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Thickness dependent tribological and magnetic behavior of two-dimensional cobalt telluride (CoTe₂)

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Abstract

Two-dimensional (2D) layered transition-metal based tellurides (chalcogens) are known to harness their surface atoms' characteristics to enhance topographical activities for energy conversion, storage, and magnetic applications. The gradual stacking of each sheet alters the surface atoms' subtle features such as lattice expansion, leading to several phenomena and rendering tunable properties. Here, we have evaluated thickness-dependent mechanical properties (nanoscale mechanics, tribology, potential surface distributions, interfacial interaction) of 2D CoTe₂ sheets and magnetic behavior using surface probe techniques. The experimental observations are further supported and explained with theoretical investigations: density functional theory and molecular dynamics. The variation in properties observed in theoretical investigations unleashes the crucial role of crystal planes of the CoTe₂. The presented results are beneficial in expanding the use of the 2D telluride family in flexible electronics, piezo sensors, tribo-generators, and next-generation memory devices.

1. Introduction

Transition metal dichalcogenides (TMDs) have drawn significant research interest among the family of two-dimensional (2D) materials due to their layer-dependent properties [1]. The origin of these characteristics is due to their honeycomb structure with a unique symmetry and higher surface-to-volume ratio. One of the intriguing features of TMDs, which makes them exceptional, is their tunable bandgap, which varies as the number of layers changes from indirect at multilayer to direct at single layer [2, 3], making them potential candidates for a wide range of electronics, optoelectronics, energy storage, and catalytic applications [4–6]. Therefore, the investigation of the thickness-dependent properties of emerging TMDs have been receiving increased attention in recent years. Cao *et al* revealed that the fracture strength of graphene paper could be improved by

decreasing its thickness [7]. Enhancement in film resistivity of WS₂ was observed with decreasing thickness by Romanov *et al* [8]. The strong dependence on the layer number of NbSe₂ sheets was observed in their superconductivity transition temperature values [9]. In the field of nanoscale lubrication, there is clear evidence for the role of thickness over a variety of 2D materials for altering the friction force values [10]. The TMDs (NbTe₂, VTe₂, Cr₂S₃, etc) are experimentally proven to exhibit magnetic behavior when the layer thickness is decreased [11–13]. However, only a few TMDs have been explored experimentally on the nanoscale, as well-controlled layer thickness up to monolayer is preferable to study the layer-dependent properties of these materials.

Among various TMDs, ditelluride transition metals are gaining attention due to their metallic characteristics in contrast to other related structures, such as selenides and sulfides [14]. Also, tellurides

exhibit unique bandgap sensitivity at lower dimensions under applied strain conditions [15–17]. 2D CoTe₂ is a layered material having a hexagonal structure wherein six Te atoms surround one Co atom. Several reports have experimentally proven that CoTe_x, in the composition range of $x = 1.3$ up to 2 is metallic due to the decrease in the emission at the Fermi level with the Te content [18]. Recent studies on CoTe₂ nanosheets reported that they have good electrical conductivities up to $4.0 \times 10^5 \text{ S m}^{-1}$, with high breakdown current densities up to $2.1 \times 10^7 \text{ A cm}^{-2}$ [19], and linear magnetoresistance up to 9 T [20]. Negedu *et al* reported that CoTe₂ could behave as a piezoelectric material, and applying small forces (up to 1 N) can result in 5 V of output voltage. They further used 2D CoTe₂ to fabricate piezo and triboelectric nanogenerators, which showed excellent high-temperature stability and gave out an output voltage of about 10 V [21]. At the atomic and nano scales, atomic force microscopy (AFM) sub-modes provide the opportunity to correlate morphology and structure with mechanical, electrical and magnetic characteristics. Significant advances in the study of 2D materials have been made recently owing to developments in AFM-based characterization techniques [22]. In this regard, a variety of suspended graphene membranes' nanomechanical characteristics were mapped by Clark *et al*. It has been found that the force–displacement behavior of monolayer graphene was similar to that obtained with conventional nanoindentation [23]. Additionally, during the fabrication of 2D materials like graphene and MoS₂, the impact of structural defects on strain, doping, and mechanical stiffness was investigated [24]. SPM (scanning probe microscopy)-based local deformation tests were adopted by Susarla *et al* to identify strain-induced ripples at the scratched edges of WS₂/MoS₂ heterostructures, showing a significant interlayer coupling [25]. Oligoglycine tectomer functionalized probe were employed to examine the interfacial interactions between biomolecules and 2D materials. The investigation focused on the tectomer's varying susceptibilities to modify the characteristics of graphene and single- and multilayer MoS₂ [26]. Hence, it would be interesting to comprehensively investigate the nanoscopic size and thickness-dependent CoTe₂ properties using different SPM techniques, and it is one of the objectives of the present study.

In the present work, the synthesis of 2D CoTe₂ was carried out using the liquid phase exfoliation (LPE) method through simple sonication for layer-by-layer exfoliation from the bulk CoTe₂. It is prepared from vacuum induction melting as it is a scalable technique and produces good quality (crystalline with a small number of impurities) nanomaterials at a reasonable cost [27]. X-ray diffraction (XRD) technique and microscopy images confirmed the formation of 2D layered CoTe₂ nanoflakes. The produced

2D CoTe₂ was extensively investigated through atomically resolved transmission electron microscopy to determine the lattice spacing as a function of the number of layers. The samples were further investigated through nano mechanics (mechanical mapping), tribo-mechanics (lateral force microscopy (LFM)), surface potential distribution (Kelvin probe force microscopy (KPFM)) and nanoscale magnetism. We also carried out fully atomistic computer (density functional theory (DFT) and *ab initio* molecular dynamics (AIMD)) simulations to better interpret the experimental data and associated physicochemical mechanisms. The obtained results add important information on the emerging class of tellurides and their use in applications for next-generation electronic devices.

2. Materials and methods

2.1. Experimental details

Bulk CoTe₂ was prepared with vacuum induction melting method by using cobalt and tellurium (99.99% purity) in a stoichiometric ratio of 17.5 wt% of cobalt and 82.5 wt% of tellurium for the composite formation. The alloy was made by melting the elements in a quartz tube at a temperature of 1050°C in a melting chamber under an argon atmosphere. The melting chamber was kept at a high vacuum condition of 10^{-5} mbar for obtaining pure alloy and preventing oxidation. Then, the prepared composite was furnace cooled and converted to powder using mortar and pestle. From these powdered bulk samples, 2D CoTe₂ samples were prepared by taking 50 mg of the bulk sample in 150 ml of isopropyl alcohol and ultrasonicated in a probe sonicator ($f = 30 \text{ kHz}$) for 5 h at room temperature to obtain exfoliated CoTe₂ sheets. The 2D CoTe₂ powdered sample was mixed into 10 ml of IPA and ultrasonicated for up to 30 minutes. The dispersion was spin-coated over the Si wafer at 1000 rpm for 1 minute. The prepared sample was further used for the doing AFM analyses.

