Single-layer Ag$_2$S: A two-dimensional bi-directional auxetic semiconductor

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ABSTRACT: Two-dimensional auxetic materials have attracted considerable attention due to their potential applications in medicine, tougher composites, defense and so on. However, they are scare especially at low dimension, as auxetic materials are mainly realized in engineered materials and structures. Here using first-principles calculations, we identify a compelling two-dimensional auxetic material, single-layer Ag$_2$S, which possesses large negative Poisson’s ratios in both in-plane and out-of-plane directions, but anisotropic ultra-low Young’s modulus. Such a coexistence of simultaneous negative Poisson’s ratios in two directions is extremely rare, which is mainly originated from its particular zigzag-shaped buckling structure. In addition, contrary to the previously known metal-shrouded single-layer M$_2$X (M = metal, X = nonmetal), single-layer Ag$_2$S is the first nonmetal-shrouded M$_2$X. Electronic calculations show that it is an indirect-gap semiconductor with gap value of 2.83 eV, and it can be turned to be direct with strain. These intriguing properties make single-layer Ag$_2$S a promising auxetic material in electronics and mechanics.

KEYWORDS: two-dimensional, auxetic material, buckling structure, ultra-low Young’s modulus
Last few years have witnessed the rapid development of two-dimensional (2D) materials.\textsuperscript{1-17} Compelling properties superior to three-dimensional (3D) materials endow them with broad applications in diverse fields. Examples mainly include graphene\textsuperscript{1-3}, phosphorene\textsuperscript{4-6}, hexagonal boron nitride (h-BN)\textsuperscript{7-9}, transition metal chalcogenides (TMCs)\textsuperscript{10-12} and transition metal halides (TMHs)\textsuperscript{13-15}. Among them, single-layer (SL) M\textsubscript{2}X (M = metal, X = nonmetal) have triggered enormous interest due to their promising prospects in sensors, energy storage and spintronics, significantly enriching the family of 2D materials.\textsuperscript{18-20} A vital member in M\textsubscript{2}X is MXene, which can be synthesized by selective etching of the A group from MAX phases. However, the exposed metal elements exhibit high surface activity, tending to absorb atoms or molecules in the ambient environment. And the intrinsic metallic feature also hampers their applications in electronics and optoelectronics. Besides MXene, other conventional SL M\textsubscript{2}X, such as alkaline earth sub-nitrides (Ca\textsubscript{2}N, Sr\textsubscript{2}N and Ba\textsubscript{2}N), suffer from the same problems.\textsuperscript{21-23} Recently, we proposed the first semiconducting SL M\textsubscript{2}X, T-Tl\textsubscript{2}O, with a high carrier mobility at 2017.\textsuperscript{24} Soon afterwards, H-Tl\textsubscript{2}O and Tl\textsubscript{2}S with different phases were reported with a semiconducting nature as well as many interesting behaviors.\textsuperscript{25,26} Currently, all the reported M\textsubscript{2}X possess a metal-shrouded structure, a SL M\textsubscript{2}X with a nonmetal-shrouded structure and a semiconducting characteristic has yet to be reported so far.

Young’s modulus and Poisson’s ratio are important parameters to estimate the material’s mechanical properties. For materials with a positive Poisson’s ratio (PPR), an expansion (shrink) in the transverse direction will occur when a compressive (tensile) strain is acted in the longitudinal direction. Compared with PPR materials, those with unusual negative Poisson’s ratio (NPR), which are referred to as auxetic materials, attract more attention lately due to their intriguing features such as toughness, shear resistance, enhanced sound and vibration absorption.\textsuperscript{27} As a result, NPR materials hold great potential in medicine, tougher composites, defense and many other areas.\textsuperscript{28-30} Although auxetic materials are theoretically allowable, they are mainly realized in traditional engineered materials and structures. 2D auxetic materials with NPR are even more scare. Only several cases, including \textalpha-\textsuperscript{31,32} and \textdelta-\textsuperscript{33} phosphorene, TiN\textsuperscript{34}, Zn\textsubscript{2}C/Cd\textsubscript{2}C\textsuperscript{35,36} and Borophane\textsuperscript{37} are reported, significantly mismatching the great potential of auxetic materials. Therefore, it is desirable to search for new 2D auxetic materials, specially, with large NPR.

