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Metal Chalcogenide Frameworks

A Rare (3,4)-Connected Chalcogenide Superlattice and Its Photoelectric Effect**

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The usefulness of cadmium chalcogenide clusters and their organized superlattices in optical, electronic, and catalytic applications[1] has prompted researchers to synthesize cadmium chalcogenide nanostructures of different shapes and sizes. In particular, self-assembly of structurally well-defined cadmium chalcogenide clusters is of interest because their uniform sizes and precisely known structures allow the study of quantum-confinement effects and collective properties at the lower size limit of quantum-dot structures.[2–6] The availability of different cluster sizes and their various spatial organizations may lead to new applications in optoelectronic and catalytic applications.

An interesting property of cadmium chalcogenides is their optical response. As photofunctional materials, the cadmium chalcogenide system has been widely studied in solar-energy conversion, semiconductor surface sensitization and modification, and nanoelectronics. Nanoelectronic devices, which may eventually replace microelectronics in communications and computer technology, require the size of a semiconductor to be reduced to nanoscale proportions. Such a size reduction will enhance its electronic, magnetic, and optical properties, and thus enable new applications. In the area of nanostructured materials, chalcogenide clusters such as $[Cd_{17}S_4(SPh)_{28}]^{2-}$ (called C1 cluster, the first member of the series of capped supertetrahedral clusters denoted as Cn, $n = 1, 2, 3 \ldots$) and $[Cd_{32}Se_{14}(SePh)_{36}(PPh_3)_4]$ (C2) lie at the extreme lower limit of the size spectrum of nanoparticles.[7] Thus, the optical response of these individual clusters and their self-assembled covalent superlattices may have potential applications in nanoelectronics.

Recent developments in metal chalcogenides have resulted in a number of 4-connected frameworks with topologies related to polymorphs of SiO_2 such as cristobalite and quartz.[5,8–10] However, to our knowledge, no three-dimensional (3D) framework built from 4- and 3-connected cadmium chalcogenide clusters was known prior to this work. Three-connected centers, when present alone, tend to form low-dimensional structures. However, in combination with 4-connected centers, they can form interesting 3D open-framework architectures.[11] Herein we report a novel 3D (3,4)-connected framework material built from $[Cd_{17}S_4(SPhMe\text{-}3)_{28}]^{2-}$ C1 clusters (HSPhMe-3 = 3-methylbenzenethiol).

This material with the formula $[\{(NH_4)_2[Cd_{17}S_4(SPhMe\text{-}3)_{24}(SPhMe\text{-}3)_{4/2}]_3[Cd_{17}S_4(SPhMe\text{-}3)_{24}(SPhMe\text{-}3)_{3/2}(SPhMe\text{-}3)]_4\}_n]$ has the boracite-type topology and exhibits photoelectric behavior. Note that it is difficult to realize oxide-based framework topologies in chalcogenides because of the different bonding geometries surrounding S and O sites. Our research, however, demonstrates that when chalcogenide clusters are used as pseudo-atoms, more diverse oxide-based network topologies become accessible.

Boracite, a magnesium chloroborate ($Mg_3B_7O_{12}Cl$), is an interesting mineral with a (3,4)-connected net[12] based on corner-sharing BO_3 triangles and BO_4 tetrahedra. Boracite and its derivatives are of particular interest because of their polar structures and technological applications related to their unique piezoelectric, pyroelectric, ferroelectric, electro-optical, and nonlinear optical properties.[13]

Although the derivatives of boracite widely occur in borate-based inorganic materials, its topological type is rarely found in non-oxidic 3D frameworks,[14] even though some coordination polymers[15] with boracite-type topology are known. One of our interests is the construction of various spatially organized 3D semiconducting superlattices from clusters of different size.

The material reported here is denoted as CMF-4 (CMF = capped metal–chalcogenide framework) and is synthesized under solvothermal conditions at 85 °C. $Cd(SPhMe\text{-}3)_2$ serves as the source for both Cd^{2+} and SPhMe-3.[16] Thiourea is used as the S^{2-} source. The S^{2-} source is essential for the growth of large clusters whose cores are made of tetrahedrally coordinated S sites, SM_4. The solvent is acetonitrile/water or acetone/water. CMF-4 was obtained as colorless crystals after several weeks. Its structure[17] was determined from single-crystal X-ray diffraction data collected at 150 K on an APEX II diffractometer.