The diffraction patterns and crystalline phase information of the sample were taken from Bruker, D8 Advance XRD with Cu- $k\alpha$ radiation having 1.5406 Å wavelength (λ) with 40 kV voltage and 40 mA current as operating conditions. WiTec UHTS Raman spectrometer 300 VIS, Germany, having an excitation wavelength of 532 nm was used for Raman spectrum analysis at room temperature. To study the surface composition and oxidation states of exfoliated CoTe₂, the PHI 5000 Versa probe-III scanning XPS (x-ray photoelectron spectroscopy) microprobe was used. To study topographical, compositional, and crystalline properties FEI, Themis 60–300, and FEI-Ceta 4k \times 4k camera high-resolution transmission electron microscopy (HRTEM) were used.

AFM was used for nanoscale imaging, potential mapping, lateral force microscopy (LFM) and magnetic force microscopy (MFM). All these characteriz-

ations were carried out using the Bruker Dimension Icon instrument at room temperature with 35% relative humidity. The AFM was positioned in the insulated box over an anti-vibrant stage to mitigate the environmental noise and building vibrations. For each mode, specific cantilevers were used for measurements as follows:

AFM was carried out with quantitative nanomechanical mapping mode, ‘an areal collection of force–displacement spectroscopy’ for measuring the variation in mechanical properties such as modulus, adhesion, and indentation along the thickness changing from monolayer to bulk. For the measurements, probe stiffness, driving frequency, and tip radii were taken at values of $5 \pm 0.5 \text{ N m}^{-1}$, 150 kHz, and $10 \pm 2 \text{ nm}$, respectively. For calibration of the cantilever, Sader’s method [28], as well as thermal tuning, were used. The uniqueness of peak force (PF)-AFM in tapping mode is that the maximum normal force applied at each point on the sample surface can be controlled using a feedback system that keeps the maximum force constant while scanning. Silicon nitride probes and Sn doped Si probe (Model: RTESPA-150, Bruker) with stiffness and drive frequency of $5 \pm 0.5 \text{ N m}^{-1}$ and 150 kHz approximately, and tip radii of $10 \pm 2 \text{ nm}$ were used for the measurement. LFM: to measure the lateral force by sliding the tip apex in trace and retrace direction a silicon cantilever of stiffness 0.4 N m^{-1} (Model: CSG10, NT-MDT) was used. KPFM: PF-Kelvin probe microscopy (Model: PFQNE-AL) to measure contact potential difference (CPD, volts). MFM: Bruker MESP probes (cobalt–chromium coating on tip apex) have been used for the investigation. The influence of the localized magnetic field has been measured through phase image in interleave mode.

2.2. Theoretical detail

In order to obtain further insights and to better interpret the experimental results, we carried out *ab initio* calculations at the DFT level. We use the cut-off energy of 250 Ry and k -points mesh of $2 \times 2 \times 2$ within the local density approximation functional and Ceperley and Alder parametrization [29] and single zeta basis. We assume that when forces in each atom are less than 0.05 eV \AA^{-1} , the convergence criteria to the optimization process were achieved. All calculations were performed with SIESTA software [30].

We considered, in our theoretical analyses, structural models to mimic the experimental conditions, i.e. the CoTe_2 layers were deposited on silicon oxide (silica, SiO_2). We deposited at the substrate slab fragments of 2D CoTe_2 corresponding to from one up to four layers at three different crystallographic orientations: [001], [010], and [001]. The heterolayer structures are then fully geometrically optimized.

Once we obtained these optimized structures, we carried out two types of analyses: (i) the energy layer adhesion, and; (ii) a Tip indentation on the 2D CoTe_2 layers. The Tip was modeled using a triangular Si_3N_4 : shaped/pyramid, which is the same tip material used in the AFM measurements. The adhesion of layers was calculated considering the work necessary to extract each layer from different sizes, using the expression (1) [31]:

$$W_{\text{ad}} = \frac{E_{\text{SiO}_2} + E_{2\text{DCoTe}_2} - E_{\frac{2\text{DCoTe}_2}{\text{SiO}_2}}}{A} \quad (1)$$

where $E_{\text{SiO}_2} + E_{2\text{DCoTe}_2}$ are total energy values for the isolated SiO_2 and 2D CoTe_2 , respectively, $E_{2\text{DCoTe}_2/\text{SiO}_2}$ is the total energy value for the 2D heterostructure $\text{CoTe}_2/\text{SiO}_2$, and A is the contact area between them. From equation (1), we calculated the work of adhesion (W_{ad}) for different separation values of sample and substrate. The W_{ad} values were estimated from the universal binding energy relation curves [31], which is a fitting process to calculate the work of adhesion as a function of 2D CoTe_2 number layers and their separation distance from the silica substrate.

