

Two-dimensional organization of $[\text{ZnGe}_3\text{S}_9(\text{H}_2\text{O})]^{4-}$ supertetrahedral clusters templated by a metal complex

Nanfeng Zheng,^a Xianhui Bu^b and Pingyun Feng^{*a}

Received (in Berkeley, CA, USA) 8th February 2005, Accepted 11th April 2005

First published as an Advance Article on the web 22nd April 2005

DOI: 10.1039/b501775k

Under the structure-directing effect of a metal complex formed *in situ*, supertetrahedral $[\text{ZnGe}_3\text{S}_6(\text{H}_2\text{O})(\text{S}_3)_{1/2}]^{1-}$ clusters alternate with tetrahedral $\text{Zn}(\text{H}_2\text{O})(\text{S}_3)_{1/2}^{1-}$ units to form a two-dimensional wide bandgap semiconductor that shows photocatalytic activity for H_2 production from aqueous solution.

Research involving porous chalcogenides has received increasing attention since 1989 and represents a distinct direction for the generation of microporous materials other than oxides and metal-organic frameworks.^{1–9} Through the integration of open framework architecture with semiconducting and photocatalytic properties, chalcogenides could extend applications of open-framework materials beyond those of traditional oxides.^{10–14}

Two traditional approaches in the synthesis of open framework materials involve the use of organic molecules (*e.g.*, protonated amines) or hydrated inorganic cations as structure-directing agents. Both approaches have been successfully extended to the synthesis of chalcogenides.^{7,8} The structure-directing by metal complexes has been recognized as a useful approach for the synthesis of both silicates and phosphates, but for open-framework chalcogenides, few examples containing metal complexes as structure-directing agents have been reported.⁹ Structure-directing by metal complexes is particularly interesting because it opens up the possibility of preparing chiral porous materials by using common chiral metal complexes as structure-directing agents.^{15,16}

Herein we report a layered chalcogenide framework structure (denoted UCR-28) templated by a chiral complex ion formed *in situ*. The structure consists of infinite sulfide sheets terminated at corners by covalently bonded water molecules. UCR-28 is a wide bandgap semiconductor that shows photocatalytic activity for hydrogen production from aqueous solution.

To synthesize UCR-28, 126.9 mg of GeO_2 , 172.3 mg of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 177.4 mg of sulfur and 2.0656 g of tris(2-aminoethyl)amine were mixed and stirred for 20 min in a 23 mL Teflon-lined stainless steel autoclave. After sealing the vessel and heating it at 190 °C for 5 days, colorless crystals of UCR-28 were obtained in a yield of ~79%.

The extended structure of UCR-28 determined from single crystal X-ray diffraction data[†] is shown in Fig. 1. This structure consists of a layered framework with the composition of $[\text{Ge}_3\text{S}_6\text{Zn}(\text{H}_2\text{O})\text{S}_3\text{Zn}(\text{H}_2\text{O})]^{2-}$ and a divalent charge-balancing complex ion (*i.e.*, $\text{Zn}(\text{C}_6\text{N}_4\text{H}_{18})(\text{H}_2\text{O})^{2+}$). There are several unique structural features. One is that water molecules are covalently incorporated onto the two-dimensional sulfide sheets, which is