CMF-4 has a rather large I-centered tetragonal unit cell (cell volume > 70000 Å^3) and is formed by 3D assembly of $[Cd_{17}S_4(SPhMe\text{-}3)_{28}]^{2-}$ nanoclusters. Adjacent clusters are joined together through corner-sharing SPhMe-3 groups. The framework composition of the covalent superlattice consists of alternating 4-connected and 3-connected centers in the ratio 3:4, which leads to the overall framework for-

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mula $[\{Cd_{17}S_4(SPhMe\text{-}3)_{24}(SPhMe\text{-}3)_{4/2}\}_3\{Cd_{17}S_4(SPhMe\text{-}3)_{24}(SPhMe\text{-}3)_{3/2}(SPhMe\text{-}3)\}_4]^{2-}$.

The building block is the C1 cluster (Figure 1 a), which contains 17 cadmium sites ($[Cd_{17}S_4(SPhMe\text{-}3)_{28}]^{2-}$). The C1 cluster is the first member in a series of tetrahedral clusters denoted as capped (C) tetrahedral clusters.[8] The core of the C*n* clusters is a regular fragment of the cubic zinc blende type phase (CdS_4 in CMF-4), and the four corners are barrelanoid cages having the characteristics of the hexagonal wurtzite-type phase. Each C1 cluster has three different sulfur sites: four inner μ_4-S^{2-} sites, 24 SPhMe-3 surface ligands and four corner SPhMe-3 groups. C*n* clusters with other types of surface ligands are also known.[2b,5,7a,9–10]

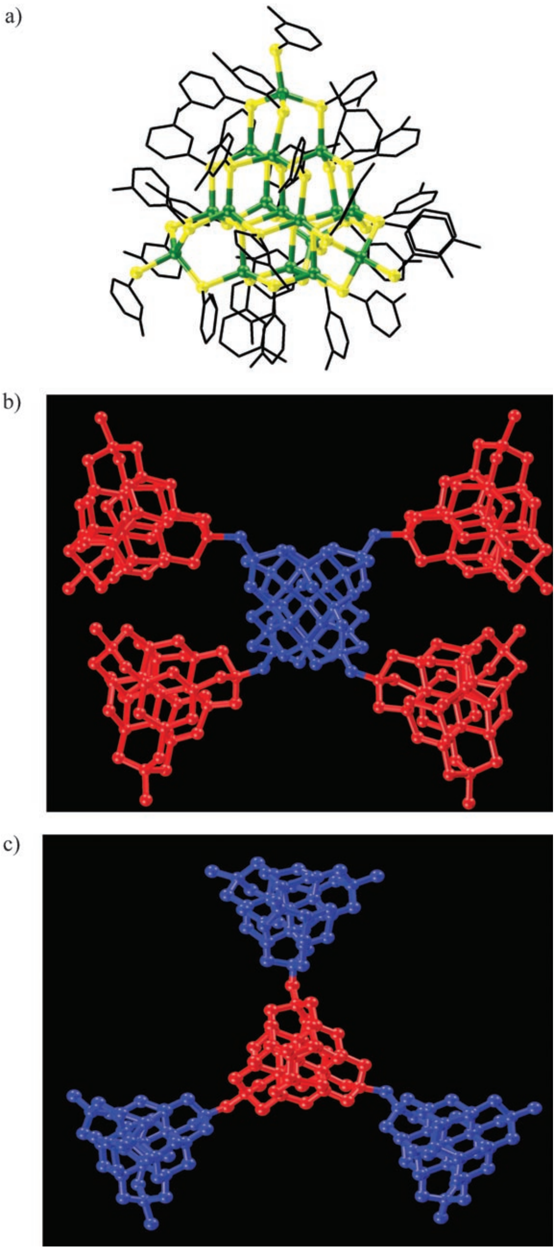

Figure 1. a) The first member C1 of the series of capped supertetrahedral clusters C*n* with composition $[Cd_{17}S_4(SPhMe\text{-}3)_{28}]^{2-}$. b) The C1-cluster-decorated 4-connected node (blue) in CMF-4 showing intercluster connectivity through SPhMe-3 ligands. c) The C1-cluster-decorated 3-connected node (red) in CMF-4. Organic surface ligands in (b) and (c) are omitted for clarity.

Topological analysis reveals that CMF-4 has a (3,4)-connected twofold-interpenetrating framework with boracite-type topology. The C1 clusters (Figure 1 a) exhibit two different connectivities: 4-connected units (blue in Figure 1 b) similar to $\{B\}O_4$ tetrahedra in boracite, and 3-connected units with one terminating corner (red in Figure 1 c) similar to $\{B\}O_3$ triangles in boracite.[18] These two building blocks are assembled to form a 3D framework (Figure 2 a). By considering C1 clusters as pseudotetrahedral atoms, CMF-4 can be reduced to a simple boracite-type net (Figure 2 b). The 4-connected C1 clusters (purple in Figure 2 b) have the Schäfli notation $6_2.6_2.8.8.8.8$, and the 3-connected C1 clusters (red in Figure 2 b) 6.6.6. The overall framework carries negative charges, which are balanced by NH_4^+ cations formed by decomposition of thiourea.

