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Crystal of Semiconducting Quantum Dots Built on Covalently Bonded T5 $[\mathrm{In}_{28}\mathrm{Cd}_6\mathrm{S}_{54}]^{-12}$: The Largest Supertetrahedral Cluster in Solid State

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The past decade has witnessed an intense research effort on nanoparticles or quantum dots (QDs), stemming from both fundamental and technological interests.[1−11] Nanoparticle systems most extensively studied thus far are colloidal dots, in which individual dots are randomly distributed over the space.[1−10] For practical use in the optical laser devices that require strong intensity and sharp line width, periodically assembled arrays of dots (i.e., a crystal built upon individual dots) are highly desirable. In addition, the periodic lattice of dots also provides opportunities for studying collective physical phenomena attributed to the interactions among individual dots. The novel collective phenomena include, for example, the energy transfer[12] and the Dyvydov excitonic splitting.[13] One way to build a solid crystal of dots is by the "bottom-up" approach, for example, arranging dots into an array using periodic templates.[11−12,14] However, two unfavorable factors exist, which make this approach less attractive. First, an ensemble of colloidal dots with uniform size must be generated in advance. Second, it has been noted that this method generally produces crystals with large dot−dot separations or long-range weak dipole−dipole interactions. Consequently, the collective excitation is rather difficult to observe in these systems.

When crystals built upon nanoclusters have an open-framework porous structure, the large porosity often changes their dielectric properties drastically and thus allows a strong interaction with incident lights, leading to important applications in photonics. Furthermore, many porous structures are suitable for adsorption, catalysis, and phase separation. Thus, the crystal of giant molecular clusters may simultaneously possess useful catalytic and dielectric/optical properties, making them promising multifunctional materials as semiconducting analogues of photonics and zeolites. Here we report on $[\mathrm{In}_{28}\mathrm{Cd}_6\mathrm{S}_{54}]\cdot[(\mathrm{CH}_3)_4\mathrm{N}]_{12}[(\mathrm{HSCH}_2\mathrm{COOH})_2]_{3.5}$ (**1**), a new open-framework crystal structure with supertetrahedral T5 cluster $[\mathrm{M}_{35}\mathrm{S}_{56}]$ as the building unit. Both experimental and theoretical methods are employed to investigate the electronic structure of **1**, and the results indicate that it is a semiconductor with a 3.0-eV band gap.

Single crystals of **1** were grown under solvothermal conditions.[15] The structure of **1** is built on the $\mathrm{In}_{28}\mathrm{Cd}_6\mathrm{S}_{56}$ unit, the largest metal−sulfur nanocluster (23 × 23 Å) found in the solid state to date (Figure 1a).[16] The $\mathrm{In}_{28}\mathrm{Cd}_6\mathrm{S}_{56}$ clusters in Figure 1a have a supertetrahedral T5 geometry.[17] Each $\mathrm{In}_{28}\mathrm{Cd}_6\mathrm{S}_{56}$ nanocluster forms covalent bonds with four neighboring units, via its four terminal S atoms, generating a layered structure (Figure 1b). The shortest interlayer S···S distance is 7.14 Å. The structure is highly porous with a calculated nonframework void space of ∼54% of the crystal volume.[18a] For an isolated metal chalcogenide Tn cluster, the composition of $\mathrm{M}_l\mathrm{Q}_m$ (M = metal atom, Q = chalcogen atom) can be calculated using the formula $l = [n(n+1)(n+2)]/6$ and $m = [(n+1)(n+2)(n+3)]/6$, thus, the isolated T5 cluster should contain 35 metal atoms and 56 chalcogen atoms.[18] The structure refinement of **1** reveals that the metal site at the center of the supertetrahedron is vacant. Those bonded to two-coordinated S only or to both two- and three-coordinated S are occupied by indium [In(1)−In(5)], while the remaining sites are shared equally by In and Cd [M(6)−M(7)],[18] which are bonded only to three-coordinated S. Thus, the structure comprises pseudo-T5 clusters $[\mathrm{In}_{28}\mathrm{Cd}_6\mathrm{S}_{56}]$. The Cd/In ratio was determined by quantitative elemental analysis, from which a composition of In:Cd = 28:6 was obtained.[16] In forming a 2D network, each pseudo-T5 cluster coordinates to each of its four neighboring clusters, via a terminal S atom, giving rise to $[\mathrm{In}_{28}\mathrm{Cd}_6\mathrm{S}_{52+(4\times1/2)}]^{-12}$ or $[\mathrm{In}_{28}\mathrm{Cd}_6\mathrm{S}_{54}]^{-12}$ as the actual composition. Note that the number of Cd atoms in **1** is fewer than what was proposed for T5 (In:Cd = 22:13).[18a] This is likely due to the unrealistically high negative charges and, thus, instability in $[\mathrm{In}_{22}\mathrm{Cd}_{13}\mathrm{S}_{54}]^{-16}$.[19] The layers in **1** stack along [001] with a staggered stacking sequence.[20] The M−S bond lengths of 2.405(5)−2.505(5) Å are comparable to those found in other Tn clusters and in the zinc blende structure of CdS with the following general trend: In−S(two-coordinate) bonds are the shortest [2.405(5)−2.479(4) Å], In/Cd−S(three-coordinate) bonds are slightly longer [2.465(4)−2.491(4) Å], and In−S(three-coordinate) bonds [2.497(7)−2.505(5) Å] are the longest. The difference in the trend of In/Cd−S bonds compared to the smaller T_n clusters is a direct consequence of the missing metal center. The cations and guest molecules that take up the voids are disordered. On the basis of the results of elemental and IR analysis,[16] we conclude that there are 12 $(\mathrm{Me}_4\mathrm{N})^+$ cations and 3.5 $(\mathrm{HOOCCH}_2\mathrm{S})_2$ molecules per cluster in the crystal.