In this work, we report the first nonmetal-shrouded M\textsubscript{2}X, SL Ag\textsubscript{2}S. It is a semiconductor with
an indirect band gap of 2.84 eV. SL Ag$_2$S displays a zigzag-shaped buckling structure, which is similar to that of Zn$_2$C and Cd$_2$C, but the latter are metal-shrouded. Such a particular buckling structure of SL Ag$_2$S gives rise to low Young’s modulus in the $x$ direction ($Y_{11}$), indicating its flexibility against strain. Strain engineering can be an effective approach to tune the electronic properties, and the strained systems exhibit high stability when large-scale strains exerted on them. Meanwhile, a direct-indirect-direct transition of the band gap is observed upon increasing the strain from -10% to 25%. More importantly, NPRs are identified in SL Ag$_2$S in both in-plane and out-of-plane directions. As mono-directional NPR is rarely identified, the special bi-directional NPR phenomena is super rare, rendering SL Ag$_2$S as an attractive auxetic material with unique properties and potential applications in nanoelectronics and micromechanics.

**Computational Details.** All structural calculations are performed using density functional theory (DFT) as implemented in the Quantum Espresso package (QE). The generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE) is used for electron exchange-correlation interactions. The cut-off energy is set to 80 Ry. The convergence criteria for energy and force are set to $1 \times 10^{-5}$ eV and 0.01 eV/Å, respectively. The vacuum space along the $z$ direction is set to 20 Å to avoid spurious interactions induced by periodic images. A k-grid of $5 \times 9 \times 1$ is employed for structure relaxation. Calculations of the electronic properties are carried out based on DFT as implemented in the Vienna ab initio simulation package (VASP) code. The Heyd-Scuseria-Ernzerhof (HSE06) functional is used for giving more accurate electronic structures. The phonon calculations are carried out with a $4 \times 4 \times 1$ supercell using the PHONOPY code, which is based on the finite-displacement method. AIMD simulations are performed with a $4 \times 4 \times 1$ supercell at 300 K for 5 ps with a time step of 1 fs.

**Results and Discussion.** Bulk Ag$_2$S is a room-temperature ductile semiconductor. The crystal structure of bulk Ag$_2$S is displayed in Fig. 1(a). It can be viewed as a layered structure in which zigzag-shaped layers are connected by Ag-S bonds [highlighted in green in Fig. 1(a)]. SL Ag$_2$S is constructed according to the zigzag-shaped layer in the bulk structure. The unit cell of SL Ag$_2$S contains two S atoms and four Ag atoms, featuring an orthorhombic lattice with the lattice constant $a$ and $b$ being 6.53 and 4.69 Å, respectively. This structure can be considered as a net made up of two kinds of zigzag Ag-S atomic chains: one is with a large buckle along the $x$ direction, while another is with a small buckle along the $y$ direction. The angle $\alpha$ of Ag-S-Ag along $x$ direction
is 85.57 °, and β along y direction is 148.55 °. It is interesting to find that the configuration of SL Ag2S is similar to that of Zn2C and Cd2C proposed by Meng et al.; see Fig. S1. All of these three 2D materials have zigzag-shaped buckling structures. The difference in structures between them is that, the former is with two S atom layers sandwiching three Ag atom layers, forming a nonmetal-shrouded configuration, but the latter are metal-shrouded. For the experimental feasibility to produce SL Ag2S, it can be achieved by growing a Ag2S layer on suitable substrate materials, similar to the relation between silicene and bulk silicon materials.

