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Two silver chalcogenidoantimonates synthesized in piperazine and their high performances for visible-light driven Cr(VI) reduction



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ABSTRACT

In the synthesis of organic hybrid metal chalcogenides, piperazine (pip) has been widely applied as a template or charge-balancing agent in the structure assembly, but application of piperazine as a solvent to synthesize organic hybrid metal chalcogenides has not been reported. In this work, two new two-dimensional layered organic hybrid silver chalcogenidoantimonates, namely $[pipH_2]_{0.5}[Ag_2SbS_3]$ (1), $[pipH_2]_{0.5}[Ag_2SbSe_3]$ (2), have been synthesized by using piperazine as reaction medium. Both compounds possess the similar honeycombed anionic bilayers, and the biprotonated piperazine cations are resided between the bilayers. Thermal stabilities and optical properties of compounds 1 and 2 have been studied. Moreover, compounds 1 and 2 exhibited excellent photocatalytic activities for reducing aqueous Cr(VI) under visible light irradiation.

1. Introduction

Organic hybrid metal chalcogenides have various structure types due to the combination of organic ligands and metal chalcogen components [1], leading to the promising properties of ion exchange [2-4], photocatalysis [5–7], electrocatalysis [8–10], photoluminescence [11–13], electrochemical energy storage [14–17], etc. These materials are usually synthesized by using relatively mild synthesis methods, such as room temperature solution synthesis [18], hydro(solvo)thermal [19-21], ionothermal [22,23], surfactant-thermal [24-27], and amine-thiol mixed solvothermal method [28,29]. All these synthetic methods involve the utilization of solvents, and the properties of the solvents have significant impacts on the compositions and structures of the as-synthesized organic hybrid metal chalcogenides [30]. On the one hand, the solvent can play the role of dissolving the reactants and mass transfer. On the other hand, a lot of organic amines can participate in the structure assembly, and play the role of charge-balancing or structure-directing agent [31]. Therefore, expanding solvent systems is crucial to the development of organic hybrid metal chalcogenides.

The temperature for the synthesis of organic hybrid metal

chalcogenides by hydro(solvo)thermal method is mostly higher than 100 °C. The melting point of piperazine is 109 °C, and its molecules could easily form hydrogen bonds with metal chalcogen species, so piperazine in molten state can be applied as a good solvent. In addition, piperazine molecule contains two secondary amine groups, which can be monoprotonated or diprotonated in the reaction process, and this variable protonated form enables it to have a higher compatibility with the metal chalcogen frameworks. In addition, piperazine can be easily dissolved in water, which facilitates the separation of the target products from piperazine by washing with water. In the past decades, the solvents used in the synthesis of organic hybrid metal chalcogenides are mainly water and conventional organic solvents, while piperazine were usually applied as an organic ligand to participate in the structure assembly, such as [pipH][GaS₂] [32], [pipH₂][pipH][AsS₄] [28], [pipH₂][Mn₂As₂S₆] [33], [pipH]₂[AgAsS₄] [28] etc. Using piperazine as a solvent to synthesize organic hybrid metal chalcogenides has not been reported. Therefore, due to the promising solvent property of piperazine, it can be used as reaction medium in the preparation of new crystalline organic hybrid metal chalcogenides.

Based on the above assumptions, by using piperazine as a solvent and

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structure directing agent, we synthesized two new silver chalcogenidoantimonates, namely $[pipH_2]_{0.5}[Ag_2SbS_3]$ (1), $[pipH_2]_{0.5}[Ag_2SbSe_3]$ (2). The two compounds are isostructural and feature two-dimensional honeycombed anionic bilayers, where biprotonated piperazine cations act as structure-directing counterions and reside between the bilayers. In addition, both compounds are n-type semiconductors, and exhibit excellent photocatalytic performances for reducing water-soluble Cr(VI) under visible light irradiation.

