Realization of vertical metal semiconductor heterostructures via solution phase epitaxy

Xiaoshan Wang¹, Zhiwei Wang¹, Jindong Zhang¹, Xiang Wang¹, Zhipeng Zhang¹, Jialiang Wang¹, Zhaohua Zhu¹, Zhuoyao Li¹, Yao Liu¹, Xuefeng Hu², Junwen Qiu², Guohua Hu³, Bo Chen⁴, Ning Wang¹,⁴, Qiyuan He⁴, Junze Chen⁴, Jiaxu Yan¹, Wei Zhang², Tawfique Hasan³, Shaozhou Li⁵, Hai Li⁶, Hua Zhang⁣, Qiang Wang⁶, Xiao Huang¹ & Wei Huang¹,⁵,⁷

The creation of crystal phase heterostructures of transition metal chalcogenides, e.g., the 1T/2H heterostructures, has led to the formation of metal/semiconductor junctions with low potential barriers. Very differently, post-transition metal chalcogenides are semiconductors regardless of their phases. Herein, we report, based on experimental and simulation results, that alloying between 1T-SnS₂ and 1T-WS₂ induces a charge redistribution in Sn and W to realize metallic Sn₀.₅W₀.₅S₂ nanosheets. These nanosheets are epitaxially deposited on surfaces of semiconducting SnS₂ nanoplates to form vertical heterostructures. The ohmic-like contact formed at the Sn₀.₅W₀.₅S₂/SnS₂ heterointerface affords rapid transport of charge carriers, and allows for the fabrication of fast photodetectors. Such facile charge transfer, combined with a high surface affinity for acetone molecules, further enables their use as highly selective 100 ppb level acetone sensors. Our work suggests that combining compositional and structural control in solution-phase epitaxy holds promises for solution-processible thin-film optoelectronics and sensors.
Heterostructures constructed from layered materials such as graphene, metal chalcogenides and black phosphorus (BP) have aroused particular interest due to their combined advantageous features and the emergence of unusual properties/functions. As a group of the mostly studied layered materials, transition metal chalcogenides (TMCs) like MoS$_2$ and WS$_2$ exist in different crystal phases such as the 2H and 1T polytypes with distinct electronic properties. Their semiconductor-to-metal transition (i.e., 2H-to-1T) can be realized via Li-intercalation, strain engineering, e-beam/laser irradiation or doping/alloying. This attractive feature allows for the formation of 2H/1T (semiconductor/metal) phase junctions that exhibit much reduced contact resistance compared to that of using noble metal contacts (e.g., Au) which normally interface with semiconducting TMCs with large Fermi level misalignment. Besides TMCs, post-TMCs such as SnS$_2$ and InSe are another important group of layered materials, exhibiting attractive electronic and optoelectronic properties for a wide range of applications, including transistors, photodetectors, and sensors. Similar to many other semiconducting materials, the type of metal contact with post-TMCs plays a critical role in tuning their functional performance. However, due to the less metallic nature of post-transition metals, post-TMCs are generally semiconductors regardless of their crystal phases, such as the 2H, 4H, and 1T polytypes. Consequently, contacting post-TMCs with metallic layered materials to achieve low interfacial resistance remains a big challenge.

To date, much effort has been devoted to the preparation of various heterostructures based on layered materials, which display different geometric arrangements such as the lateral and vertical heterostructures. In particular, to prepare vertical heterostructures in which dissimilar layered crystals are stacked one above the other in a pre-designed sequence, solid-state procedures, including dry transfer, chemical vapor deposition (CVD) and chemical vapor transport (CVT) method have mostly been applied. This is because these methods allow good control over the spatial arrangement of the layers as well as the deposition sequence. Compared to these solid-state methods, solution-phase approaches are advantageous in terms of relatively easier procedures, low-cost setups, and most importantly, scalability. However, direct wet-chemical growth of vertical heterostructures of layered metal chalcogenides has thus far been challenging.

In view of their potential applications, heterostructures/heterojunctions such as InSe/graphene, MoTe$_2$/MoS$_2$, MoS$_2$/perovskite, and graphene/MoS$_2$/graphene have recently shown promising performance in photodetectors, due to the improved charge separation/transport and enhanced light adsorption. Meanwhile, development of gas sensors for detection of volatile organic compounds are important in applications such as environmental monitoring and non-invasive diagnosis of diseases based on breath analysis. Chemiresistive sensors based on metal oxides/sulfides have been used for detection of volatile organic compounds, however, high operating temperatures (typically ≥150 °C) are usually required to achieve good sensitivity and selectivity. Very recently, layered materials such as SnS$_2$, WS$_2$ and Ti$_3$C$_2$T$_x$ have demonstrated great potential for room-temperature gas detection. It is expected that creation of heterostructures may realize further improved sensing performance.

In this contribution, nanosheets of SnS$_2$, a typical n-type semiconductor, are used as synthesis templates for the surface deposition of layered Sn$_{0.5}$W$_{0.5}$S$_2$ nanosheets, which show 83% metallic phase, leading to the formation of metal/semiconductor vertical heterostructures. Kelvin probe force microscope (KPFM) and tunneling atomic force microscopy (TUNA) analyses suggest the formation of ohmic-like contact at the Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ interface. The resultant heterostructures are fabricated into chemiresistive sensors to detect acetone at room temperature and exhibit a good selectivity and a minimum detectable concentration down to 100 ppb. The good sensing performance could be attributed to the low charge transfer resistance at the Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ interface that enables a much increased signal-to-noise ratio, and the alloying induced enhancement in surface gas adsorption.