For comparison, three other configurations of Ag2S are considered, which are shown in Fig. S2. Configurations I (H-phase) and II (T-phase) are conventional configurations of M2X, which can be found in Tl2O and Tl2S. Configuration III is similar to that of the nonmetal-shrouded Ag2S we proposed here, but with a parallel configuration (P-phase) of atomic chains along y direction. We calculate the energy differences ∆E between these configurations and the nonmetal-shrouded structure, which are presented in Fig. S2. Clearly, the nonmetal-shrouded configuration is more stable than configurations I, II or III in energy. Furthermore, we depict the simulated STM image of Ag2S in Fig. S3(a) as a reference to the experimental observation. Electron localization function (ELF) is calculated to figure out the bonding characteristic in Ag2S. As shown in Fig. S3(b), electrons are mainly localized around S atoms, reflecting ionic bonding characteristic between S and their nearest neighboring Ag atoms.

**Fig. 1** (a) Crystal structure of bulk Ag2S. (b) Top and side views of crystal structure of SL Ag2S. Unit cell and coordination environment of the S atom are also plotted in the rectangles with dashed lines.
To estimate the stability of SL Ag$_2$S, we first calculate its phonon curves, which are shown in Fig. S4(a). Eighteen branches can be seen, among which three are acoustical and fifteen are optical. Only a tiny imaginary frequency (0.17 cm$^{-1}$, <<10 cm$^{-1}$; 1 THz $\sim$ 33 cm$^{-1}$) is found around the $\Gamma$ point, suggesting SL Ag$_2$S is dynamically stable. The maximal frequency is 9.7 THz, implying the soft Ag-S bonding. AIMD simulations are further performed to check the thermal stability of SL Ag$_2$S. As we can see from Fig. S4(b), the free energy of the proposed structure fluctuates slightly during annealing at 300 K for 3 ps. These results are vigorous proofs for the stability of SL Ag$_2$S. Mechanically, a stable 2D structure should meet the Born-Huang criteria given by $C_{11}, C_{22}, C_{66} > 0$; $C_{11} + C_{22} - 2C_{12} > 0$, where $C_{ij}$ are the elastic constants. The calculated values are $C_{11} = 2.87$ N/m, $C_{22} = 63.65$ N/m, $C_{12} = 2.42$ N/m and $C_{66} = 3.49$ N/m for SL Ag$_2$S, fully satisfying the mechanical stability criteria. To confirm the accuracy of the method we adopt, we also calculate the elastic constants of phosphorene and SL SnSe for comparison. Our results of $C_{11} = 103.32$ N/m, $C_{22} = 29.07$ N/m, $C_{12} = 33.19$ N/m, $C_{66} = 21.83$ N/m for phosphorene and $C_{11} = 37.86$ N/m, $C_{22} = 22.07$ N/m, $C_{12} = 18.59$ N/m, $C_{66} = 17.99$ N/m for SnSe agree well with the available theoretical values.

The band structure of SL Ag$_2$S is shown in Fig. 2. SL Ag$_2$S is a semiconductor with an indirect band gap of 2.84 eV. The conduction band minimum (CBM) is located at the A point along the M-Y line, while valence band maximum (VBM) is positioned at the Y point. Ag and S atoms have comparable contributions to VBM and CBM. The lowest conduction band along M-Y line is so flat that the energy difference between A and Y is only 17.3 meV, thus forming a quasi-direct band gap of 2.86 eV. As we can see from the partial density of states (PDOS) plotted in Fig. 2(a), the CBM is mainly composed of Ag-p, Ag-d and S-p states, while VBM is mainly contributed by Ag-d and S-p states. A sharp peak can be seen in the conduction band, which is attributed to the flat band along M-Y line. What’s more, strong s-p and p-d hybridization are evidently shown in the PDOS, stabilizing the Ag$_2$S structure. To further investigate the characteristic of charge distribution, we calculate the partial charge density; see Fig. 2(b). The results can vividly reflect the orbital distribution of the band edge, agreeing well with the information observed in band structure and PDOS.
Unique structures usually lead to intriguing mechanical performance. It is thus of great interest to explore the mechanical behaviors of SL Ag$_2$S by calculating the in-plane Young’s modulus $Y(\theta)$ and Poisson’s ratio $\nu(\theta)$ on the basis of the elastic constants. The Young’s modulus $Y(\theta)$ and Poisson’s ratio $\nu(\theta)$ along the in-plane $\theta$ can be expressed as follows \(^51\):