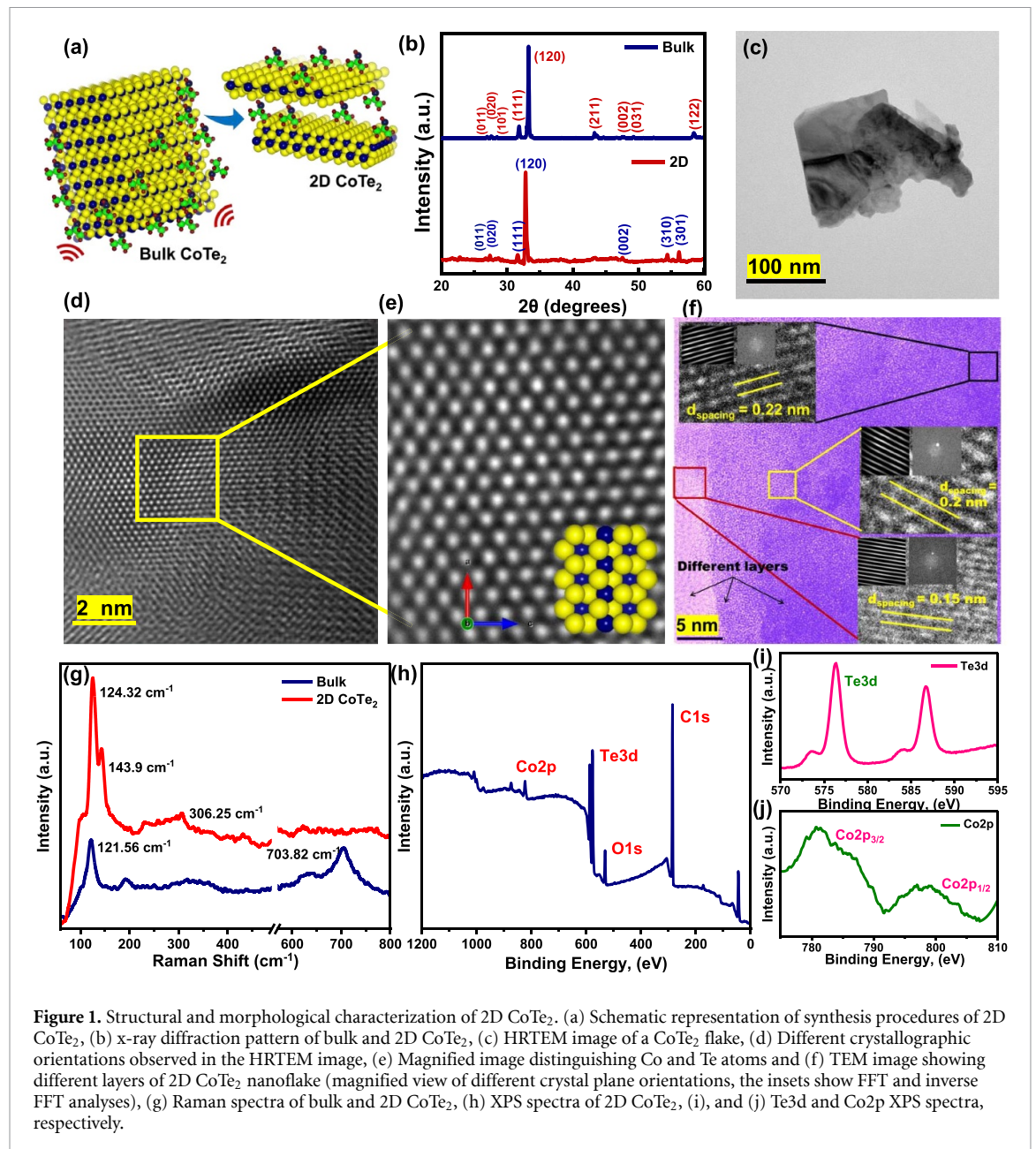
For the analysis of Si_3N_4 Tip penetration on the 2D $\text{CoTe}_2/\text{SiO}_2$ heterostructure, we performed AIMD simulations with an NVT ensemble and integration time of $dt = 1.0 \text{ fs}$. We simulated the Tip processes assuming indentation step movements of 0.5 \AA , in which, for each step, an AIMD run of 0.5 ps is performed. When the Si_3N_4 Tip penetrates the CoTe_2 , it produces a compressive stress (negative value) along the Z direction. It relates to the force through the expression:

$$S_z = -\frac{F}{A} \quad (2)$$

where S_z is the stress component along the Z direction, F is the force applied to the system, and A is the contact area at which the force is applied.

3. Results and discussion

The schematic representation of the formation of layered 2D CoTe_2 from its bulk counterpart is described in figure 1(a) where probe sonication has been used to carry out LPE. The crystalline arrangement was investigated through XRD patterns for both bulk and exfoliated 2D CoTe_2 , shown in figure 1(b), indexed to non-centrosymmetric space group Pnn2 (No. 34) with lattice parameters of $a = 5.329 \text{ \AA}$, $b = 6.322 \text{ \AA}$, and $c = 3.908 \text{ \AA}$. An intensity difference was observed due to the exfoliation of CoTe_2 into preferential planes. The peaks were observed at 28.3° , 31.7° , 32.9° , 47.2° , 54.31° , and 58.2° , in exfoliated CoTe_2 , which are characteristic peaks of orthorhombic crystalline structures. HRTEM images of the polycrystalline telluride flakes



of different thicknesses are presented in figure 1(c). The atomic resolution identifies different crystallographic plane orientations (figure 1(d)) with different atomic arrangements. A zoom-in region of a particular plane in figure 1(e) confirms the presence of two types of atoms: Co and Te, which are depicted by white and black color balls, respectively. The Co atomic number is smaller than Te's, thus, it shows a weaker contrast compared to Te. The arrangement of Co and Te are shown using blue and yellow colors, respectively (figure 1(e)), revealing the CoTe₂ hexagonal structure. The distinction between the CoTe₂ structures with a different number of layers (consequently, having different contrasts) can be clearly seen in figure 1(f). The insets show the FFT (fast fourier transform) and inverse FFT analysis of

the plane orientation observed in these different layers. The d_{spacing} was calculated for the different layers of the CoTe₂ nanoflake, indicating a gradual increase with thin layers having d_{spacing} value of approximately 0.15 nm and thick layers having 0.22 nm. This plays a crucial role in influencing the mechanical properties, surface chemistry, surface potential, and magnetic properties as discussed in the subsequent sections.

The Raman spectra of bulk and 2D CoTe₂ is as shown in figure 1(g). The prominent peaks were obtained at 124.32, 143.9 and 306.25 cm⁻¹ for the exfoliated sample. The A¹ mode at 124.32 cm⁻¹ can be attributed to the movement of atoms in the basal plane found in most of the tellurides [32]. The E² mode at 143.9 cm⁻¹ is associated with asymmetric stretching predominantly along the

c-axis [33]. Compared to the 2D CoTe₂, an additional peak observed at 703.82 cm⁻¹ in the case of bulk was assigned to the stretching mode of the TeO₃ trigonal pyramid units [34]. The XPS spectra of the samples are shown in figure 1(h) with the presence of the characteristic peaks of cobalt, tellurium, oxygen and carbon. Figure 1(i) shows the core level region of Te 3d having peaks at 576 eV and 587 eV, which corresponds to the Te⁴⁺ state i.e. Te 3d_{5/2} and Te 3d_{3/2}, respectively [35]. The other two peaks might be due to surface oxide formation with Co while exfoliating. Figure 1(j) shows the deconvoluted peaks of 2D CoTe₂ where the peaks at about 780 eV and 798 eV are mainly due to Co 2p_{3/2} core level and Co 2p_{1/2} spin-orbit coupling, respectively [36].