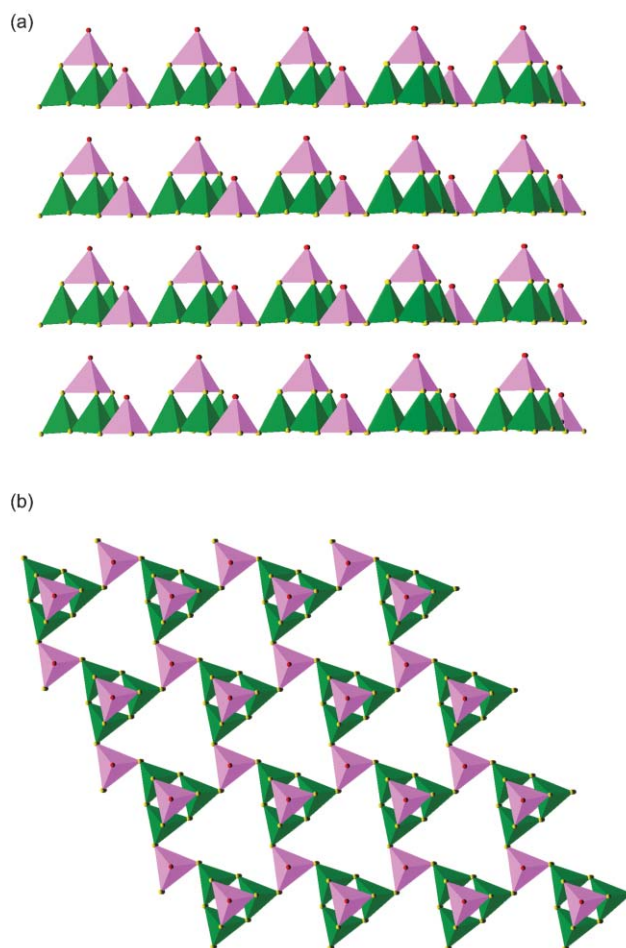


Fig. 1 The side view (a) and top view (b) of the two-dimensional sheet in UCR-28: green tetrahedra, GeS_4 ; pink tetrahedra, $\text{ZnS}_3(\text{H}_2\text{O})$; yellow spheres, S; red spheres, H_2O .

quite uncommon among open-framework sulfides. Another important feature is that a chiral zinc complex ion serves as the structure-directing agent to direct the formation of the sulfide sheet. This demonstrates the feasibility of synthesizing open-framework chalcogenides with various complex ions as charge-balancing and space-filling species. We anticipate that an expansion of this approach, which makes use of pre-formed chiral complex ions, could provide a useful route for the synthesis of chiral open-framework chalcogenides that are quite rare so far.

Within each infinite sheet, each supertetrahedral $[\text{ZnGe}_3\text{S}_6(\text{H}_2\text{O})(\text{S}_3)_{1/2}]^{1-}$ cluster (denoted T2 cluster) is connected to three $\text{Zn}(\text{H}_2\text{O})(\text{S}_3)_{1/2}^{1-}$ tetrahedra (denoted T1 cluster) through

*pingyun.feng@ucr.edu

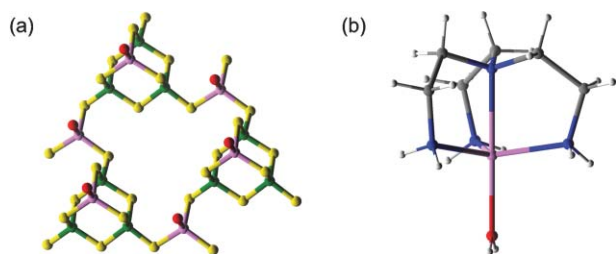


Fig. 2 (a) The 9-member ring window made from the alternating T2 and T1 clusters. (b) The structure of the templating agent in UCR-28: green, Ge; pink, Zn; yellow, S; red, O; blue, N; grey, C; white, H.

corner-sharing sulfurs and *vice versa*. The adamantane-shaped T2 cluster is the 2nd member of the series of supertetrahedral cluster and has the general formula of M_4X_{10} (M and X represent cationic and anionic sites, respectively) for an isolated cluster (Fig. 1).^{2,5,7} Unlike most other chalcogenides in which all four corners of a supertetrahedron are connected to adjacent clusters, both $[\text{Ge}_3\text{S}_9\text{Zn}(\text{H}_2\text{O})^{4-}]$ T2 clusters and $[\text{ZnS}_3(\text{H}_2\text{O})^{4-}]$ T1 clusters are 3-connected due to the corner termination by one water molecule on each zinc site. The alternation of T2 and T1 clusters gives rise to the formation of windows with 9-membered rings (6 Ge^{4+} ions and 3 Zn^{2+} ions) (Fig. 2(a)). All layers are stacked along the *c*-axis in the eclipsed configuration resulting in straight 9-ring channels with an interlayer spacing of 8.37 Å.