$$Y(\theta) = \frac{C_{11}C_{22} - C_{12}^2}{C_{11} \sin^4 \theta + A \sin^2 \theta \cos^2 \theta + C_{22} \cos^4 \theta},$$

$$\nu(\theta) = \frac{C_{12} \sin^4 \theta - B \sin^2 \theta \cos^2 \theta + C_{12} \cos^4 \theta}{C_{11} \sin^4 \theta + A \sin^2 \theta \cos^2 \theta + C_{22} \cos^4 \theta},$$

where $A = (C_{11}C_{22} - C_{12}^2)/C_{66} - 2C_{12}$ and $B = C_{11} + C_{22} - (C_{11}C_{22} - C_{12}^2)/C_{66}$. The results are plotted in Fig. 3. Young’s modulus reflects the flexibility or rigidity of materials, and a flexible material harbors a low Young’s modulus. The Young’s modulus $Y(\theta)$ of SL Ag$_2$S exhibits strong anisotropy due to its anisotropic structure, implying the different mechanical responses against the same strain along different directions; see Fig 3(a). The Young’s modulus reaches its highest value of 61.61 N/m at $\theta = 90^\circ$ and 270 $^\circ$ ($Y_{22}$), while the value is as low as 2.78 N/m at $\theta = 0^\circ$ and 180 $^\circ$ ($Y_{11}$). This indicates SL Ag$_2$S has moderate rigidity against deformation along the $y$ direction but becomes much soft along the $x$ direction. As comparison, the Young’s modulus is 1000 N/m for graphene\(^52\), and 330 N/m for MoS$_2$\(^53\). It is noteworthy that the Young’s modulus of SL Ag$_2$S along $x$ direction is
lower than that of most of the previously reported 2D materials and probably the lowest among 2D materials. Such a small value implies extraordinary flexibility of SL Ag$_2$S along $x$ direction, which can be ascribed to its buckled nature. Poisson’s ratio is defined by the ratio of the strain in the transverse direction to that of the longitudinal direction, reflecting the mechanical responses of the system against uniaxial strains. The Poisson’s ratio $\nu(\theta)$ of SL Ag$_2$S also shows obvious anisotropy, with the maximum value being achieved along $y$ direction; see Fig. 3(b). Most remarkably, the rare NPR is obtained in SL Ag$_2$S along diagonal direction and nearby areas and reaches its highest value of -0.12 at 54°, indicating Ag$_2$S is an auxetic material. This in-plane NPR value is significantly larger than that of tetra-silicene (-0.055)$^{54}$, PN (-0.078)$^{49}$, and comparable to that of Be$_3$C$_2$ (-0.16)$^{55}$, AsN (-0.176)$^{49}$ and $\delta$-phosphorene (-0.267)$^{33}$. Such the interesting NPR along diagonal direction is also observed in V-V binary compounds with an $\alpha$ phase.$^{49}$

**Fig. 3** (a) Young’s modulus and (b) Poisson’s ratio of SL Ag$_2$S as a function of the angle $\theta$. $\theta = 0$° corresponds to the $x$ axis. NPR is represented with wine red, while PPR is shown with yellow-black gradient.