The morphology of the 2D CoTe₂ flakes of different thicknesses and their corresponding mechanical response against calibrated tip apex was investigated through AFM; see experimental section for calibration of cantilevers. The nanoscale mapping through PF tapping probe microscopy (PF-AFM) is useful to obtain the mechanical properties of the telluride sheets under elastic conditions (i.e. without damage) of varying thickness from 1 up to 9 nm, figures 2(a) and (c). Thus, the concurrent maps of modulus, adhesion force, and indentation depth were obtained in a single acquisition for a valid comparison, assuming unaffected tip radii [37]. The Derjaguin–Muller–Toporov (DMT) [38] contact mechanical model was used, as it is applicable for stiff samples having low surface energies and includes van der Waals forces outside the contact region. As per this model, the tip–sample surface interaction force under the influence of adhesion force can be given by the relation (3):

$$F = \frac{4}{3} E^* \sqrt{R(d - d_0)^3} + F_{\text{adhesion}} \quad (3)$$

where R is the tip radius, d_0 is the surface rest position, $(d - d_0 = \delta$ (nm)) is the sample deformation under tip indentation depth. E^* is referred as effective elastic modulus of tip and sample, and F_{adhesion} is the adhesion force during contact. The contact mechanics in the DMT conditions is useful to obtain the mechanical properties over various thickness of 2D CoTe₂ shown in figures 2(c) and (d). The retraction force–displacement curves for 2D CoTe₂ nanoflakes from monolayer to bulk are illustrated in figure 2(b). From these retraction force calculations, we observed a gradual reduction in the adhesion force ‘pull-out’. Figures 2(e)–(g) summarizes the trend of average values of adhesion force (nN), modulus (GPa), and indentation depth (nm) values from several telluride sheets showing decreasing adhesion force, modulus, and increasing indentation depth at fixed normal force value. The adhesion force values depend on two major factors: the interfacial contact area between

the tip apex-topmost layer of the 2D material under deformation and the interfacial interaction through static electric charges.

The indentation depth (δ) represents the vertical separation between jump-to-contact and maximum force point in the approach curve of the force–distance spectroscopy (see supplementary information (SI) figure S6) [39]. The increment of indentation depth (nm) indicates the higher contact area with increasing thickness (figure 2(g)) results in higher adhesion force as observed in graphene (see inset figure 2(e)). Nevertheless, the lowering of adhesion force in the telluride sheets confirms the predominance of the static interfacial charges for determining the interfacial interaction (i.e. the metallic tip experiences a repulsion force from the thicker telluride sheets). Further, the increment of the indentation depth also explains the softness (1: 1.4 ± 0.5 GPa, 2: 0.8 ± 0.5 GPa and bulk: 0.6 ± 0.5 GPa) with increasing thickness, similar to the graphene sheets (see the inset of figure 2(f)) of varying Young’s modulus from 2.4 TPa to 1 TPa from monolayer to bulk [40, 41]. The additional factor responsible for mechanical characteristics with thickness is increasing the lattice constant, which leads to weak binding between metal and chalcogenides. During indentation, the interlayer stacking error, i.e. interlayer sliding in multilayer 2D materials, can also be a factor for the decrease in modulus values with increasing thickness [42]. Thus, 2D CoTe₂ sheets share a similar mechanical response with graphene layers with distinct interfacial interaction that will be discussed through the surface potential map by KPFM in the subsequent section. One of the advantages of having low adhesion forces is the potential use of the 2D CoTe₂ sheets as a solid-state lubricant and tribo-generators [21]. The friction map generated from shear forces between the sliding tip and the telluride sheets shows lower resistance to sliding/delamination, figure 2(h) (inset concurrent friction map). The average values of friction force (nN) decrease with thickness, as shown in figure 2(i). This tribological trend is in good agreement with the pioneer works of Lee *et al* [10] and Filleter *et al* [43], addressing the frictional behavior of 2D materials for different thicknesses. This trend is observed (although with different frictional values) for the majority of 2D materials, including graphene and MoS₂ [44–46]; see inset figure 2(h). It has been proposed that thin layers of a 2D material with weak interlayer and substrate interactions are susceptible to deform out-of-plane (‘a puckering effect’) under shear forces, as depicted in schematic figure (S2) in the SI. When the AFM tip slides over the surface of the sample with a finite normal force, a puckered structure (i.e. temporary wrinkle-like topology) is formed around the tip, which increases the contact area and thus induces higher friction. However, as the number of layer increases, the bending rigidity increases

