Research Article

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Soft Science

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3	Controlled low dimensionality in flexible hybrid inorganic-organic superlattices
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26	Abstract

27 Control of electron and phonon transport by manipulating dimensionality is essential

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for the performance of advanced electronic materials and devices, such as quantum 28 electronics, thermoelectrics, and superconductors which may also lead to yet 29 undiscovered, emergent electronic or thermal phenomena. In this paper, we report a 30 series of hybrid inorganic-organic superlattice structures, in which metallic TiS₂ 31 32 monolayers are spatially confined between soft and insulating organic molecules of varying thicknesses. By choosing different organic molecules that increase the 33 interlayer distance, the electrons inside the TiS₂ layers gradually become 34 two-dimensional, with increasing density of states as seen by the effective mass of 35 electrons increasing from 5.3 m_0 to 8.6 m_0 , where m_0 is the mass of a bare electron. In 36 addition, the DFT calculation confirms a transition of electron distribution from bulk to 37 2D, due to the suppressed interlayer coupling. The result demonstrates that 38 thermoelectric transport of two-dimensional electrons can be realized in a 3D 39 40 inorganic/organic superlattice, thus enabling the access of the interesting properties of individual 2D materials in the bulk form, which may provide new opportunities in 41 flexible thermoelectrics. 42

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Keywords: TiS₂, inorganic-organic superlattices, two-dimensional electrons, flexible

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47 **INTRODUCTION**

The emergence and popularity of two-dimensional materials (2D) have opened up new 48 49 opportunities for achieving superb thermoelectric properties compared with their bulk counterparts, as evidenced by tremendous theoretical predictions and some 50 experimental reports^[1-8]. However, as the thickness of the individual 2D materials is 51 restricted to a few atoms, the maximum heat and current loads allowed through the 52 devices are severely limited, which are not practical for macroscopic thermoelectric 53 applications with energy conversion power to the level of Watts. Although there have 54 been many efforts to integrate 2D materials into thick film or 3D structure, fabrication 55 techniques might introduce undesired doping and defects that compromise electronic 56 57 properties and leads to the disappearance of the 2D states and their superb properties^[9-11]. Realizing the promising thermoelectric properties of 2D materials in a 58

3D bulk structure is strongly desired for practical integration into thermoelectricdevices with large thermal and electrical loads.

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There have been several strategies to realize 2D electronic states in a bulk structure. It 62 has been proposed by Hicks and Dresselhaus that confining a conducting thin layer 63 inside the insulating layers, can result in 2D electrons^[12]. The density of states 64 increased, leading to a high Seebeck coefficient and hopefully improved thermoelectric 65 performance^[12]. This idea was later validated by the observation of the giant Seebeck 66 coefficient in SrTiO₃/SrTi_{0.8}Nb_{0.2}O₃ superlattices, where two-dimensional electron gas 67 can be formed at the interfaces^[13]. On the other hand, by confining electrons into 68 69 two-dimensional electron gases in GaN/AlN/Al_{0.2}Ga_{0.8}N superlattices, electron mobility can be greatly enhanced to achieve the improvement of ZT^[14]. Meanwhile, 2D 70 71 materials have been widely recognized to provide a platform in which unconventional pairing states appear in the high-temperature superconductors of layered WTe₂^[15] and 72 73 FeSe^[16]. Further, dimensionality-tuned properties have been demonstrated in these layered compounds: distinctively different critical temperature T_c can be observed in 74 structures with different interlayer spacing^[17, 18]. Intuitively, a crossover of transport 75 76 regime from 3D to 2D can be expected, if the interlayer spacing is changed. Such 77 dimensionality crossover leads to the discovery of novel superconductors like $Na_xCo_2O_4 \cdot yH_2O$ where water molecules are inserted between conducting CoO_2 78 79 layers^[19]. Besides effective control of electron transport, phonon transport can also be tailored by dimensionality crossover. Low dimensional structures appear to have the 80 81 ability to focus phonons along particular directions leading to ultra-low thermal conductivity^[20, 21] as well as unusually high thermal conductivity^[22]. 82

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In our previous work, we studied thermoelectric properties of bulk inorganic-organic 84 85 superlattices, in which the inorganic conducting layers are spatially separated by insulating organic layers^[23]. Enhanced thermoelectric properties have been discovered, 86 together with superior mechanical flexibility. However, 2D electron states and superior 87 thermoelectric properties were not obtained in the hybrid system, as the interlayer 88 distance is limited to 9.65 Å and the interlayer coupling interaction was not decoupled. 89 In this paper, by choosing organic molecules of different sizes through a chemical 90 91 solvent exchange process, the distance between the neighboring inorganic layers is

92 modulated and the insulating organic component can become an electrostatic barrier confining the electrons inside the inorganic layers. Such intercalation leads to a 93 quantum well structure and 2D transport of charge carriers can be realized in inorganic 94 layers. This dimensionality control is demonstrated by the change of effective mass of 95 electrons, as well as the electron density distribution as a function of the interlayer 96 distance. Although thermoelectric ZT has not been optimized, this paper demonstrates 97 that dimensionality crossover can be achieved in a 3D bulk material, enabling the 98 99 access of interesting properties of individual 2D materials in the bulk form, which may provide new opportunities in flexible thermoelectrics. 100

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103 EXPERIMENTAL

We developed an electrochemical processing technique that can synthesis a superlattice structure inside a bulk single crystal. This process opens up the van der Waals gap of a layered material, like TiS₂, through an electrochemical reaction, followed by ion exchange or solvent exchange to diversify and tune the composition.

