

Electronic supplementary information (ESI)

Nonlayered tellurene as an elemental 2D topological insulator: experimental evidence from scanning tunneling spectroscopy†

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Characterization of 2D nanoflakes via transmission electron microscopy (TEM)

TEM images were recorded to obtain microstructures and chemical composition of tellurene nanoflakes. In general, a large quantity of random-shaped 2D objects was found in image. A typical micrograph has been presented in Fig. S1a. The average size of the flakes was about 80 nm. One of nanoflakes was further characterized through high-resolution mode of TEM (Fig. S1b) demonstrating a crystalline nature of tellurenes. In addition, fast-Fourier transform (FFT) photograph (inset of Fig. S1b) demonstrates that the crystalline features were retained during their liquid phase exfoliation process. Another HR-TEM image (Fig. S1c) exposed the distinct lattice planes of the nanoflakes. In order to obtain more information regarding the nanoflakes' composition, they were characterized by energy dispersive X-ray spectroscopy (EDX). The EDX studies (Fig. S1d) evidenced presence of elemental tellurium in the exfoliated nanoflakes. Peaks of copper have resulted due to use of carbon-coated copper grids while recording TEM images. We further recorded HR-TEM images at the edge of a tellurene nanoflake (Fig. S1e). The edge was clean with no signature of further nucleation at the margin of tellurene nanoflakes during the exfoliation process.

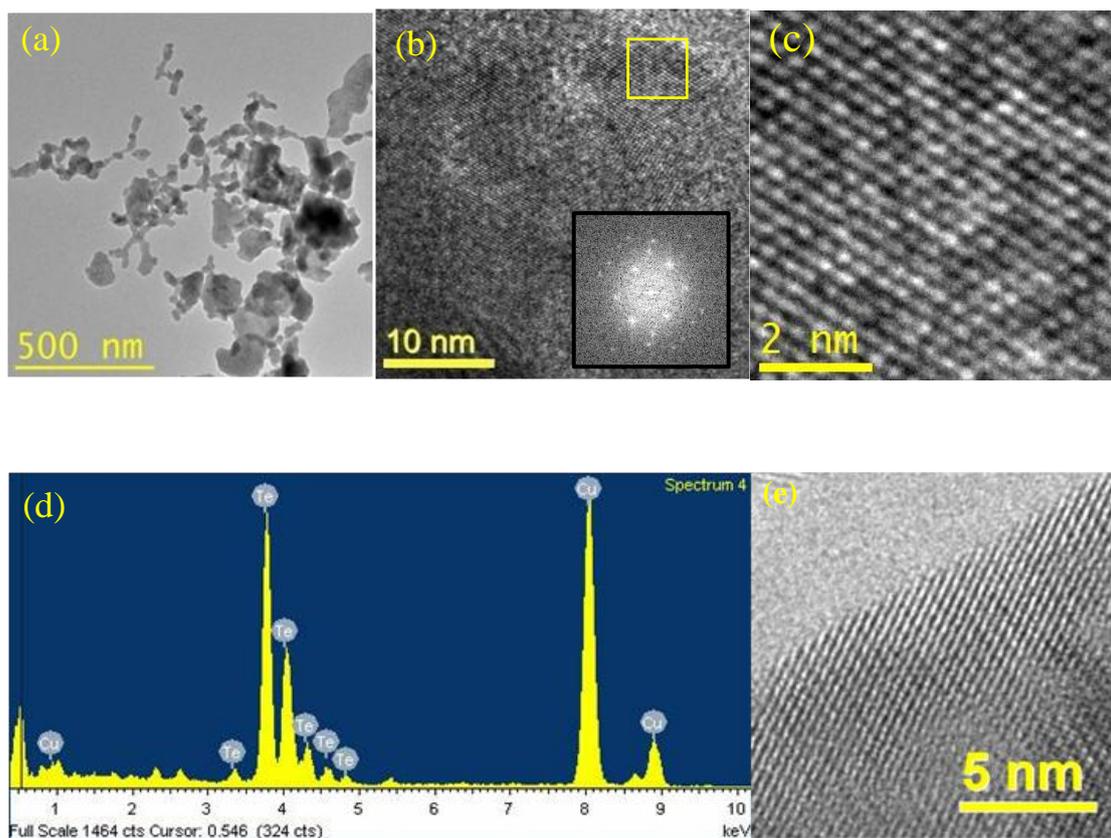


Fig. S1 (a) TEM and (b) HRTEM images of tellurene nanoflakes showing their 2D morphology. Inset of (b) represents a typical FFT photograph. (c) A HR-TEM image, as obtained on the squared region of (b), illustrating their crystalline lattices. (d) EDX obtained from tellurene nanoflakes. (e) An HR-TEM image recorded on an edge of a tellurene nanoflake evidencing no additional nucleation at the edge of the nanoflake.