As mentioned above, $\alpha$ phase V-V binary compounds harbor in-plane NPR along diagonal direction,$^{49}$ while $\alpha$-phosphorene and $\alpha$ phase group-IV monochalcogenides possess out-of-plane NPR.$^{31,32,50}$ Despite the fact that phosphorene shares isoelectronic and similar structure with its analogues, they behave different mechanic responses. One question then naturally arises: Are there any auxetic materials owning in-plane and out-of-plane NPRs simultaneously? The particular structure of Ag$_2$S urges us to explore the out-of-plane mechanical properties of SL Ag$_2$S extensively. Following the previous studies$^{34,37}$, the strain range of -6%~6% is considered here to estimate the Poisson’s ratio. The response of lattice parameters of SL Ag$_2$S to uniaxial strains are shown in
Fig. 4. Strain is defined as $\varepsilon = (l - l_0)/l_0$, where $\varepsilon = \varepsilon_x, \varepsilon_y, \varepsilon_z$ indicates the relative strain along $x$, $y$ and $z$ directions, respectively; $l = a, b, c$ represents the lattice parameter along $x$, $y$, $z$ directions under strain, respectively; and $l_0 = a_0, b_0, c_0$ is the corresponding lattice constant without strain. The Poisson’s ratio can be obtained by fitting $\varepsilon_{rs} = -\nu_1\varepsilon_s + \nu_2\varepsilon_s^2 + \nu_3\varepsilon_s^3$, where $\varepsilon_s$ and $\varepsilon_{rs}$ indicate strain and resultant strain, and $\nu_1$ could be regarded as the Poisson’s ratio. From Fig. 4(a) we can see that the lattice parameter $b$ decreases linearly with increasing $a$, and vice versa, consisting with the in-plane PPR along $x$ and $y$ directions analyzed above. PPR is also observed between $x$ and perpendicular $z$ direction, with the layer thickness $c$ decreasing with the increase of the lattice parameter $a$. As shown in Fig. 4(b), surprisingly, the layer thickness $c$ increases with increasing of the lattice parameter $b$, indicating that extremely large NPR emerges between $y$ and perpendicular $z$ direction. The NPR reaches up to -0.52, much larger than that of $\alpha$-phosphorene (-0.027)$^{31,32}$ and SnSe (-0.17)$^{50}$, exhibiting pronounced NPR properties.

![Graphs](image)

Fig. 4 The mechanical response of SL Ag$_2$S under uniaxial strain along (a) $x$ and (b) $y$ directions. The evolution of local structure of SL Ag$_2$S during uniaxial tensile strain in the (c) $x$ and (d) $y$ direction.

The origin of the NPR in SL Ag$_2$S can be understood by the competition of two contrary effects: the responses of $\varepsilon_z$ to $\varepsilon_x$ and $\varepsilon_y$. As mentioned above, resulting from the particular structure of SL Ag$_2$S, the compression (expansion) along either $x$ or $y$ direction would give rise to the...
increase (decrease) of the strain along the z direction, and thus increasing (decreasing) the buckling height along the z direction. The strain along z direction induced by $\varepsilon_x$ and $\varepsilon_y$ is donated as $\varepsilon_{z1}$ and $\varepsilon_{z2}$, respectively. And $\varepsilon_z = \varepsilon_{z1} + \varepsilon_{z2} = -A\varepsilon_x - B\varepsilon_y (A, B > 0)$. If A is large enough, the first term will be larger than the second one, i.e. $|\varepsilon_{z1}| > |\varepsilon_{z2}|$. When applying tensile strain along x direction ($\varepsilon_x > 0$), Ag$_2$S will compress along the y direction ($\varepsilon_y < 0$). Considering $\varepsilon_{z1} < 0$, $\varepsilon_{z2} > 0$ and $|\varepsilon_{z1}| > |\varepsilon_{z2}|$, thus $\varepsilon_z < 0$. Therefore, the buckling height of SL Ag$_2$S would decrease with increasing the strain along the x direction, namely, PPR; see Fig. 4(c). When applying tensile strain along y direction ($\varepsilon_y > 0$), Ag$_2$S will compress along the x direction ($\varepsilon_x < 0$). Considering $\varepsilon_{z1} > 0$, $\varepsilon_{z2} < 0$ and $|\varepsilon_{z1}| > |\varepsilon_{z2}|$, thus $\varepsilon_z > 0$. Therefore, the buckling height of SL Ag$_2$S would increase with increasing the strain along the y direction, namely, NPR; see Fig. 4(d). The whole process can also be explained by re-entrant mechanism previously exploited in auxetic foam, where the structure is built with coupling orthogonal hinges, and when one of the hinges opens in a particular direction, the other hinge will close in a vertical direction.\textsuperscript{31,56,57}

