Flexible n-type thermoelectric materials by organic intercalation of layered transition metal dichalcogenide TiS₂

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Organic semiconductors are attracting increasing interest as flexible thermoelectric materials owing to material abundance, easy processing and low thermal conductivity. Although progress in p-type polymers and composites has been reported, their n-type counterpart has fallen behind owing to difficulties in n-type doping of organic semiconductors. Here, we present an approach to synthesize n-type flexible thermoelectric materials through a facile electrochemical intercalation method, fabricating a hybrid superlattice of alternating inorganic TiS₂ monolayers and organic cations. Electrons were externally injected into the inorganic layers and then stabilized by organic cations, providing n-type carriers for current and energy transport. An electrical conductivity of 790 S cm⁻¹ and a power factor of 0.45 mW m⁻¹ K⁻² were obtained for a hybrid superlattice of TiS₂/(hexylammonium)(H₂O)(DMSO)₀, with an in-plane lattice thermal conductivity of 0.12 ± 0.03 W m⁻¹ K⁻¹, which is two orders of magnitude smaller than the thermal conductivities of the single-layer and bulk TiS₂. High power factor and low thermal conductivity contributed to a thermoelectric figure of merit, ZT, of 0.28 at 373 K, which might find application in wearable electronics.

Organic semiconductors, such as conjugated polymers, have been successfully applied to thin-film electronics¹⁻³ and optoelectronic devices⁴⁻⁵ and are attracting attention as a potential thermoelectric material⁶⁻⁷. Owing to their flexibility and easy processing, organic semiconductors and composites can offer new opportunities for flexible power generation, Peltier cooling and sensor networks for wearable technologies, which is not possible with the conventional brittle and usually toxic inorganic thermoelectric materials. Thermoelectric energy conversion efficiency is determined by the thermoelectric figure of merit (ZT), defined as S²σT/k, where S, σ, T and k represent Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. Great progress has been made on p-type polymers and composites, especially those based on poly(3,4-ethylenedioxythiophene) polystyrene sulphonate (PEDOT–PSS), which might find application in wearable electronics.

We synthesized an inorganic/organic superlattice with facile two-step chemical processes, including electrochemical intercalation and solvent exchange (Fig. 1a and Supplementary Section 1 and Supplementary Fig. 1). TiS₂ single crystals were synthesized using the chemical vapour transport method⁸ and were used as the host material. The TiS₂ crystals were used as the cathode in electrochemical reaction cells with the organic salt dissolved in a solvent and used as the electrolyte. When an electrical potential was applied, part of the Ti⁴⁺ in TiS₂ was reduced to Ti³⁺ and the TiS₂ layers were negatively charged with additional carriers, as suggested by the X-ray photoelectron spectroscopy result (Supplementary Fig. 2). The organic cations in the electrolyte were intercalated into the van der Waals gap, driven by Coulomb force, and an inorganic/organic superlattice was formed. Owing to the cation–dipole effect, the solvent molecules are co-intercalated with the organic cations (see Supplementary Fig. 1), which can be

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changed into other polar solvent molecules as desired by a solvent exchange reaction.$^{11}$