Optical properties of tellurene nanoflakes

In Fig. S2, we have presented an optical absorption spectrum of tellurene in dispersed solution. The spectrum shows that tellurium nanoflakes have a broad and monotonically decreasing absorbance in a wide wavelength range starting from 325 to 1200 nm. The spectrum matched the reported result.^{S1}

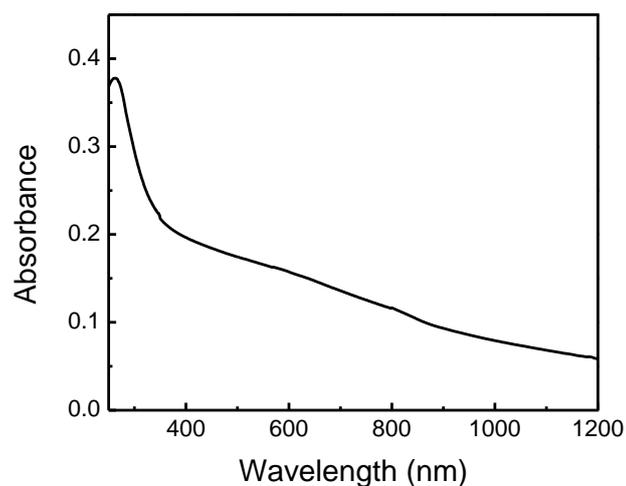


Fig. S2 Optical absorption spectrum of alpha-tellurene in ethanol dispersion.

Analysis of Raman spectroscopy

As presented in Fig. S3, Raman spectra of bulk tellurium and tellurene nanoflakes exhibit three significant Raman-active modes. For all the spectra, we have used a Lorentzian function to fit them. The goodness of fitting was determined by using the value of COD (R^2); in doing so, all parameters were refined until a convergence of the quality factor was 1.0. Here COD refers to coefficient of determination. Interestingly, when monolayers of tellurene were analyzed, the E^1 mode led to a split to doublets with frequencies at 94 and 102 cm^{-1} for transverse (TO) and longitudinal (LO) phonons, respectively, due to an appreciable effective dynamic charge induction. In contrast to the bulk counterpart, we have observed a shift in the A^1 and E^2 modes towards a higher frequency.

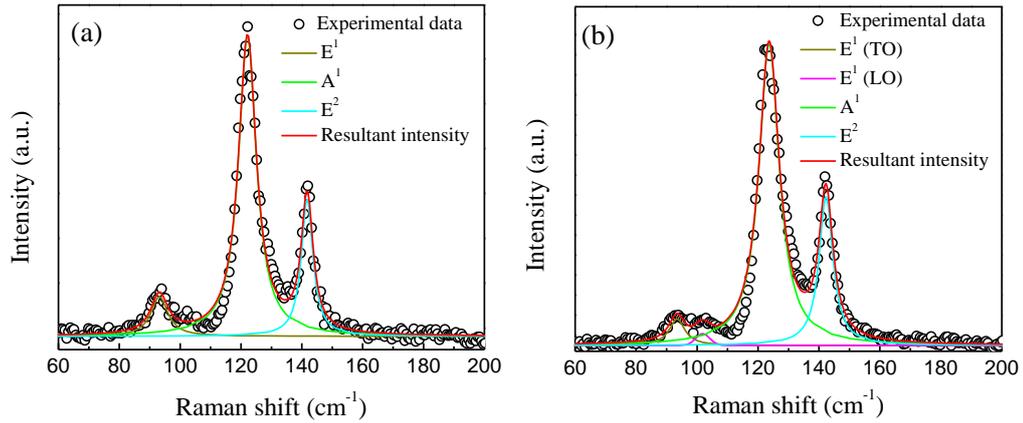


Fig. S3 Raman spectra for (a) tellurium bulk and (b) exfoliated tellurene monolayers with different modes have been fitted through a Lorentzian function.