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109 TiS₂ single crystals with a typical size of 4 mm \times 4 mm \times 100 μ m were grown by the 110 chemical vapor transport method using excess sulfur as the transport agent. The hybrid inorganic-organic superlattice compositions were then prepared using 111 an 112 electrochemical process. A TiS₂ single crystal and a platinum plate were used as the 113 cathode and anode respectivley. A solution of heyxlammonium (HA) chloride dissolved 114 in dimethyl sulfoxide (DMSO) was used as the electrolyte. The electrochemical reaction was pefromed under a voltage of 1.8 V for 20 minutes. Part of the Ti⁴⁺ was 115 116 reduced to a valence state of Ti³⁺. The TiS₂ layer was therefore negatively charged and 117 the positive organic cation in the electrolyte was interacted driven by the Coulumb 118 force. After the intercalation, the thickness of TiS₂ increased to 2.5 times the original 119 thickness. At the same time, the uncharged solvent molecules entered the superlattice 120 together due to the cation-dipole effect. The as-synthesized TiS₂/HA/DMSO was then 121 treated in glycerin and H₂O overnight for solvent exchange and cation transfer 122 respectively. The thickness decreased by $\sim 30\%$ after the solvent exchange with water. 123 The fabricated hybrid material was then analyzed with XRD and High-angle annular 124 dark-field scanning transmission electron microscopy (HAADF-STEM). The transport

properties of the samples were measured with homemade apparatuses. The seebeck 125 coefficient was measured by the sople of voltage as a function of the temperature 126 diffrenence. The electrical conductivity was measured by the Van der Pauw method. 127 The thermal conductivity was obtained by using the parallel conductance method^[24]. 128 129 All the measurements were calibrated using some reference samples, such as TiS₃ and Mg₂Si, with accuracies within 5%. All the samples were fabricated independently and 130 measured twice or 3 times to ensure the repeatability of the results. The Hall coefficient 131 was measured using the Van der Pauw technique under a reversible magnetic field of 132 0.5T (ResiTest8300, Rigaku). The cross-plane thermal conductivity was obtained by 133 134 multiplying the thermal diffusivity measured by the laser flash analysis method, the 135 heat capacity measured by differential scanning calorimetry (DSC), and the density 136 calculated by mass over volume.

137

138 **RESULTS AND DISCUSSION**

139 Chemical and structural analysis of the inorganic-organic superlattices

 TiS_2 single crystal is a typical layered transition metal dichalcogenide (TMDC) with a 140 141 trigonal space group (pN3m), consisting of a Ti layer sandwiched between two layers 142 of S atoms in an octahedral configuration^[25]. Each three-atom slab is stacked with its 143 neighboring layers via relatively weak van der Waals interactions. The prepared hybrid material maintained the same basal plane as that of the TiS₂ single crystal while 144 145 expanded along the c-axis. Different from the brittle pristine TiS₂ single crystal, the hybrid superlattices became soft and flexible. For instance, a 54-µm-thick 146 TiS₂/HA/DMSO superlattice sample can still keep the resistance change no more than 147 148 2% when the bending radius is 2mm (Supplementary Figure 3).

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Structure analysis of the hybrid materials demonstrated the increase of the lattice constant in the c-axis direction, namely the interlayer distance between the TiS_2 monolayers. The most obvious evidence for the expansion of the interlayer distance came from XRD. The shift of the (001) peaks reflected the change of the interlayer distance. The (001) peak of bulk TiS_2 locates at 15.5° , corresponding to its interlayer distance of 5.9 Å (as shown in Figure 1A). After the intercalation of the organic molecules, all of the (001) peaks shifted to lower angles.

Despite that the same intercalant HA was used, we find that the interlayer distance and 158 thermal stability of the superlattice structures are sensitive to the solvent. When 159 different solvent molecules were exchanged into the superlattices, the corresponding 160 interlayer distance changed accordingly (Supplementary Figure 1). The interlayer 161 162 distance for TiS₂/HA/DMSO, TiS₂/HA/glycerin, and TiS₂/HA/H₂O were measured to be 13.97Å, 13.84 Å, and 9.65Å respectively. However, the thermal gravimetric analysis 163 164 (TGA) showed that TiS₂/HA/DMSO is not stable and decomposes gradually when the 165 sample was heated above 40°C in air. The thermal instability issue can be solved by exchanging solvent molecules with higher boiling point, such as H₂O and glycerin. 166 167 Thermal stability of the composition of TiS₂/HA/glycerin showed improvement, which 168 remains stable up to 70°C. Further, the incorporation of H_2O enabled the hybrid 169 material to remain stable until 120°C in the air (Supplementary Figure 2).