Hexylammonium (HA) chloride dissolved in dimethylsulfoxide (DMSO) was chosen here as the electrolyte, which results in a hybrid superlattice of TiS$_2$[(HA)$_x$(DMSO)$_y$]$_z$ after the electrochemical intercalation reaction (Fig. 1a). The hybrid superlattice was then immersed in water to form TiS$_2$[(HA)$_x$(H$_2$O)$_y$(DMSO)$_z$] after most of the DMSO molecules were exchanged with water molecules (Fig. 1a). Thermogravimetric differential thermal analysis was performed on the samples to study their thermal stability. Supplementary Section 2 and Supplementary Fig. 3). TiS$_2$[(HA)$_x$(DMSO)$_y$]$_z$ was found to have low thermal stability and continuously lost weight when it was heated above room temperature. In contrast, TiS$_2$[(HA)$_x$(H$_2$O)$_y$(DMSO)$_z$] maintained its weight and was stable up to 120 °C, which is suitable for thermoelectric application around room temperature. To quantitatively determine the composition of the samples, the samples were dispersed in heavy water D$_2$O and mechanically crushed, then ultrasonically pulverized and heated in a sealed glass tube at 150 °C. The compositions of the hybrid superlattices were determined to be TiS$_2$[(HA)$_{0.08}$(DMSO)$_{0.35}$] and TiS$_2$[(HA)$_{0.08}$(H$_2$O)$_{0.22}$(DMSO)$_{0.35}$] by NMR analysis of the filtered solution containing all of the organic components (see Supplementary Section 3 and Supplementary Fig. 4). The sample microstructure was first studied by X-ray diffraction (XRD) analysis (Supplementary Fig. 5). Pure TiS$_2$ crystallizes with a trigonal space group (p$\overline{3}$m) and only (00l) peaks were observed perpendicular to the basal plane. The c-axis lattice constant ($d$), namely, the interlayer distance, was calculated to be 5.69 Å. After intercalation of the organic molecules, all of the (00l) peaks shifted to lower angles, suggesting an increase in the c-axis lattice constant and an expansion of the TiS$_2$ layers. The interlayer distance ($d$) became 13.97 Å for TiS$_2$[(HA)$_{0.08}$(DMSO)$_{0.35}$], and the value decreased to 9.65 Å for TiS$_2$[(HA)$_{0.08}$(H$_2$O)$_{0.22}$(DMSO)$_{0.35}$] after the solvent exchange.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was used to observe the cross-section of the inorganic/organic superlattices. TiS$_2$[(HA)$_{0.08}$(H$_2$O)$_{0.22}$(DMSO)$_{0.35}$] was not stable under the high vacuum environment required for transmission electron microscopy observation and thus a clear image could not be obtained. A clear image was obtained for TiS$_2$[(HA)$_{0.08}$(DMSO)$_{0.35}$] owing to its much higher stability. In Fig. 1b, c, the bright points represent the inorganic TiS$_2$ layer and the dark areas represent the organic molecules, which shows that the length of the unit cell was 9.65 Å, consistent with the XRD results. The HAADF-STEM observations clearly demonstrated that the TiS$_2$ and organic layers stacked alternatingly, forming a stage-1 compound. As TiS$_2$[(HA)$_{0.08}$(H$_2$O)$_{0.22}$(DMSO)$_{0.35}$] was converted from the TiS$_2$[(HA)$_{0.08}$(DMSO)$_{0.35}$] precursor by solvent exchange reactions, it can be concluded that the latter compound is also a stage-1 compound.

HAADF-STEM can also provide information on the orientation of the hexylammonium ions with long alkyl chains. According to the shape of the dark area in Fig. 1c and the long chains in the hexylammonium molecules, the molecules were inclined by about 30° relative to the TiS$_2$ plane. This geometrical configuration was

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**Figure 1** | Synthesis of TiS$_2$-based inorganic/organic superlattices. a, TiS$_2$ single crystal was first electrochemically intercalated into a TiS$_2$[(HA)$_x$(DMSO)$_y$]$_z$ superlattice, where a bilayer structure of the hexylammonium ions was formed owing to DMSO stabilization. A superlattice of TiS$_2$[(HA)$_x$(H$_2$O)$_y$(DMSO)$_z$] was then formed by the solvent exchange process after immersion in water, where the hexylammonium ions change to a monolayer configuration. b, HAADF-STEM image of the TiS$_2$[(HA)$_x$(H$_2$O)$_y$(DMSO)$_z$] hybrid superlattice showing a wavy structure. c, Magnified HAADF-STEM image of TiS$_2$[(HA)$_x$(H$_2$O)$_y$(DMSO)$_z$].
confirmed by polarized Fourier transform infrared spectroscopy (FTIR) measurements (Supplementary Section 4 and Supplementary Fig. 6). The FTIR measurement shows that the chains in the hexylammonium molecules were inclined by 31.8° relative to the TiS$_2$ layers in TiS$_2$[\((HA)_{0.08}(H_2O)_{0.22}(DMSO)_{0.03}\)]$_x$, and the tilting angle of 28° was observed by polarized FTIR measurements in TiS$_2$[\((HA)_{0.19}(DMSO)_{0.03}\)]. Considering that the expansion of the unit cell \(\Delta d = 8.28\) Å in TiS$_2$[\((HA)_{0.19}(DMSO)_{0.03}\)] was almost twice that of TiS$_2$[\((HA)_{0.08}(H_2O)_{0.22}(DMSO)_{0.03}\)] \(\Delta d = 3.96\) Å, it can be deduced that the hexylammonium ions formed a bilayer structure in TiS$_2$[\((HA)_{0.08}(DMSO)_{0.03}\)] (Fig. 1a). The hydrophobic methyl groups in DMSO are compatible with the alkyl group in hexylammonium and can stabilize the paraffin-type bilayer structure. However, the bilayer structure could not be maintained and a monolayer of hexylammonium ions was formed when most of the DMSO molecules were exchanged with water (Fig. 1a). Such a solvent exchange process results in a much more stable structure where the organic molecules were confined inside a narrower space between inorganic TiS$_2$ layers.