2. Experimental section

2.1. Materials and general methods

All chemicals were purchased as analytical grade and used without further purification. Elemental analyses (EA) of C, H, and N were performed using a German Elementary Vario EL cube instrument. The mapping analyses of Cu, Ag, Sb, S and Se have been performed on a JEOL JSM-7800F scanning electron microscope. Room-temperature optical diffuse reflectance spectra of powder samples were obtained using a Germany Analytikjena Specord 50 spectrophotometer. Thermogravimetric analyses (TGA) were carried out with a METTLER TOLEDO at a heating rate of 10 °C/min under a nitrogen atmosphere. Powder X-ray diffraction (PXRD) patterns were collected at room temperature on a Rigaku Smartlab diffractometer using CuK α radiation ($\lambda = 1.5406$ Å) in the 2 θ range of 5–65°.

2.2. Synthesis

Synthesis of $[pipH_2]_{0.5}[Ag_2SbS_3]$ (1). A mixture of AgNO₃ (0.99 mmol, 0.168 g), Sb₂S₃ (0.49 mmol, 0.166 g), S (3.94 mmol, 0.126 g) and piperazine (23.22 mmol, 2.000 g) were mixed and sealed in an autoclave equipped with a Teflon liner (25 mL), then heated at 190 °C for 6 days and cooled to room temperature. The products were filtrated and washed several times with ethanol and deionized water to obtain yellow flake-like crystals of 1 with a yield of 44.3% (0.212 g, based on Sb). Elemental analysis calcd (%) for 1: C 5.03%, H 1.26%, N 2.93%; found(%): C 5.17%, H 1.05%, N 2.65%.

Synthesis of $[pipH_2]_{0.5}[Ag_2SbSe_3]$ (2). A mixture of AgNO₃ (0.99 mmol, 0.169 g), Sb (0.50 mmol, 0.061 g), Se (1.59 mmol, 0.126 g) and piperazine (23.57 mmol, 2.030 g) were mixed and sealed in an autoclave equipped with a Teflon liner (25 mL), then heated at 190 °C for 6 days and cooled to room temperature. The products were filtrated and washed several times with ethanol and deionized water to obtain red flake-like crystals of 2 with a yield of 57.1% (0.177 g, based on Sb). Elemental analysis calcd (%) for 2: C 3.88%, H 0.98%, N 2.26%; found(%): C 3.59%, H 0.87%, N 1.95%.

2.3. Single-crystal structure determination

All single-crystal X-ray diffraction data were collected on a Rigaku XtaLAB mini-II CCD diffractometer equipped with graphitemonochromated MoK α radiation ($\lambda = 0.71073$ Å) at room temperature. The crystal structures were solved by direct methods and and refined by full-matrix least-squares on F^2 using the SHELX-2016 program package [34]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Detailed crystallographic data and structure-refinement parameters of compounds 1–2 are summarized in Table 1. The corresponding selected bond lengths and bond angles data are listed in Tables S1–S2 in the Supporting Information (SI).

2.4. Preparation of photoelectrodes

Typical fabrication of working electrode was described as follow: ITO substrates were prepared by immersing ITO electrode in the distilled water, ethanol, and isopropanol by sonication, and then dried in vacuum. 5 mg of fully-grinded sample was added in the mixing solvent of distilled Table 1

Crystallographic data	and structure refinement	for compounds 1–2
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Compound	1	2
Empirical formula	C2H6NAg2SbS3	C2H6NAg2SbSe3
Formula weight	477.75	618.45
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Á	6.3720(13)	6.5588(5)
b/Å	20.439(4)	20.6713(10)
c/Á	6.8395(14)	7.0920(7)
$\alpha/^{\circ}$	90.00	90.00
$\beta/^{\circ}$	117.19(3)	117.539(10)
γ/°	90.00	90.00
$V/Å^3$	792.3(3)	852.58(11)
Ζ	4	4
T/K	293(2)	293(2)
Measured refls.	4827	10087
Independent refls.	1618	2062
R _{int}	0.0842	0.0680
GOF	1.000	1.084
${}^{\mathrm{a}}R_1 \ (I > 2\sigma(I))$	0.0466	0.0467
$^{b}wR(F_{2}) (I > 2\sigma (I))$	0.0770	0.1284

water (200 µL), ethanol (40 µL), and Nafion (10 µL) for 2 h sonication. Then 40 µL of the colloid was taken and dripped onto the ITO substrates with an area of 1×1 cm². Finally, the as-prepared working electrode was dried in vacuum for 3 h.