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We have thus examined the structure of the most stable compound $TiS_2/HA/H_2O$ using HAADF-STEM. As shown in Figure 1B, the bright points represent the inorganic TiS_2 layer and the interlayer distance is measured to be 9.65 Å, consistent with the XRD results. The dark area is filled with organic molecules, which support the gaps between inorganic layers. Therefore, the superlattice structure of hybrid inorganic-organic material is confirmed by the HAADF-STEM imaging showing a clear alternating stacking pattern of TiS_2 and organic layers(as shown in Figure 1C).

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For the other compositions, TiS₂/HA/DMSO and TiS₂/HA/glycerin, which have lower 179 180 stability and cannot be observed by HAADF-STEM, the stacking structure of the 181 inorganic-inorganic superlattices can be analyzed with the one-dimensional (1D) 182 electron density map along the c-axis. The 1D electron density maps are derived from 183 the Fourier transform of the XRD results (see Supplementary Material), as shown in 184 Figure 1D and E. Three sharp peaks located at -1.4, 0, and 1.4 Å represent the triple atomic planes in TiS₂. Organic molecules in the interlayer spacing contributed to the 185 186 small peaks appearing between the neighboring strong triple peaks, indicating relatively ordered spatial arrangements. The similar peaks next to the triple peaks by 1.4 Å 187 appeared in all the electron density maps, which should belong to the ammonium head 188 189 groups of HA cations. There are also some relatively strong symmetric peaks located in 190 the interlayer space of the superlattices. These peaks are attributed to the electronegative oxygen and sulfur atoms in the neutral polar molecules, such as DMSO
and glycerin, exchanged into the superlattice. Through the cation-dipole effect, they
were also regularly arranged between the inorganic layers.

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With different sizes of the intercalated molecules, we have demonstrated that the interlayer distance is controllable, which indicates great opportunities for tunable thermal, electronic, and thermoelectric properties. In the following sections, detailed experimental characterization and theoretical analysis will be performed to demonstrate dimensionality-controlled thermoelectric transport properties.

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Figure 1. Crystal structure of TiS₂ single crystal and the hybrid inorganic-organic superlattices with different interlayer distances. (A) TiS₂ single crystal. (B) HAADF-STEM image of the TiS₂/HA/H₂O. (C) TiS₂/HA/H₂O. (D) TiS₂/HA/DMSO corresponding to the 1-D electron density map along the c-axis. (E) TiS₂/HA/ glycerin corresponding to the 1-D electron density map along the c-axis.

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208 Electrical transport properties of the inorganic-organic superlattices

The transport properties of TiS_2 single crystals and the hybrid inorganic-organic superlattices were measured, as shown in Table 1. As a result of the high density of electronic states (mainly composed of the 3-fold degenerate t_{2g} orbitals of the 3*d* electrons of the Ti atom) around the Fermi level, TiS_2 showed a high Seebeck

coefficient and power factor^[26]. The transport properties strongly depended on the 213 214 growth conditions which might induce nonstoichiometry (interstitial Ti atoms) and other defects^[27]. We grew TiS₂ single crystals using excess sulfur rather than the 215 conventional iodine as a transport agent to avoid impurities. The obtained TiS₂ single 216 217 crystals show a Seebeck coefficient of -160 μ V K⁻¹, which was lower than that of the nearly stoichiometric sample, because of the extra electrons donated by the interstitial 218 219 Ti atoms. Hall measurement showed a carrier concentration of 3.4×10^{20} cm⁻³. Assuming each interstitial Ti atom contributes 4 electrons, the actual composition of the single 220 crystal was calculated to be $Ti_{1.0049}S_2$. 221

222

223 Table 1. Electrical transport properties of TiS₂ single crystal and the hybrid

Compositions	T.	In-pla	ne pro	perties			Cross-plane
Compositions	I d	S	σ	n	μ	<i>m</i> *	σ
TiS ₂	~	-160	409	3.40	7.24	5.3	0.51
A	40	-75	363	8.48	2.67	8.3	0.14
В	70	-75	534	9.11	3.66	8.6	0.16
С	120	-78	781	7.59	6.41	6.2	2.73

224 inorganic-organic superlattices

225 Composition A, TiS₂/HA/DMSO; composition B, TiS₂/HA/glycerin; composition C,

226 TiS₂/HA/H₂O; T_d , decomposition temperature in °C; S, Seebeck coefficient in μ V K⁻¹;

227 σ , electrical conductivity in S cm⁻¹; *n*, the carrier concentration in 10²⁰ cm⁻³; μ , mobility 228 in cm² V⁻¹ s⁻¹; *m**, effective mass in *m*₀ which is the mass of a bare electron.