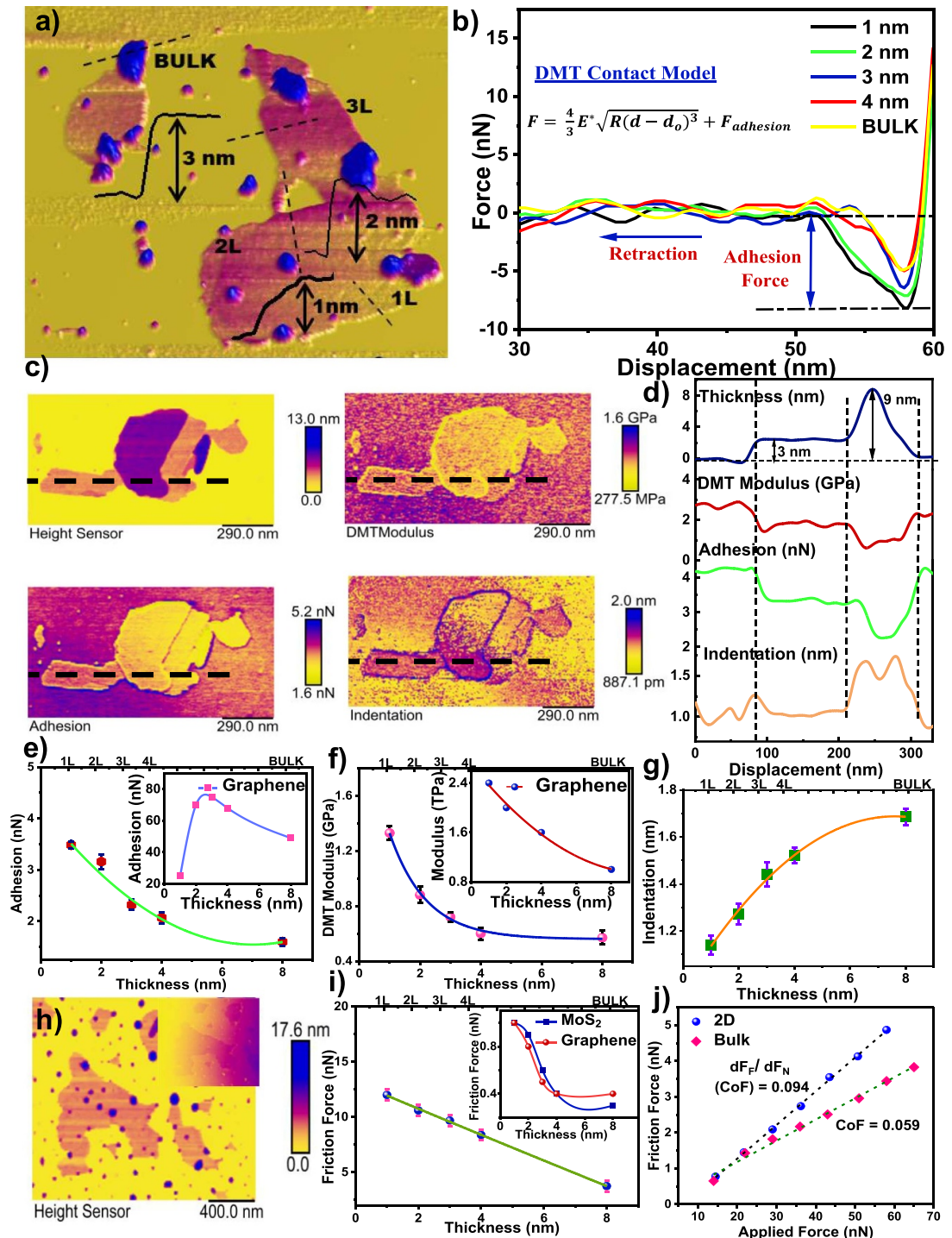


Figure 2. The concurrent surface chemistry (adhesion force) and mechanical response (DMT modulus, indentation map) from CoTe₂ sheets. (a) AFM topography of 2D CoTe₂ layers distributed from monolayer to bulk at different locations, (b) The force–displacement retraction curves from a few layers to bulk show an adhesion force (pull-out) from different thicknesses. The inset presents the contact-mechanical model used to measure the mechanical properties under the influence of the adhesion forces, (c), (d) Topographical images and corresponding line profile of 2D CoTe₂. The dashed line shows the thickness of an individual sheet and its mechanical response toward the AFM tip apex sheet quantified through the line profile. (e)–(g) Variation in average values of adhesion, modulus, and indentation as a function of the thickness. The insets show a comparison with graphene [40, 47]. (h), (i) Frictional map and its characteristics at different thicknesses compared to other 2D materials (inset [45]), and (j) Calculation of the friction coefficient from the applied force Vs. friction force graph of a fixed thickness.

along the vertical direction, suppressing the puckering and consequently lowering the friction force. A generalized form of nanoscale frictional feature can be described through the coefficient of friction values through a first derivative of load-dependent friction

(figure 2(j)). The estimated value of 0.094 brings tellurides close to the category of graphene and MoS₂ as good solid-state lubricants.

DFT and AIMD simulations were carried out using structural models to mimic the experimental

conditions of the contact interaction of the 2D CoTe₂ layers with a SiO₂ (silica) substrate. We used a Si₃N₄ shaped/pyramid tip (the same tip material used in the AFM measurements) to simulate the indentation processes. The adhesion energy variations and the structural distortions of the 2D layers during the simulated indentations. See the experimental section for details. The adhesion energy (J m^{-2}) is measured as a function of the separation distance (\AA) between the telluride sheet/s ($1l$ and $2l$) against the SiO₂ surface (see figures 3(a) for the telluride crystal plane [010]). The optimized structures showed that the charge in the SiO₂ substrate remains practically the same, and no significant charge transfer has been observed from CoTe₂ to the SiO₂ substrate. A slight decrease in the adhesion energy value from $1l$ (1.7 J m^{-2}) to $2l$ (1.66 J m^{-2}) corroborates the trend observed from force–distance spectroscopy measurements. The in-depth analysis indicates that negative static charges on the interface of CoTe₂/SiO₂ (26 me) decrease as a function of the number of layers that play a crucial role in determining the adhesion energy value. It is important to remark that this trend of adhesion energies has been observed for other crystal planes [100] and [001], see SI (figure S5), which suggests that the above-mentioned trend is crystal-oriented dependent and consistent with the different static charges' values 126 and 35 meV along [100] and [001] plane respectively. Also, we considered our structures in vacuum and defectless, while the experiments were in an ambient environment (35% of relative humidity) and comprised structural defects, as evidenced by the microscopy results. Broadly, the adhesion energy of CoTe₂–SiO₂ depends on the crystal plane interfacing the silica substrate, and lies in the range of $0.97\text{--}1.70 \text{ J m}^{-2}$, which is similar to other 2D materials, such as $1l$ graphene–SiO₂ (0.72 J m^{-2}) [48], MoS₂–SiO₂ (0.17 J m^{-2}) [49]. Graphene has shown a parabolic trend in the adhesion energy from $1l$ to $3l$ ($2l$: 1.4 J m^{-2} and $3l$: 1.3 J m^{-2}), indicating saturation of one type of charge at the bilayer [50].

We also estimated Young's modulus (Y_M) values from the DFT simulations. The procedure is to introduce small strain values ($\sim 1\%$) along the X and Y directions separately and then obtain the Y_M values from the slope of the stress versus strain curves. The Y_M values for different crystallographic directions as a function of the number of layers are presented in figure 3(b). It is observed that the different crystallographic directions do not show the same trends. The obtained numbers are consistent with the corresponding experimental ones. The simulated indentation procedures were performed through AIMD simulations. We considered a rigid indenter (Si₃N₄) that is moved (perpendicularly) toward the CoTe₂/SiO₂ structure up to a penetration depth of 0.5 \AA , as schematically shown in figure 3(c) for the case of CoTe₂ [100] plane. The corresponding AIMD snapshots at

different time frames (fs) show a gradual penetration of the indenter and accumulation/dissipation of induced stress through each layer to the silica substrate, which is different for each crystallographic direction. The corresponding results for the [010] and [001] directions are presented in the SI based on the atomic charge distribution. [100] undergoes a minor deformation (up to the depth of 3.5 \AA) due to an efficient stress transfer to the silica substrate (silica amortization). Figure 3(d) presents the force as a function of the depth values. We can see from this figure that the general trend is that the force decreases as the depth value increases. The same behavior was observed for the other crystallographic directions (results presented in the SI). Although the values from the simulations are larger than those experimentally obtained (expected as the simulations considered pristine defect less structures), the qualitative behavior is the same experimentally observed and further validates the thickness softness effect.

