

# Synthesis and Characterization of Ultrathin FeTe<sub>2</sub> Nanocrystals

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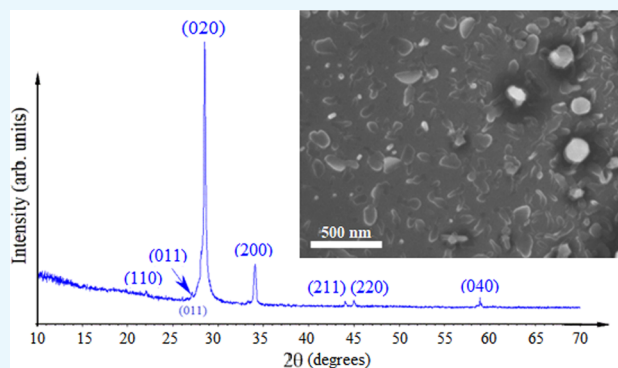
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**ABSTRACT:** Ultrathin crystals including monolayers have been reported for various transition-metal dichalcogenides (TMDCs) with van der Waals bonds in the crystal structure. Herein, we report a detailed synthesis procedure and characterization of ultrathin iron ditelluride crystals. This material crystallizes in an orthorhombic marcasite *Pnmm* crystal structure whose bonding is dominantly covalent and without loosely connected van der Waals (vdW) bonds, making monolayer FeTe<sub>2</sub> synthesis less straightforward than other TMDC monolayer syntheses. The chemical vapor deposition synthesis process described is simple, effective, and results in a range of crystal thicknesses from approximately 400 nm down to the FeTe<sub>2</sub> monolayer.



## INTRODUCTION

Iron ditelluride (FeTe<sub>2</sub>) is one of the several transition-metal dichalcogenide crystals first synthesized and observed by Steffan Tengner in 1938.<sup>1</sup> FeTe<sub>2</sub> is known to form in either marcasite-type or pyrite-type crystals, depending on the synthesis conditions. The orthorhombic marcasite structure is the more common crystal phase formed under ambient conditions, while the cubic pyrite phase is formed through high-temperature and high-pressure synthesis techniques.<sup>2</sup>

Marcasite FeTe<sub>2</sub> adopts either a *Pnmm*<sup>1,3</sup> or *Pnn2*-type<sup>4</sup> orthorhombic unit cell, where Fe is octahedrally coordinated by Te. Density functional theory found no significant energy difference between the two arrangements.<sup>5</sup> Early studies show that FeTe<sub>2</sub> crystals have an anisotropic antiferromagnetic ground state below about 80 K and a possible ferromagnetic (FM) state below approximately 30 K.<sup>6–8</sup> The electronic structure features a reported band gap of 0.35–0.67 eV, as deduced from electrical transport measurements.<sup>7,9</sup> FeTe<sub>2</sub> thin films have been found to feature a low thermal conductivity value of 1.20 W m<sup>-1</sup> K<sup>-1</sup>.<sup>10</sup> Electron-doped marcasite FeTe<sub>2</sub> crystals are a good candidate for thermoelectric applications due to the sharp increase in density of states around the band edges, which favors a large increase in the thermoelectric power factor  $S^2\sigma$ , where  $S$  is the thermopower and  $\sigma$  is the electrical conductivity.<sup>5</sup>

FeTe<sub>2</sub> nanoparticles have previously been synthesized using solution-based methods, where all reactions take place between 120 and 300 °C. Low-temperature hydrothermal synthesis produced 25 nm diameter spherical nanoparticles<sup>11</sup> and nanorods<sup>12</sup> that can be indexed to orthorhombic FeTe<sub>2</sub>. FM FeTe<sub>2</sub> nanocrystallites<sup>13</sup> were also prepared using a hydro-

thermal method. Hot-injection solvothermal methods under atmospheres of inert gases like nitrogen and argon have produced FeTe<sub>2</sub> nanorods,<sup>14</sup> a colloidal solution of FeTe<sub>2</sub> nanocrystals,<sup>15</sup> and magnetic spherical FeTe<sub>2</sub> crystallites that aggregate into treelike architectures.<sup>16</sup> Irregular FeTe<sub>2</sub> nanocrystallites<sup>13,16</sup> with dimensions on the order of several hundred nanometers were found to be ferromagnetic at room temperature. These solutions utilize relatively mild temperatures and deliver crystals of variable morphologies. However, they are also relatively time-consuming, require complicated precursor solution syntheses prior to the FeTe<sub>2</sub> formation reaction, and necessarily involve filtration, washing, and drying/resuspension steps. These steps not only add extensive hands-on involvement but can also be a source of contamination.