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After the intercalation of HA ions, the Seebeck coefficient became -75 μ V K⁻¹ and the 230 231 electrical conductivity became 363 S cm⁻¹ at room temperature. During the electrochemical process, the TiS₂ layers were electrochemically reduced, so the carrier 232 concentration in the TiS₂ layers increased and was equal to the density of the 233 intercalated organic cations according to the requirement of charge neutrality. Hall 234 measurement demonstrated that the carrier concentration increased to 8.48×10^{20} cm⁻³. 235 Meanwhile, the mobility became 2.67 cm² V⁻¹ s⁻¹, which was reduced compared with 236 that of the TiS₂ single crystal. Since the electrons were primarily localized within the 237 TiS₂ layers and the conduction pathway was well preserved, there should be minimal 238

additional scattering in the inorganic-organic superlattice. The electrons in pure TiS_2 were mainly scattered by acoustic phonons^[28], where the electron effective mass also played an important role. In this quantum well system, the electron effective mass may be changed, which will be analyzed later.

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The incorporation of neutral glycerin molecules almost did not change the 244 concentration of the organic cations (the HA ions), and therefore should not influence 245 the electron density in the TiS_2 layers. The electrical conductivity increased from 363 S 246 cm⁻¹ to 534 S cm⁻¹. Hall measurement showed that this increase was mainly due to an 247 increase in mobility. The polar glycerin molecules with relatively a high dielectric 248 249 constant in the van der Waals gap of TiS_2 may help screen the deformation potential 250 induced by the lattice vibrations of the TiS₂ layers, which decreased the acoustic 251 phonon scattering effect and enhanced the electron mobility^[29].

252

253 For the TiS₂/HA/H₂O case, with the highest thermal stability among the three different 254 materials, the Seebeck coefficient had a slight improvement in comparison with the two 255 previous samples. The electrical conductivity was much larger in comparison with the previous two samples. Hall measurement confirmed that the carrier concentration only 256 257 slightly decreased, possibly because of a loss of organic cations during the ion exchange process which can reduce the corresponding negative electron density in the 258 259 inorganic TiS₂ layers. Meanwhile, the mobility increased to a value close to that of the pristine TiS₂ single crystals. 260

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Two-dimensional electron transport in the inorganic-organic superlattices

Since the intercalated molecules are insulating, the electron pathway is dominantly inside the inorganic TiS₂ layers, likely confined inside the TiS₂ monolayers and determined by the scattering processes inside each TiS₂ layer^[28]. Using the volume fraction of the inorganic component derived from the interlayer distance measured by XRD, the real carrier concentration inside the TiS₂ layers can be estimated. Then the effective mass m^* can be deduced from the Seebeck coefficient *S* and the carrier concentration $n^{[30]}$:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m * T(\frac{\pi}{3n})^{2/3}$$
(1)

The results show that the effective mass of all the inorganic-organic superlattices 272 increased from that of the pristine TiS₂ single crystal, as shown in Figure 2A. The TiS₂ 273 layers are spatially confined between the insulating organic molecules, which can 274 behave as electrostatic potential barriers. Two-dimensional electron gas (2DEG) could 275 form inside the TiS₂ layers, which increased the density of states at the edge of the 276 conduction band and enhance the effective mass. As shown in Fig. 2A, the 277 dimensionality crossover is evidenced by the continuously increased effective mass and 278 decreased mobility with the expanding interlayer distances^[31]. Since the insulating 279 organic molecules filling the van der Waals gaps have a much wider bandgap than TiS₂, 280 they can be considered as potential barriers separating the conducting TiS₂ layers that 281 282 resemble 2D potential wells. With larger interlayer distances, the width of the potential barriers also increased, hence the interlayer electron transport is suppressed, which 283 284 resulted in an increased effective mass and decreased mobility. Ultimately, large spacing leads to a stack of effectively isolated TiS₂ monolayers. Our previous work 285 286 calculated the electronic structure of the TiS₂ monolayer, in which electrons are completely confined two-dimensionally and the effective mass is doubled compared 287 288 with the bulk value^[1]. The observed increased effective mass from 5.3 m_0 for single crystal TiS₂ to 8.3 m₀ for TiS₂/HA/DMSO with a large interlayer spacing of 13.97 Å 289 suggests we almost approach the monolayer limit. 290

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The formation and the tunability of 2DEG are also manifested in the temperature 292 dependence of electric conductivity, as shown in Figure 2B. The inorganic-organic 293 superlattices have a highly anisotropic electrical conductivity and the cross-plane 294 electrical conductivities are about 800~2000 times lower than the in-plane values, 295 which can be explained by regarding the organic layers as potential barriers suppressing 296 interlayer charge transport. In addition, the temperature dependence of electrical 297 conductivity for the two compounds $TiS_2/HA/DMSO$ (d = 13.97 Å) and 298 TiS₂/HA/glycerin (d = 13.84 Å) is much weaker than the pristine TiS₂ and 299 TiS₂/HA/H₂O with smaller interlayer distances. With large widths and heights of 300