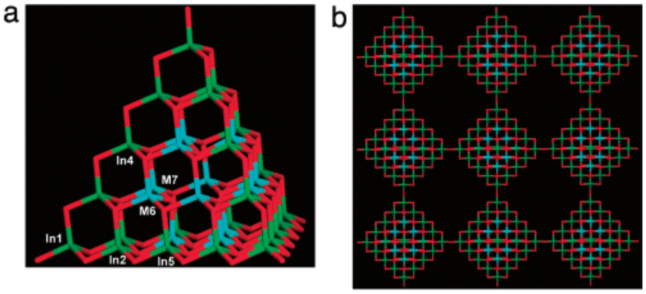

Figure 1. (a) View of a "defected" $[\mathrm{In}_{28}\mathrm{Cd}_6\mathrm{S}_{56}]^{-12}$ cluster in **1**. In (green), In/Cd (blue), S (red). (b) View of the two-dimensional network of the $[\mathrm{In}_{28}\mathrm{Cd}_6\mathrm{S}_{56}]^{-12}$ clusters along the *c*-axis.

The crystal of T5 clusters is a novel periodic structure combining InCdS quantum dots and open space (i.e., antidots). T5 clusters are nearly regular tetrahedral, with an edge of 23.3 Å in length (calculated on the basis of the van der Waals radius of S, 1.80 Å), thus each T5 cluster is a 2-nm dot of the same size, and the

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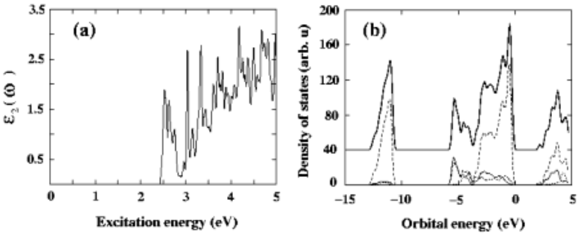

Figure 2. (a) Imaginary part of dielectric function for the T5 crystal structure. (b) Total density of states (upper panel) and partial density of states (lower panel: dashed line for S, solid line for In, dotted line for Cd).

disadvantage of size distribution plaguing colloidal dots is removed. Unlike the usual array of colloidal dots,[11,12] in which the distance between neighboring dots is very large (typically more than 5 nm), the T5 clusters are linked by sharing terminal S atoms (at the outermost vertexes), giving rise to a layer containing pores of ~20 Å dimension. The shared S atom at the corner forms a natural point contact between the neighboring T5 cluster pairs. Electrons are confined in each cluster by the potential barrier associated with the open space. Meanwhile, the point contacts allow electrons in one cluster to hop into the other. This provides a more interesting regime to study electron transport on the nanometer scale. By contrast, the electrons in the arrays of colloidal dots can only exchange energy by weak dipole–dipole interaction, and thus, the collective effect is small.