The development of a more facile synthesis method for FeTe<sub>2</sub> nanocrystals is of high interest, particularly methods that can produce relatively clean materials for future studies. It has been known for some time that nanocrystals with vdW bonds in the crystal structure, such as TMDCs, can be produced using chemical vapor deposition methods.<sup>17–21</sup> The synthesis of ultrathin TMDC nanocrystals has enabled many important discoveries.<sup>22–24</sup>

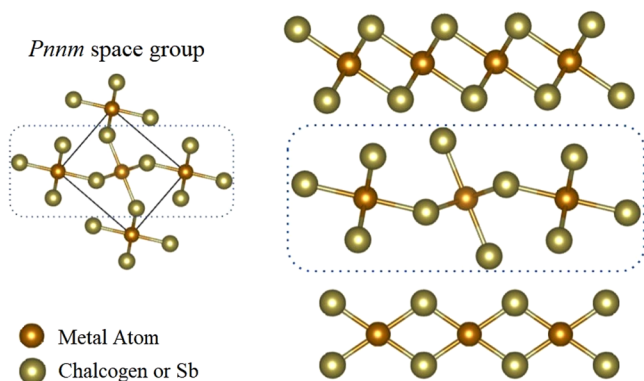
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Since neither marcasite nor pyrite crystals are vdW solids, monolayer FeTe<sub>2</sub> was formerly considered nonexistent.<sup>25</sup> This conclusion was reasonable, as it can be seen in Figure 1 that



**Figure 1.** Comparison of marcasite *Pnmm* space group with the 1T (*P31m*, CdI<sub>2</sub>-type) and 2H (*P63/mmc*, NbS<sub>2</sub>-type) crystal structures of transition-metal dichalcogenides. Note the absence of van der Waals bonds in the marcasite crystal structure.

neither the 1T nor 2H atomic layer structures common in TMDCs are directly derived from the *Pnmm* space group crystal unit cell. However, multiple first-principles studies, where monolayer FeTe<sub>2</sub> was studied,<sup>5,26–29</sup> concluded that it is possible for this material to be energetically stable in monolayer form in ambient conditions based on calculated phonon-dispersion frequencies. When both the octahedral (T) and trigonal-prismatic (H) coordinations of Fe were compared, it was found that the H phase had lower energy than the T phase,<sup>2</sup> making it the more thermodynamically favorable of the two. As a result, most first-principles calculations of monolayer FeTe<sub>2</sub> consider the H phase.

The magnetic state of monolayer FeTe<sub>2</sub> is predicted to be either FM or ferromagnetic with calculated moment values in the range from 1.08 to 2  $\mu_B$ .<sup>5,28,29</sup> Magnetocrystalline anisotropy (MCA) that favors the in-plane direction<sup>28</sup> and the MCA dependence on an applied electric field for multiple MTe<sub>2</sub> compound monolayers<sup>27</sup> were predicted. The FeTe<sub>2</sub> easy axis flips from in-plane to out-of-plane as the applied electric field increases, giving monolayer FeTe<sub>2</sub> excellent potential for applications in magnetic memory devices. Magnetic anisotropy has also been noted in experiments on bulk FeTe<sub>2</sub> crystals.<sup>7</sup>

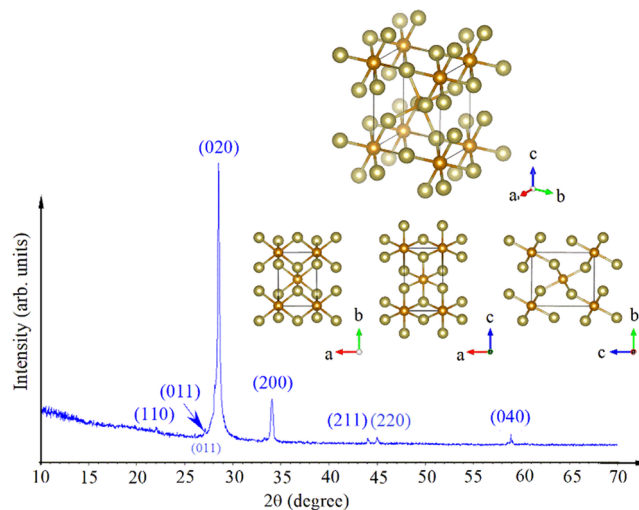
There is some debate about the electronic character of the FeTe<sub>2</sub> monolayer. Two studies found it to exhibit semi-conducting behavior, with band gaps of 0.87<sup>2</sup> and 0.35 eV,<sup>5</sup> which are on the order of those observed in TMDCs. However, other studies found FeTe<sub>2</sub> monolayer to exhibit metallic behavior<sup>25,26,28</sup> and half-metallicity,<sup>27,29</sup> making it a potential candidate for applications in spintronics as spin valves. Gudelli et al.<sup>5</sup> also found in their first-principle theoretical study of the thermoelectric properties of monolayer FeSe<sub>2</sub> and FeTe<sub>2</sub> that marcasite FeTe<sub>2</sub> is a good thermoelectric material that favors electron doping. Its hole and electron concentrations were calculated to be  $9.2 \times 10^{19}$  and  $1.4 \times 10^{21} \text{ cm}^{-3}$  for the thermopower values of 96 and  $-74 \text{ mV K}^{-1}$  at 300 and 600 K, respectively. FeTe<sub>2</sub> also had calculated relaxation times of  $2.3 \times 10^{-14}$  and  $3.1 \times 10^{-14} \text{ s}$  at those respective temperatures.