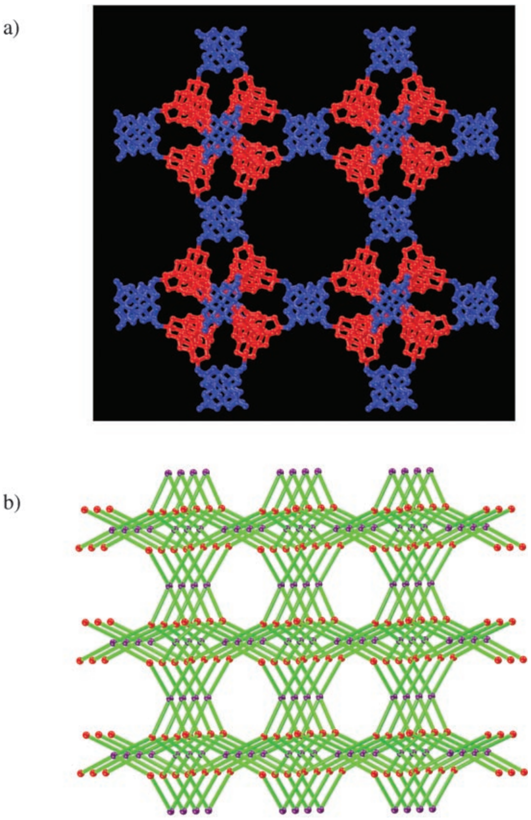

Figure 2. a) 3D framework of CMF-4 showing C1 clusters at tetrahedral and triangular nodes of the boracite net. Blue: 4-connected C1 clusters; red: 3-connected C1 clusters. Organic surface ligands are omitted for clarity. b) A simplified net diagram for boracite based on 4- and 3-connected nodes. Purple: 4-connected nodes, red: 3-connected nodes.

The diffuse-reflectance spectrum of CMF-4 was measured on a Shimadzu UV-3101PC double-beam double-monochromator spectrophotometer by using $BaSO_4$ powder as 100% reflectance reference. The diffuse-reflectance spectrum shows that CMF-4 has the absorption onset at about 430 nm, corresponding to a band gap of 2.88 eV (Figure 3). Thermo-

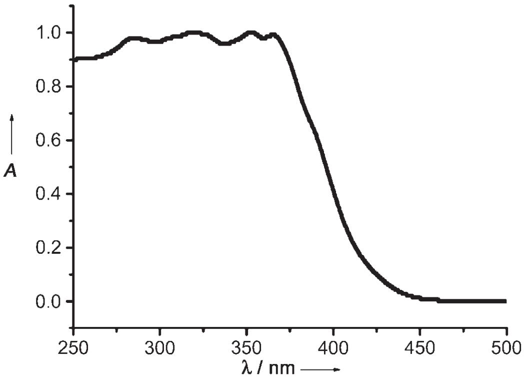

Figure 3. The UV/Vis absorption spectrum of CMF-4.

gravimetric/differential scanning calorimetric analysis, performed on a TA instruments SDT Q600 under flowing N_2 atmosphere, showed that CMF-4 is stable up to 230 °C.

To probe the optical behavior of CMF-4, a photoelectrochemical cell consisting of an SnO_2(F-doped)/CMF-4/nafion electrode, a Pt-foil counterelectrode and a Ag/AgCl (saturated KCl) reference electrode was constructed (a more detailed description is given in the Supporting Information), and the generation of transient photocurrent, in the presence of 1 M Na_2SO_3 aqueous solution as sacrificing agent, was recorded (Figure 4) with a Solartron SI 1287 electrochemical interface instrument. Visible light ($\lambda > 400$ nm) was obtained from a 350-W xenon lamp by using a filter. A sharp photocurrent was generated when the SnO_2(F-doped)/CMF-4/nafion electrode was subjected to excitation with visible light. The photogenerated electrons in CMF-4 are collected by SnO_2 to generate anodic current. Thus, a steady photocurrent can be observed in the CMF-4-based photoelectrochemical cells. The on–off cycles of illumination confirmed the reproducibility of the transient photocurrent response of the CMF-4 film (Figure 4). The I–V characteristic of the SnO_2(F-doped)/CMF-4/nafion electrode shows increased photocurrent generation with increasing anodic potential, and this suggests that the CMF-4 film shows n-type semiconductor behavior.[19]