2.5. Photoelectrochemical measurements

CHI660E electrochemical workstation was used for photoelectrochemical measurements. A three-electrode system was set up by using Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode, ITO electrode coated with target sample as working electrode, and 0.5 M sodium sulfate solution (pH = 7) as electrolyte. A 300 W Xe lamp (PL-X300D) equipped with a cutoff filter was used as the light source ($\lambda \ge 420$ nm).

2.6. Mott-Schottky measurement

The Mott-Schottky plots were also tested by CHI660E electrochemical workstation, and the three-electrode system was set up as above. The Mott-Schottky plots were measured at the frequencies of 250, 500, and 1000 Hz by the standard three-electrode system.

2.7. Photoelectrochemical measurements

The photocatalytic activities of compounds 1 and 2 were tested for the photocatalytic reduction of Cr(VI) under visible light irradiation using a 300 W Xe lamp with a 400 nm cutoff filter. Typically, 50 mg catalyst powder was added into 50 mL Cr(VI) solution with a concentration of 50 mg/L, which was prepared by dissolving K₂Cr₂O₇ into distilled water. Then, the initial pH was adjusted to the desired value (3-9) with 0.1 M NaOH or H₂SO₄. Before illumination, the suspension was magnetically stirred in the dark for 2 h at room temperature to obtain absorption-desorption equilibrium. During illumination, approximately 2 mL of suspension was sampled from the reactor at given time intervals, the photocatalyst was separated from the suspension by centrifugation (8000 rpm, 10 min). Finally, the Cr(VI) content was measured colorimetrically at $\lambda_{max} = 540$ nm using the standard diphenylcarbazide (DPC) method [35]. Furthermore, the stability and repeatability of 1 and 2 were investigated by the photocatalytic reduction of Cr(VI). After each cycle, the photocatalyst was separated from the suspension by centrifugation (8000 rpm, 10 min). Then the photocatalyst was soaked in HNO_3 (pH = 3) aqueous in order to remove Cr(OH)3 deposited on the surface of samples. At last, the photocatalyst was collected by centrifugation (8000 rpm, 10 min) and washed with deionized water and ethanol, dried in vacuum at 60 °C overnight, and continued for a new cycle.

3. Results and discussion

3.1. Synthesis

Crystals of compounds 1 and 2 were synthesized under the similar reaction conditions by reacting AgNO₃, Sb₂S₃ or Sb, S or Se powder, and piperazine at 190 °C for 6 days. They all featured two dimensional anionic bilayers, where biprotonated piperazine cations acted as chargebalanced agent and filled between the bilayers. We have tried four piperazine derivatives instead of piperazine in the synthesis of 1 and 2, including AEP (1-(2-aminoethyl)piperazine), BAPP (1,4-bis(3-aminopropyl)piperazine, N-methylpiperazine, and N-ethylpiperazine. When we used 1-(2-aminoethyl)piperazine (AEP) instead of piperazine as a solvent, the crystals of 1 and 2 could also be obtained. It was clear that AEP can be decomposed to piperazine cations under such reaction conditions [36]. Moreover, in the synthesis of 1, when we used BAPP instead of piperazine as a solvent, black block-like crystals of AgSbS2 (PDF#19-1137) were obtained (Fig. S6). However, when we used N-methylpiperazine or N-ethylpiperazine to replace piperazine in the synthesis of 1, no crystals can be obtained. In the synthesis of 2, when we used BAPP, N-methylpiperazine or N-ethylpiperazine instead of piperazine as a solvent, all these reactions can produce red plate-like crystals. However, due to the poor quality of the crystals, we cannot collect single crystal XRD data to solve the structures. Nevertheless, the PXRD patterns of these red plate-like crystals match well with the simulated PXRD patterns of 2 (Figuer S7), suggesting that the red plate-like crystals may possess the similar inorganic frameworks as that of compound 2. In addition, we also investigated the effect of reaction temperature to the synthesis of 1 and 2. We found that 190 °C was the most suitable temperature for the crystal growth of compounds 1 and 2, since lower yields of the target crystals were obtain at 160 °C, and only a small amount of unknown powder was formed at and below 140 °C.