It is clear that FeTe<sub>2</sub> is a material with promising qualities for future applications that remains relatively unstudied experimentally. With the lack of efficient large-scale syntheses of this

material being an obstruction of progress in this field, it is vital to further develop its nanomaterial production methods. In this work, we present a chemical vapor deposition process to synthesize FeTe<sub>2</sub> nanocrystals of various sizes down to monolayer thickness. This more facile process allows for nanocrystal synthesis directly on the substrate from simple powder precursors in a relatively short interval of time. Crystal structure and unit cell parameters of deposited nanostructures were investigated through X-ray diffraction. A scanning electron microscope (SEM) was used to obtain images confirming nanoparticle deposition, lateral sizes, and morphologies. The energy-dispersive X-ray spectroscopy (EDS) capability of the SEM was used to determine the chemical composition of nanostructures within the sample. Raman spectroscopy also confirmed that FeTe<sub>2</sub> phase crystals formed in this experiment. Atomic force microscopy (AFM) data was used to calculate and compare the lateral and vertical size dimensions of deposited nanostructures.

## RESULTS

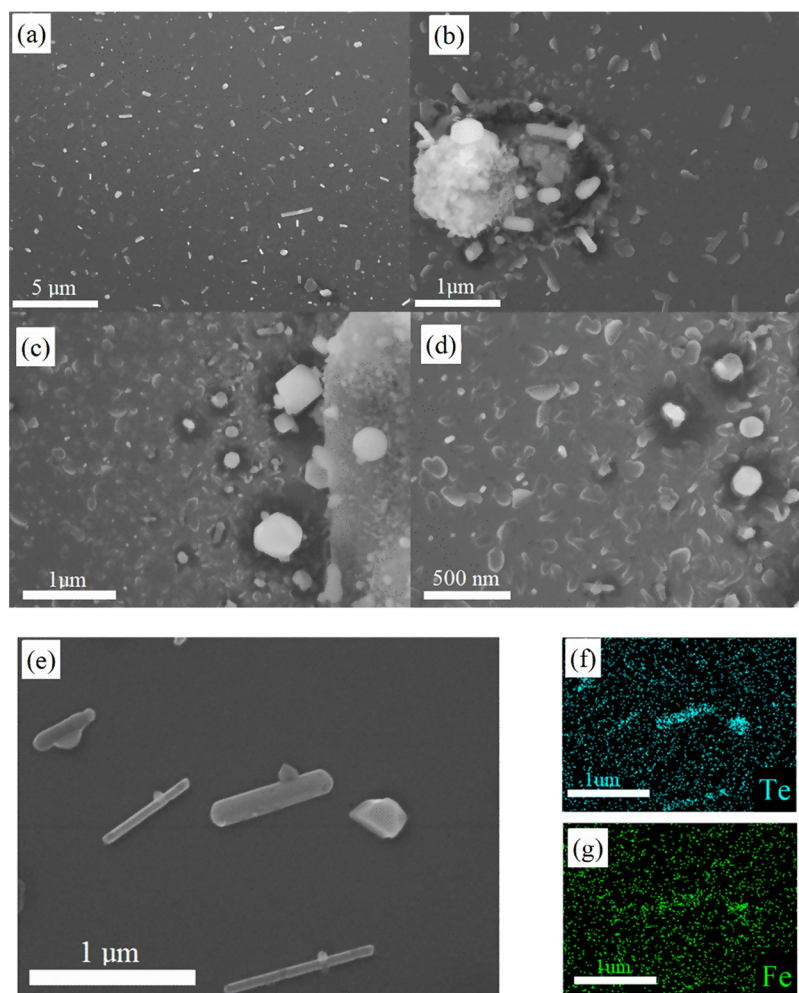
**X-ray Diffraction and Energy-Dispersive Spectroscopy.** Figure 2 shows the X-ray diffraction scan of the substrate



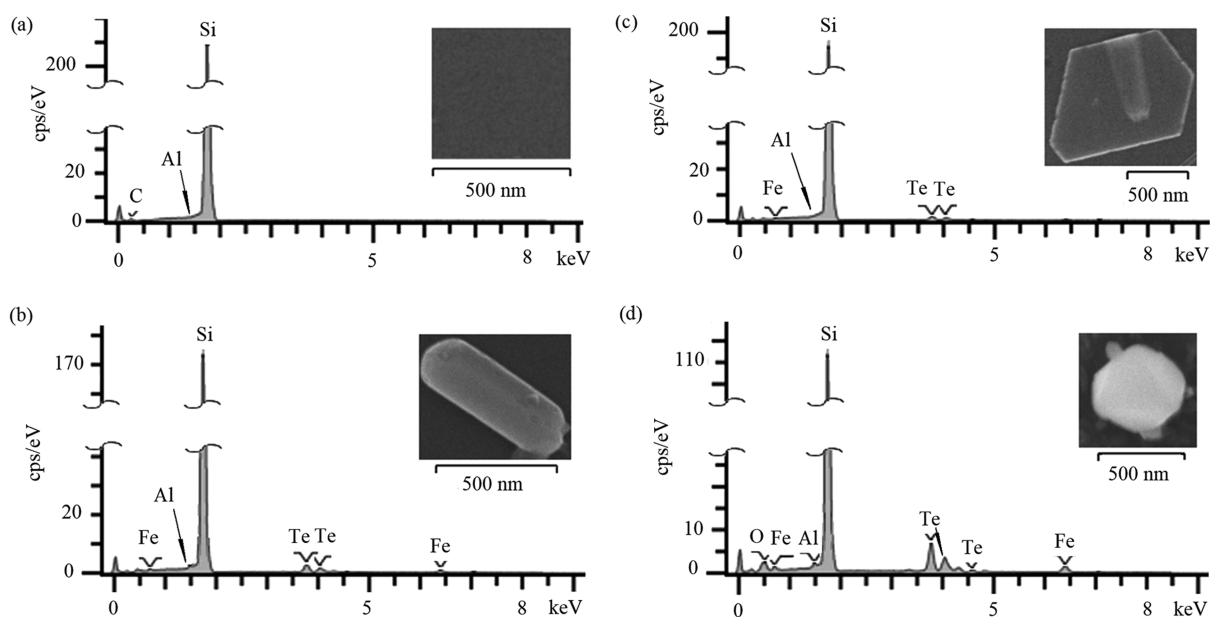
**Figure 2.** X-ray diffraction pattern for deposited FeTe<sub>2</sub> crystals. The inset shows the FeTe<sub>2</sub> crystal structure.