While a number of Tn clusters including T2 $[Ge_4S_{10}]^{4-}$,[21a–b] T3 $[In_{10}S_{20}]^{10-}$,[21c–e] and T4 $[M_4In_{16}S_{35}]^{14-}$ [M = Mn, Co, Zn, and Cd][18] have been reported thus far, very little is known about the materials properties of this family. We conducted both experimental measurements and first-principle density functional calculations to reveal the electronic structure and optical properties of **1**. The optical absorption spectrum of the compound gave a sharp absorption edge at 3.0 eV,[22] clearly indicating that the compound is a semiconductor. Concluding that the crystal of a T5 structure is a semiconductor is important; it suggests that the size-tunable band-edge electronic properties, such as band-gap and oscillator strength, are all available in the supertetrahedral structure. It also suggests that each T5 cluster will indeed behave like a colloidal semiconductor dot, but the coupling between the neighboring clusters is much stronger. The DFT calculations for this complex T5 crystal structure (with 176 atoms inside a unit cell) were performed using the local density functional approximation (LDA)[23] and the pseudopotential method[24] employing an efficient mixed-basis set (i.e., combining atomic orbitals and plane waves) to handle the large number of atoms. The method has been extensively applied to study the optical and electrical properties of ZnTe-based hybrid materials[25a] and ferroelectric $Pb(Ti_xZr_{1-x})O_3$.[25b] The calculated imaginary part of dielectric function, shown in Figure 2a, reveals that the LDA absorption edge is 2.45 eV. It is well-known that the LDA generally underestimates the band gap. Here we estimate the band-gap correction using a similar material CdS (sphalerite), in which the LDA predicts the band gap of 2.16 eV, and the experimental gap is 2.55 eV.[26] Accordingly we add a band-gap correction of 0.39 eV to our calculated LDA gap of the T5 crystal, and the corrected gap will be 2.84 eV. This is in good agreement with experimental value of 3.0 eV. The calculated total and partial density of states for the crystal of the T5 structure is shown in Figure 2b. We see that the density of states (DOS) near the top of the valence band is very large, in contrast to the normal zinc blende III–V semiconductors.[27] These band-edge states are dominated by sulfur lone-pair orbitals, which give rise to a small band dispersion due to their weak bonding. As a result, the band-edge transitions, as shown in Figure 2a, have a sharp intensity. This is remarkably useful since efficient laser and solar cell devices require large intensities of band-edge transitions.

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Supporting Information Available: Tables of atomic coordinates of all atoms, isotropic and anisotropic thermal parameters, bond distances and angles (PDF), and crystallographic data for the compound (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) $InCl_3$ (0.112 g, 0.5 mmol) and $CdCl_2$ (0.092 g, 0.5 mmol) were added to the solution of $HSCH_2COOH$ (0.31 mL, 4.5 mmol) and $(C_2H_5)_3N$ (0.62 mL, 4.5 mmol) in 10 mL MeCN. The mixture was stirred for 3 h to give a white slurry. The slurry was transferred into a 23-mL Telflon-lined stainless steel vessel, followed by addition of $(CH_3)_4NCl$ (0.115 g, 1 mmol) and elemental sulfur (0.064 g, 2 mmol). The vessel was sealed and heated at 145 °C for 5 days. After cooling to room temperature, the product was isolated by washing with ethanol and ether. Light yellow octahedral-shaped crystals formulated as $[In_{28}Cd_6S_{54}]\cdot[(CH_3)_4N]_{12}[(SCH_2COOH)_2]_{3.5}$ were collected.
(16) Crystal data of **1**: M = 7148.8, tetragonal, space group $P4_2/nmc$, a = 19.623(3) Å, c = 24.818(5) Å, V = 9556(3) Å^3, Z = 2, $F(000)$ = 6738, D_c = 2.484 g·cm^{-3}, μ(Mo Kα) = 4.660 mm^{-1}, 118 variables refined on F^2 with 3314 observed reflections collected at 293 K (θ_{max} = 25.34°) with $\geq 2\sigma(I)$ yielding R1 = 0.0980, wR2 = 0.1866, GOF = 1.459. The elemental microanalysis data for **1** are as follows: Calculated: C, 10.28; H, 2.19; N, 2.31; Cd, 9.6; In, 45.04. Found: C, 10.26, H, 2.30; N, 2.32; Cd, 9.99; In, 44.85. IR (cm^{-1}) 2977, 2671(b), 2481(b), 1693(s), 1464(s), 1396(s), 1196(s), 1029 (s).
(17) A supertetrahedron is obtained by extending a basic MQ_4 (T1) tetrahedral unit to form a tetrahedrally shaped cluster. The resultant cluster is a fragment of cubic zinc blende structure. It is generally notated as T*n*, where *n* is the number of tetrahedral subunits linked along each edge. A crystal of supertetrahedral clusters is a periodic lattice built upon T*n*.
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