In order to investigate the effect of viscosity of piperazine to the crystallization of compounds **1** and **2**, we have mixed different auxiliary

solvents with piperazine to reduce the viscosity of the solvents in the reactions. When adding 0.5 mL or 1 mL of H_2O in the syntheses of 1 and 2, the target crystals with good quality can also be produced. However, when adding 2 mL of H_2O in the synthesis of 2, no crystals can be produced. Clearly, adding a small amount of water in the reactions could reduce the viscosity of piperazine, and improve the crystal quality of compounds 1 and 2, while adding too much water in the reaction systems may reduce the concentration of piperazine and hinder the crystallization of 2. What's more, we have tried to add 1 mL of acetonitrile, DMF, methanol, or ethanol in the syntheses of 1 and 2. However, the crystals of 1 and 2 with lower yield and bad quality were obtained, and some unknown powders were also produced, indicating that some side reactions were occurred in the presence of these organic solvents.

3.2. Crystal structure

Single crystal X-ray analysis reveals that both compounds 1 and 2 crystallize in monoclinic space group $P2_1/n$. Due to the isomorphic feature of 1 and 2, only the structure of 1 will be described as an example in detail. The structure of compound 1 is presented as a two-dimensional $[Ag_2SbS_3]_n^n$ anionic layer, with biprotonated piperazine cations in the interlayer voids. The asymmetric unit of 1 contains two Ag atoms, one Sb atom, three S atoms, and half a biprotonated piperazine cation. The Ag atoms adopt two coordination geometry, where Ag(1) atom coordinates with three S atoms to form a Ag(1)S₃ triangular pyramid, Ag(2) atom coordinates with four S atoms to form a Ag(2)S4 tetrahedron. Sb(1) atom coordinates with three S atoms to form a Sb(1)S₃ triangular pyramid. The Sb(1)S₃, Ag(1)S₃ triangular pyramids and Ag(2)S₄ tetrahedron connect with each other via corner-sharing S atoms, and these triangular pyramids and tetrahedrons are arranged in an order of Sb(1)-Ag(1)-Ag(2)-Sb(1) along the c-axis to form a {Ag₂SbS₇} chain (Fig. 1a). Then the adjacent {Ag₂SbS₇} chains connect with each other via corner-sharing S atoms to set up a honeycomb monolayer along the ac-plane. As shown in Fig. 1b, there are three types of six-membered rings in the monolayer,



Fig. 1. (a) The Sb(1)S₃, Ag(1)S₃ triangular pyramids and Ag(2)S₄ tetrahedron connect with each other to form a {Ag₂SbS₇} chain. (b) The {Ag₂SbS₇} chains connect with each other via corner-sharing S atoms to set up a honeycomb monolayer along the *ac*-plane. (c) Two monolayers connect with each other through Ag(2)-S(1) and Ag(1)-Sb(1) bonds to build up a honeycomb-like [Ag₂SbS₃]^{*n*} anionic bilayer. (d) Two-dimensional bilayers of **1** viewed along the *a*-axis, piperazine cations are located between the bilayers. H atoms are omitted for clarity.

and all these six member rings are made up of two Ag atoms, one Sb atom, and three S atoms with different twisting angles. Two such honeycomb-like monolayers connect with each other through Ag(2)-S(1) and Ag(1)-Sb(1) bonds to build up a honeycomb-like $[Ag_2SbS_3]_n^n$ anionic bilayer (Fig. 1c). The center projection of the bilayer structure of compound **1** along the *a*-axis is shown in Fig. 1d, where the biprotonated piperazine cations are served as charge-balancing agents and separate the bilayers. The bond angles of S(2)-Sb(1)-S(1), S(1)-Ag(1)-S(3), S(3)-Ag(2)-S(2) are 101.6(1)°, 101.74(9)°, 105.86(9)°, respectively. The bond lengths of Ag-S and Sb-S are in the ranges of 2.562(3) Å-2.860(4) Å and 2.413(3) Å-2.452(3) Å, respectively. The Ag(1)-Sb(1) bond length is 2.8949(12) Å. Fig. S1 displays the EDX mapping images of **1** and **2**, which approve the even distribution of Ag, Sb, S or Se elements in the crystals.