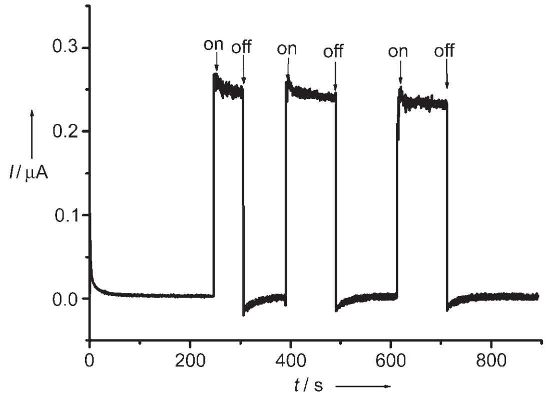

Figure 4. Transient photocurrent response of SnO_2 (F-doped)/CMF-4/nafion at 0 V versus Ag/AgCl (saturated KCl) with and without illumination with visible light. Electrolyte: 1.0 M Na_2SO_3 (pH 12; NaOH was used to adjust the pH value).

The mechanism of photocurrent generation can be explained as follows: Photoinduced charge separation in the CMF-4 film is the primary step, followed by hole transfer to the SO_3^{2-} anion in the solution and electron transfer to the collecting electrode. A steady photocurrent is thus observed in this photoelectrochemical cell.

In conclusion, a novel chalcogenide cluster superlattice with boracite topology (decorated with $[Cd_{17}S_4(SPhMe\text{-}3)_{28}]^{2-}$ C1 clusters) has been synthesized. The assembly of large $[Cd_{17}S_4(SPhMe\text{-}3)_{28}]^{2-}$ C1 clusters into the (3,4)-connected superlattice is unprecedented. The superlattice structure exhibits interesting photoelectric properties. This work represents a step forward towards the synthesis of novel semiconductor superlattices that may be useful for applications in nanoelectronics.

Experimental Section

Typical synthetic procedure for CMF-4: A mixture of $Cd(SPhMe\text{-}3)_2$ (100 mg), thiourea (50 mg), acetone (4.0 g), and water (2.0 g) was placed in a glass vial and stirred for 1 h. The solution was then heated at 85 °C for 2–3 weeks. Pale yellow crystals were obtained in 45 % yield (based on Cd). Elemental analysis (%) calcd: C 41.84, H 3.51, N 0.08; found: C 41.34, H 3.67, N 0.36. FTIR (KBr pellet, Figure S3): $\tilde{\nu} = 3400$ (br, NH_4^+), 3050 (aromatic CH), 1580 (aromatic ring), 1560 (aromatic ring), 1470 (aromatic ring), 1080 (CS), 975 (aromatic ring), 810 (aromatic ring), 705 (aromatic ring), 425 cm^{-1} (CdS).

Preparation of SnO_2 (F-doped)/CMF-4/nafion electrode: A piece of conducting F-doped SnO_2 glass was cleaned by sonication successively in water, acetone, and isopropyl alcohol. CMF-4 (50 mg) was dispersed in an ethanolic solution (1 mL, 1.5 wt %) of nafion and the mixture was thoroughly mixed by ultrasonic agitation for 30 min. This CMF-4 suspension (50 μL) was drop-cast onto a piece of above cleaned and dried F-doped SnO_2 glass. The film was dried in air; the active area of the modified electrode was 0.8 × 1.3 cm. The thickness and morphology of the film were characterized by SEM (Supporting Information). The average thickness of the film was about 15 μm.

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[17] Crystal data for CMF-4, $C_{1288}H_{1296}N_2S_{212}Cd_{119}$, tetragonal, space group $I\bar{4}$, $a = 41.1322(3)$, $c = 42.0792(8)$ Å, $V = 71192.0(15)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.722\ \text{g cm}^{-3}$, $F(000) = 36230$, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 150$ K, $2\theta_{\max} = 35.0°$, 22569 reflections collected, 19646 of which were unique; final GOF = 1.03, $R1 = 0.093$, $wR2 = 0.208$, R indices based on 123948 reflections with $I > 2\sigma(I)$ (refinement on F^2) and 1401 parameters. The high $R(F)$ is in part related to the disorder of surface organic ligands, which limits the resolution of the diffraction data to 35° (data resolution 1.18 Å) in 2θ. However, such data resolution is adequate for resolving the Cd–S cluster structure with a Cd–S distance of about 2.4 Å. CCDC 655254 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..

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