after deposition. All diffraction peaks can be indexed in the orthorhombic *Pnmm* (58) space group, with the calculated lattice parameters  $a = 5.262(2) \text{ \AA}$ ,  $b = 6.2608(2) \text{ \AA}$ , and  $c = 3.871(2) \text{ \AA}$ . These values correspond well to the reported standard values<sup>10,13</sup> with no impurity present.

Diffraction peaks can be seen at 28.49° (020) and 34.01° (200), and weak peaks at 22.05° (110), 27.11° (011), 44.00° (211), 44.98° (220), and 58.92° (040). The strongest peak is at 28.49° (020), and the peak for its parallel plane (040) is visible as well. Due to the orthorhombic lattice structure of this crystal, the (200) plane is also symmetrical to the (020) and (040) planes. The symmetry of the two largest peaks indicates the preferential orientation of crystals on the substrate with their  $\{0k0\}$  faces aligned to the substrate direction, or faces of the type  $\{200\}$  or  $\{100\}$ . The presence of peaks for the (110) and (220) planes, which are symmetrical, as well as the (211) and (011) planes, indicate that although there is preferential orientation along the (010) plane, the deposits have a certain range of preferred crystallization.



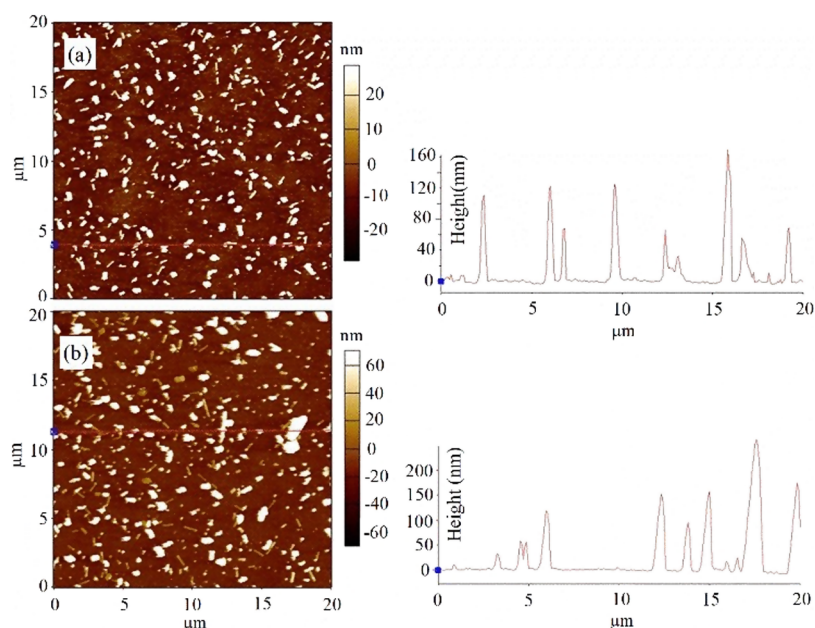
**Figure 3.** (a–e) Scanning electron microscope images at various magnifications of the as-synthesized  $\text{FeTe}_2$  nanocrystals. (f, g) Elemental mapping of target nanocrystals for tellurium (f) and iron (g) concentrations.



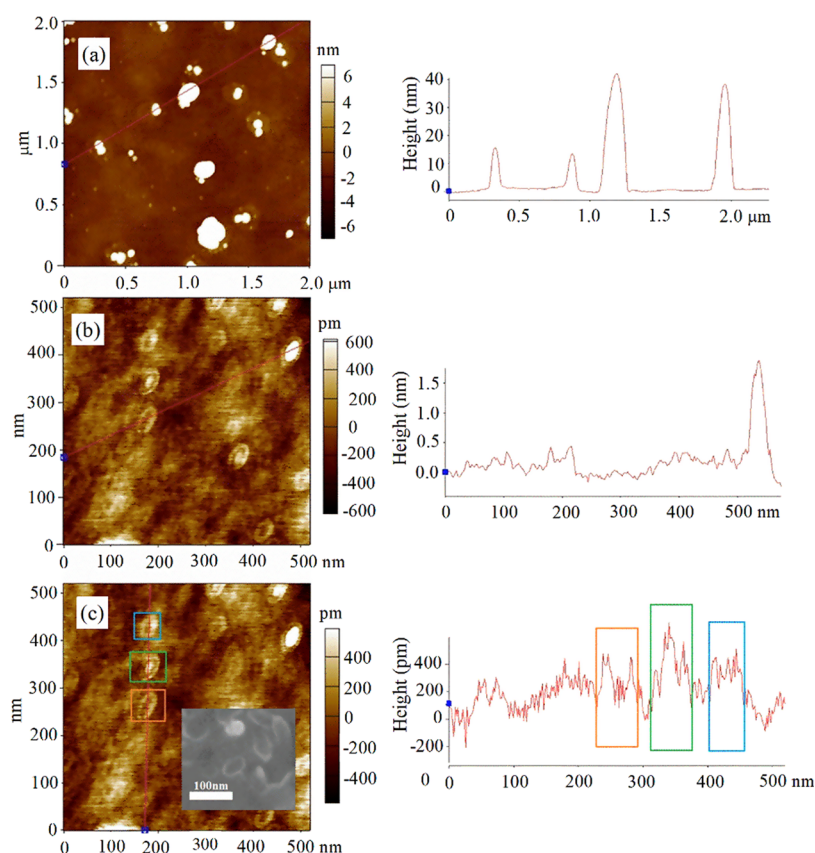
**Figure 4.** Energy-dispersive X-ray spectroscopy spectra taken on a substrate before deposition (a) and on selected crystals (b–d).