Actually, there are two types of $[Ag_2SbS_3]_n^{n-}$ anionic bilayers with K⁺ and organic amine cations. The first type of $[Ag_2SbS_3]_n^{n}$ anionic bilayer formed in [enH][Ag₂SbS₃] [37,39] is constructed by two [Ag₂SbS₆] $_{n}^{7n-1}$ anionic monolayers, which are built up by connecting [AgS₃] triangles, [AgS₃] trigonal pyramids, and [SbS₃] trigonal pyramids via corner-sharing S atoms (Fig. S8). Consequently, 6-membered and 10-membered rings are alternately formed in the $[Ag_2SbS_6]_n^{7n}$ anionic monolayer. The second type of $[Ag_2SbS_3]_n^{n-}$ anionic bilayer formed in KAg₂SbS₃ [38] and [enH₂][Ag₄Sb₂S₆] [39] is also constructed by two $[Ag_2SbS_6]_n^{7n-}$ anionic monolayers. However, this type of $[Ag_2SbS_6]_n^{7n-}$ anionic monolayer is set up by connecting distorted [AgS₄] tetrahedra, [AgS₃] trigonal pyramids, and [SbS₃] trigonal pyramids via corner-sharing S atoms, where only 6-membered rings are generated (Fig. S9). In this work, we synthesized two silver chalcogenidoantimonates with molecular formulas of [pipH2]0.5[Ag2SbS3] (1) and $[pipH_2]_{0.5}[Ag_2SbSe_3]$ (2). Both compounds feature $[Ag_2SbQ_3]_n^{n}$ (Q = S, Se) anionic bilayers, which are isostructural to the second type of $[Ag_2SbS_3]_n^{n-}$ anionic bilayers in KAg₂SbS₃ [38] and $[enH_2][Ag_4Sb_2S_6]$ [39]. In the structure of KAg₂SbS₃, the twisted $[Ag_2SbS_3]_n^{n-}$ anionic bilayers are stacked in an AA sequence along the *a*-axis, where K⁺ cations are located between the layers (Fig. S10a). In the structures of $[enH_2]$ [Ag₄Sb₂S₆] and compounds 1–2, the $[Ag_2SbQ_3]_n^{n-}$ anionic bilayers are stacked in an ABA sequence along the *a*-axis, where $[enH_2]^{2+}$ and $[pipH_2]^{2+}$ cations are located between the layers, respectively (Figs. S10b–c).

3.3. PXRD and thermal analyses

Powder X-ray diffraction (PXRD) patterns of compounds **1** and **2** are consistent with their simulated PXRD patterns based on the single-crystal X-ray diffraction data (Fig. S2), indicating that these compounds are pure phase. The differences of peak intensity in the spectrogram may be caused by the preferred orientation effects of powder samples.

The thermal stabilities of compounds **1** and **2** were investigated by thermogravimetric analysis (TGA) from 30 to 800 °C with a heating rate of 10 °C/min under N₂ atmosphere. As shown in Fig. S3, compounds **1** and **2** all experienced a significant weight loss stage, which can be attributed to the release of piperazine molecule and the collapse of anionic framework. Compounds **1** and **2** have similar weight loss curves, which may be due to their structural isomorphism. Specifically, compound **1** showed a total weight loss of 12.58% in the range of 30–330 °C, which corresponds to the loss of half a piperazine molecule (9.62%) and half a H₂S molecule (3.56%) per formula unit. The weight loss of compound **2** between 30 and 420 °C was due to the removal of half a piperazine molecule (6.96%) and half a H₂Se molecule (6.38%) per formula unit.



