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Hydrazine-hydrothermal method to synthesize three-dimensional chalcogenide framework for photocatalytic hydrogen generation

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ABSTRACT

A novel chalcogenide, $[Mn_2Sb_2S_5(N_2H_4)_3]$ (1), has been synthesized by the hydrazine-hydrothermal method. X-ray crystallography study reveals that the new compound **1** crystallizes in space group $P\bar{1}$ (no. 2) of the triclinic system. The structure features an open neutral three-dimensional framework, where two-dimensional mesh-like inorganic layers are bridged by intra- and inter-layer hydrazine ligands. Both two Mn1 and Mn2 sites adopt distorted octahedral coordination. While two Sb1 and Sb2 sites exhibit two different coordination geometries, the Sb1 site is coordinated with three S atoms to generate a SbS_3 trigonal-pyramidal geometry, and the Sb2 site adopts a SbS_4 trigonal bipyramidal coordination geometry. It has an optical band gap of about ~2.09 eV, which was deduced from the diffuse reflectance spectrum, and displays photocatalytic behaviors under visible light irradiation. Magnetic susceptibility measurements show compound **1** obeys the Curie–Weiss law in the range of 50–300 K.

1. Introduction

Crystalline chalcogenide materials not only have fundamental interests in their diverse structures but also pose significant synthetic challenges and display unique structure–property correlations [1–3]. The potential applications of chalcogenide materials can be found in superconductors [4], field-effect transistors [5], visible-light photocatalysts [6], gas separators [7], nonlinear optical generators [8], photoluminescence [9], photoconductors [10], thermoelectrics [11], ion exchangers [12], fast ion conductors [13], porous materials [14], and magnetism [15]. In particular, a broad range of chalcogenide-based semiconducting materials is being considered for solar energy conversion due to current energy problems. It is believed that high crystallinity and large surface area are two basic requirements for enhanced visible-light-driven photocatalytic activities. At the same time, an appropriate narrow band gap (around 2.0 eV) with the right positions of bands is also very important for photocatalysis. Therefore, finding a good synthetic condition to satisfy the above requirements is a big challenge.

Among the various synthetic methods to prepare chalcogenides [16–23], the solvo(hydro)thermal method has proved to be an efficient way of producing crystalline porous chalcogenide frameworks. In particular, hydrazine is a basic solvent with strong coordination and reduction ability. The use of hydrazine in solvo(hydro)thermal synthesis could be promising to produce novel porous crystalline chalcogenide materials [24–27]. Here, we report the synthesis, structural characterization, optical property, magnetic property, and visible-light photocatalytic behavior of a new three-dimensional neutral hydrazine-bridged chalcogenide framework $[Mn_2Sb_2S_5(N_2H_4)_3]$ (**1**). Note that it is first time that metal-hydrazine chalcogenide chemistry is extended towards Mn/pnictide-hydrazine chalcogenides.

2. Experimental section

2.1. Materials and general methods

All reagents were purchased commercially and used without further purification. Elemental analyses (N, H and S) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. The elemental analyses of Mn, Sb and S have been examined with the aid of an EDX-equipped JEOL/JSM-6360A SEM. The IR spectrum was obtained on a Perkin-Elmer FT-IR spectrophotometer in the 500–4000 cm^{-1} region with a KBr pellet. Thermal stability studies were carried out on a TGA Q500 instrument under N_2 at a heating

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rate of 10 °C/min. Powder X-ray diffraction data were recorded on a Bruker D8 Advance diffractometer with a graphite-monochromatized Cu$K\alpha$ radiation. The operating 2θ angle ranges from 10° to 65°. The DC magnetic susceptibility measurements were made on an MPMS magnetometer at temperatures between 5.0 and 300 K.