301 potential barriers formed by DMSO and glycerin molecules, the tunneling process 302 dominating the interlayer electron transport is suppressed. In contrast, $TiS_2/HA/H_2O$ 303 has a short interlayer distance hence the potential barrier is much narrower, resulting in 304 the stronger coupling of charge carriers between neighboring TiS_2 layers and a metallic 305 electrical conductivity in the cross-plane direction. The temperature dependence of 306 electrical conductivity in $TiS_2/HA/H_2O$ is therefore similar to the pristine TiS_2 . 307



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Figure 2. Demonstration of the gradual two-dimensionalization of electrons with increasing interlayer distance. (A) Effective mass and mobility in the in-plane direction as a function of interlayer distance. (B) the temperature dependence of the cross-plane electrical conductivity of the hybrid organic/inorganic superlattices, in which (a), (b), (c), (d) represents TiS₂ single crystal, TiS₂/HA/DMSO, TiS₂/HA/glycerin, and TiS₂/HA/H₂O respectively.

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In addition to the experimental characterizations, we also performed density functional theory (DFT) calculations to provide theoretical insights into the confinement of electron gas inside TiS_2 monolayers by changing the interlayer distances. We calculated the electronic DOS of the conduction band as a function of the interlayer distance of TiS_2 , as shown in Figure 3. For bulk TiS_2 , the DOS at conduction band edge showed a gradual increase, but the DOS of the monolayer TiS_2 has a sharp increase at the band edge, which is a typical feature for 2DEG. For the structure with intermediate interlayer distances (9.65 Å and 13.9 Å), the slope of the DOS at the band
edge is between the bulk TiS₂ and single layer TiS₂. This DOS clearly showed a
bulk-to-2D transition of the electronic structure.

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327

Figure 3. Electronic density of states of the conduction band, as a function of the distance between TiS_2 layers.

330

We can also visualize such transition of electron distribution from 3D to 2D by 331 calculating the valance electron distributions (Fig. 4A-D). In bulk TiS₂, the electron 332 density cloud of different TiS₂ layers is overlapped with each other, forming a 333 three-dimensional distribution. However, the electrons in each monolayer become 334 decoupled from the neighboring layers when the inter-layer distance increases. Our 335 DFT simulation of DOS and the spatial electron density distribution indicate that 336 increasing the van der Waals gap between TiS2 layers can suppress the inter-layer 337 coupling and the electron transport in these intercalated compounds gradually becomes 338 two-dimensional-like. 339

340



Figure 4. Demonstration of the gradual two-dimensionalization of electrons with
increasing interlayer distance. The valance electron distribution of (A) bulk TiS₂, (B)
TiS₂ with van der Waals gap of 9.65 Å, (C) TiS₂ with van der Waals gap of 13.9 Å and
(D) single layer TiS₂.

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348 Thermoelectric performance as a function of interlayer distance

It is important to realize that careful control of interlayer spacing is important to avoid excessive reduction of the electrical conductivity that compromises the thermoelectric performance. While opening the van der Waals gaps between TiS_2 layers can enhance the effective mass of electrons, it does not always improve the power factor, because the loss in mobility could counterbalance the gain in the Seebeck coefficient. In addition, the large volume fraction of the insulating organic molecules also decreases the electrical conductivity.

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In addition to the electrical properties, increasing the Van der Waals gap by organic molecule intercalation can result in much lower phononic thermal conductivities and thereby an enhanced ZT value. Through the parallel thermal conductance method, the thermal conductivity of the pristine TiS_2 single crystal was measured to be 4.45 W m⁻¹ K^{-1} along the in-plane direction. The corresponding values for $TiS_2/HA/DMSO$, $TiS_2/HA/glycerin$, and $TiS_2/HA/H_2O$ were measured to be 0.76, 0.83, and 0.69 W m⁻¹ K^{-1} respectively, which were about 6 times lower than that of the starting TiS_2 single

crystal (Table 2). As the thermal conductivity is contributed by both phonons and 364 electrons, the Wiedemann-Franz law was used to estimate the electronic thermal 365 conductivity^[32]. The lattice thermal conductivity of TiS₂ single crystal was calculated to 366 be 4.24 W m⁻¹ K⁻¹ and the values for the three compositions become $0.22 \sim 0.54$ W m⁻¹ 367 K⁻¹, which were significantly lower than the value of TiS₂. The huge reduction of the 368 thermal conductivity from pure TiS₂ to the hybrid materials is because of the interaction 369 between TiS₂ and the dangling organic molecules which provides extra scattering 370 channels for TiS₂ vibrational modes, as shown in our previous work using molecular 371 dynamics simulations^[23]. Meanwhile, the thermal conductivity of TiS₂/HA/H₂O is 372 lower than the other two hybrid materials, which may be due to the distorted and wavy 373 374 structure, as shown in supplementary Fig. 4. This wavy structure may be due to the strong interaction between TiS₂ and the organic molecules that are confined within a 375 narrow space ($\triangle d=3.75$ Å) Owing to the significant decrease of thermal conductivity, 376 the ZT value of the hybrid inorganic-organic superlattices achieved remarkable 377 improvement compared with the TiS₂ single crystal. In general, the thermoelectric 378 properties of the inorganic-organic superlattice change with the change of the interlayer 379 380 distance (Figure 5).