The hardened in-plane E^2 vibration mode in thinner tellurene is known to appear due to an enhancement in interlayer long-range Coulomb interactions.^{S2} For the A^1 mode, the observed shift towards the higher frequency is in contrast to layered van der Waals (vdW) materials, which usually show a shift of their out-of-plane vibration modes towards low frequencies. As a result of unique chiral-chain vdW structure of tellurene, the lattice deformation within the 2D plane gives rise to the attenuated inter-chain vdW interactions and enhanced intra-chain covalent interactions in tellurene monolayers leading to more effective restoring forces on tellurium atoms and thereby hardened out-of-plane A^1 vibration mode. We can hence conclude that stiffening of vibrational modes in tellurene monolayers is related to its structure reconstruction or spontaneous rearrangements, where extra bonds were formed between adjacent chains in tellurene nanoflakes.

XRD patterns of tellurene

The crystalline phase of bulk tellurium was compared with that of exfoliated nanoflakes through record of XRD patterns (Fig. S4). As expected, tellurium exhibited highly crystalline

nature yielding sharp and intense patterns with peak positions analogous to previous report.^{S1} In case of exfoliated nanoflakes, though the crystal structure remained unaltered, we have observed a shift in peak positions towards lower angles. Such a change has occurred due to the compressive strains developed in the basal plane of alpha-tellurene. One can thus infer that a change in lattice spacing in the strained lattice occurred during the sonication-induced exfoliation process. The results are hence in compliance with the shift in Raman-active modes upon exfoliation.

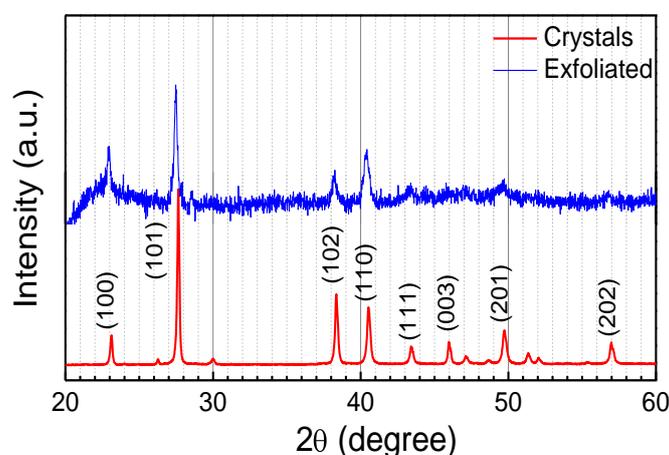


Fig. S4 XRD patterns of tellurium crystals and tellurene.

Fourier-transform infrared spectroscopy (FTIR)

It is mandatory to remove DMF from the nanoflakes before they were characterized in a STM. We therefore used FTIR spectroscopy to infer their absence. Tellurene nanoflakes in ethanol dispersion were considered for FTIR measurements. The spectrum, as presented in Fig. S5, shows several characteristic peaks of different functional groups. More importantly, the spectrum did not show any trace of peaks C=O and C-N stretching vibrations at around 1675 and 1214 cm^{-1} , which are signatures of DMF. The results hence infer that DMF could be removed properly from the nanoflakes making them ready for STM measurements.

Absence of vibrations near 661 and 787 cm^{-1} which correspond to symmetrical stretching of Te-O bond further infers absence of oxygen in the nanoflakes.

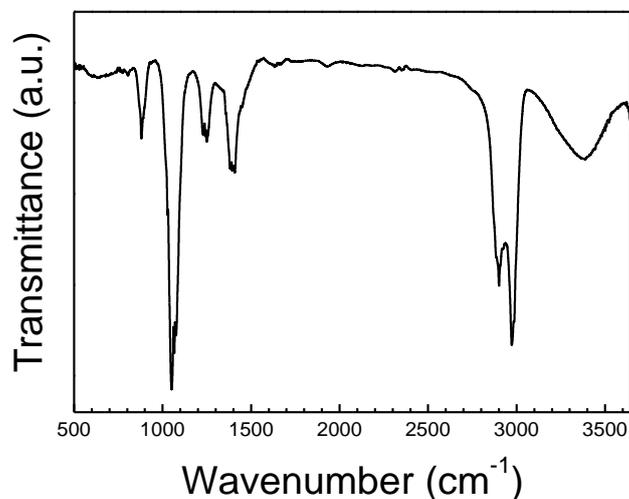


Fig. S5 FTIR spectrum of tellurene nanoflakes in ethanol dispersion inferring absence of DMF.

Scanning tunneling microscopy/spectroscopy at room temperature (STM/S)

We have recorded dI/dV spectra of tellurene nanoflakes at room temperature. As usual, we have recorded the spectra at the interior and also at the periphery to investigate the gapped and metallic states, respectively. The measurements were carried out at different tip-approach conditions (Figs. S6a and 6b). Interestingly, the position of Dirac point and also the band-edges remained unaltered when compared with the results obtained at 80 K. The results infer robust nature of topologically-protected tellurene upon temperature variation. A topography and line profile (to estimate the thickness) recorded at room temperature have been presented in Figs. S6c and S6d, respectively. The profile showed that the nanoflake had a thickness of 0.5 nm which is optimum for observing QSHI phase in tellurene.