2.2. Synthesis

A mixture of Mn (1.0 mmol, 0.055 g), Sb_2S_3 (0.4 mmol, 0.136 g), S (1.0 mmol, 0.032 g), and hydrazine monohydrate (4 mL, 98%) was mixed in a 23 mL Teflon-lined stainless steel autoclave. (*Note: More attention should be paid due to hydrazine monohydrate toxicity and strongly reducing ability.*) The autoclave was sealed and heated at 140 °C for 7 days without any disturbance. Then, the autoclave was taken out and cooled to room temperature at its natural cooling rate. The dark-red crystals **1** were isolated in 70% yield (based on Sb_2S_3), washed several times with deionized water, acetone, and ethanol, and air-dried. The crystals appear to be stable in air for months. Anal. calc. for $Mn_2Sb_2S_5N_6H_{12}$ **1**: H, 1.99%; N, 13.83%; S, 26.31% (calculated). Found: H, 2.13%; N, 14.05%; S, 26.85% (experimental). EDS analysis of Mn/Sb/S ratio in **1**: 1:1:2.4.

2.3. Single-crystal structure determination

A dark-red block of crystal of $0.25 \times 0.20 \times 0.12$ mm^3 from reaction **1** was mounted on a glass fiber. Single crystal X-ray diffraction data were collected on a Bruker APEX II CCD diffractometer equipped with a graphite-monochromatized Mo$K\alpha$ radiation source ($\lambda = 0.71073$ Å) at 293 K. Empirical absorption was performed, and the structure was solved by direct methods and refined with the aid of a SHELX-TL program package. All hydrogen atoms were calculated and refined using a riding model. The anisotropic refinement converged to $R_1 = 0.0693$, $wR_2 = 0.2256$ for $I > 2\sigma(I)$ data. Because of the disorder of the free N_2H_4 molecules, it was impossible to locate them in the final structural refinement and this can account for the relatively high R_1 value. Crystallographic data and structural refinements are summarized in Table 1. Atomic positions and anisotropic displacement parameters are provided in Table 2. Selected bond lengths and angles are listed in Table 3. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. 779023. Copy of this data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/datarequest/cif.

Table 1
Crystallographic data for $Mn_2Sb_2S_5(N_2H_4)_3$.

Empirical formula	$Mn_2Sb_2S_5(N_2H_4)_3$
Formula weight	609.78
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a (Å)	8.814(2)
b (Å)	8.858(2)
c (Å)	8.947(2)
α (deg.)	70.04(3)
β (deg.)	85.98(3)
γ (deg.)	64.07(3)
V (Å^3)	587.9(2)
Z	2
D_{cal} (g/cm^3)	3.264
μ (mm^{-1})	7.493
GOF	1.173
R_1[a]	0.0693
wR_2[b]	0.2256

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2
Atomic positions and equivalent isotropic displacement parameters for $Mn_2Sb_2S_5(N_2H_4)_3$.

Atom	x	y	z	U_{eq} (Å^2)[a]
Sb(1)	0.82148(17)	0.76464(18)	0.30025(16)	0.0145(5)
Sb(2)	1.34105(17)	1.00431(18)	0.15462(16)	0.0138(5)
Mn(1)	0.8799(4)	1.1962(4)	0.0485(4)	0.0163(7)
Mn(2)	0.5455(4)	1.1831(4)	0.4089(4)	0.0162(8)
S(1)	0.8910(7)	0.6845(7)	0.0600(6)	0.0180(11)
S(2)	0.5838(7)	0.6847(7)	0.3626(6)	0.0166(11)
S(3)	0.6598(6)	1.0850(7)	0.1685(6)	0.0136(11)
S(4)	1.1253(7)	0.8921(7)	0.2030(6)	0.0157(11)
S(5)	1.2814(7)	1.1266(7)	0.3726(6)	0.0152(11)
N(1)	0.687(3)	1.493(2)	−0.096(2)	0.026(4)
N(2)	0.801(2)	1.210(3)	0.399(2)	0.022(4)
N(3)	0.402(2)	1.466(2)	0.246(2)	0.021(4)
N(4)	0.856(2)	1.303(2)	0.256(2)	0.019(4)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Bond lengths (Å) and angles (deg.) for $Mn_2Sb_2S_5(N_2H_4)_3$.