Figure 5. In-plane thermoelectric properties of TiS_2 and the hybrid inorganic-organic superlattices as a function of interlayer distance.

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386 The cross-plane thermal conductivity was measured using the laser flash method. The electronic thermal conductivity can be neglected compared with the lattice thermal 387 conductivity because of the low cross-plane electrical conductivity. As shown in Table 388 2, TiS_2 shows anisotropy of thermal conductivity due to the anisotropic bonding 389 390 strengths: strong covalent bonding inside the layers and weak van der Waals force between the layers. However, this anisotropy ratio between in-plane and cross-plane 391 392 thermal conductivity decreased after the organic molecule intercalation. This could be attributed to the increased scattering rates of vibrational modes inside TiS2 due to the 393 394 anharmonic coupling with the organic molecules, which is demonstrated by molecular

395 dynamics simulations in our previous work^[23].

396

Table 2. Thermal transport and thermoelectric properties of TiS₂ single crystal

398 and the hybrid inorganic-organic superlattices

Compositions	Cross-plane properties		In-pla	In-plane properties				
	К	κL	$S^2\sigma$	К	КL	ZT		
TiS ₂	1.92	1.92	1.05	4.45	4.24	0.07		
А	0.50	0.50	0.20	0.76	0.54	0.08		
В	0.49	0.49	0.30	0.83	0.51	0.11		
С	0.11	0.11	0.48	0.69	0.22	0.21		

399 Composition A, TiS₂/HA/DMSO; composition B, TiS₂/HA/glycerin; composition C,

400 TiS₂/HA/H₂O; $S^2\sigma$, power factor in mW m⁻¹ K⁻¹; κ , thermal conductivity in Wm⁻¹K⁻¹; κ_L ,

401 lattice thermal conductivity in W m⁻¹ K⁻¹; ZT, the dimensionless figure of merit.

402

403 CONCLUSIONS

In summary, we presented a series of materials with a hybrid organic/inorganic 404 405 superlattice structure, in which the inorganic conducting TiS₂ layers are spatially confined between the soft organic molecules. The interlayer distance was 406 407 systematically tuned by different organic molecules from 9.65-13.96Å. Gradual dimensional crossover of the electrons from 3D to 2D was demonstrated with 408 409 increasing interlayer distance, which was evidenced by the increase of effective mass from 5.6 to 8.3 m₀. Meanwhile, the electron distribution was analyzed through DFT 410 calculation, which confirms the dimensional crossover of electrons with the increasing 411 412 interlayer distance.

413

Atomically thin 2D materials show great potential in thermoelectric energy conversion due to their superb electronic properties, but the higher thermal conductivities of 2D materials could lead to a low thermoelectric figure of merit^[33]. The result demonstrates that thermoelectric transport of two-dimensional electrons can be realized in a 3D inorganic/organic superlattice, thus enabling the access of the interesting properties of individual 2D materials in the bulk form, which may provide new opportunities in flexible thermoelectrics. Many other layered materials such as Bi₂Te₃ and the transition

421	metal dichalcogenides NbS ₂ , TaS ₂ , VS ₂ , CrS ₂ , MoS ₂ , WSe ₂ can be intercalated to make
422	both n- and p-type inorganic/organic superlattices materials and realize potentially high
423	thermoelectric properties.
424	
425	
426	DECLARATIONS
427	Authors' contributions
428	Wrote and reviewed the manuscript: Yin SJ, Qian X, Koumoto K, Yang RG, Wan CL
429	
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431	Not applicable.
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439	All authors declared that there are no conflicts of interest.
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444	Consent for publication
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450	REFERENCES
451	1. Zhang RZ, Wan CL, Wang YF, Koumoto K: Titanium sulphene:
452	two-dimensional confinement of electrons and phonons giving rise to improved

thermoelectric performance. *Phys Chem Chem Phys* 2012; 14:15641-15644.