As discussed above, the thickness dependence of 2D CoTe₂ sheets influences their mechanical properties and interfacial adhesion energy. Its critical effect also applies to surface electric potentials and localized magnetic fields, sensed by separate functionalized probes of metallic and magnetized coating (cobalt–chromium) coatings, respectively. The CPD (volts) observed during PF-KPFM measurements shows topography (figure 4(a)) corresponding to surface potential distribution of different thicknesses, figures 4(b) and (c). The average values of work function (eV) were calculated from surface potential values using an expression (SI equation (4)) showing a decreasing trend with thickness, inset of figure 4(c). The decreasing values of work function with increasing thickness indicate higher electron concentration at the thick layer. This phenomenon can be explained by electrostatic interlayer screening [51], i.e. charge redistribution among each layer induced from the substrate as observed in graphene by Kim and co-workers [52]. Therefore, increasing the negative charges with the addition of a telluride layer repels the similar negative charges on the sliding probe responsible for the lower adhesion with higher thickness. Nevertheless, interlayer interaction (in a thick sheet) against the tip apex cannot be ignored [53]. One can stimulate the surface with biasing and modulate the static charge interaction, consequently, adhesion force from 2D material for the desired application [26].

The magnetostatic interaction between the stray magnetic field from the CoTe₂ and magnetic sensor was investigated as the function of thickness. The magnetized probe (see experimental section) is slid at constant lift height (LH) to detect the force gradient of the stray field. The vertical force gradient from different sheet thicknesses shifts the magnetic sensor resonance frequency (f_o) proportionally. The frequency

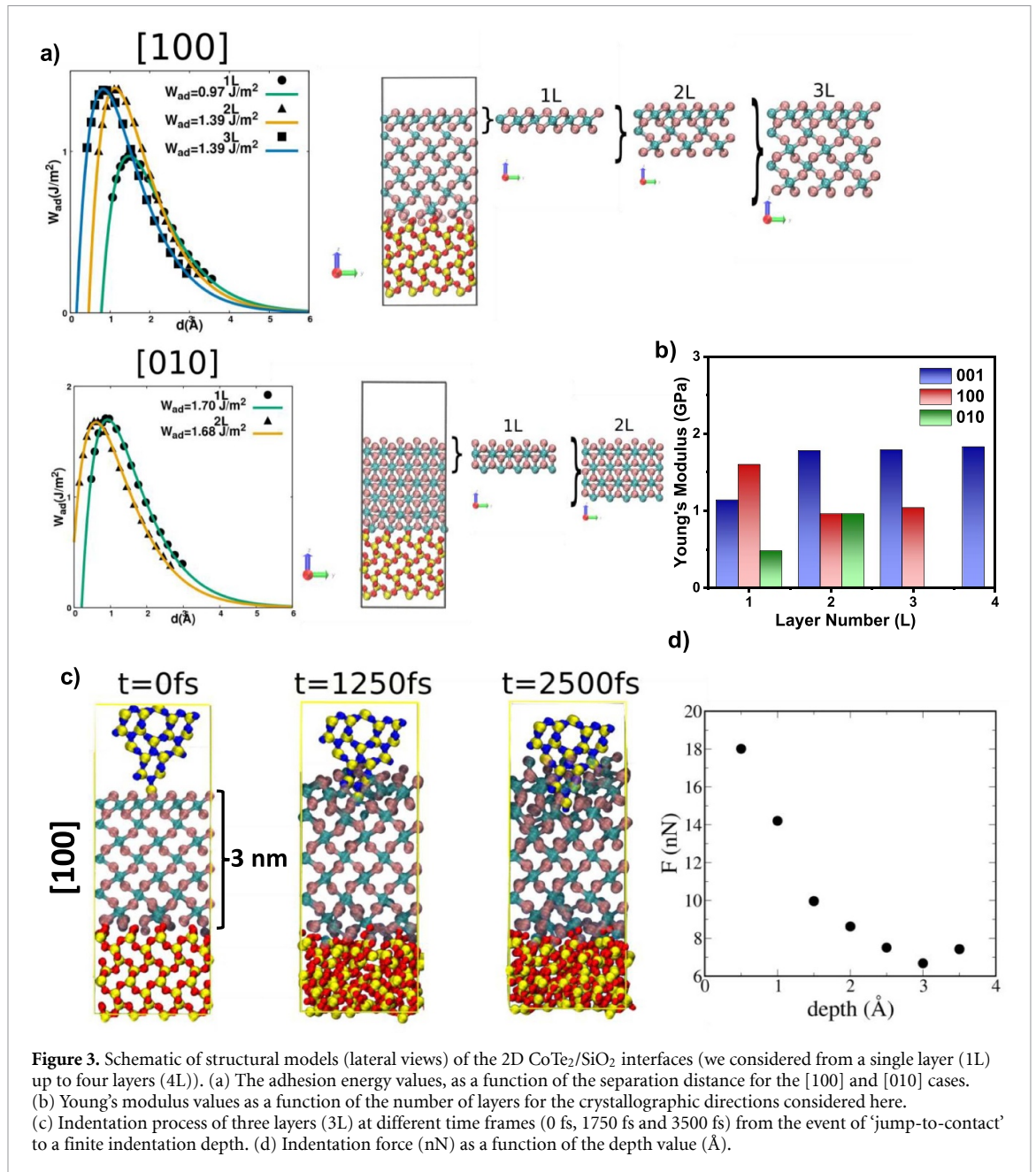
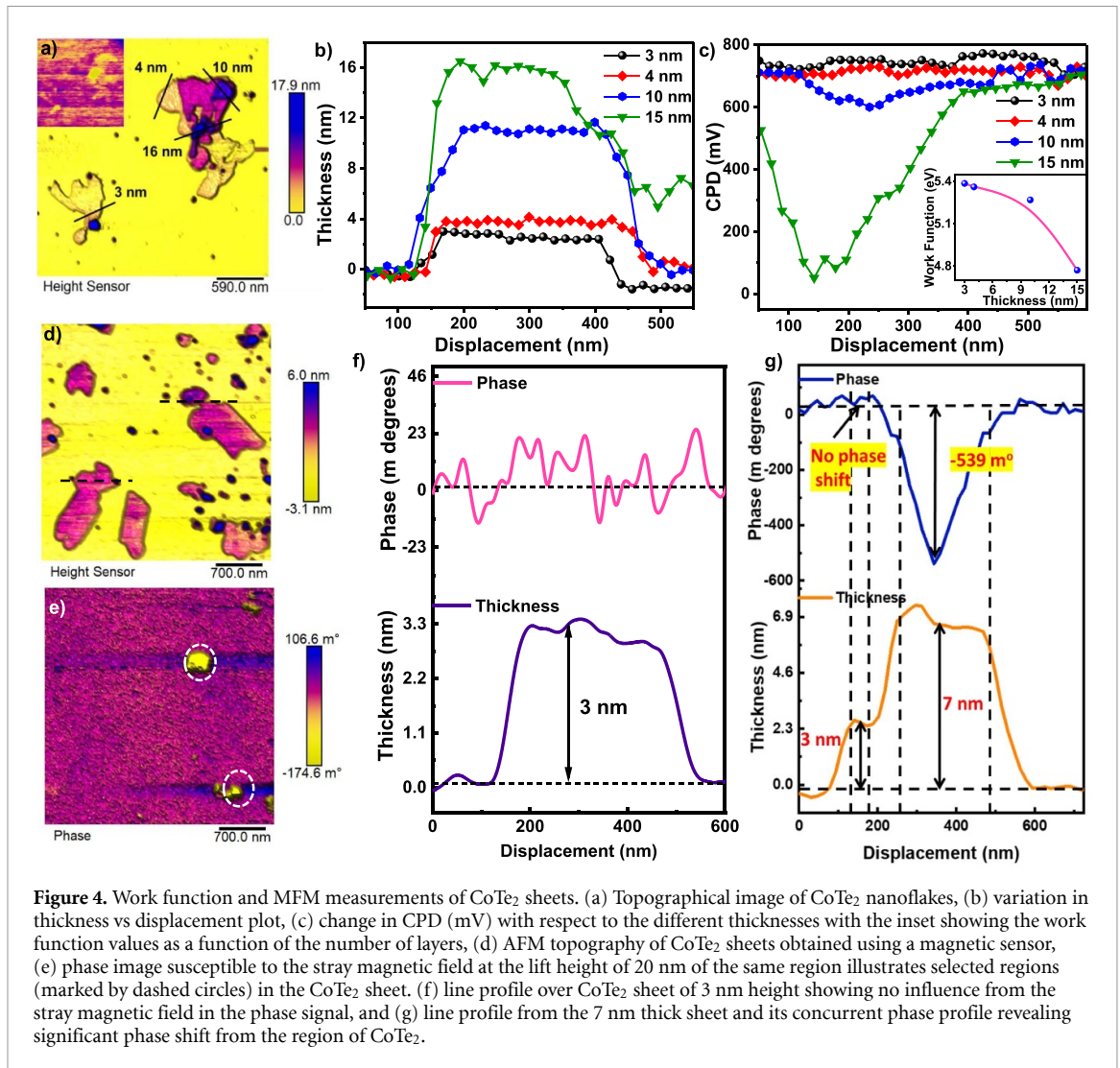