**Results**

**Synthesis and characterizations of Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2**. As a representative post-TMC, SnS$_2$ has been widely studied and applied in phototransistors and sensors for its favorable band structure and relatively high surface electronegativity. Typically, SnS$_2$ nanoplates were synthesized via a hydrothermal reaction with thiourea (CS(NH$_2$)$_2$) and tin tetrachloride hydrate (SnCl$_4$·5H$_2$O) as the precursors for S and Sn, respectively (see the Methods section for the detailed procedure). As shown in the scanning electron microscope (SEM), transmission electron microscope (TEM) and atomic force microscopy (AFM) images in Supplementary Figs. 1 and 2, hexagonal nanoplates with edge lengths ranging from 200 to 700 nm and an average thickness of 43 nm were obtained. As confirmed by the selected area electron diffraction (SAED) and X-ray diffraction (XRD) analyses, the nanoplates are α-SnS$_2$ with a 1T structure (space group P3m1), where $a = 3.65$ and $c = 5.90$ (ICSD no. 42566) (Supplementary Figs. 1c and d). By adding (NH$_4$)$_2$H$_2$(W$_2$O$_7$)$_6$ to the precursors of the aforementioned synthesis solution, alloyed Sn$_1$–xW$_x$S$_2$ nanosheets were in-situ synthesized and hybridized with SnS$_2$ nanosheets as shown in Fig. 1a, b. These heterostructures show an average lateral size of 750 nm (Fig. 1a) and an average thickness of 60 nm (Fig. 1c and Supplementary Fig. 3). The side-view TEM image in Fig. 1d clearly shows a SnS$_2$ nanoplate covered by Sn$_1$–xW$_x$S$_2$ nanosheets on both its basal faces forming a vertical heterostructure. The deposited Sn$_{1-x}$W$_x$S$_2$ nanosheets are typically 6–9 nm in thickness (Supplementary Fig. 4). Energy dispersive X-ray spectroscopy (EDX) mapping of a typical heterostructure reveals the distribution of Sn, W, and S elements (Fig. 1e), in which the center of the heterostructure shows a higher concentration of Sn compared to the edge. EDX line analysis of the cross-section of a typical heterostructure, which was prepared by cutting with focused ion beam (FIB), further indicates that the SnS$_2$ nanoplate was covered by Sn$_{1-x}$W$_x$S$_2$ nanosheets (Fig. 1f). EDX spot analyses on edges of Sn$_{1-x}$W$_x$S$_2$ nanosheets suggest $x = 0.5$, confirming Sn$_{0.5}$W$_{0.5}$S$_2$ nanosheets were obtained (Supplementary Fig. 5).

The structural properties of the heterostructures were investigated with XRD and high resolution TEM (HRTEM) analysis. In the XRD pattern in Fig. 2a, besides the characteristic peaks for 1T-SnS$_2$, two relatively broader peaks observed at 8.9° and 17.8° could be attributed, respectively, to the (001) and (002) planes of Sn$_{0.5}$W$_{0.5}$S$_2$ nanosheets with an enlarged interlayer spacing of about 1.0 nm. The enlarged spacing, which was also observed in side-view HRTEM images (Supplementary Fig. 6), may result from the use of CS(NH$_2$)$_2$ and (NH$_4$)$_2$H$_2$(W$_2$O$_7$)$_6$ in our synthesis, leading to the intercalation of NH$_4^+$ ions in between the adjacent layers. This was also confirmed by X-ray photoelectron spectroscopy (XPS) analysis (Supplementary Fig. 7). The crystal structure of a typical heterostructure was further investigated by taking its SAED pattern. As shown in Fig. 2b, two sets of patterns both along the [001] zone axis show the epitaxial registry. The hexagonal pattern with six inner and six outer spots can be assigned to 1T-SnS$_2$, and the measured (100) lattice spacing is 3.16 Å, in good agreement with the XRD result (Fig. 2a). The other set of pattern for Sn$_{0.5}$W$_{0.5}$S$_2$ shows elongated spots, forming discontinued ring segments. This may
result from the curled structure of the Sn0.5W0.5S2 nanosheets as well as possible misorientation. The measured lattice spacing for Sn0.3W0.7S2 (100) planes was 3.0 Å, corresponding to a lattice parameter of a = 3.46 Å. This reasonably falls in between that of WS2 (a = 3.16 Å) and SnS2 (a = 3.65 Å). Note that the mismatch between the (100) planes of SnS2 and Sn0.3W0.7S2 is 5%, which can be tolerated in van der Waals epitaxial growth of layered materials.36 The top-view HRTEM image in Fig. 2c distinctly shows the relatively darker region for the SnS2 nanoplate covered with Sn0.3W0.7S2, and the brighter region for the periphery Sn0.3W0.7S2 nanosheet. The lattice fringes extend continuously from the SnS2/Sn0.3W0.7S2 center to the Sn0.3W0.7S2 edge, further confirming the epitaxial growth mode. Moiré patterns could be observed in some areas due to the overlap of Sn0.3W0.7S2 and SnS2 at small misorientation angles. For example, as shown in Fig. 2d, a Moiré pattern with a periodicity of 4.0 nm was observed when the Sn0.3W0.7S2 overlayer made a misorientation angle of 3° with SnS2 (see the detailed analysis in Supplementary Fig. 8). Note that the overlapping of two hexagonal lattice patterns normally produces a hexagonal Moiré pattern37, which was not observed in the present work. This may be due to the fact that the Sn0.3W0.7S2 nanosheets showed lattice distortion with varied interlayer spacings (0.6–1.0 nm, Supplementary Fig. 6), and thus were deviated from being perfectly flat on the SnS2 nanoplate. As a result, only short-range line-like Moiré patterns were observed38. High resolution scanning TEM (STEM) images of the edge area of a heterostructure show the 1T-phase-like atomic arrangement of Sn0.3W0.7S2 (Supplementary Fig. 9). It is interesting that zigzag lattice patterns for 1T or Td phases which have been previously observed in TMCs such as WS2 and WTe2,40,41 were not observed in Sn0.3W0.7S2. Based on our density functional theory (DFT) calculation results shown in Supplementary Table 1 and Supplementary Fig. 10, the W–S bonds tend to be shorter than the Sn–S bonds in the alloyed system, resulting in a distortion from the perfect in-plane symmetric 1T lattice. The distorted 1T structure was also reflected in the Raman spectrum in Supplementary Fig. 11, where in addition to the peaks at 310, 351, and 414 cm−1 that correspond to the SnS2-like A1g, WS2-like E2g, and WS2-like A1g modes, respectively, the active modes observed at 171 cm−1 and 224 cm−1 in the lower frequency region could be attributed to distorted 1T-WS2.12,35. The dominant distorted 1T-phased W–S coordination was further confirmed by XPS analysis (Fig. 2e). It has been reported that the XPS band positions of a metal element are sensitive to their oxidation states, coordination geometries, and Fermi levels42,43. Normally in the W 4f spectra, the doublet peaks (32.1 and 34.2 eV) associated with W in the 1T-phased structure are downshifted by 0.6 eV relative to those associated with W in the 2H structure (32.7 and 34.8 eV). The deconvolution of the W 4f bands thus could enable the quantitative estimation of the 1T and 2H phase concentrations.7. No such case, from the deconvoluted peak areas (Fig. 2e), the concentrations of the distorted 1T and 2H phases were calculated to be 83% and 17%, respectively. For the Sn 3d spectrum, the peak positions match well with the 1T-SnS2 structure (Fig. 2f).44. The formation of 1T or distorted 1T structures have been observed previously in TMCs when they were intercalated with alkali metal ions (e.g., Li+, K+ etc.)39,45 or synthesized in the
presence of ammonium containing precursors35 and hydrazine hydrate46. According to previous theoretical calculations, the presence of the positive counterions could cause an increase of the electron density of the d-orbital of the transition metals, leading to the stabilization of the 1T or distorted 1T phase47. Therefore, the realization of the distorted 1T-Sn0.5W0.5S2 in our present work might also be a result of the intercalated NH4+ cations from CS(NH2)2 and (NH4)10H2(W2O7)6 used in the synthesis solution.

