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Nanocluster with One Missing Core Atom: A Three-Dimensional Hybrid Superlattice Built from Dual-Sized Supertetrahedral Clusters

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In addition to having size-dependent properties, nanoclusters also behave like large pseudo-atoms and serve as building blocks for construction of superlattices with properties that differ from either individual clusters or the bulk.[1−5] While colloidal nanoparticles usually self-assemble into close-packed lattices, supertetrahedral clusters that are regular fragments of the zinc blende-type lattice can form covalent lattices with large pore size and high pore volume.[6−13] Unfortunately, the size of the known tetrahedral cluster is still small, and only a few types are currently known. In addition, their superlattices invariably consist of clusters of identical size.

For discrete supertetrahedral clusters denoted as T*n* ($n > 1$), the formulae for *n* from 2 to 5 are M_4X_{10}, $M_{10}X_{20}$, $M_{20}X_{35}$, and $M_{35}X_{56}$, respectively, where M is a metal ion and X is a chalcogen. T2 and T3 clusters have no core atoms, but regular T4 and T5 clusters have X and MX_4 cores, respectively. In terms of size, these clusters can be considered as lower limits of colloidal nanoclusters. Prior to this work, the largest known supertetrahedral cluster is T4 with 20 metal atoms.[12,13]

Here we report a novel nanocrystal superlattice (denoted as UCR-15) that extends the size of supertetrahedral clusters from 20 metal ions in a T4 cluster to 34 metal ions in a pseudo-T5 cluster, $[In_{34}S_{54}]^{6-}$. These pseudo-T5 clusters are coupled to T3 clusters to form a 3D framework. UCR-15 is the first example of a covalent open framework built from supertetrahedral clusters of different sizes, thus opening up new possibilities in the construction of nanoporous semiconducting frameworks.

To prepare crystals of UCR-15, indium metal (115.9 mg), sulfur (70.6 mg), $CdCl_2{\cdot}2.5H_2O$ (43.9 mg), and dipiperidinomethane (2.0335 g) were mixed in a Teflon-lined stainless steel autoclave. After addition of distilled water (3.0215 g), the mixture was stirred for 10 min. The vessel was then sealed and heated at 190 °C for 6 d. The autoclave was subsequently allowed to cool to the room temperature. Transparent, pale yellow crystals were obtained with about 50% yield. Elemental analyses using an EDAX attachment on a scanning electron microscope and an inductively coupled plasma spectrometer showed that divalent Cd^{2+} ions were not detectable in crystals.

The most prominent structural feature of UCR-15 is the presence of the T5 cluster with one missing core atom, $[In_{34}S_{54}]^{6-}$ (Figure 1).[14] A complete, discrete T5 cluster consists of 35 metal atom sites and 56 anion sites. For a 3D framework with a bi-coordinated S^{2-} bridge between two adjacent clusters, the number of anion sites per cluster is reduced by two. A key structural feature of a complete T5 cluster is the presence of a tetrahedral MS_4 core. All other atoms are located on faces, edges, and corners of the cluster. In an ideal T5 cluster, the metal site at the core would be bonded to four tetrahedrally coordinated S^{2-} sites. In UCR-15, the metal atom at the center of the T5 cluster is missing.

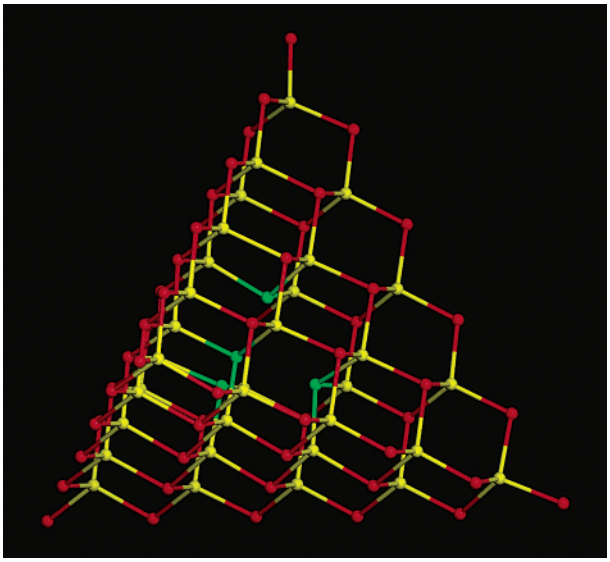

Figure 1. Structural diagram of the pseudo-T5 cluster $(In_{34}S_{54})^{6-}$ showing the missing core site surrounded by four core S^{2-} ions (in green). Yellow: In^{3+}; Red: S^{2-} ions on the surface of the cluster.

A significant conceptual advance as a result of this work is that larger clusters can be made in simple binary systems such as indium sulfide. We can envision a whole family of coreless nanoclusters with sizes larger than T5. For example, a T6 cluster with a missing T2 core ($M_{56}X_{84} - M_4 = M_{52}X_{84}$), a T7 cluster with a missing T3 core ($M_{84}X_{120} - M_{10} = M_{74}S_{120}$), and a T8 cluster with a missing T4 core ($M_{120}S_{165} - M_{20}S = M_{100}S_{164}$) would be the next three members in this family. The superlattices formed from these clusters are unusual because they would contain both inter- and intra-cluster pores.