Sb(1)–S(3)	2.427(6)	Mn(1)–S(4)#1	2.632(6)
Sb(1)–S(1)	2.445(5)	Mn(1)–S(1)#1	2.651(6)
Sb(1)–S(2)	2.463(5)	Mn(2)–N(3)	2.235(17)
Sb(2)–S(4)	2.457(5)	Mn(2)–N(2)	2.357(18)
Sb(2)–S(5)	2.461(5)	Mn(2)–S(3)	2.569(6)
Sb(2)–S(1)#1	2.734(6)	Mn(2)–S(5)#3	2.602(6)
Sb(2)–S(2)#2	2.778(6)	Mn(2)–S(2)#4	2.644(6)
Mn(1)–N(4)	2.310(19)	Mn(2)–S(5)#5	2.648(6)
Mn(1)–N(1)	2.357(19)	N(1)–N(3)#6	1.46(3)
Mn(1)–S(3)	2.558(6)	N(2)–N(4)	1.45(3)
Mn(1)–S(4)	2.574(6)	N(4)–Mn(1)–S(1)#1	88.8(5)
S(3)–Sb(1)–S(1)	97.60(18)	N(1)–Mn(1)–S(1)#1	83.2(5)
S(3)–Sb(1)–S(2)	98.62(18)	S(3)–Mn(1)–S(1)#1	176.6(2)
S(1)–Sb(1)–S(2)	97.60(18)	S(4)–Mn(1)–S(1)#1	88.0(2)
S(4)–Sb(2)–S(5)	96.49(18)	S(4)#1–Mn(1)–S(1)#1	92.58(19)
S(4)–Sb(2)–S(1)#1	88.57(17)	N(3)–Mn(2)–N(2)	92.2(7)
S(5)–Sb(2)–S(1)#1	93.14(17)	N(3)–Mn(2)–S(3)	90.6(5)
S(4)–Sb(2)–S(2)#2	92.16(17)	N(2)–Mn(2)–S(3)	80.5(5)
S(5)–Sb(2)–S(2)#2	88.92(17)	N(3)–Mn(2)–S(5)#3	171.7(5)
S(1)#1–Sb(2)–S(2)#2	177.72(16)	N(2)–Mn(2)–S(5)#3	84.3(5)
N(4)–Mn(1)–N(1)	84.3(7)	S(3)–Mn(2)–S(5)#3	96.25(19)
N(4)–Mn(1)–S(3)	87.8(5)	N(3)–Mn(2)–S(2)#4	84.1(5)
N(1)–Mn(1)–S(3)	97.0(5)	N(2)–Mn(2)–S(2)#4	99.0(5)
N(4)–Mn(1)–S(4)	92.9(5)	S(3)–Mn(2)–S(2)#4	174.6(2)
N(1)–Mn(1)–S(4)	170.8(5)	S(5)#3–Mn(2)–S(2)#4	88.98(19)
S(3)–Mn(1)–S(4)	91.6(2)	N(3)–Mn(2)–S(5)#5	88.8(5)
N(4)–Mn(1)–S(4)#1	173.4(5)	N(2)–Mn(2)–S(5)#5	168.3(5)
N(1)–Mn(1)–S(4)#1	89.4(5)	S(3)–Mn(2)–S(5)#5	87.93(18)
S(3)–Mn(1)–S(4)#1	90.86(18)	S(5)#3–Mn(2)–S(5)#5	96.13(19)
S(4)–Mn(1)–S(4)#1	93.65(19)	S(2)#4–Mn(2)–S(5)#5	92.66(19)

Symmetry transformations used to generate equivalent atoms:
#1 $-x+2, -y+2, -z$; #2 $x+1, y, z$; #3 $-x+2, -y+2, -z+1$.
#4 $-x+1, -y+2, -z+1$ #5 $x-1, y, z$ #6 $-x+1, -y+3, -z$.

2.4. Optical properties

The optical diffuse reflectance spectra were measured at room temperature on a Perkin-Elmer Lambda 900 UV–vis-NIR spectrometer equipped with an integrating sphere. $BaSO_4$ was used as the reference material, and the polycrystalline samples were ground well before the measurement. The absorption (α/S) data were calculated from the reflectance using the Kubelka–Munk function: $\alpha/S = (1-R)^2/2R$, in which R is the reflectance at a given wavelength, α is the absorption coefficient, and S is the scattering coefficient [28].