Formation process of Sn0.5W0.5S2/SnS2. To investigate the formation process of the Sn0.5W0.5S2/SnS2 vertical heterostructures, intermediate products were collected at different reaction intervals for characterizations. At the beginning of the synthesis process, the precursors, i.e., (NH4)10H2(W2O7)6 and SnCl4·5H2O, reacted to produce Sn(HWO4)2 hydrate46. According to previous theoretical calculations, the formation of W–S bond is less favored compared to that of the Sn–S bond (step 1 in Fig. 3d). As the reaction proceeded further, the oxide of Sn and W with a formula of Sn0.17WO3 based on XRD measurements (Supplementary Table 2). Based on our control experiments, Sn0.17WO3 nanorods could form at 180 °C and decompose at temperatures above 200 °C (Supplementary Fig. 15). This suggests that the Sn0.17WO3 nanorods forming at the beginning of the hydrothermal reaction gradually decomposed at 220 °C (step 1 in Fig. 3d), providing additional Sn and W ions with a high W/Sn ratio (>30) (Supplementary Table 2). Such a high W/Sn ratio could drive the growth of alloyed Sn0.5W0.5S2 nanosheets on the surface of SnS2 even though the formation of W–S bond is less favored compared to that of the Sn–S bond (step 2 in Fig. 3d). In addition, we also tried to extend the Sn–W binary system to Sn–Mo system, but found that, under certain conditions, Sn1+xMo2S2 nanosheets grew epitaxially on SnS2 mainly via the edge growth. This phenomenon might be due to the different synthesis energies required for basal growth or edge growth3, which requires our further investigation.

Electronic properties of Sn0.5W0.5S2/SnS2. Alloying has been a powerful approach to tune the bandgaps of TMCs or to achieve their semiconductor-to-metal transition9,52. However, alloying between layered TMC and post-TMC has not been reported so far, and thus the electronic properties of such alloys could be of great interest for potential applications. DFT calculations were performed to understand the electronic properties of the distorted 1T-Sn0.5W0.5S2 deposited on 1T-SnS2 with and without NH4+ intercalation. The detailed results of the optimized crystal structures, calculated Bader charges, band structures and density of states (DOS) are shown in Fig. 4, Supplementary Figs 16 and 17 and Supplementary Table 1. In contrast to a five-layer semiconducting 1T-SnS2 which shows no DOS at the Fermi level (Fig. 4b), a four-layer distorted 1T-Sn0.5W0.5S2 on a monolayer...
IT-SnS2 exhibits intrinsic metallic behavior with observable DOS at the Fermi level, dominantly contributed from the W and S atoms and slightly from the Sn atoms (Fig. 4d). The calculated Bader charge of W atoms in distorted 1T-Sn0.5W0.5S2 is 0.20 e higher compared to that in 1T-WS2, whereas the Bader charge of Sn atoms in distorted 1T-Sn0.5W0.5S2 is 0.10 e lower compared to that in 1T-SnS2 (Fig. 4a, c and Supplementary Fig. 16). This suggests a charge redistribution in the Sn0.5W0.5S2 alloy by charge transfer from W to Sn atoms. Similarly, the distorted 1T-Sn0.5W0.5S2 with intercalated NH4+ ions (20 mol%) also shows the metallic behavior (Supplementary Fig. 17). To experimentally verify the calculated results, the electronic properties of the SnS2 nanoplates and Sn0.5W0.5S2/SnS2 heterostructures were measured by fabrication of back-gated thin film field effect transistors (Supplementary Fig. 18). The drain current (I_d) vs. drain-source voltage (V_ds) curves at varied gate voltages reveal that the SnS2 nanoplates are typical n-type semiconductors (Supplementary Fig. 18c, d) suggesting the metallic charge transport through the Sn0.5W0.5S2 nanosheets, consistent with the theoretical predictions.