Figure 3. Schematic of structural models (lateral views) of the 2D CoTe₂/SiO₂ interfaces (we considered from a single layer (1L) up to four layers (4L)). (a) The adhesion energy values, as a function of the separation distance for the [100] and [010] cases. (b) Young's modulus values as a function of the number of layers for the crystallographic directions considered here. (c) Indentation process of three layers (3L) at different time frames (0 fs, 1750 fs and 3500 fs) from the event of 'jump-to-contact' to a finite indentation depth. (d) Indentation force (nN) as a function of the depth value (\AA).

shift (Δf) is detected through the phase of oscillations. In the present set-up, the cantilever phase signal upper shift indicates the magnetic sensor repulsion from the stray magnetic field and vice-versa for the downshift (see scale bar in figure 4(e)). The phase image reveals that a limited region of the CoTe₂ sheet is susceptible to the magnetic field, which is quantified through the phase signal profile. It is observed that thicker CoTe₂ (around 7 nm) showed the signature of the magnetic attraction, which was not observed in the thinner sheets of 3 nm (see figures 4(f) and (g)). It is worth mentioning that MFM technique is well suited for highly magnetized samples, nevertheless ineffective toward weak stray fields generated from subtle magnetic regions [54]. DFT simulations were also carried out to investigate sub-nanoscale

magnetic properties of 2D CoTe₂ through the calculation of collinear spin polarization (see SI, figure (S5) for details). It was observed that magnetic moment (μ) increased with thickness for the crystal direction [100], as follows: ($\mu_{1L} = 0.43 \mu_B$, $\mu_{2L} = 0.56 \mu_B$, and $\mu_{3L} = 0.58 \mu_B$). For the other crystal planes ([010], and [001]), different trends were observed ($\mu_{1L} = 0.62 \mu_B$, and $\mu_{2L} = 0.57 \mu_B$), ($\mu_{1L} = 0.77 \mu_B$, $\mu_{2L} = 0.62 \mu_B$, $\mu_{3L} = 0.57 \mu_B$), respectively, where, μ_B is the Bohr magneton constant. The DFT results also indicate that the magnetization of CoTe₂ is direction-dependent, it increases for [100], and decreases to [010] and [001].

Since the magnetic contrast in MFM is highly dependent on the LH, we carried out MFM measurements at various LHs to investigate the magnetic



properties of 2D CoTe₂ with different thicknesses. Through MFM, concurrent height profile information and interleave phase signal have been observed. The phase response is a consequence of the interaction between the magnetized AFM probe's field and the magnetic domains (parallel and antiparallel) from the sample operated at vertical separations (so-called LHs). Thus, different LHs reveal valuable information about the gradient of stray magnetic fields from 2D CoTe₂, as shown in figure 5(a). The MFM images exhibit resolution details of the surface magnetic domains at the LHs from 20 nm to 25 nm and decrease after 35 nm for all thicknesses. The corresponding plot profiles at different LHs, as shown in figure 5(b), align with the morphology of the 2D CoTe₂. A distinguishable magnetic characteristic has been observed between 3 and 6 nm thickness 2D CoTe₂ for LHs of 20 nm and 25 nm. The negative phase shift reflects the attractive interaction between the probe and the sample, found higher in the 6 nm thickness sample. This is because, under the attractive magnetic field interaction, the resonance frequency

($\omega_0 \approx 73.43$ KHz) of the cantilever decreases, resulting in negative phase shift change ($\Delta \text{phase}^\circ$). Lowering of LH further increases the $\Delta \text{phase}^\circ$, indicating a higher magnetic moment of the thicker layer than thin 2D CoTe₂. It is suggested that nominal positive values of $\Delta \text{phase}^\circ$ imply lesser magnetic response or the dominance of electrostatic repulsion [55, 56].