In Fig. 1b, the layers in the hybrid superlattice are distorted, forming a wavy structure with a nanoscale wavelength (~20 nm). It is well known that inorganic nanolayers tend to roll up and form nanotubes under a suitable treatment. One driving force for the rolling up of the nanolayers is the asymmetry of their structure on the two sides of the layer. TiS$_2$[\((HA)_{0.08}(H_2O)_{0.22}(DMSO)_{0.03}\)] was converted from TiS$_2$[\((HA)_{0.04}(DMSO)_{0.03}\)] where almost half of the hexylammonium ions were extracted during the solvent exchange reaction. The remaining hexylammonium ions may have been distributed non-uniformly on the two sides of each TiS$_2$ layer. The positive ammonium group at the end of the hexylammonium molecule may have aggregated, giving rise to a locally high density of positive charges. By forming a curved structure, the atomic crowding of the negatively charged sulphur atoms on the inner side of the layer could compensate for this local aggregation of positive charges. As the TiS$_2$ monolayers in the inorganic/organic superlattice were quite large (millimetre-order), they tended to be distorted on the nanoscale instead of forming a large tube.

Figure 2 shows the in-plane thermoelectric transport properties of TiS$_2$[\((HA)_{0.08}(H_2O)_{0.22}(DMSO)_{0.03}\)] in comparison with those of the single crystal TiS$_2$ host material before organic intercalation. During the single-crystal growth, the introduction of interstitial Ti atoms readily occurred in the van der Waals gap in the TiS$_2$ layers and induced non-stoichiometry, resulting in additional electron carriers in the single-crystal TiS$_2$ (ref. 15). A carrier concentration of $3.4 \times 10^{20}$ cm$^{-3}$ was obtained by the Hall measurement for the single crystal. However, even at such high carrier concentration, the Seebeck coefficient is still very high, $−171$ µV K$^{-1}$ at room temperature, owing to the high density of states of the TiS$_2$ conduction band that is mainly composed of three $t_{2g}$ states of Ti 3d orbitals, where the electron carrier does not significantly alter the chemical potential. With the increasing temperature, the electrical conductivity decreased and the absolute Seebeck coefficient increased, indicating the behaviour of a typical degenerate semiconductor.

After the intercalation of the hexylammonium ions, the in-plane Seebeck coefficient decreased to $−78$ µV K$^{-1}$ and the electrical conductivity increased to 790 S cm$^{-1}$ at room temperature. During the electrochemical process, the TiS$_2$ layers were electrochemically reduced and the negative charge was balanced by the intercalated hexylammonium ions (that is, the organic cations) according to the requirement for electrical neutrality. The total carrier density in the hybrid material increased to $7.59 \times 10^{20}$ cm$^{-3}$ after
the electrochemical intercalation, as shown by the Hall measurement. This corresponds to an effective carrier concentration of $1.29 \times 10^{11}$ cm$^{-2}$ for the TiS$_2$ layers, if we assume that electrons are confined inside them. The in-plane mobility is calculated to be $6.41 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, using $\mu = \sigma / (nq)$, where $\mu$, $\sigma$, $n$ and $q$ are mobility, electrical conductivity, carrier concentration and unit electron charge, respectively. This value is comparable to that of the TiS$_2$ single crystal ($7.24 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$), which indicates that the electronic transport is still confined along the TiS$_2$ layers in the hybrid superlattice. The positive hexylammonium ions could potentially scatter the electrons inside the TiS$_2$ layers by Coulomb interaction. However, because of the presence of the polar water molecules with a high static dielectric constant ($\varepsilon_r = 80$) that surround the positive hexylammonium ions, the Coulomb force can be effectively screened, and the electron mobility inside the TiS$_2$ layers can remain almost unaffected. Overall, the in-plane electrical transport properties of the hybrid superlattice exhibited degenerate semiconducting behavior similar to the host single-crystal TiS$_2$; the electrical conductivity decreases and the absolute Seebeck coefficient increases with increasing temperature. The in-plane power factor of TiS$_2[(\text{HA})_{0.06}(\text{H}_2\text{O})_{0.22}(\text{DMSO})_{0.03}]$ was 0.45 mW m$^{-1}$ K$^{-2}$ at room temperature, lower than that of TiS$_2$, 1.05 mW m$^{-1}$ K$^{-2}$. However, this value is very close to the highest value reported for flexible thermoelectrics, 0.47 mW m$^{-1}$ K$^{-2}$ for a p-type conducting polymer PEDOT–PSS (ref. 7), and much higher than that of n-type organometallic poly(K(NiI,1,2,2-ethenetetrathiolate)) (0.07 mW m$^{-1}$ K$^{-2}$; ref. 19) and n-type (Zn,Al)O/hydroquinone hybrid material (0.018 mW m$^{-1}$ K$^{-2}$). It is even higher than that of a flexible inorganic Bi$_2$Te$_3$ thin film (0.18 mW m$^{-1}$ K$^{-2}$) where the porous structure was introduced to increase the flexibility, which also severely deteriorates the electrical conductivity.