To examine the interface property between a SnS2 nanoplate and the surface deposited Sn0.5W0.5S2/SnS2, its surface potential, which correlates to its work function, was analyzed by KPFM in air. A PtIr tip was used as the probe, and a SiO2/Si substrate sputtered with Au/Cr with a theoretical work function (ϕ_Au) of 5.100 eV was used as the potential reference. The 2D potential image of a typical Sn0.5W0.5S2/SnS2 heterostructure is shown in Fig. 5a, where the color variation reflects the local surface potential difference (ΔV = ϕ_Au − ϕ_sample) (details on the calculation of the surface potentials are given in the Methods section). It can be seen that the surface potential of the Sn0.5W0.5S2/SnS2 heterostructure is 0.029 V lower than that of Au to give an estimated work function of 5.071 eV (Fig. 5a). On the other hand, an SnS2 nanoplate exhibits a work function of 5.110 eV (Fig. 5b). The decrease in surface potential after deposition of Sn0.5W0.5S2 on SnS2 suggests that the metallic Sn0.5W0.5S2 possesses a lower work function than that of the n-type SnS2. Although based on DFT calculations, the work function of distorted 1T-Sn0.5W0.5S2 is 5.62 eV which is much higher than that of SnS2, it can be substantially lowered to 2.87 eV by introducing an NH4+ intercalation with a molar concentration of about 20% (Supplementary Table 1). Such work function modulation induced by doping or chemical absorbates has also been reported previously. This also explains why the experimentally measured work function of Sn0.5W0.5S2 nanosheets with partial NH4+ intercalation was lower than that of SnS2. Therefore, an ohmic contact should form at the Sn0.5W0.5S2/SnS2 heterointerface (Fig. 5c), affording a low charge transfer resistance. This was further confirmed by measuring I–V curves on individual SnS2 nanoplates or Sn0.5W0.5S2/SnS2 heterostructures deposited on highly oriented pyrolytic graphite (HOPG) with TUNA (Fig. 5d, e). The I–V curve for a SnS2 nanoplate is highly asymmetric and the onset of the current rectification is at 3.50 V (Fig. 5d), indicating the presence of Schottky barrier at the PtIr tip/n-type SnS2 interface, provided that the work function for PtIr, HOPG, and SnS2 is 5.50, 4.60, and 5.11 eV, respectively. In sharp contrast, the I–V curve for Sn0.5W0.5S2/SnS2 is almost linear and symmetric with respect to 0 V, suggesting that the contact at SnS2/Sn0.5W0.5S2 interface is ohmic-like (Fig. 5e).

**Sn0.5W0.5S2/SnS2 for photodetectors.** The advantage of the facile charge transport across the ohmic-like heterointerfaces was demonstrated in fabrication of thin film photodetectors based on the Sn0.5W0.5S2/SnS2 heterostructures. Figure 6a shows the I–V curves of the device under 405 nm laser illumination with power...
intensity varied from 0.45 to 1.05 mW. A clear rise of the photocurrent with increasing illumination intensity was observed, indicating the effective conversion of photon flux to photo-generated carriers. In addition, the Sn0.5W0.5S2/SnS2 photodetector showed symmetric and linear I–V plots, which is in sharp contrast to the non-linear I–V curves observed for SnS2-based device (Supplementary Fig. 19a). This further indicates the low resistance contact formed between the semiconducting and metallic components in Sn0.5W0.5S2/SnS2. The temporal photoresponse of the photodetectors was measured as well as shown in Fig. 6b, c and Supplementary Figs. 19b, c. The Sn0.5W0.5S2/SnS2 photodetector showed an abrupt rise of photocurrent with a fast response time of 42.1 ms (defined as the time required to increase 90% from the minimum to maximum current density), which is comparable and outperforms some previously reported TMC based photodetectors 58,59. This value is also about 50 times shorter than that of the SnS2-based photodetector (2.10 s) (Supplementary Fig. 19c). Such markedly shortened response time suggests the rapid transport of charge carriers across the Sn0.5W0.5S2/SnS2 heterointerfaces60,61. Note that a relatively large dark current and thus a much reduced on/off ratio were observed for the Sn0.5W0.5S2/SnS2-based device as compared with the SnS2 device. This was due to the metallic nature of the Sn0.5W0.5S2 nanosheets. The similar phenomenon was reported previously in photodetectors based on graphene composite62,63.