**Scanning Electron Microscopy.** Figure 3a–e consists of several medium- and high-magnification SEM images of the

crystallized deposition products on the substrate. As can be seen in the medium-magnification image (a), the chemical vapor



**Figure 5.** Atomic force microscope images at two different areas (a, b) with scan sizes of  $20\ \mu\text{m}$  with line scans corresponding to the horizontal red lines across each image.

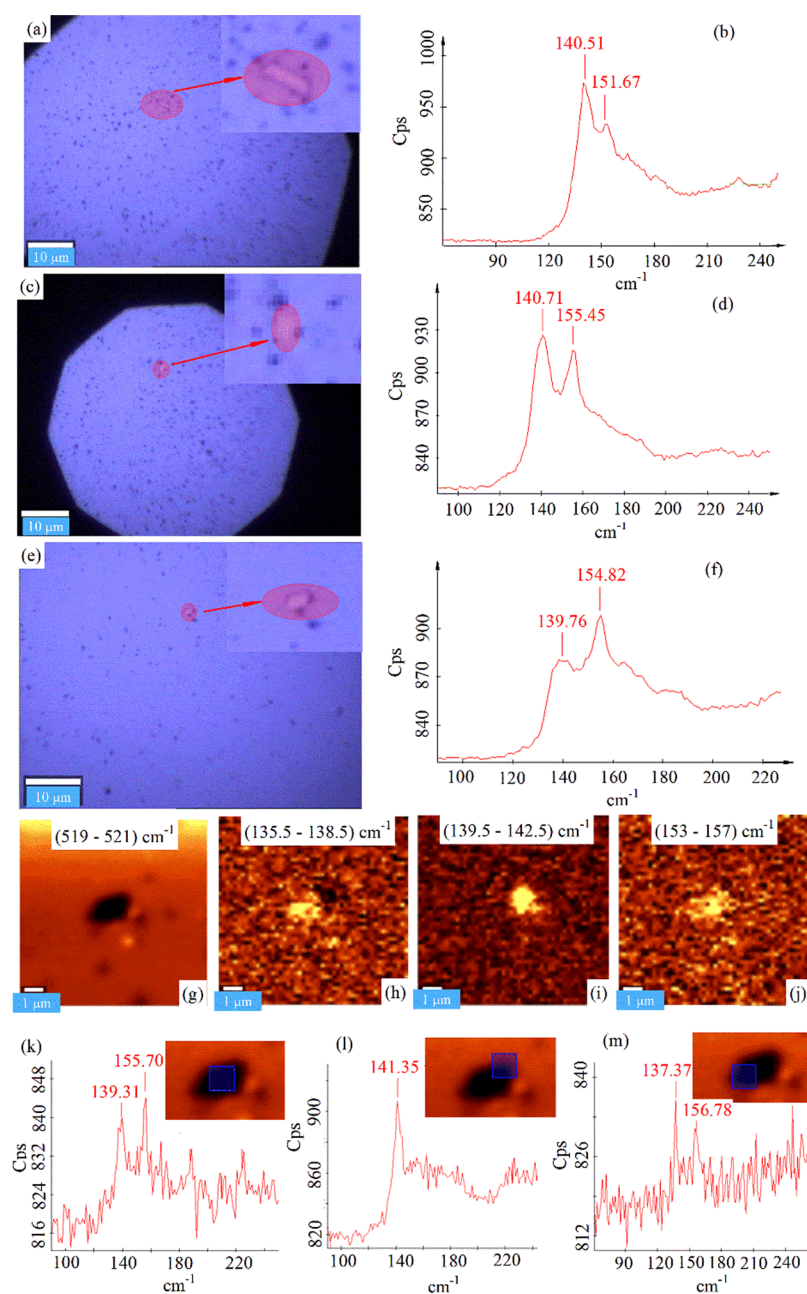


**Figure 6.** Atomic force microscope images with scan sizes of (a)  $2.0\ \mu\text{m}$  and (b, c)  $500\ \text{nm}$  and their accompanying line scans. (c) Boxes to designate the borders of each scanned nanoplate and an inset that shows a proportionate scanning electron microscope image of nanoplates for comparison.

deposition process delivers results with a high dispersibility and nanostructures that range in size and morphology. The nanoparticles produced in this reaction can be separated into three classes based on the order of their largest lateral dimension: those with dimensions greater than  $1\ \mu\text{m}$ , those

with dimensions between  $100\ \text{nm}$  and  $1\ \mu\text{m}$ , and those with all lateral dimensions less than  $100\ \text{nm}$ .