454		[DOI: 10.1039/c2cp42949g]
455	2.	Huang W, Luo X, Gan CK, Quek SY, Liang G: Theoretical study of
456		thermoelectric properties of few-layer MoS2 and WSe2. Phys Chem Chem Phys
457		2014; 16:10866-10874. [DOI: 10.1039/c4cp00487f]
458	3.	Hippalgaonkar K, Wang Y, Ye Y, et al: High thermoelectric power factor in
459		two-dimensional crystals of $\operatorname{Mo} {\operatorname{Mo}} - {\operatorname{S}}_{2}$
460		Review B 2017; 95:115407. [DOI: 10.1103/PhysRevB.95.115407]
461	4.	Wu J, Chen Y, Wu J, Hippalgaonkar K: Perspectives on Thermoelectricity in
462		Layered and 2D Materials. Advanced Electronic Materials 2018; 4:1800248.
463		[DOI: 10.1002/aelm.201800248]
464	5.	Kayyalha M, Maassen J, Lundstrom M, Shi L, Chen YP: Gate-tunable and
465		thickness-dependent electronic and thermoelectric transport in few-layer MoS2.
466		Journal of Applied Physics 2016; 120:134305. [DOI: 10.1063/1.4963364]
467	6.	Pallecchi I, Manca N, Patil B, Pellegrino L, Marré D: Review on thermoelectric
468		properties of transition metal dichalcogenides. Nano Futures 2020; 4:032008.
469		[DOI: 10.1088/2399-1984/ab92f4]
470	7.	Shimizu S, Shiogai J, Takemori N, et al: Giant thermoelectric power factor in
471		ultrathin FeSe superconductor. Nature Communications 2019; 10:825. [DOI:
472		10.1038/s41467-019-08784-z]
473	8.	Cao Y-D, Sun Y-H, Shi S-F, Wang R-M: Anisotropy of two-dimensional ReS2
474		and advances in its device application. Rare Metals 2021. [DOI:
475		10.1007/s12598-021-01781-6]
476	9.	Novak TG, Kim K, Jeon S: 2D and 3D nanostructuring strategies for
477		thermoelectric materials. Nanoscale 2019; 11:19684-19699. [DOI:
478		10.1039/c9nr07406f]
479	10.	Huang H, Cui Y, Li Q, et al: Metallic 1T phase MoS2 nanosheets for
480		high-performance thermoelectric energy harvesting. Nano Energy 2016;
481		26:172-179. [DOI: 10.1016/j.nanoen.2016.05.022]
482	11.	Li D, Gong Y, Chen Y, et al: Recent Progress of Two-Dimensional
483		Thermoelectric Materials. Nano-Micro Letters 2020; 12:36. [DOI:
484		10.1007/s40820-020-0374-x]
485	12.	Hicks LD, Dresselhaus MS: Effect of Quantum-Well Structures on the
486		Thermoelectric Figure of Merit. Physical Review B 1993; 47:12727-12731.
487		[DOI: 10.1103/PhysRevB.47.12727]
488	13.	Ohta H, Kim S, Mune Y, et al: Giant thermoelectric Seebeck coefficient of
489		two-dimensional electron gas in SrTiO3. Nature Materials 2007; 6:129-134.
490		[DOI: 10.1038/nmat1821]
491	14.	Sztein A, Bowers JE, DenBaars SP, Nakamura S: Polarization field engineering
492		of GaN/AlN/AlGaN superlattices for enhanced thermoelectric properties.
493		Applied Physics Letters 2014; 104:5. [DOI: 10.1063/1.4863420]
494	15.	Zhang H, Rousuli A, Shen S, et al: Enhancement of superconductivity in
495		organic-inorganic hybrid topological materials. Science Bulletin 2020;
496		65:188-193. [DOI: 10.1016/j.scib.2019.11.021]

497	16.	Shi MZ, Wang NZ, Lei B, et al: FeSe-based superconductors with a
498		superconducting transition temperature of 50 K. New Journal of Physics 2018;
499		20:123007. [DOI: 10.1088/1367-2630/aaf312]
500	17.	Harshman DR, Mills AP: Concerning the Nature of High-T(C)
501		Superconductivity - Survey of Experimental Properties and Implications for
502		Interlayer Coupling. Physical Review B 1992; 45:10684-10712. [DOI:
503		10.1103/PhysRevB.45.10684]
504	18.	Burrard-Lucas M, Free DG, SedImaier SJ, et al: Enhancement of the
505		superconducting transition temperature of FeSe by intercalation of a molecular
506		spacer layer. Nature Materials 2013; 12:15-19. [DOI: 10.1038/NMAT3464]
507	19.	Takada K, Sakurai H, Takayama-Muromachi E, Izumi F, Dilanian RA, Sasaki T:
508		Superconductivity in two-dimensional CoO2 layers. Nature 2003; 422:53-55.
509		[DOI: 10.1038/nature01450]
510	20.	Qian X, Zhou JW, Chen G: Phonon-engineered extreme thermal conductivity
511		materials. Nature Materials:15. [DOI: 10.1038/s41563-021-00918-3]
512	21.	Huang Y, Wan C: Controllable fabrication and multifunctional applications of
513		graphene/ceramic composites. Journal of Advanced Ceramics 2020; 9:271-291.
514		[DOI: 10.1007/s40145-020-0376-7]
515	22.	Xu XF, Chen J, Zhou J, Li BW: Thermal Conductivity of Polymers and Their
516		Nanocomposites. Advanced Materials 2018; 30:10. [DOI:
517		10.1002/adma.201705544]
518	23.	Wan C, Gu X, Dang F, et al: Flexible n-type thermoelectric materials by organic
519		intercalation of layered transition metal dichalcogenide TiS2. <i>Nature Materials</i>
520		2015; 14:622-627. [DOI: 10.1038/nmat4251]
521	24.	Zawilski BM, Littleton RT, Tritt TM: Description of the parallel thermal
522		conductance technique for the measurement of the thermal conductivity of
523		small diameter samples. <i>Review of Scientific Instruments</i> 2001; 72:1770-1774.
524		[DOI: 10.1063/1.1347980]
525	25.	Fang CM, deGroot RA, Haas C: Bulk and surface electronic structure of
526		1T-TiS2 and 1T-TiSe2. <i>Physical Review B</i> 1997; 56:4455-4463. [DOI:
527		10.1103/PhysRevB.56.4455]
528	26.	Imai H, Shimakawa Y, Kubo Y: Large thermoelectric power factor in TiS2
529		crystal with nearly stoichiometric composition. <i>Physical Review B</i> 2001;
530		64:241104. [DOI: 10.1103/PhysRevB.64.241104]
531	27.	Barry JJ, Hughes HP, Klipstein PC, Friend RH: STOICHIOMETRY EFFECTS
532		IN ANGLE-RESOLVED PHOTOEMISSION AND TRANSPORT STUDIES
533		OF TI1+XS2. Journal of Physics C-Solid State Physics 1983; 16:393-402. [DOI:
534		10.1088/0022-3719/16/2/022]
535	28.	Wan C, Wang Y, Wang N, Norimatsu W, Kusunoki M, Koumoto K:
536		Intercalation: Building a Natural Superlattice for Better Thermoelectric
537		Performance in Layered Chalcogenides. Journal of Electronic Materials 2011;
538		40:1271-1280. [DOI: 10.1007/s11664-011-1565-5]
539	29.	Cardona M, Christensen NE: Acoustic Deformation Potentials and

