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Unsaturated Mn complex decorated hybrid thioarsenates: Syntheses, crystal structures and physical properties

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ABSTRACT

The incorporation of unsaturated $[\text{Mn}(1,2\text{-dap})]^{2+}$, $[\text{Mn}(1,2\text{-dap})_2]^{2+}$, $[\text{Mn}(2,2\text{-bipy})]^{2+}$ (1,2-dap=1,2-diaminopropane) complex cations with thioarsenate anions of $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ and $[\text{As}^{\text{V}}\text{S}_4]^{3-}$ led to three new hybrid manganese thioarsenates, namely, $[\text{Mn}(1,2\text{-dap})_2\text{MnAs}_2\text{S}_6]$ (**1**), $[\text{Mn}(1,2\text{-dap})_2\{\{\text{Mn}(1,2\text{-dap})\}_2\text{As}_2\text{S}_8\}]$ (**2**) and $(\text{NH}_4)[\text{Mn}(2,2\text{-bipy})_2\text{AsS}_4]$ (**3**). In compound **1**, the unsaturated $[\text{Mn}(1,2\text{-dap})]^{2+}$ complexes, $[\text{MnS}_4]^{6-}$ tetrahedra and $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ trigonal-pyramids are condensed to form the 1D $[\text{Mn}(1,2\text{-dap})_2\text{MnAs}_2\text{S}_6]$ chain, whereas compound **2** features 2D layer composed of $[\text{Mn}(1,2\text{-dap})]^{2+}$ and $[\text{Mn}(1,2\text{-dap})_2]^{2+}$ complexes as well as $[\text{As}^{\text{V}}\text{S}_4]^{3-}$ tetrahedral units. For compound **3**, two $[\text{As}^{\text{V}}\text{S}_4]^{3-}$ anions bridge two $[\text{Mn}(2,2\text{-bipy})]^{2+}$ complex cations into a butterfly like $\{\{\text{Mn}(2,2\text{-bipy})\}_2\text{As}_2\text{S}_8\}^{2-}$ anionic unit. Magnetic measurements indicate the ferrimagnetic behavior for compound **1** and antiferromagnetic (AF) behaviors for compounds **2–3**. The UV–vis diffuse-reflectance measurements and electronic structural calculations based on density functional theory (DFT) revealed the title compounds belong to semiconductors with band gaps of 2.63, 2.21, and 1.97 eV, respectively. The narrow band-gap of compound **3** led to the efficient and stable photocatalytic degradation activity over organic pollutant than N-doped P25 under visible light irradiation.

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1. Introduction

In the past several decades, metal thioarsenates have drawn enormous interest because of their fascinating structural diversities and potential applications in many areas such as fast-ion conductivity, absorption, ion exchange, photocatalyst and photoelectric materials [1–12]. Since 1996, solvothermal reaction in polyamine solution has become a versatile route for synthesizing inorganic–organic hybrid thioarsenates. Subsequently, a large amount of thioarsenate secondary building units (SBUs) have been reported and characterized, such as $[\text{As}_2\text{S}_5]^{4-}$, $[\text{As}_3\text{S}_7]^{5-}$, $[\text{As}_4\text{S}_9]^{6-}$, $[\text{As}_3\text{S}_6]^{3-}$ and $[\text{As}_4\text{S}_8]^{4-}$, etc [13–17]. Now, an effective strategy for the development of new thioarsenates is to design and construct new SBUs via incorporation of other heteroatoms into the single metal thioarsenate anionic frameworks, including main group 13, 14 metals as well as transition metals (TM) [18–28]. Generally speaking, the thiophilic d^{10} TM ions (Cu^+ , Ag^+ , Zn^{2+} , Cd^{2+} , Hg^{2+}) are able to form various $[\text{TMS}_x]$ building units

including TMS_2 , TMS_3 , TMS_4 , etc, which further integrate with $[\text{As}_x\text{S}_y]^{n-}$ moieties to form ternary TM–As–S anionic frameworks, whereas the former 3d transition metals, such as Mn^{2+} , Fe^{2+} , Co^{2+} and Ni^{2+} , are favored to be coordinated by chelating amines, leading to $[\text{TM}(\text{amine})_n]^{2+}$ complex cations as counter cations and structure-directing agents. Furthermore, the unsaturated TM complexes can also effectively incorporate the thioarsenate anionic frameworks to form inorganic–organic hybrid thioarsenates via TM–S covalent bonds. Such strategy not only enhances the structural diversities but also integrate the electronic, optical, and magnetic properties of TM ions with the host inorganic frameworks.