The in-plane thermal conductivities of the TiS$_2$ single crystal and TiS$_2[(\text{HA})_{0.06}(\text{H}_2\text{O})_{0.22}(\text{DMSO})_{0.03}]$ were measured to be 4.45 W m$^{-1}$ K$^{-1}$ and 0.69 W m$^{-1}$ K$^{-1}$ using the parallel thermal conductance method developed for small samples, respectively (see Supplementary Section 5 and Supplementary Fig. 7 for details). The experimental value of the TiS$_2$ single crystal is close to the literature value. As a result of the significant reduction in the thermal conductivity, the in-plane ZT value has been tripled in TiS$_2[(\text{HA})_{0.06}(\text{H}_2\text{O})_{0.22}(\text{DMSO})_{0.03}]$ and reached 0.28 at 373 K, which is the highest for n-type flexible thermoelectrics and is close to that of the most promising p-type organic material, PEDOT–PSS (ref. 7).

Both phonons and electrons contribute to the thermal conductivity, and the electronic contribution can be comparable to the phonon contribution in high-efficiency thermoelectric materials. After subtracting the electronic thermal conductivity that was estimated according to the Wiedemann–Franz law using a calibrated Lorentz constant (see Supplementary Section 8), the in-plane lattice thermal conductivity was estimated to be 4.2 W m$^{-1}$ K$^{-1}$ for the TiS$_2$ single crystal and an ultralow value of 0.12 W m$^{-1}$ K$^{-1}$ was obtained for TiS$_2[(\text{HA})_{0.06}(\text{H}_2\text{O})_{0.22}(\text{DMSO})_{0.03}]$ at 300 K. The ultralow thermal conductivities across inorganic/organic interfaces have been studied for planar self-assembled monolayers and nanocrystal arrays. Low cross-plane thermal conductivity has also been reported for inorganic/organic superlattices. However, the in-plane thermal conductivity of inorganic/organic superlattices has not been reported. Assuming the TiS$_2$ layers and the organic molecules formed a parallel thermal circuit along the in-plane direction of the hybrid superlattice, the thermal conductivity was estimated to be $2.59 \text{ W} \text{m}^{-1} \text{K}^{-1}$, almost half of the thermal conductivity of bulk TiS$_2$, which is much higher than the measured value.
To explain such ultralow thermal conductivity of TiS\(_2\)[(HA)\(_{0.08}\)(H\(_2\)O)\(_{0.22}\)(DMSO)\(_{0.03}\)], we conduct the equilibrium molecular dynamics simulations with the Green–Kubo method to understand the fundamental phonon transport mechanisms in both bulk TiS\(_2\) and the hybrid superlattice material with hexylammonium molecules. The details of interatomic potential parameters and computation methodology can be found in Supplementary Section 9 and Supplementary Fig. 10, and the Supplementary Movie. In our simulations, we observed an eightfold reduction in lattice thermal conductivity when the TiS\(_2\) bulk is intercalated by organic components. This reduction is significantly higher than the simple volumetric averaging, indicating that the coupling between the inorganic and organic parts plays an important role in phonon transport in the in-plane direction. As the thermal conduction in the inorganic part is much better than the organic part, the low thermal conductivity of the hybrid material could be attributed to the reduction in the thermal conductivity of the inorganic layer after the intercalation. To qualitatively explain the difference in the phonon dynamics between bulk TiS\(_2\) and the hybrid material, we calculate the spectral energy density\(^27\), \(\phi(k, \omega)\) with phonon wavevector \(k\) and frequency \(\omega\) of the bulk TiS\(_2\) and the TiS\(_2\) layer from the hybrid material, as shown in Fig. 3a–d. The positions of peaks, \(\omega_k\), in the spectral energy density distribution for a given wavevector, \(k_0\), correspond to the phonon dispersion that the material supports, and the broadening of the peak in the frequency domain is related to the phonon relaxation time. The smaller the broadening is, the longer is the relaxation time. In both materials, the three acoustic branches are clearly distinguishable. For all acoustic dispersions, larger broadening can be observed for the hybrid case. Figure 3e shows the spectral energy density at \(0.25\pi/a_{\perp}, 0, 0\) as an example, indicating the increased phonon scattering rates in the hybrid material. The stronger scattering in the hybrid material can be understood as a result of the inorganic TiS\(_2\) layers being ionically combined with the dangling hexylammonium ions. The electrostatic interaction is much stronger than weak van der Waals interaction, which is dominant in the bulk TiS\(_2\).