Prior to this work, it appeared that divalent metals were essential for construction of supertetrahedral clusters larger than T3.[12,13] For supertetrahedral clusters with tetrahedral S^{2-} sites, it has been suggested that divalent metal ions such as Cd^{2+} are needed around tetrahedral S^{2-} sites to satisfy the bond valence rule.[12,13] Because a regular T4 cluster consists of a M_4S unit, the bond valence rule was used to explain the incorporation of divalent metals into the T4 cluster with the ternary composition $(M_4In_{16}S_{33})^{10-}$ where M = Cd, Zn, Mn, Fe, Co.[12,13] In UCR-15, the absence of the metal ion from the T5 core leads to the reduction in the coordination number from 4 to 3 for four-core sulfur sites. This shows that different avenues exist toward the creation of larger nanoclusters.

Another novel feature that distinguishes UCR-15 from other supertetrahedra-based open frameworks is the presence of two

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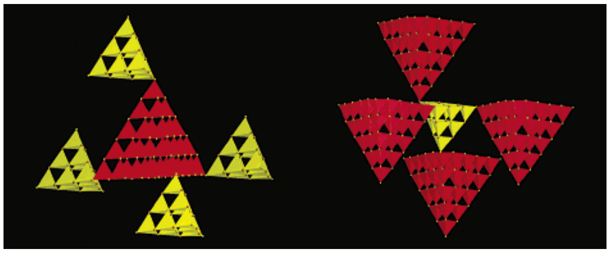

Figure 2. Four T3 clusters are joined together by a pseudo-T5 cluster and vice versa.

different clusters. For building superlattices from colloidal nanoclusters, the size variation is in general detrimental because it tends to disrupt the close packing of nanoparticles. Here, the pseudo-T5 supertetrahedron alternates with the regular T3 $(In_{10}S_{18})^{6-}$ supertetrahedron to form a covalent 3D framework. Each pseudo-T5 cluster is surrounded with four T3 clusters and vice versa (Figure 2).

When both T3 and pseudo-T5 clusters are replaced with T4 clusters, the framework of CdInS-44 and UCR-5MInS (M = Zn, Mn, Co) is obtained. The formation of the alternating T3 and pseudo-T5 framework in UCR-15, however, significantly reduces the overall framework negative charge with −0.273 charge per metal site. In comparison, the charge per metal site in the T4−T4 framework is −0.5, almost twice as negative as the T3−T5 framework. In the study of oxide open framework materials, it was suggested that the host−guest charge density matching plays an important role in the formation of four-connected zeolite-type materials.[15,16] Here, the host−guest charge density matching may also be an important factor in the formation of the T3−T5 framework. In the simplest approximation, the charge density of a fully protonated amine molecule can be approximated by its C/N ratio. Thus, the more negatively charged T4−T4 framework is formed when 1,4-bis(3-aminopropyl)piperazine (the C/N ratio = 2.5) is used as the structure-directing agent whereas the less negative T3−T5 framework is formed when dipiperidinomethane (the C/N ratio = 5.5) is used in the synthesis.

The topological type of UCR-15 resembles that of the cubic ZnS lattice (Figure 3). In other words, inter- and intra-cluster connectivities are the same. There are two identical interpenetrating lattices. Even with the formation of two interpenetrating lattices, the framework of UCR-15 is still highly open. More than half of the crystal volume (55%) is occupied by disordered guest species as calculated by PLATON.[17]

Fluorescent spectra were measured on a SPEX Fluorolog-3 system equipped with a 450-W xenon lamp. UCR-15 showed a broad emission (fwhm = 100 nm) centered at about 512 nm when excited at 440 nm. In comparison, UCR-1CdInS that consists of only T4 supertetrahedra displays photoluminescence at about 521 nm when excited at 401 nm. These observations, coupled with our earlier discovery of photoluminescence between 400 and 430 nm in open framework oxides[18] indicate that these novel open-framework materials have a broad range of photoluminescent properties in addition to their potential porosity.

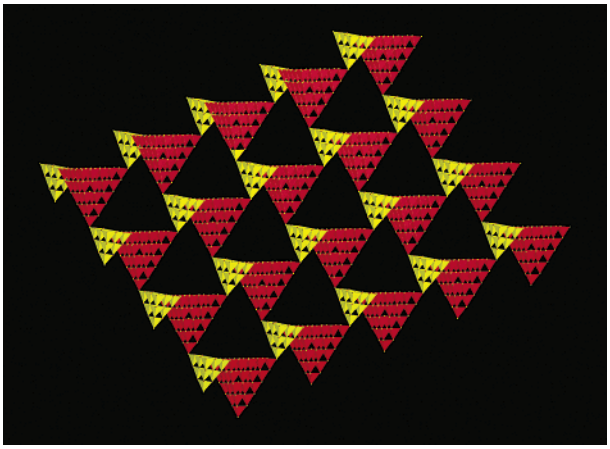

Figure 3. Three-dimensional framework of UCR-15. Yellow: T3 clusters; Red: T5 clusters. Only one set of superlattice is shown for clarity.

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Supporting Information Available: Crystallographic data including positional parameters, thermal parameters, and bond distances and angles (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Crystallographic data for $(In_{34}S_{54})(In_{10}S_{18})(C_{11}H_{24}N_2)_6$: space group $I4_1/a$, $a = 24.597(6)$ Å, $c = 44.09(2)$ Å, $V = 26674(13)$ Å^3, $Z = 4$, Mo Kα, $2\theta_{max} = 40°$, $R(F) = 7.69\%$ for 265 parameters and 2616 reflections with $I > 2\sigma(I)$. Results of the elemental analysis (in wt %) for UCR-15 are 8.50 (calcd 9.36) for C, 1.41 (calcd 1.71) for H, and 1.60 (calcd 1.99) for N.
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