Three germaniums and one zinc cation are used to build a T2 cluster. All germanium sites are tetrahedrally coordinated to sulfur atoms with the Ge-S bond length ranging from 2.169(1) to 2.244(1) Å. In comparison, only three sulfur atoms (Zn-S 2.325(1) Å) are bonded to the zinc site because the fourth corner of the Zn site is occupied by one water molecule (Zn-O 2.068(7) Å). The same bonding environment around the Zn site within each T2 cluster is also found for the zinc site within each $[\text{ZnS}_3(\text{H}_2\text{O})^{4-}]$ T1 cluster.

In UCR-28, the divalent $\text{Zn}(\text{C}_6\text{N}_4\text{H}_{18})(\text{H}_2\text{O})^{2+}$ complex ion functions as the structure-directing agent for the formation of the inorganic sheet. In addition to organic amines and pure inorganic cations, the structure direction by complex ions provides an alternative approach to control the formation of framework structures. As shown in Fig. 2(b), the zinc ion in the complex $\text{Zn}(\text{C}_6\text{N}_4\text{H}_{18})(\text{H}_2\text{O})^{2+}$ is trigonal bipyramidal and has a

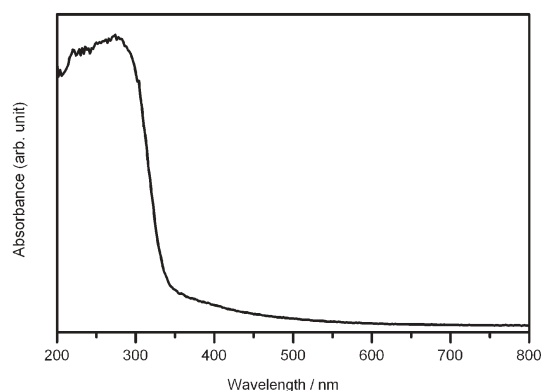


Fig. 3 The diffuse reflection spectrum of UCR-28.

coordination number of five, four from tris(2-aminoethyl)amine ligand and one from water molecule. The ligand water molecule is located near the center of the 9-membered ring. Each 9-ring is built up from three T2 clusters and three T1 tetrahedra and encapsulates one complex molecule so that the negative charge from the sulfide sheet is balanced by the charge on the metal complex. It is of particular interest that the metal complex $\text{Zn}(\text{C}_6\text{N}_4\text{H}_{18})(\text{H}_2\text{O})^{2+}$ is chiral, which is likely responsible for the space group symmetry of the crystal (P3).

The diffuse reflectance spectrum of UCR-28 was measured on a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer by using BaSO_4 powder as 100% reflectance reference. As shown in Fig. 3, optical absorption data derived from the reflectance showed that UCR-28 is a wide gap semiconductor with the adsorption band edge at 360 nm (3.4 eV) accompanied by a shoulder up to 500 nm (2.5 eV). As a semiconductor, UCR-28 exhibited photocatalytic activity for hydrogen production from aqueous solution containing Na_2SO_3 as the sacrificial agent.¹⁷

We thank the support of this work by CSULB (X. B.), the NSF (P. F.), Beckman Foundation (P. F.), and the donors of the Petroleum Research Fund (administered by the ACS) (X. B. and P. F.). P. Y. is an Alfred P. Sloan research fellow and Camille Dreyfus Teacher-Scholar.