Crystal morphology was not found to be size-dependent, with multiple configurations present throughout the sample. The most common structure, seen in Figure 3a,b, consists of oblong plates with rounded edges. These elongated oval or rectangular



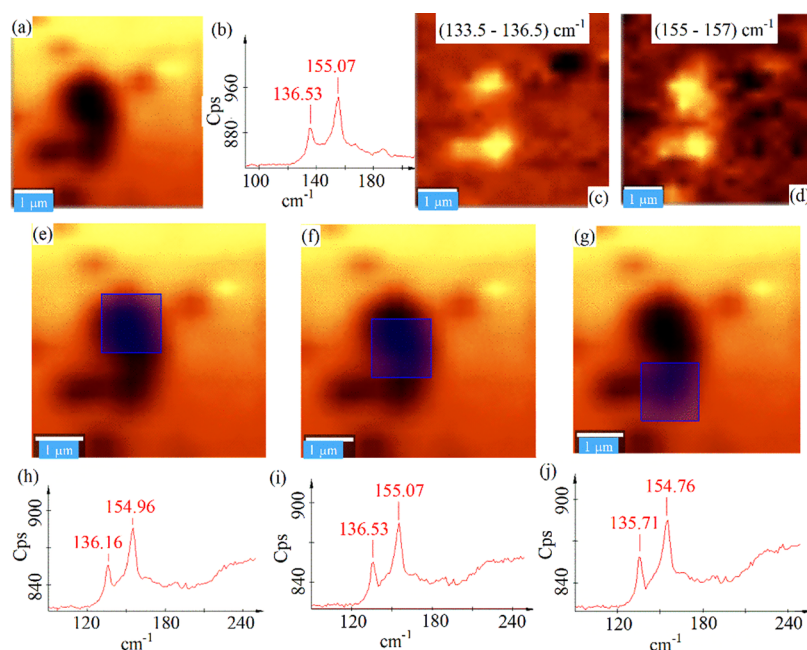
**Figure 7.** Raman peaks of  $\text{FeTe}_2$  nanoplates with lateral dimensions above  $1 \mu\text{m}$  of oblong (a, b) and two different rounded shapes (c–f). (g) Two-dimensional mapping at  $520.7 \text{ cm}^{-1}$  Si crystalline Raman peak. Since  $\text{FeTe}_2$  nanoplates block the Si Raman signal, the shape and dimension of the dark feature in the mapping are used to identify the nanocrystal. (h–j) Raman intensity peak mapping for the crystal (e). Position dependence of Raman peaks of  $\text{FeTe}_2$  (k–m); scale identical to (g).

structures are seen across all size ranges, with their length being their largest dimension. A less common morphology, visible in the bottom right corner of Figure 3a,c, is that of the elongated hexagonal particle, which is often darker in color than the oblong structures.

More common than the hexagonal particles are structures like those seen in Figure 3c, where deposits form from the clusters of smaller oblong and spherical particles. The spherical crystallites that make up the deposit in Figure 3c can also be seen individually in Figure 3d. Their lateral dimensions are all less than  $100 \text{ nm}$ , but their relative brightness indicates a significant thickness. The morphology that makes up the majority of the deposited particles in Figure 3d consists of oblong nanoplates with irregular edges. These also have lateral dimensions in the

tens and hundreds of nanometers, but their dimness indicates a relatively lower vertical dimension. Most deposited structures have one elongated dimension. Elemental mapping (Figure 3f–g) done through energy-dispersive X-ray spectroscopy (EDS) confirms that deposited nanostructures are composed of both iron and tellurium.

The ratio of iron (Fe) to tellurium (Te) in structures of different sizes and morphologies as observed through EDS can be seen in Figure 4. The oblong structures (Figure 4b) have a Fe/Te ratio of 1:2, whereas deposits in (c) and (d) show the width of formation with Fe/Te ratio of 1:1.81 and 1:2.16, respectively. This indicates that different morphologies may result from minor fluctuations in molar ratio. Based on these observations and those from the diffractogram in Figure 2,



**Figure 8.** (a) Two-dimensional mapping at  $520\text{ cm}^{-1}$  of Si crystalline Raman peak, analogous to Figure 7g. (b) Raman peaks, (c, d) Raman intensity, and (e–j) position peak mapping of oblong  $\text{FeTe}_2$  nanoplates with lateral dimensions below  $1\ \mu\text{m}$ .

synthesized nanocrystals exhibit the orthorhombic marcasite  $\text{FeTe}_2$  crystal structure. The deviation from ideal stoichiometry could arise from the interference with the silicon substrate, which could generate a stronger signal than the relatively thin deposited nanoparticles. The relatively high percentages of oxygen seen only in Figure 4d could be an evidence of oxidation and may indicate size-based air instability.