Surely, the former 3d transition metals (Mn^{2+} , Fe^{2+} , Co^{2+} and Ni^{2+}) are also able to form $[\text{TMS}_4]$ tetrahedra as building units of inorganic frameworks similar to those of thiophilic d^{10} TM ions, which have been reported in some hybrid chalcogenides [29–39]. Among these former TM ions, Mn^{2+} ion has been proved to be a perfect center metal for the follow reasons: (1) comparing with other former TM ions, the Mn^{2+} with the $3d^5$ half-occupied orbital is more likely to resemble the thiophilic d^{10} ions; (2) the paramagnetic Mn^{2+} ion ($S=5/2$) can convert nonmagnetic parent

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semiconductors to intriguing magnetic materials due to the coupling of the localized magnetic moments with the band electrons through the exchange interactions; (3) the tetrahedral coordinated Mn^{2+} ion acting as recombination center for the excited electron-hole pairs exhibits a strong photoluminescence emission originating from the 3d–3d transition [40].

Up to now, many organic–organic hybrid thioarsenates containing $[\text{MnS}_4]$ tetrahedra, $[\text{MnS}_6]$ octahedra or unsaturated $[\text{TM}(\text{amine})_n]^{2+}$ complexes as building units have been reported with various structures and intriguing magnetic properties. For example, Guo group adopted unsaturated $[\text{Mn}(2,2\text{-bipy})]^{2+}$ complex, $[\text{MnS}_6]$ octahedron, $[\text{As}^{\text{V}}\text{S}_4]^{3-}$ tetrahedron or $[\text{As}_2^{\text{III}}\text{S}_5]^{4-}$ dimer as building units to form a 1D $\text{Mn}_3(2,2\text{-bipy})_3(\text{As}^{\text{V}}\text{S}_4)_2$ neutral wavelike chain and 2D $\text{Mn}_2(2,2\text{-bipy})\text{As}_2\text{S}_5$ layer featuring AF ordered states with Néel temperatures of 19 and 24 K, respectively [41]. $[\text{Mn}(\text{phen})]_3(\text{As}^{\text{V}}\text{S}_4)(\text{As}^{\text{III}}\text{S}_3)$ features a noncentrosymmetric polar packing arrangement based on unsaturated $[\text{Mn}(\text{phen})]^{2+}$ complexes, $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ and $[\text{As}^{\text{V}}\text{S}_4]^{3-}$ units, and exhibit coexistence of antiferromagnetic order and nonlinear optical properties [42]. In addition, there are also many similar hybrid Mn–As–S phases with phen, 2,2-bipy or N_2H_4 as coordination ligands have been characterized including $(\text{CH}_3\text{NH}_3)[\{\text{Mn}(\text{phen})_2(\text{As}^{\text{V}}\text{S}_4)\} \cdot \text{phen}]$, $[\text{Mn}(\text{phen})_2(\text{As}_2^{\text{III}}\text{S}_4)]$, $\{[\text{Mn}(\text{phen})]_3(\text{As}^{\text{III}}\text{S}_3)_2\} \cdot \text{H}_2\text{O}$, $\{[\text{Mn}(2,2\text{-bipy})_2]_2(\text{As}^{\text{V}}\text{S}_4)[\text{As}^{\text{III}}\text{S}(\text{S}_5)]\}$, $[\text{NH}_4]_8[\text{Mn}_2\text{As}_4\text{S}_{16}]$, $[\text{Mn}(\text{NH}_3)_6][\text{Mn}_2\text{As}_2\text{S}_8(\text{N}_2\text{H}_4)_2]$ and $[\text{NH}_4][\text{MnAs}_3\text{S}_6]$, etc [43–49].

Intrigued by the rich structural types and potential physical properties of inorganic–organic hybrid thioarsenates, we undertook systematic studies in Mn–As–S phases with 1,2-dap molecule as ligand, about which much less is known compared with the π -conjugated ligands. Our exploratory studies afforded two new hybrid thioarsenates, namely, $[\text{Mn}(1,2\text{-dap})_2]_2\text{MnAs}_2\text{S}_6$ (**1**), $[\text{Mn}(1,2\text{-dap})_2][\{\text{Mn}(1,2\text{-dap})_2\text{As}_2\text{S}_8\}]$ (**2**). Compound **1** features 1D chain based on $[\text{Mn}(1,2\text{-dap})]^{2+}$ complex and $[\text{MnS}_4]^{6-}$ tetrahedron and $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ trigonal-pyramid, whereas compound **2** shows 2D layer composed of $[\text{Mn}(1,2\text{-dap})]^{2+}$ and $[\text{Mn}(1,2\text{-dap})_2]^{2+}$ complex as well as $[\text{As}^{\text{V}}\text{S}_4]^{3-}$ tetrahedron. The bridging actions of $[\text{As}^{\text{III}}\text{S}_3]^{3-}$ and $[\text{As}^{\text{V}}\text{S}_4]^{3-}$ units lead to the short Mn···Mn distances as well as interesting ferrimagnetic and antiferromagnetic behaviors for compounds **1** and **2**, respectively. Furthermore, we also adopted 2,2-bipy ligand to prepare a new compound of $(\text{NH}_4)[\text{Mn}(2,2\text{-bipy})_2]\text{AsS}_4$ (**3**) with 0D isolated unit and antiferromagnetic ordered state. The UV–vis diffuse-reflectance measurements revealed that the compounds possess narrow band gaps and visible light absorption, and sample **3** exhibits efficient heterogeneous photocatalytic activity under visible light irradiation. Herein, we report their syntheses, crystal structures, band structures, magnetic and photocatalytic properties.