540		Heterostructure Band Offsets in Semiconductors. Physical Review B 1987;
541		35:6182-6194. [DOI: 10.1103/PhysRevB.35.6182]
542	30.	Snyder GJ, Toberer ES: Complex thermoelectric materials. Nature Materials
543		2008; 7:105-114. [DOI: 10.1038/nmat2090]
544	31.	Ohta H, Mune Y, Koumoto K, Mizoguchi T, Ikuhara Y: Critical thickness for
545		giant thermoelectric Seebeck coefficient of 2DEG confined in
546		SrTiO3/SrTi0.8Nb0.2O3 superlattices. <i>Thin Solid Films</i> 2008; 516:5916-5920.
547		[DOI: 10.1016/j.tsf.2007.10.034]
548	32.	Kim H-S, Gibbs ZM, Tang Y, Wang H, Snyder GJ: Characterization of Lorenz
549		number with Seebeck coefficient measurement. APL Materials 2015; 3. [DOI:
550		10.1063/1.4908244]
551	33.	Gu XK, Li BW, Yang RG: Layer thickness-dependent phonon properties and
552		thermal conductivity of MoS2. Journal of Applied Physics 2016; 119:8. [DOI:
553		10.1063/1.4942827]
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586	Supplementary	Material:	Controlled	low	dimensionality	in	hybrid
587	organic-inorgani	c superlattice	es				
588							
589	One-dimensional	electron den	sity map calcu	ilated f	rom XRD results		
590	X-ray diffraction spectrum reflects the electronic and atomic structure information of						
591	the material, which	h can be reve	rsed from the X	CRD res	ults.		
592	The electron densi	ity along the c	e-axis could be	obtaine	d by		
593							

$$\rho(z) = \sum_{j=1}^{\infty} F_{00l} \cos\left(\frac{2\pi l z}{c}\right)$$
(S1)

where l, F_{001} , and c represents the Miller index of the (001) crystal plane, structure factor of the 001 reflections, and the interlayer distances, respectively.

597 The structure factors of the 00l reflections F_{00l} were derived from their intensities 598 corrected for Lorentz-polarization effects

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$$|F_{00l}| = (l/Lp)^{1/2}$$
(S2)

600

where I is the intensity of the peak intensity and L_p is the Lorentz-polarization factor which can be written as

603

$$Lp = (1 + \cos^2 2\theta) / (\sin^2 \theta \cos \theta)$$
(S3)

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The absolute values for F_{001} can be derived by Eq. (4). The signs (phase) of the structure factor can be directly obtained instead from the scattering contributions of the inorganic atoms framework by assuming that the contribution from the intercalated organic molecules is relatively small.

$$F_{00l} = \sum_{j=1}^{N} 2f_i \cos(2\pi l z_i)$$
(S4)

where f_i is the scattering factor of j atom, z_i is its fractional coordinate on the c axis. Using Eq. (5), the sign for each F₀₀₁ was determined and combined with the absolute value in Eq. (4), and the one dimensional electron density map can be derived. **XRD result**



Supplementary Figure 1. XRD result of hybrid inorganic-organic superlattices,
showing the shift of (001) peaks as the result of the intercalation of organic molecules.
The origin (001) peak of TiS₂ single crystal is marked by the asterisk.

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622 **TGA result**



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626 Flexibility test



Supplementary Figure 3. The sheet resistance R as a function of bending radius (r) for 629 a 54- μ m-thick TiS₂/HA/DMSO sample, where R₀ is the corresponding value of its 630 original state before bending.



638	Supplementary Figure 4.	HAADF-STEM figure of TiS ₂ /HA/H ₂ O
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