are well known in small clusters, and (C₅R₅)M fragments likewise typically exhibit positive Gaussian curvature. In one example, Cp₃Ti fragments cap the corners of NaF clusters.[75] But to go beyond this exceeds the scope of this article.

4. Conclusion

This article is intended as a survey of some of the uses of nanostructured matter here at DuPont. We also examine the topological roles of the various pieces that comprise selected binary or ternary inorganic cluster compounds, and how these pieces might—or might not—be adapted to building larger nanocluster particles. Because “inorganic” chemistry includes such a tremendous diversity of species, preferred bonding trends, and coordination numbers and geometries, we have used the language of “curvature” as a way of articulating relationships among disparate entities that otherwise may not seem to have much in common. Our hope is that this article will challenge our fellow chemists to view the curvature as being exhibited by groups of atoms, especially five- or seven-membered rings, as in [12]. By manipulating their curvature, atomic centers that in one case bond together as an infinite level surface can in other cases be encouraged to close into polyhedra. See D. L. Thorn, R. L. Harlow, N. Herron, Inorg. Chem. 1995, 34, 2629.


There were 362 “hits” responding to compounds having, either simply or embedded within them, this general “cubane” structural type; see [33]. An example is (Cd(SPh)₄(SPh)₆: A.-K. Duhme, H. Strasdeit, Naturforsch. 1985, B49, 119. Iron- and molybdenum-containing compounds of this sort have been extremely important in bioinorganic chemistry; see R. H. Holm, Acc. Chem. Res. 1977, 10, 427. D. Coucouvanis, ibid. 1981, 14, 201.

There were 3 “hits” responding to the general connectivity of Figure 6d [33]. The “hits” contain a large proportion of tetrahedrally coordinated metal centers, e.g., Fe (16 hits) and Ni (seven hits). An example is (FeI₂(Ni(PMePh₂)₄)₂: C. Junghams, W. Saak, S. Pohl, Acc. Chem. Res. 1977, 10, 427. D. Coucouvanis, ibid. 1981, 14, 201.

There were 43 “hits” responding to the general connectivity of Figure 6e [33]. This structure precludes tetrahedrally coordinated metal centers, thus the “hits” contain a large proportion of square-planar/tautrahedral Co–Mo–W, and a very small representation by Fe (three hits) and Ni (zero hits). An example of this structural type is (Co(P(Et)₃)₄)₂: M. Stegerwald, T. Siegrist, S. M. Stuczynski, Inorg. Chem. 1991, 30, 2256.

As cluster chemists, we admit that any claim to general, rational, deliberate syntheses of clusters/nanoparticles is foolhardy. Lewis Carroll’s poem nicely summarizes the cluster chemist’s situation: “You boil it in sawdust: you salt it in glue: You condense it with locusts and tape: Still keeping one principal object in view— To preserve its symmetrical shape.” (from The Hunting of the Snark).

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[46] There were 186 “hits” ([33]) for structures having this general connectivity. Many of the “basic acetate” compounds have other carboxylato groups in place of the bridging acetate. The particular compound (μ-3-oxo)-hexakis(μ-2-benzoato)-dioxo-tetrahydrofuran-tri-vanadium, described by F. A. Cotton, G. E. Lewis, G. N. Mott, *Inorg. Chem.* 1982, 21, 3127 is very closely related to the compound sketched in Figure 10b [18].
[50] For example, Zr$_6$(OH)$_4$O$_4$(methacrylate)$_{12}$, reported by G. Kickelbick, U. Schubert, *Chem. Ber./Red.* 1997, 130, 473. The vinylic groups are “fully accessible for further reactions”.