Nanfeng Zheng,^a Xianhui Bu^b and Pingyun Feng^{*a}

^aDepartment of Chemistry, University of California, Riverside, California 92521, USA. E-mail: pingyun.feng@ucr.edu; Fax: 01 951 827 4713; Tel: 01 951 827 2043

^bDepartment of Chemistry and Biochemistry, California State University, 1250 Bellflower Blvd., Long Beach, California 90840, USA

Notes and references

† Crystallographic data for UCR-28, $[\text{Ge}_3\text{S}_6\text{Zn}(\text{H}_2\text{O})\text{S}_3\text{Zn}(\text{H}_2\text{O})][(\text{Zn}(\text{C}_6\text{N}_4\text{H}_{18})(\text{H}_2\text{O}))]$, trigonal, space group P3, $a = 9.6014(10)$, $c = 8.3735(13)$ Å, $V = 668.51(14)$ Å³, $Z = 1$. Data collection at 298 K on a SMART 1000 CCD diffractometer with Mo-K α radiation. $2\theta_{\text{max}} = 56.6^\circ$, $R1 = 0.0327$, $wR2 = 0.0560$ for 85 parameters and 1993 reflections with $I > 2\sigma(I)$. Hydrogen atoms for three water molecules are not located or refined. CCDC 262154. See <http://www.rsc.org/suppdata/cc/b5/b501775k/> for crystallographic data in CIF or other electronic format.

- R. L. Bedard, S. T. Wilson, L. D. Vail, J. M. Bennett and E. M. Flanigen, in *Zeolites: Facts, Figures, Future. Proceedings of the 8th International Zeolite Conference*, ed. P. A. Jacobs and R. A. van Santen, Elsevier, Amsterdam, 1989, pp. 375–387.
- C. L. Cahill and J. B. Parise, *J. Chem. Soc., Dalton Trans.*, 2000, 1475.
- S. Dhingra and M. G. Kanatzidis, *Science*, 1992, **258**, 1769.
- R. W. J. Scott, M. J. MacLachlan and G. A. Ozin, *Curr. Opin. Solid State Mater. Sci.*, 1999, **4**, 113.
- H. Li, A. Laine, M. O’Keeffe and O. M. Yaghi, *Science*, 1999, **283**, 1145.
- H. Ahari, A. Lough, S. Petrov, G. A. Ozin and R. L. Bedard, *J. Mater. Chem.*, 1999, **9**, 1263.
- N. Zheng, X. Bu, B. Wang and P. Feng, *Science*, 2002, **298**, 2366.
- N. Zheng, X. Bu and P. Feng, *Nature*, 2003, **426**, 428.
- R. Stahler, C. Nather and W. Bensch, *J. Solid State Chem.*, 2003, **174**, 264.
- E. M. Flanigen, in *Introduction to Zeolite Science and Practice*, ed. H. van Bekkum, E. M. Flanigen and J. C. Jansen, Elsevier, New York, 1991, pp. 13–34.
- M. E. Davis, *Nature*, 2002, **417**, 813.
- X. Bu, N. Zheng and P. Feng, *Chem. Eur. J.*, 2004, **10**, 3356.
- X. Bu, N. Zheng, Y. Li and P. Feng, *J. Am. Chem. Soc.*, 2002, **124**, 12646.
- W. Su, X. Huang, J. Li and H. Fu, *J. Am. Chem. Soc.*, 2002, **124**, 12944.
- K. Morgan, G. Gainsford and N. Milestone, *J. Chem. Soc., Chem. Commun.*, 1995, 425.

16 S. M. Stalder and A. P. Wilkinson, *Chem. Mater.*, 1997, **9**, 2168.

17 The photocatalytic reaction was performed in a Pyrex reaction cell connected to a closed gas evacuation and accumulation system. 0.500 g of UCR-28 was suspended in a 270 ml 0.5 M Na₂SO₃ aqueous solution. After the system was evacuated, about 80 Torr of Ar gas was introduced into the reaction cell. The catalyst suspension was then irradiated by a

300 W Xe lamp equipped with a heat absorbing filter. The amount of hydrogen produced was analyzed using an online gas chromatograph with a thermal conductivity detector (TCD). About 6.5 μmol h⁻¹ g⁻¹ of hydrogen could be produced over UCR-28 without any co-catalyst. For comparison, ZnS was able to produce hydrogen at a rate of 20 μmol h⁻¹ g⁻¹ under similar conditions.