Sn0.5W0.5S2/SnS2 for gas sensing. The presence of a metallic component in a thin film channel may pose some limitation to its optoelectronic performance, such as the relatively large dark current observed in the aforementioned Sn0.5W0.5S2/SnS2 photodetector. However, the metallic structure might become an advantage for applications like sensors. As another proof of concept demonstration of the advantage of solution-processible functional materials, the Sn0.5W0.5S2/SnS2 heterostructures were deposited on Au interdigitated electrodes to fabricate chemiresistive gas sensors for detection of volatile organic compounds such as acetone, which is a potential biomarker for diabetes and lung cancer64. For comparison, SnS2-based gas sensors were also fabricated. The response–recovery curves of the gas sensors were measured under gas flows with increasing concentrations (typically 0.1–50 ppm) at room temperature (Fig. 7a, b and Supplementary Figs. 20 and 21). Taking sensing of acetone for example, the resistance of the Sn0.5W0.5S2/SnS2 sensor decreased upon exposure to acetone and the decrease in resistance (ΔR = R₄ – R₀) with increasing acetone concentration (Fig. 7a, b and Supplementary Fig. 20). A minimum detectable concentration of 0.1 ppm was achieved. This is 20 times lower compared to that of the sensor based on SnS2, which only afforded a minimum detectable concentration of 2 ppm (Supplementary Fig. 21), and to the best of our knowledge, outperforms other reported metal sulfide/oxide chemiresistive acetone sensors. More importantly, our sensor
showed the best sensitivity (i.e., sensing response, $\Delta R/R_0$) at 100 ppb levels among all reported chemiresistive sensors operating at room temperature (Supplementary Table 3). Furthermore, as shown in Supplementary Fig. 22, a typical Sn$_0.5$W$_0.5$S$_2$/SnS$_2$ sensor was repeatedly exposed to 1 ppm acetone and then back to N$_2$ gas for 10 cycles and showed an almost constant sensing response of 1.88 ± 0.07% (by taking standard deviation of the results from 10 cycles), indicating its good repeatability.
The improved sensitivity after deposition of Sn$_{0.5}$W$_{0.5}$S$_2$ nanosheets on SnS$_2$ nanoplates could be attributed to the following reasons. First, the formation of an ohmic-like contact between Sn$_{0.5}$W$_{0.5}$S$_2$ and SnS$_2$ that allowed rapid charge transfer across the metal–semiconductor interface partly led to a 35 times reduction in background noise and thus a much higher signal to noise (S/N) ratio (Supplementary Fig. 23) 27. Second, it can be noted that, the response/recovery time of the Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ gas sensor was longer than that of the SnS$_2$ gas sensor (Fig. 7a and Supplementary Fig. 21), pointing to a chemical adsorption-related sensing pathway 64,65. To confirm this, we calculated the adsorption energy of acetone on the different sensing materials (Fig. 7c). The adsorption energy of acetone on Sn$_{0.5}$W$_{0.5}$S$_2$ is 2.37 eV which is much larger compared to that on SnS$_2$ (0.40 eV). This indicates that acetone molecules interact more strongly with Sn$_{0.5}$W$_{0.5}$S$_2$. It is worth noting that the NH$_4$+-intercalated Sn$_{0.5}$W$_{0.5}$S$_2$ nanosheets towards acetone, with the adsorption energy slightly reduced by 0.09 eV. As further shown in Fig. 7d, there is an obvious charge accumulation on Sn$_{0.5}$W$_{0.5}$S$_2$ due to charge transfer from the absorbed acetone molecule. Third, one of the advantages of using low-dimensional materials in gas sensing as compared with bulk crystals is their large specific surface areas, which are beneficial for providing large interfaces for channel–gas interaction 25. Indeed, the deposition of wrinkled Sn$_{0.5}$W$_{0.5}$S$_2$ nanosheets on SnS$_2$ nanoplates increased the specific surface area from typically 6.25 to 11.37 m$^2$/g based on the Brunauer–Emmett–Teller (BET) measurements as shown in Supplementary Fig. 24. However, in spite of the beneficial effects from the large specific surface area of the wrinkled Sn$_{0.5}$W$_{0.5}$S$_2$ nanosheets and their strong interaction with acetone, increasing the amount of Sn$_{0.5}$W$_{0.5}$S$_2$ nanosheets on SnS$_2$ did not further improve the sensing performance, but on the contrary, led to poorer sensitivity with a minimal detectable concentration of only 1 ppm (Supplementary Fig. 25). This suggests that the concentration of the metallic phase present in the hybrid sensing film should not be too high, otherwise, the gas-induced doping effect on the semiconducting SnS$_2$ would be substantially weakened. Therefore, the presence of the semiconductor/metal heterostructures with a low charge transfer barrier, combined with sufficient active surfaces for strong gas adsorption are important in achieving low sensitivity in our thin film based gas sensors.

The selectivity of the Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ sensor was also investigated by comparing its sensing response towards acetone with other electron donating gases like diethyl ether and propanal, neutral gas like toluene, and electron withdrawing gas like NO$_2$ (Fig. 7e, Supplementary Fig. 26). The response of the Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ sensor towards diethyl ether and propanal was 10 times lower compared to that towards acetone at 2 ppm. This is largely due to the weaker electron donating ability of diethyl ether and propanal compared to that of acetone (Fig. 7e). Under the exposure of toluene, the sensor showed no response. In sharp contrast, when responding to NO$_2$, an electron withdrawing gas, the sensor showed increased resistance (Fig. 7e, Supplementary Fig. 26e), agreeing with the fact that SnS$_2$ is an n-type semiconductor (Supplementary Fig. 18b).
Discussion

The epitaxial growth of metallic Sn$_{0.5}$W$_{0.5}$S$_2$ nanosheets on the surfaces of SnS$_2$ nanoplates was realized via a solution-phase epitaxial deposition process. Importantly, an alloyed metal oxide (i.e., Sn$_{0.17}$W$_2$O$_7$) was identified as an intermediate product which formed at 180°C and decomposed subsequently at 220°C to provide additional Sn and W ions with a high W/Sn ratio of about 30. We proposed that this high W/Sn concentration could drive the formation of alloyed Sn$_{0.5}$W$_{0.5}$S$_2$ nanosheets despite the fact that the formation of Sn–S bond requires less energy compared to that of the W–S bond. Although 1T-SnS$_2$ is a semiconductor, alloyed Sn$_{0.5}$W$_{0.5}$S$_2$ showed 83% distorted 1T structure, which is metal-like as predicted by theoretical calculations. KPFM and TUNA measurements on a Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ heterostructure suggested the formation of omnic-like contact at the heterointerface, resulting in a low charge transfer resistance. The rapid charge transport at the Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ heterointerface allowed for the fabrication of fast photodetector with a short response time of 42 ms. Additionally, when the Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ heterostructures were fabricated into thin films for gas sensing, a much-enhanced signal-to-noise ratio was achieved partly due to the presence of metallic Sn$_{0.5}$W$_{0.5}$S$_2$ layers. Furthermore, Sn$_{0.5}$W$_{0.5}$S$_2$ showed much enhanced surface adsorption of acetone than SnS$_2$ based on theoretical calculations. As a consequence, selective and sensitive detection of acetone was achieved with an ultralow minimum detectable concentration of 100 ppb at room temperature. This, combined with large sensing area and high-yield preparation of functional hybrid nanomaterials, meets demonstrates a promising way towards the facile, economic and high-yield preparation of functional hybrid nanomaterials. Synthesis of layered materials through alloying among elements with distinct electronic and chemical properties is expected to bring about more materials and unusual phenomena.

Methods

Materials. Ammonium tungstate hydrate ((NH$_4$)$_{10}$H$_2$(W$_2$O$_7$)$_6$, 99.99%), ammonium molybdate tetrahydrate ((NH$_4$)$_2$MoO$_4$·4H$_2$O, 99.0%), thiouria (CS(NH)$_2$, 99.0%) and tin tetrachloride hydrate (SnCl$_4$·2H$_2$O, 99.9%) were purchased from Sigma-Aldrich (Shanghai, China). Ethanol (C$_2$H$_5$OH, ACS, 99.9%) was purchased from J&K chemical (Shanghai, China). The gaseous analytes (CH$_3$COCH$_3$, (CH$_3$CH$_2$)$_2$O, CH$_3$CH$_2$CHO, C$_6$H$_5$CH$_3$, and NO$_2$) which were diluted with N$_2$ gas were puriﬁed using Milli-Q3 System (Millipore, France).