It is noted that the degree of reduction in the thermal conductivity obtained in the present equilibrium molecular dynamics simulations is still less than the experimental observation. This is because other scattering mechanisms besides the interfacial coupling can potentially further reduce the thermal conductivity, which is worthy of further investigation. One possibility is the wavy structure of the layers observed in Fig. 1. As a reference, we measured the thermal conductivity of TiS\(_2\)[(HA), (PEG)], where the layers were aligned straight owing to the long chain structure of polyethylene glycol (PEG; see Supplementary Section 10 and Supplementary Fig. 11). The lattice thermal conductivity of the flat hybrid superlattice TiS\(_2\)[(HA), (PEG)] was measured to be \(0.56\) W m\(^{-1}\) K\(^{-1}\), 4–5 times higher than the wavy TiS\(_2\)[(HA)\(_{0.08}\)(H\(_2\)O)\(_{0.22}\)(DMSO)\(_{0.03}\)]. This can be further explained using the thermal conductivity accumulation as a function of mean free path (see Supplementary Fig. 10e). The phonons with a mean free path above 10 nm (the half-wavelength of the wavy structure) that contribute to 82% of the total thermal conductivity would be strongly scattered by the wavy structure. In addition, local atomic disordering of the TiS\(_2\) layers in the hybrid superlattice in the wavy structure could be another additional phonon scattering mechanism. Compared with the sharp peaks of XRD for TiS\(_2\) single crystals, the peaks of TiS\(_2\)[(HA)\(_{0.08}\)(H\(_2\)O)\(_{0.22}\)(DMSO)\(_{0.03}\)] become broadened (Supplementary Fig. 5), which is a sign of structural disordering as further confirmed by HAADF-STEM (Supplementary Fig. 12).

Apart from the low thermal conductivity, the hybrid superlattice became mechanically flexible compared with a TiS\(_2\) single crystal. The flexural modulus was measured to be \(\sim 145\) MPa at 300 K, which is two orders of magnitude lower than that of a TiS\(_2\) single crystal and even lower than a typical plastic material (such as Teflon), as shown in Fig. 4a. In the TiS\(_2\) single crystal, the TiS\(_2\) layers were connected by van der Waals forces, but the interlayer interaction was significantly reduced by the expansion of the interlayers, as a result of the intercalation of organic molecules. Moreover, the organic molecules that occupy the space between neighbouring TiS\(_2\) layers could also accommodate deformations and contribute to the flexibility. Therefore, the two-dimensional TiS\(_2\) monolayers could be freely deformed and were highly flexible. When the material was attached to the surfaces of glass tubes with different radii, the electrical resistance slightly changed under bending deformation.

Figure 4 | Flexibility tests. a. The flexural modulus of the TiS\(_2\)[(HA)\(_{0.08}\)(H\(_2\)O)\(_{0.22}\)(DMSO)\(_{0.03}\)] hybrid superlattice is two orders of magnitude lower than that of TiS\(_2\) and is even lower than that of a typical plastic material, Teflon. F represents the applied force for bending the sample in the measurement. b. The sheet resistance \(R\) as a function of bending radius \(r\) for a 0.3-mm-thick TiS\(_2\)[(HA)\(_{0.08}\)(H\(_2\)O)\(_{0.22}\)(DMSO)\(_{0.03}\)] crystal, where \(R_0\) is the corresponding value of its original state before bending. Detailed error analysis is available in the Supplementary Information.
within 5% of the resistance of the original state, even when the bending radius was 1.5 mm (Fig. 4b). This result firmly suggests that the material can be attached to any curved surface to fabricate flexible thermoelectric generators or coolers.