**Atomic Force Microscopy.** Figure 5 shows topographic atomic force microscopy images of the substrate surface with varying scan sizes. Each scan captures information about the vertical dimensions of the different size classes of deposited nanostructures. Images in Figure 5a,b, with scan sizes of  $20\ \mu\text{m}$ , confirm the high dispersibility of the nanostructures as seen through SEM. Their line scans show the vertical dimensions of features crossed by the matching line across the image. Nanocrystals with a dimension greater than  $1\ \mu\text{m}$  were found to have vertical dimensions ranging from 100 to 250 nm, and even up to 400 nm (not shown). Nanoparticles in the class with maximum lateral dimensions equal to or less than  $1\ \mu\text{m}$  have thicknesses ranging from 10 to 150 nm.

The nanocrystals measured in Figure 6 are significantly smaller, with lateral dimensions under 250 nm. Those measured in Figure 6a can be compared to the bright, round particles seen clustered together in Figure 6c. These particles have maximum lateral dimensions between 88 and 214 nm, and thicknesses in the range of 12–50 nm. For all particles discussed thus far, their height ranged between 10 and 33% of their largest lateral dimension. However, the particles in Figure 6b were found to have a significantly reduced height to length ratio.

The particles in Figure 6b appear to be the flat, irregularly shaped  $\text{FeTe}_2$  nanoplates seen in Figure 3d. These crystals are in the lowest size range of those observed for both the SEM and AFM, and these images are directly compared in Figure 6c. These particles have smaller lateral dimensions than those in Figure 5a, with lengths measured between 43 and 62 nm. Their vertical dimensions are significantly lower, with thicknesses between approximately 400 pm and 2 nm, or between 0.5 and

3% of their lateral dimensions. These measurements are on the order of the lattice parameters found when analyzing the sample diffraction pattern, with the smallest lattice parameter measuring 386 pm. This indicates that the nanocrystals in Figure 6b,c are single to quadruple molecular layers of  $\text{FeTe}_2$  unit cells.

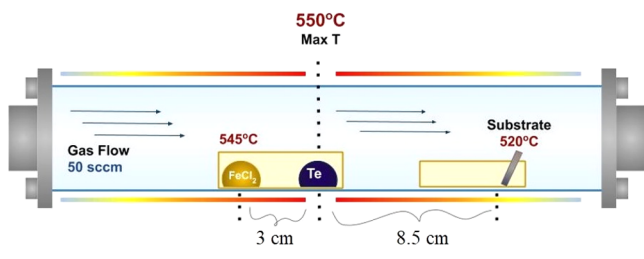
**Raman Spectroscopy.** Raman peaks for bulk  $\text{FeTe}_2$  crystals were previously reported at 119 and  $137\text{ cm}^{-1}$  at room temperature.<sup>7</sup> A  $154\text{ cm}^{-1}$  peak was also observed at low temperature,<sup>7</sup> and at room temperature in a different study.<sup>30</sup> The first two peaks are attributed to the  $B_{1g}$  mode associated with antiphase Te–Te vibration, whereas the  $154\text{ cm}^{-1}$  mode is associated with  $A_{1g}$  in-phase mixed Te–Te stretching related to mutual Fe–Te motion within  $\text{FeTe}_6$  octahedron and is sensitive to changes in bond lengths.<sup>7,30</sup> Raman spectra in this work (Figures 7 and 8) support the X-ray diffraction and energy-dispersive X-ray conclusion that  $\text{FeTe}_2$  phase crystals were formed in this experiment.

We note that the elongated, oblonglike nanocrystals of several micron size show somewhat lower  $A_{1g}$  frequency and somewhat higher  $B_{1g}$  frequency when compared to bulk crystals (Figure 7a,b). In contrast, both frequencies are slightly increased in the rounded crystals (Figure 7c–f) of about  $1\ \mu\text{m}$  size. Interestingly, peak intensity mapping of one such round-shape nanoplate (Figure 7g–j) reveals that the broad  $B_{1g}$  mode (Figure 7f) splits into weak intensity bulk crystal like  $137\text{ cm}^{-1}$  and strong intensity  $\sim 141\text{ cm}^{-1}$  vibration, whereas the weak  $A_{1g}$  mode shows a small shift to higher frequencies compared to bulk crystal. The selected spot Raman spectroscopy suggests that the  $A_{1g}$  mode tends to diminish near the crystal edge (Figure 7k–m).

Both  $B_{1g}$  ( $136\text{ cm}^{-1}$ ) and  $A_{1g}$  ( $155\text{ cm}^{-1}$ ) modes were observed in nanoplate crystals with lateral dimensions below  $1\ \mu\text{m}$  (Figure 8a,b), confirming the synthesis of submicron  $\text{FeTe}_2$  nanoplates. Both modes are more intense near submicron crystal edges (Figure 8c,d), even though position mapping indicates the presence of both peaks along the crystallite length (Figure 8e–j). This could suggest that the  $\text{FeTe}_2$  nanoplate growth mechanism

involves the reaction of Fe vapor from sublimed FeCl<sub>2</sub> (Scheme 1) with Te powder particle of several hundred micron sizes,

### Scheme 1. Schematic Diagram for FeTe<sub>2</sub> Chemical Vapor Deposition Synthesis



where FeTe<sub>2</sub> growth is facilitated along the lateral edges of Te powder. As nanoplates grow to micron (Figure 7e–m) and oblong rodlike shapes of several micron lateral lengths (Figure 7a–d), small Raman peak shifts imply changes in Fe–Te and Te–Te bond lengths in mesoscale FeTe<sub>2</sub>.