Preparation of SnS$_2$ nanoplates. In a typical process, 0.25 mmol of SnCl$_2$·2H$_2$O and 3.75 mmol of CS(NH)$_2$ were dissolved in 19.45 mL DI water and stirred for 2 h to form a homogeneous solution. This solution was transferrred to a 25 mL Teflon-lined stainless steel autoclave, heated to 220°C in an electrical oven and then maintained at this temperature for 12 h before being cooled down naturally to room temperature. The obtained product was centrifuged at 8000 rpm for 10 min, and the precipitate was washed with DI water for three times before further characterization.

Preparation of Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ heterostructures. In a typical process, 0.25 mmol of (NH$_4$)$_2$H$_2$(W$_2$O$_7$)$_6$, 7.5 mmol of CS(NH)$_2$, and 0.5–0.625 mmol of SnCl$_2$·2H$_2$O were dissolved in 19.45 mL DI water and stirred at 80°C for 2 h to form a homogeneous solution. This solution was then transferred to a 25 mL Teflon-lined stainless steel autoclave, heated to 220°C in an electrical oven and then maintained at this temperature for 60 h before being cooled down naturally to room temperature. The obtained product was centrifuged at 8000 rpm for 10 min, and the precipitate was washed with DI water for three times before further characterization.

Characterizations. Scanning electron microscope (SEM, JEM, JSM-7800FS, Japan), transmission electron microscope (TEM, JEM, 2100 Plus, Japan) and high resolution transmission electron microscope (HRTEM, JEM, 2100 F, Japan) coupled with energy dispersive X-ray (EDX) spectroscopy were used to investigate the compositional, morphological and structural features of the samples. X-ray diffraction (XRD, Rigaku SmartLab, Japan) was performed using CuKa radiation (λ = 1.54 Å). X-ray photodetector spectroscopy (XPS, PHI 5000 VersaProbe, Japan) measurements were conducted on the different metal sulfide nanomaterials, and the binding energies were corrected for specimen charging effects using the C 1s level at 284.6 eV as the reference. Raman spectra (Horiba HR800, France) of the samples were collected with a 532 nm laser. Semiconducto parameter analyzer (Tektronix Keithley 4200, America) and probe station (Lake Shore TTPX, America) were used to investigate the semiconductors heterostructures properties of the samples. A commercial atomic force microscopy (AFM, Dimension ICON with Nanoscope V controller, Bruker) was used to investigate the electrical properties of the individual nanomaterials in air. Inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700x, America) was used to measure the concentration of Sn and W ions in the synthesis solution. Brunauer–Emmett–Teller (BET, Micromeritics, ASAP2460, USA) measurements were carried out to determine the specific surface area and pore size distribution of various samples.

Semiconducting property characterization. After Au (50 nm)/Cr (30 nm) drain and source electrodes were deposited onto a SiO$_2$ (285 nm)/Si substrate via thermal evaporation through a shadow mask, SnS$_2$ nanoplates or Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ heterostructures were in-wafer were drop-casted onto the substrate, aligning the channel to the contact and drain source electrodes with a channel length of 11 μm. The semiconducting properties of the channel material were then characterized using a 5×5×2400 semiconductors characterization system operating at 77 K in vacuum (5×10⁻¹⁶ Torr).

KPFM and TUNA measurements. After Au (50 nm)/Cr (30 nm) was coated onto a SiO$_2$ (285 nm)/Si substrate via thermal evaporation, SnS$_2$ nanoplates or Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ heterostructures were in-wafer were drop-casted onto the substrate. A KPFM (Dimension ICON with Nanoscope V controller, Bruker) was then used to characterize the surface potential of the SnS$_2$ nanoplates or Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ heterostructures at ambient conditions. The contact potential difference between the tip (PtIr) and the sample surface ($V_{CPD}$), which is also referred to as the surface potential can be calculated by using the following equations:

$$\Delta V_{CPD} = \frac{1}{e} (\phi_t - \phi_e)$$

$$\Delta V_{CPD} = \Delta V_{CPD}(film) - \Delta V_{CPD}(substrate)$$

where $\phi_e$, $\phi_s$, and $\phi_f$ represent the work functions of the probe tip, the substrate, and the sample film, respectively.

Fabrication of photodetector and photoresponse measurement. Au (15 nm in thickness) interdigitated electrodes with a 10 μm spacing were deposited onto a SiO$_2$ (300 nm)/Si substrate via magnetron sputtering through a shadow mask. After that, 0.5 μL of a concentrated dispersion (6.0 mg/mL) of Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ heterostructures was drop-casted on the electrodes. The current–voltage (I–V) characteristics of individual SnS$_2$ nanoplates or Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ heterostructures were measured using the C 1 s level at 285 nm/µm substrate via thermal evaporation through a shadow mask, SnS$_2$ nanoplates or Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ heterostructures were in-wafer were drop-casted onto the substrate, aligning the channel to the contact and drain source electrodes with a channel length of 11 μm. The semiconducting properties of the channel material were then characterized using a 5×5×2400 semiconductors characterization system operating at 77 K in vacuum (5×10⁻¹⁶ Torr).