We also investigate the effect of defects on Ag$_2$S. Three defect configurations are considered, with defect formation energies of 1.62 eV, 1.20 eV and 1.05 eV respectively for S$_V$ (3×3 supercell with one S vacancy), Ag$_1$V (3×3 supercell with one Ag vacancy) and Ag$_2$V (3×3 supercell with one Ag vacancy). The calculated formation energy suggests that it is hard but still possible to form defects. The optimized structures of defect systems are shown in Fig. S5, from which we can see that the structures maintain their zigzag shape, which are the main reason for negative Poisson’s ratio. Therefore, the effect of defects on auxetic property is negligible.

At last we also investigate the strain engineering on the electronic properties of SL Ag$_2$S. We wish to mention that the discussion on compressive strain here is more about academic interest rather than for practical applications because it is difficult to apply compressive strain in experiment and the compressed structure is prone to form buckling. Here, we only focus on the strain along x direction, and the y direction is fixed. To verify the feasibility of the realization of Ag$_2$S under uniaxial strains along x direction, we first explore their stability by calculating the phonon frequencies. As shown in Fig. S6, only slight imaginary frequency is observed even within the range from -10% to 25%, demonstrating their exceptional stability against strain. It should be noted that the slight imaginary frequency around the $\Gamma$ point is caused by the difficulty to achieve numerical convergence when using first-principles calculations for 2D materials.\textsuperscript{58} Fig. 5 presents
the evolution of band edge level and energy gap of SL Ag₂S under different uniaxial strain along \( x \) direction. The CBM shifts up to higher energy level when strain increases from -10% to 20%, but shifts down to lower energy level from 20% to 25%. Similar variation tendency can be seen in the energy gap \( E_g \) as VBM changes slightly with strain. To further analyze the electronic properties, we plot the band structures of the strained systems in Fig. S7. The CBM is located at the Y point when the compressive strain is exerted. When increasing strain from 0% to 15%, the conduction band at the Y point rises to higher energy level, and the CBM moves to one particular point along the M-Y line. Upon further increasing the tensile strain, the conduction band at the Y point down-shifts to lower energy level, thus the CBM shifts to the Y point again. The VBM is always at the Y point regardless of the magnitude of strain. Therefore, a direct-indirect-direct transition of band gap can be observed as the strain increase from -10% to 25%. The sensitivity to strain and direct-indirect-direct band gap transition renders SL Ag₂S a favorable material in electromechanics.

![Fig. 5]

**Fig. 5** Band edge positions and band gap of SL Ag₂S under uniaxial strains along \( x \) direction. The green, yellow and blue circles represent the CBM, VBM and band gap \( E_g \), respectively. The solid lines are linear fittings to the data.

**Conclusion.** In this work, we propose a novel SL M₂X, Ag₂S. Different from all the previously reported SL M₂X which features a metal-shrouded structure, SL Ag₂S exhibits a nonmetal-shrouded structure. Its stability is confirmed by the phonon spectra, AIMD simulations and elastic constants. SL Ag₂S is an indirect-gap semiconductor. Arising from its particular structure, the zigzag-shaped configuration, SL M₂X shows low Young’s modulus, rendering it as a flexible material against
strain. Significantly, SL Ag$_2$S is an auxetic materials. Moreover, it displays extremely large negative Poisson’s ratios in both in-plane and out-of-plane direction, which are extremely rare in the 2D world. And the underlying mechanism is revealed.

ASSOCIATED CONTENT

Supporting Information
Relevant structural, thermal-dynamical and electronic properties for SL Ag$_2$S.

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Notes

The authors declare no competing financial interests.

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