Fig. 2. (a) Solid-state UV-vis absorption spectra of 1 and 2. (b) Photocurrent responses of 1 and 2. The Mott-Schottky plots of 1 (c) and 2 (d) measured at the frequencies of 250, 500, and 1000 Hz by the standard three-electrode system.

3.4. Optical properties and photocurrent responses

Solid-state UV–vis diffuse reflectance data of compounds 1 and 2 were tested at room temperature and converted to optical absorption spectra by using the Kubelka-Munk function method. The absorption edges shown in Fig. 2a indicates that both compounds are semiconductors with band gaps of 2.07 eV for compound 1, and 1.95 eV for compound 2, respectively, which are consistent with their yellow and red crystal colors.

To further confirm the semiconductor characteristics of compounds **1** and **2**, the corresponding photoelectrochemical properties were investigated as well. A three-electrode photoelectrochemical cell was employed to test the photocurrent response properties of compounds **1** and **2** under visible light irradiation ($\lambda \ge 420$ nm), where the working electrode was built up by coating sample colloid on the ITO conductive glass. By periodically turning the xenon light on and off, the repeatable photocurrent responses of **1** and **2** were observed in Fig. 2b. The photoelectrodes of **1** and **2** can generate photocurrent densities of 430 nA/cm² and 495 nA/cm² with 0.6 V additional biased potential, respectively. The highly repeatable

and stable photocurrent profiles suggest that both compounds are very stable under the illuminating conditions. Mott-Schottky plots of **1** and **2** were measured at the frequencies of 250, 500, and 1000 Hz by using the same three-electrode system (Fig. 2c-d). The positive slopes of the curves further confirm the n-type semiconducting characteristics of these materials, while the flat-band potentials of **1** and **2** can be estimated as -1.09 V and -0.89 V versus Ag/AgCl, respectively.

3.5. Photoreduction of aqueous Cr(VI)

Cr(VI) is a very common heavy metal pollutant in the surface and groundwater. Due to its high solubility, acute toxicity and potential carcinogenicity, it seriously threatens the ecosystem and human health [40]. As an important class of semiconductor materials, crystalline organic hybrid metal chalcogenides are widely investigated in the areas of photocatalytic hydrogen production and degradation of organic dyes. However, there are currently few researches in the photocatalytic reduction of aqueous Cr(VI). The photocatalytic activity of compounds **1** and **2** was evaluated by the photocatalytic reduction of aqueous Cr(VI).



Fig. 3. The effect of initial concentration of Cr(VI) solution, pH of Cr(VI) solution on photocatalytic reduction rate of compounds 1 (a, c) and 2 (b, d). Recycling performance of compounds 1 (e) and 2 (f) in photocatalytic reduction of aqueous Cr(VI) under visible-light irradiation.

under visible light irradiation. Before irradiation, the suspensions were magnetically stirred in darkness for 2h to establish the absorption-desorption equilibrium. As shown in Fig. S4, when the concentration of Cr(VI) solution was 50 mg/L, the concentration of Cr(VI) showed almost no change throughout the process in the absence of photocatalysts at pH = 3. When adding compounds 1 and 2 as photocatalysts, the concentration of Cr(VI) was quickly reduced within 20 min. In the process of photocatalytic reaction, the pH of the solution has a great influence on the photocatalytic effect [41]. The pH of Cr(VI) solution was adjusted by using 0.1 M H₂SO₄ and 0.1 M NaOH solution. Fig. 3a-b shows the activity comparison of photocatalytic reduction of Cr(VI) (50 mg/L) by compounds 1 and 2 under visible light irradiation, while the pH of initial solution was adjusted to 3, 5, 7, 9. Firstly, as the pH of the solution increases, the adsorption rate of the catalyst to Cr(VI) in the solution decreases in the dark. Secondly, when the pH of the solution was 3, both compounds 1 and 2 can completely reduce Cr(VI) within 20 min. Nevertheless, the Cr(VI) reduction efficiency of compounds 1 and 2 decreased with the increase of pH. These experimental phenomena can be ascribed to the following aspects: (i) the surface of photocatalyst would be more positive at lower pH, so increasing the electrostatic attraction of $Cr_2O_7^{2-}$, HCrO₄, and CrO₄²⁻ anions (Cr(VI) exists mainly as CrO_4^{2-} in the aqueous solution with pH value above 7, whereas mostly as $Cr_2O_7^{2-}$ and HCrO₄ in the aqueous solution with pH value below 7) [42]; (ii) H⁺ is essential for the reduction of Cr(VI) according to the following equations:

In acidic solution,

$$Cr_2O_7^{2-} + 14 H^+ + 6 e^- \rightarrow 2 Cr^{3+} + 7H_2O$$
 (1)

$$HCrO_{4}^{-} + 7 H^{+} + 3 e^{-} \rightarrow Cr^{3+} + 4H_{2}O$$
 (2)

In alkaline solution,

$$CrO_4^{2-} + 4H_2O + 3 e^- \rightarrow Cr(OH)_3 + 5 OH^-$$
 (3)

All the above reactions can proceed more favorably in the solutions with lower pH, based on Le Chatelier's principle [43]; (iii) The Nernst reduction potential of $Cr_2O_7^{-2}$ and $HCrO_4$ under acidic conditions (1.36 V vs. NHE) are much higher than that of CrO_4^{-2} under alkaline conditions (-0.13 V vs. NHE) [44]. Thus, compared with CrO_4^{-2} , $Cr_2O_7^{-2}$ and $HCrO_4$ are more liable to be reduced from the viewpoint of thermodynamics. (iv) In a higher pH of solution, more Cr(III) can deposit on the surface of photocatalyst in the form of $Cr(OH)_3$, leading to the reduction of the amount of surface active sites for the adsorption and photocatalytic reactions [45,46]. In addition, we investigated the effect of different initial Cr(VI) concentrations on the photocatalytic reduction performance of photocatalysts (50 mg) under the condition of pH = 3. Even when the initial Cr(VI) concentration was as high as 100 mg/L, compounds 1 and 2 could still reduce 86.14% and 77.76% of Cr(VI) in 60 min under visible light irradiation (Fig. 3c-d), respectively.

Apart from the high Cr(VI) reduction efficiency, sustainability of the catalytic activity is also an important factor in practical applications. Therefore, recycling experiments for the reduction of Cr(VI) under visible light irradiation were conducted at pH = 3. Considering that the reduction product (Cr(III)) may deposit on the catalyst surface [47], photocatalyst was pretreated before the next cycle. In this work, after photocatalytic reduction of Cr(VI), the catalyst powder of 1 and 2 was recycled via sequential centrifugation, separation, washing and drying processes. After centrifugation, the residual catalyst powder was washed repeatedly by HNO_3 (pH = 3) to remove the adsorbed Cr(III). As presented in Fig. 3e-f, at the end of the third cycle, the Cr(VI) reduction percentage of compounds 1 and 2 can still reach 83.2% and 97.8%. Moreover, the recycled samples after three cycles were further investigated by PXRD (Fig. S5), the PXRD patterns of the recycled sample were consistent with the simulated PXRD patterns based on single crystal XRD data, which further proved the stability of compounds 1 and 2 for visible-light driven Cr(VI) reduction.

The element distribution of the crystal surface of compound **2** after each cycle experiment was investigated by EDX mapping analysis. As shown in Fig. S11a, after the first cycle experiment, when using water to wash the catalyst, there were still a lot of reduction products Cr(III) deposited on the catalyst surface. However, when washing the catalyst by HNO₃, the amount of chromium on the catalyst surface was largely decreased (Fig. S11b). We also collected the EDX mapping images of compound **2** after the second cycle experiment (Fig. S12), where the catalysts were washed by water and HNO₃, respectively. Similarly, the chromium content on the catalyst surface washed by HNO₃ is much lower than that of catalyst washed by water. Obviously, the reduction products were deposit on the catalyst surface, while most of the surface sites of the catalyst after each cycle can be free from chromium after washing with HNO₃ (pH = 3). Therefore, the trace amount of chromium on the surface of the catalyst has no great influence on the catalytic performance.