Fabrication of chemiresistive sensors and gas sensing tests. Chemiresistive gas sensors were fabricated based on SnS$_2$ nanoparticles or Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ heterostructures for sensing of various gases, including CH$_3$COOH, CH$_3$COCH$_3$, CH$_3$CH$_2$OH, CH$_3$CH$_2$CHO, CH$_3$CH$_2$NH$_2$, and NO$_2$. Typically, a drop of 100 μL aqueous solution containing 10 mM as-prepared SnS$_2$ or Sn$_{0.5}$W$_{0.5}$S$_2$/SnS$_2$ was drop-casted onto an Au interdigitated electrode (with 0.1 mm spacing over a 2 × 1 cm$^2$ area, Changshun Mega Borui Technology Co., Ltd) and then dried in oven at 60 °C. The gas sensing test was performed in an air-tight chamber with electrical feedthroughs at room temperature (25 °C). A constant current was applied to the sensor electrode, and the variation of the sensor resistance was monitored and recorded with the changes in the gas environment using a data acquisition system (34972A, Agilent) with a 20 channel multiplexer (34901A, Agilent). A typical sensing measurement cycle consisted of three sequential steps: (1) a dried N$_2$ flow was introduced into the chamber to record a baseline resistance ($R_0$); (2) a target gas, e.g., acetone, balanced in N$_2$ was introduced, and the concentration increased (0.1–30 ppm) with...
progressive cycles; and (3) when the resistance of the sensor reached equilibrium in the target gas ($R_d$), the target gas was replaced by N$_2$ to allow the resistance of the sensor to return to $R_0$. All gas flows were set at 300 sccm, precisely controlled by using mass-flow controllers.

**Computational methods.** All the computations were performed with Vienna Ab initio simulation package (VASP) which is based on the density functional theory (DFT)66,67. The exchange-correlation interaction uses the general gradient approximation (GGA) formulated by Perdew–Burke–Ernzerhof (PBE)68. All electron interactions were described with projector augmented wave (PAW) pseudo potentials. Long-range dispersion corrections have been considered within the DFT-D2 method. The dispersion coefficient $C_6$ and van der Waals radius $R_{vdW}$ for W and Sn were used in our DFT-D2 method were taken from previous reports68,69. The scale factor $S_6$ was set to 0.75 because the GGA-PBE function was employed. An 11 × 11 k-point mesh was used for the interaction of the Brillouin-zone. The cutoff energy for the plane wave basis set was restricted to 400 eV, and a vacuum region of at least 12 Å was used in building the slab models. The convergence threshold was set as $10^{-5}$ eV in energy and 0.02 eV/Å in force, respectively. As shown in Fig. 4c, a four-layer 1T-Sn$_0.5$W$_0.5$S$_2$ on a monolayer 1T-SnS$_2$ was constructed with a 2 × 2 supercell, which contains 24 Sn, 16 W and 80 S atoms, respectively. Three NH$_4^+$ ions were introduced in the four-layer 1T-Sn$_0.5$W$_0.5$S$_2$ on a monolayer 1T-SnS$_2$ system (Supplementary Fig. 10). All atoms in the structure were fully relaxed to optimize without any restriction, and the convergence threshold was set as $10^{-5}$ eV in energy and 0.02 eV/Å in force, respectively. The optimized lattice constants and work functions ($\Phi$) were summarized in Supplementary Table 1. The experimental lattice constant ($a = 3.46$ Å) was used in DFT calculations for the in-plane periodicity of the four-layer 1T-Sn$_0.5$W$_0.5$S$_2$ on a monolayer 1T-SnS$_2$ without and with intercalated NH$_4^+$ ions. To evaluate the stability of the adsorption of the acetone molecule on a three-layer 1T-SnS$_2$ and three-layer 1T-SnW$_0.5$S$_2$ without and with intercalated NH$_4^+$ ions (each system contains a 4 × 4 supercell), the adsorption was defined by $\Delta E_{ac}=E_{acetone}+E_{substrate} - E_{acetone-substrate}$ (where $E_{acetone-substrate}$ is the total energy of the acetone/substrate compound systems, whereas $E_{acetone}$ and $E_{substrate}$ are the energy of the isolated acetone molecule, and the total energies of upper two-layer relaxed and bottom-layer fixed 1T-SnS$_2$ or distorted 1T-SnW$_0.5$S$_2$ without or with intercalated NH$_4^+$ ions systems, respectively). VESTA was used for preparation of the structure models60.

**Data availability**

The data that support the findings of this study are available from the corresponding author on request.

Received: 27 January 2018 Accepted: 1 August 2018

**References**

1. Liu, Y. et al. Van der Waals heterostructures and devices. Nat. Rev. Mater. 1, 16042–16058 (2016).
2. Cho, S. et al. Phase patterning for ohmic homojunction contact in MoTe$_2$. Nat. Commun. 3, 649–658 (2015).
3. Gong, Y. et al. Vertical and in-plane heterostructures from WS$_2$/MoS$_2$. Nat. Commun. 13, 1133–1142 (2014).
4. Chhowalla, M. et al. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. Nat. Chem. 5, 263–275 (2013).
5. Loan, P. T. et al. Graphene/MoS$_2$ heterostructures for ultrasensitive detection of DNA hybridisation. Adv. Mater. 26, 4838–4844 (2014).
6. Chen, X. et al. High-quality sandwiched black phosphorus heterostructure and its quantum oscillations. Nat. Commun. 6, 7315 (2015).
7. Acker, M., Voiry, D. & Chhowalla, M. Metallic 1T phase MoS$_2$ nanosheets as supercapacitor electrode materials. Nat. Nanotechnol. 10, 313–318 (2015).
8. Song, S. et al. Room temperature semiconductor-metal transition of MoTe$_2$ thin films engineered by strain. Nano Lett. 16, 188–193 (2016).
9. Rhodes, D. et al. Engineering the structural and electronic phases of MoTe$_2$ through W substitution. Nano Lett. 17, 1616–1622 (2017).
10. Kappera, R. et al. Phase-engineered low-resistance contacts for ultrathin MoS$_2$. Nat. Mater. 13, 1128–1134 (2014).
11. Yang, Z. et al. Wafer-scale synthesis of high-quality semiconducting two-dimensional layered InSe with broadband photoresponse. ACS Nano 11, 4225–4236 (2017).
12. Ou, J. Z. et al. Physiosorption-based charge transfer in two-dimensional Sn$_2$S$_3$ for selective and reversible NO$_2$ gas sensing. ACS Nano 9, 10313–10323 (2015).
13. Stage, J. et al. High electron mobility, quantum Hall effect and anomalous optical response in atomically thin InSe. Nat. Nanotechnol. 12, 223–227 (2017).
14. Huang, Y. et al. Tin disulfide—an emerging layered metal dichalcogenide semiconductor: materials properties and device characteristics. ACS Nano 8, 10743–10755 (2014).
15. Hu, X. et al. Phase-controlled synthesis and photocatalytic properties of SnS$_2$, SnS$_2$, and Sn$_2$S$_3$ heterostructures nanocrystals. Mater. Res. Bull. 48, 2325–2332 (2013).
16. Pourbahram, A. & Chhowalla, M. Phase engineering of transition metal dichalcogenides. Chem. Soc. Rev. 44, 2702–2712 (2015).
17. Zhang, Z. et al. Hierarchical assembly of ultrathin hexagonal Sn$_2$S$_3$ nanosheets onto electropun TiO$_2$ nanofibers: enhanced photocatalytic activity based on photoinduced interfacial charge transfer. Nano Lett. 5, 606–618 (2013).