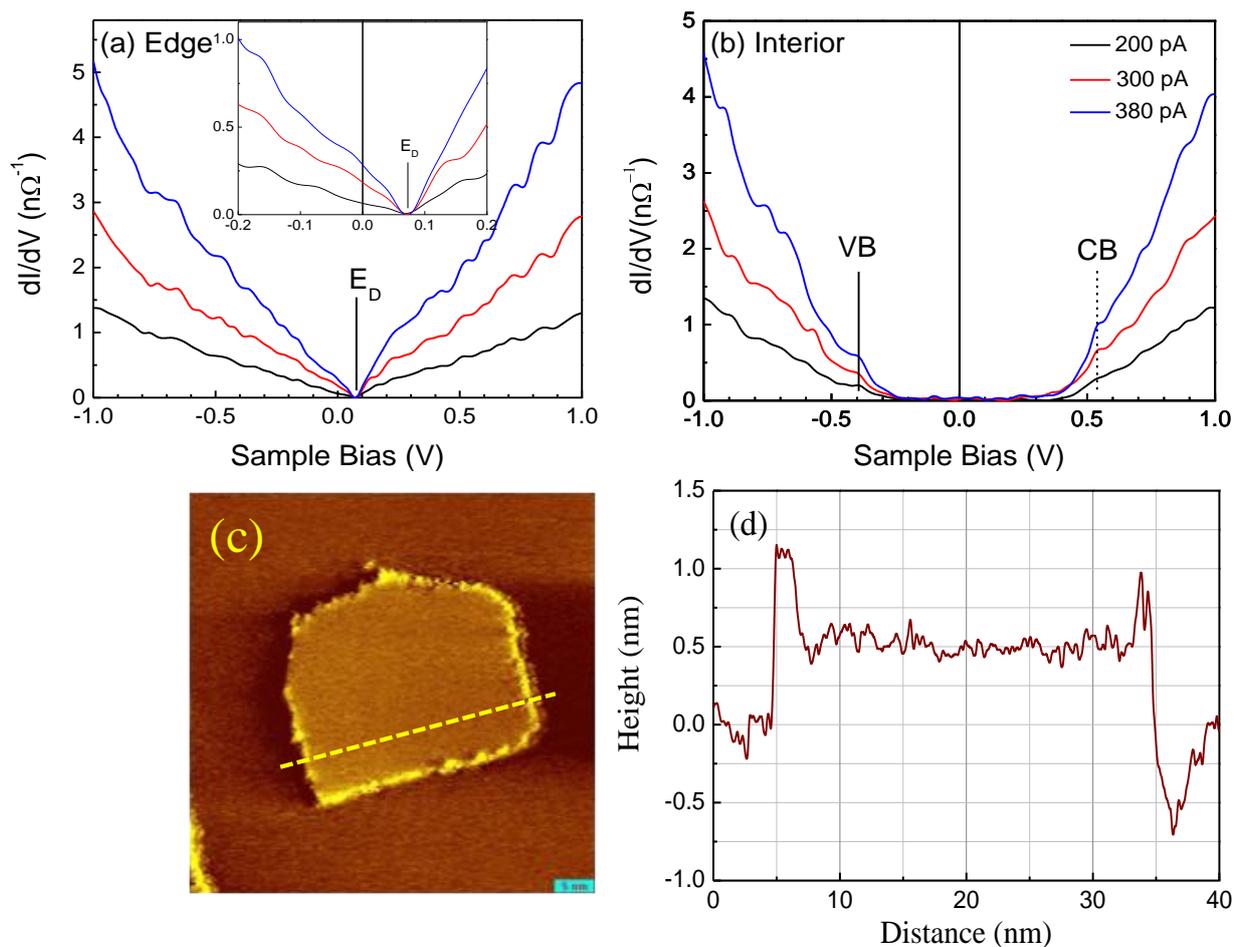


Fig. S6 Density of states (DOS) spectra of a tellurene nanoflake recorded at the (a) edge and (b) interior at three different tip-approach conditions. VB and CB edges have been marked by solid and broken lines, respectively. (c) STM topography of a tellurene nanoflake (scale bar: 5 nm; tunneling current: 400 pA; sample bias: 660 mV) and (d) a line profile on the nanoflake.

References

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