Interlayer interactions between the telluride sheets and the cumulative spin moments can explain the overall magnetic properties of 2D lamellar CoTe₂. It has been found in previous studies that the magnetic behavior of the different layers depends on the stacking sequence of the crystal. Since the interlayer van der Waals bonding is weak, this can result in different stacking polytypes. For instance, Li *et al* reported that in the monoclinic stacking sequence of CrI₃, the spin coupled to each other results in an antiferromagnetic behavior, whereas if the layers were arranged in a rhombohedral manner, it resulted in a ferromagnetic interlayer exchange [57]. It is worth noting that the linear growth of magnetic moment

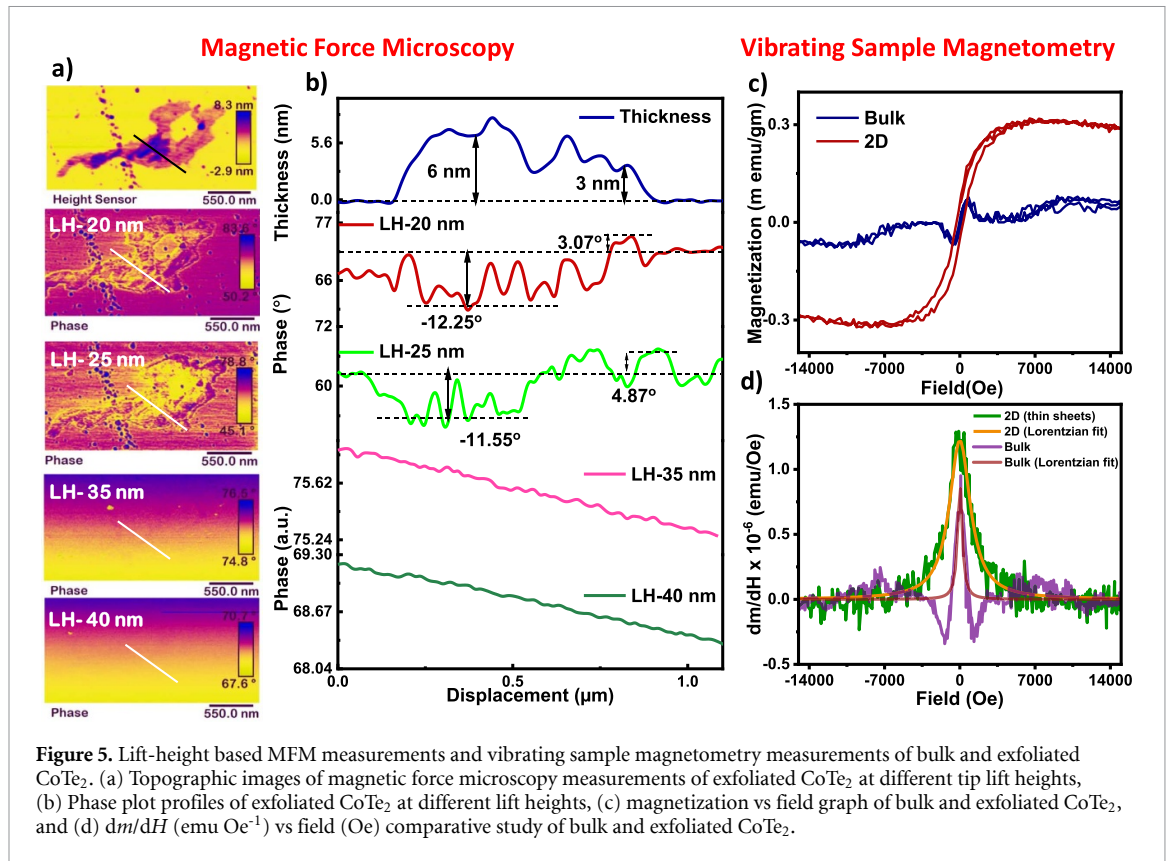


Figure 5. Lift-height based MFM measurements and vibrating sample magnetometry measurements of bulk and exfoliated CoTe₂. (a) Topographic images of magnetic force microscopy measurements of exfoliated CoTe₂ at different tip lift heights, (b) Phase plot profiles of exfoliated CoTe₂ at different lift heights, (c) magnetization vs field graph of bulk and exfoliated CoTe₂, and (d) dm/dH (emu Oe⁻¹) vs field (Oe) comparative study of bulk and exfoliated CoTe₂.

with increasing thickness is not always obvious, as observed by Li and coworkers for another TMD (MoS₂) [55]. Additional factors, such as variations in the stacking arrangement, presence of defects, vacancies, etc, could also change the cumulative spin moments and influence the lamellar material's magnetic properties [58, 59].

The macroscale magnetic behavior of 2D CoTe₂ was investigated through vibrating sample magnetometry performed at room temperature (300 K), as shown in figure 5(c). The magnetic ordering of bulk CoTe₂ is weaker as compared to 2D CoTe₂. The saturation magnetization in 2D CoTe₂ is 0.321 emu gm⁻¹, which is four times larger than the corresponding bulk value (79.61×10^{-3} emu gm⁻¹). The magnetic coercivity (H_c) and retentivity (M_r) for 2D CoTe₂ are 311.90 Oe and 384.56×10^{-6} emu, respectively, which are larger than the bulk CoTe₂ (43.77 Oe and 118.18×10^{-6} emu). The appearance of a hysteresis loop in the 2D CoTe₂ shows the presence of a soft ferromagnetic nature. According to figure 5(d), it is anticipated that the full-width half maximum of the first derivative for 2D CoTe₂ has a broader distribution of magnetic moments and hence exhibits better magnetization with respect to a given field than the bulk counterpart, which exhibits a weaker magnetization, as shown in the fitted curve. The previous work on bulk CoTe₂ reported its ferromagnetic behavior being suppressed due to strong spin fluctuations, thereby maintaining its paramagnetic nature

[60]. The current work is the first paper on magnetic and mechanical properties correlation of 2D CoTe₂. In future, a detailed temperature dependent magnetic properties studies can reveal several interesting unexplored physics of the unique CoTe₂. However, no experimental validation of changing the magnetic nature to ferromagnetic after exfoliation with varying thicknesses has been reported. Hence, our research sheds light on the intriguing magnetic properties of 2D CoTe₂ and opens new perspectives for future explorations in this dynamic area of intrinsic magnetism and spin-based electronic devices.

4. Conclusions

In summary, the present work demonstrated the thickness-dependent properties of 2D CoTe₂. The theoretical and experimental observations conclude that the crystallographic orientations and structural changes are responsible for the mechanical behavior. The surface charge distribution changes as a function of number of layers. The obtained results for nanostructured CoTe₂ were compared with other 2D materials. The magnetic behavior changes as a function of layer number, which is due to the stacking order. We have demonstrated that the number of layers can be effectively used to tune and control some electronic and/or magnetic features, that can be helpful for designing next-generation tellurides-based devices.

Data availability statement

The data cannot be made publicly available upon publication because no suitable repository exists for hosting data in this field of study. The data that support the findings of this study are available upon reasonable request from the authors.

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Conflict of interest

The authors declare no competing financial/commercial conflicts of interest.

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