**NATURE COMMUNICATIONS | DOI: 10.1038/s41467-018-06053-z | www.nature.com/naturecommunications
45. Zak, A. et al. Alkali metal intercalated fullerene-like MS₂ (M = W, Mo) nanoparticles and their properties. J. Am. Chem. Soc. 124, 4747–4758 (2002).
46. Li, H. et al. Amorphous nickel–cobalt complexes hybridized with 1T-phase molybdenum disulfide via hydrazine-induced phase transformation for water splitting. Nat. Commun. 8, 15377 (2017).
47. Cheng, Y. et al. Origin of the phase transition in lithiated molybdenum disulfide. ACS Nano 8, 11447–11453 (2014).
48. Patra, B., Chudasama, A. Synthesis, characterization and application of an inorganic organic material: p-chlorophenol anchored onto zirconium tungsten bronze crystal. Bull. Mater. Sci. 24, 265–271 (2001).
49. Xu, X. L., Schmalle, H. W. & Ginter, J. R. Crystal structure of a hexagonal tin tungsten bronze prepared by a mild reaction. Solid State Ion. 76, 221–228 (1995).
50. Albert, C. F. & Geoffroy, W. Advanced inorganic chemistry: a comprehensive text. 3rd ed. (John Wiley, New York, 1972).
51. Lv, Y. Y. et al. Composition and temperature-dependent phase transition in miscible Moₓ₋ₓWₓTe₂ single crystals. Sci. Rep. 7, 44587 (2017).
52. Gong, Y. et al. Band gap engineering and layer-by-layer mapping of selenium-doped molybdenum disulfide. Nano Lett. 14, 442–449 (2014).
53. Wu, M., Cao, C. & Jiang, J. Z. Light non-metallic atom (B, N, O and F)-doped graphene: a first-principles study. Nanotechnology 21, 255202 (2010).
54. Katagiri, Y. et al. Gate-tunable atomaically thin lateral MoS₂ Schottky junction patterned by electron beam. Nano Lett. 16, 3788–3794 (2016).
55. Yu, Y.-J. et al. Tuning the graphene work function by electric field effect. Nano Lett. 9, 3430–3434 (2009).
56. Su, W. S., Chen, Y. F., Hsiao, C. L. & Tu, L. W. Lateral and vertical two-dimensional layered topological insulator heterostructures. Adv. Mater. 28, 2801–2809 (2016).
57. Li, Y. et al. Ultrathin photodetectors based on monolayer MoS₂. Nat. Nanotechnol. 8, 497–501 (2013).
58. Shim, J. et al. High-performance 2D rhenumium disulfide (ReS₂) transistors and photodetectors by oxygen plasma treatment. Adv. Mater. 28, 6985–6992 (2016).
59. Song, X. et al. Boosting two-dimensional MoS₂/CaPbBr₃ photodetectors via enhanced light absorbance and interface carrier separation. ACS Appl. Mater. Interfaces 10, 2801–2809 (2018).
60. Ma, C. et al. Heterostructured WS₂/CH₃NH₃PbI₃ photoconductors with suppressed dark current and enhanced photodetectivity. Adv. Mater. 28, 3683–3689 (2016).
61. Lee, Y. et al. High-performance perovskite–graphene hybrid photodetector. Adv. Mater. 27, 41–46 (2015).
62. Dang, V. Q. et al. Methylammonium lead iodide perovskite–graphene hybrid channels in flexible broadband phototransistors. Carbon 105, 353–361 (2016).
63. Kim, J. S., Yoo, H. W., Choi, H. O. & Jung, H. T. Tunable volatile organic compounds sensor by using thiolated ligand conjugation on MoS₂. Nano Lett. 14, 5941–5947 (2014).
64. Calvi, A., Ferrari, A., Shudel, L., Goldoni, A. & Modesti, S. Recognizing physiosorption and chemiosorption in carbon nanotubes as sensors by double exponential fitting of the response. Sensors 16, 731–739 (2016).
65. Liu, X. et al. Segregation growth of graphene on Cu–Ni alloy for precise layer control. J. Phys. Chem. C. 115, 11976–11982 (2011).
66. Sanville, E., Kenny, S. D., Smith, R. & Henkelman, G. Improved grid-based algorithm for bader charge allocation. J. Comput. Chem. 28, 899–908 (2007).
67. Bucko, T., Hafner, J., Lebegue, S. & Angyan, J. I. Improved description of the structure of molecular and layered crystals: Ab initio DFT calculations with van der Waals corrections. J. Phys. Chem. A 114, 11814–11824 (2010).
68. Grimme, S. Semipirical GGA-type density functional constructed with a long-range dispersion correction. J. Comput. Chem. 27, 1787–1799 (2006).
69. Momma, K. & Izumi, F. VESTA3 for three-dimensional visualization of crystal, volumetric and morphology data. J. Appl. Crystallogr. 44, 1272–1276 (2011).