In summary, we present a new approach to synthesize n-type flexible thermoelectric materials through a facile electrochemical intercalation method to fabricate a hybrid superlattice of alternating inorganic TiS₂ monolayers and organic cations. This general synthesis route using organic intercalation could become a platform to fabricate hybrid inorganic/organic superlattices that would lead to the discovery of new, flexible, high-efficiency thermoelectric materials. Many other layered materials such as Bi₂Te₃, or the transition metal dichalcogenides NbS₂, TaS₂, VS₂, CrS₂, MoS₂, or even layered oxides such as Na₃CoO₂ could also be intercalated to make both n- and p-type thermoelectric materials. The infinite choices of organic molecules with various sizes and functional groups could further diversify the compositions and provide strategies to optimize the thermoelectric performance, such as dimension control¹⁸ and dielectric engineering⁹.

**Methods**

TiS₂, single crystals with a typical size of 4 mm × 4 mm × 100 μm were grown by the chemical vapour transport method using excess sulphur as the transport agent¹⁷. The hybrid inorganic/organic superlattices were then synthesized using an electrochemical intercalation process and subsequent solvent exchange processes (see Supplementary Section 1 and Supplementary Fig. 1). The obtained samples were vacuum dried for 24 h and then characterized by XRD, thermogravimetric differential thermal analysis and X-ray photoemission spectroscopy. To quantitatively determine the composition of the samples, the samples were dispersed in heavy water D₂O and mechanically crushed, then ultrasonically pulverized and heated in a sealed glass tube at 150 °C. The compositions of the hybrid superlattices were determined by NMR analysis of the filtered solution containing all of the organic components. The hybrid material was ultrasonically pulverized and a thin film was prepared by dropping the dispersion solution onto the surface of a CaF₂ substrate and analysed by FTIR to determine the orientation of the hexylammonium molecules. The cross-sections of the samples were observed by HAADF-STEM. All of the transport properties were measured on the same sample, in the sequence of thermal conductivity, Seebeck coefficient, electrical conductivity and Hall measurements (TOYO Corporation, ResiTest8300). The details of the measurement of thermal conductivity, Seebeck coefficient and electrical conductivity are discussed in Supplementary Sections 5–7 and Supplementary Figs 7–9. The bending modulus was also measured by a home-made apparatus introduced in Supplementary Section 11 and Supplementary Fig. 13. Flexibility was evaluated by attaching the hybrid superlattice to the surfaces of glass tubes with different radii and measuring the resistivity using the van der Pauw method. Classical molecular dynamics simulations are performed using the LAMMPS package for the phononic thermal conductivity (see Supplementary Section 9).

Received 24 July 2014; accepted 19 February 2015; published online 6 April 2015.

References


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Acknowledgements

The authors thank R. Sasai for polarized FTIR measurements. C.W. acknowledges financial support from a Murata Science Foundation Research Grant, a Thermal and Electrical Energy Technology Foundation Research Grant, Takahashi Industrial and Economic Research Foundation and JSPS KAKENHI Grant Number 26820295. K.Koumoto acknowledges financial support from JSPS KAKENHI Grant Number 25289226 and ThermAT. G.J.S. acknowledges support from AFOCSR-MURI and DOE-EPFC (3STEC) award number DE-SC0001239. X.G. and R.Y. acknowledge the partial support for this work from the NSF CAREER award (0846561) and AFOCSR (FA9550-11-1-0109). The simulation work used the Janus supercomputer, supported by NSF (0821794).

Author contributions

C.W. and K.Koumoto initiated the concepts. C.W. designed the experiments. C.W., F.D., T.L., Y.W., H.S., M.K., K.Koga and K.Y. conducted the experiments. X.G. and R.Y. performed the molecular dynamics simulations. C.W., X.G., G.J.S., R.Y. and K.Koumoto analysed the data and wrote the manuscript. All of the authors contributed to manuscript preparation.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to C.W. or K.K.

Competing financial interests

The authors declare no competing financial interests.