Because O_2 is a potential scavenger for photogenerated electrons, we have examined the effect of the dissolved O_2 levels in the Cr (VI) photoreduction in air-equilibrated and inert (nitrogen saturated) experiments. The dissolved O_2 levels were increased or decreased by pumping air or nitrogen in the Cr(VI) solution, accordingly, the photocatalytic activities of **1** and **2** for reducing Cr(VI) with pH of 3 were studied. As shown in Fig. S13, the dissolved O_2 in the Cr(VI) solution has nearly no influence on the photoreduction efficiency of **1** and **2**. Fig. S13 also shows that compounds **1** and **2** can adsorb nearly 40% of Cr(VI) in the darkness, indicating strong electrostatic interactions between Cr(VI) and the surface of the photocatalysts. Thus, the limited effect of the dissolved O_2 to the photoreduction of Cr(VI) may be ascribed to strong adsorption behavior of Cr(VI) on the crystals of **1** and **2**.

3.6. Possible photocatalytic mechanism

Both compounds 1 and 2 exhibited promising performances for the reduction of Cr(VI) driven by visible light irradiation, then we studied the corresponding mechanism for electron transfer. Since the CB position of a semiconductor was usually inferred by flat band measurements. As shown in Fig. 2c-d, the flat-band potentials of compounds 1 and 2 were estimated from Mott-Schottky measurements with values of -1.09 V and -0.89 V vs Ag/AgCl at pH = 7 (corresponding to -0.89 V and -0.69 V vs NHE), respectively. The slopes of Mott-Schottky plot for 1 and 2 were positive, so n-type behavior can be speculated for compounds 1 and 2. For n-type semiconductors, the CB position is 0.1 V negative than the flat band potential [48,49]. Thus, the CB position of compound 1 was estimated to be -0.99 V vs NHE, and the CB position of compound 2 was estimated to be -0.79 V vs NHE. The band gaps of compounds 1 and 2 are 2.07 eV and 1.95 eV, the VBs of 1 and 2 are calculated to be 1.08 V and 1.16 V vs NHE, respectively. According to the above experimental data and analysis, Fig. 4 shows a proposed mechanism for the photocatalytic reduction of Cr(VI) by compounds 1 and 2. Under visible light irradiation, the catalysts of 1 and 2 can produce photogenerated electrons (e⁻) and holes (h⁺), and then the as-produced photoelectrons could reduce the adsorbed Cr(VI) into Cr(III).

4. Conclusions

In summary, we used piperazine as a solvent to prepare crystalline organic hybrid metal chalcogenides, and two new silver chalcogenidoantimonates were synthesized. Both compounds possess the similar honeycombed anionic bilayers, and the biprotonated piperazine cations are resided between the bilayers. Due to the n-type semiconductivity of compounds 1 and 2, both compounds displayed promising photocatalytic activity for reduction of Cr(VI) under visible light irradiation. Furthermore, compounds 1 and 2 exhibited higher Cr(VI) reducing efficiency in the Cr(VI) aqueous solution with lower initial pH. The photocatalysts of 1 and 2 also showed good stability and recycling performance. The present study proved that piperazine could be used as a promising solvent to synthesize new crystalline organic hybrid metal chalcogenides.



Fig. 4. Schematic diagram of the Cr(VI) reduction reaction mechanism for compounds 1 and 2 under visible light irradiation.

CRediT authorship contribution statement

Huan Wang: Conceptualization, Data curation, Writing – original draft. Ji-Ming Yu: Methodology, Investigation. Ning Wang: Data curation. Lu-Lu Xiao: Data curation. Ji-Peng Yu: Data curation. Qi Xu: Data curation. Bing Zheng: Writing – review & editing. Fang-Fang Cheng: Data curation, Project administration. Wei-Wei Xiong: Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://do i.org/10.1016/j.jssc.2021.122276.

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