2. Experimental section

2.1. Materials and instruments

All the reagents and solvents except of $[\text{Mn}(2,2\text{-bipy})_3]\text{Cl}_2$ were purchased commercially and used without further purification. N-doped TiO_2 (P25) was synthesized following the previously reported method, that is, by treating commercially available TiO_2 in the NH_3 (67%)/Ar atmosphere at 550 °C for 10 h. Elemental analyses (C, H, N) were performed on a PE2400 II elemental analyzer. A Mettler TGA/SDTA 851 thermal analyzer was used to obtain TGA curves in N_2 with an increasing temperature rate of 10 °C/min^{−1} in the range of 30–800 °C. Optical diffuse reflectance spectra were measured at room temperature with a PE Lambda 900 UV/vis spectrometer in the wavelength range of 200–800 nm. The absorption spectra were calculated from reflectance spectra using the Kubelka-Munk function of $\alpha/S = (1 - R)^2/2R$, where R is the

absorption coefficient and S is the scattering coefficient. X-ray powder diffractions (XRPD) were measured on X'Pert-Pro diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of 5–80°. Magnetic susceptibility measurements were measured by using on a Quantum Design PPMS-9T magnetometer at a field of 1000 Oe in the temperature range of 5–300 K.

2.2. Synthesis of compound 1

A mixture of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (1.0 mmol), As (0.5 mmol), S (2.0 mmol), 1,2-dap (3 mL), glycol (1 mL) and H_2O (1 mL) was sealed in a stainless steel reactor with a 15 mL Teflon liner, and then heated at 160 °C for 5 days and slowly cooled to room temperature at a rate of 0.1 °C/min. Light yellow block-shaped crystals of **1** were found and subsequently determined as $[\text{Mn}(1,2\text{-dap})_2]_2\text{MnAs}_2\text{S}_6$. The crystals were easily collected by hand and washed with distilled water and ethanol (12% yield based on As). Elem. Anal. Calcd for $\text{C}_6\text{N}_4\text{H}_{20}\text{Mn}_3\text{As}_2\text{S}_6$: C, 10.99; H, 3.07; N, 8.55%; found: C, 11.02; H, 3.12; N, 8.49%.

2.3. Synthesis of compound 2

The reagents of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (1.0 mmol), As (0.5 mmol), S (2.5 mmol), 1,2-dap (4 mL) and H_2O (1 mL) were sealed in a stainless steel reactor with a 15-mL Teflon liner, and then reacted in the same condition as that of compound **1**. The product consisted of yellow block-shaped crystals of **2** and a large amount of unknown black powder. The yellow crystals were collected by hand under microscope, and washed with ethanol, dried, and then stored under vacuum (Yield: 21% based on As). Elemental analysis for $\text{C}_{12}\text{N}_8\text{H}_{40}\text{Mn}_3\text{As}_2\text{S}_8$, Calcd: C 16.61%, H 4.65%, N 12.91%; Found: C 16.57%, H 4.60%, N 12.98%.

2.4. Synthesis of compound 3

Compound **3** was synthesized by using solvothermal method at low temperature comparing with those of compounds **1** and **2**. The powder of $[\text{Mn}(2,2\text{-bipy})_3]\text{Cl}_2$ (0.5 mmol), As_2S_3 (0.5 mmol) and S (1.0 mmol) were added to the mixed solvent of acetonitrile (4 mL) and aqueous ammonia (1 mL), and the reaction mixture was kept stirring for one hour, and the mixture was allowed to react at 90 °C for one week. A large amount of red plane-shaped crystals of compound **3** were collected and washed with ethanol, dried, and then stored under vacuum (Yield: 46% based on As). Elem. Anal. Calcd for $\text{C}_{10}\text{N}_3\text{H}_{12}\text{AsMnS}_4$: C, 27.78; H, 2.79; N, 9.72%; found: C, 27.82; H, 2.70; N, 9.70%.

2.5. Crystal structure determination

Single crystals of **1–3** suitable for X-ray analyses were mounted at the apex of a glass fiber for data collection. Data collections for all compounds were performed on a Bruker SMART CCD-based diffractometer (Mo $\text{K}\alpha$ radiation, graphite monochromator) at 293 (2) K. The INTEGRATE program of the APEX2 software was used for data reductions and multi-scan absorption corrections were applied using the SCALE program for area detector. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods with the SHELXS-97 program [50]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms bonded to C and N atoms were located according to theoretical models. Crystallographic data and structural refinements for **1–3** are summarized in Table 1, and important bond lengths are listed in Table 2. Crystallographic data in CIF format for compounds **1–3** have been deposited as CCDC numbers of 1414802, 1414803 and 1414804, respectively.

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