The bond lengths and coordination numbers of surface atoms and bulk atoms are usually different; therefore, a shift in Raman frequencies could arise due to competing influences of surface atom undercoordination and bond-length changes. The undercoordination of surface atoms has a great impact on their vibrational frequency.<sup>31,32</sup> The above argument can be applied to the subtle changes of Raman peak shift seen due to the variety in size and shape among the nanoplates and between nanoplates and bulk. In particular, the atoms in crystal corners are usually undercoordinated when compared to the atoms in bulk and surface. Hence, the change in coordination number in the corners of nanoplates may influence the Fe–Te motion in Figure 7i,j. The peaks for the Te–Te mode are still observed at the corners, suggesting that the corners of the FeTe<sub>2</sub> plates are mainly terminated by Te atoms. The FeTe<sub>2</sub> plates in Figure 8 show a higher peak intensity mode of A<sub>1g</sub> Fe–Te motion compared to the B<sub>1g</sub> Te–Te mode.

The corner or edge effects are more obvious in smaller plates or elongated, oblonglike nanocrystals, so the peak intensity of the Te–Te mode is relatively higher than that of the Fe–Te mode, as shown in Figure 7a,b. For both single-selected spot Raman spectroscopy and 2D mapping over the surface areas of FeTe<sub>2</sub> plates, both Fe–Te motion (~151 cm<sup>-1</sup>) and Te–Te mode (~137–140 cm<sup>-1</sup>) peaks are observed and comparable, suggesting elementary stoichiometric structure in the FeTe<sub>2</sub> nanoplates.

## DISCUSSION

FeTe<sub>2</sub> nanocrystals are of high interest for application in the new generation of hybrid energy storage devices such as lithium–ion capacitors and sodium–ion batteries that feature high power and energy density and a good cycle retention rate.<sup>33,34</sup> Further experiments on in situ chemical vapor deposition of FeTe<sub>2</sub> ultrathin crystals in porous carbon network are therefore of high interest. Moreover, since FeTe<sub>2</sub> monolayers are predicted to preserve a ferromagnetic state due to magnetocrystalline anisotropy arising from spin-orbit coupling,<sup>28</sup> further magneto-optic experiments are of interest to test theoretical predictions. Two-dimensional materials with ferromagnetic ground states attract great interest as they are possible candidates for spintronic and memory devices but can also be valuable in fundamental science studies.<sup>35–37</sup> Finally, since reproducible switching behavior without crystal structure

changes has recently been reported in FeTe<sub>2</sub> nanostructures,<sup>38</sup> it would be of interest to investigate the size dependence of switching properties in future devices made from FeTe<sub>2</sub> ultrathin crystals.

## CONCLUSIONS

In this experiment, FeTe<sub>2</sub> nanocrystallites of varying sizes and thicknesses down to the monolayer were grown using a facile chemical vapor deposition process. The deposited nanoparticles showed a high dispersibility and lateral dimensions ranging from less than 100 nm to above a micrometer. The most common crystal morphology is that of an oblong nanoplate with rounded edges. The observed nanocrystallites have stoichiometries corresponding to FeTe<sub>2.0(2)</sub>. The X-ray diffractogram of this sample can be indexed to that of orthorhombic marcasite FeTe<sub>2</sub> with a *Pnmm* space group and no crystalline impurity phase present. The preferential orientation of deposited nanocrystals along the (010) plane is indicated by differences in relative peak intensities. Synthesized nanocrystallites have thicknesses ranging from picometers to 200 nm or between 0.5 and 33% of their largest lateral dimension. This indicates that the chemical vapor deposition process in this work is effective at synthesizing nanocrystalline FeTe<sub>2</sub> with disparate thicknesses down to the monolayer level on one substrate. Comparison of shape- and size-dependent Raman spectra suggests that FeTe<sub>2</sub> crystallites grow from the reaction of sublimed Fe on Te submicron particles on lateral edges. Future work of interest includes studies of chemical defects that could influence magnetic properties, chemical stability, and protection of dangling covalent bonds as well as size-dependent studies of magnetism in reduced dimensions using optical methods.

## EXPERIMENTAL SECTION

**Materials and Equipment.** Anhydrous iron(II) chloride (FeCl<sub>2</sub>) powder (99.5% Alfa Aesar) and Tellurium (Te) powder (99.99% Alfa Aesar) were used as chemical precursors for the synthesis of FeTe<sub>2</sub>. Metal chloride powder precursors are preferable to their pure metal counterparts due to significantly increased vapor pressures at lower temperatures. For example, FeCl<sub>2</sub> has a vapor pressure of 0.1 mmHg at 490 °C and 1 mmHg at 570 °C,<sup>39</sup> whereas pure iron requires a temperature of 1412.5 °C to reach a vapor pressure of 0.1 mmHg.<sup>40</sup> Tellurium, however, has a vapor pressure of 1 mmHg at the relatively low temperature of 520 °C<sup>39</sup> and therefore can be used in pure form. The deposition substrates used were silicon thermal oxide wafers with a 285 nm silicon oxide layer (MTI Corporation), with lateral dimensions of 5 mm and a thickness of 0.5 mm. The precursors and substrate were placed in rectangular alumina crucibles of varying dimensions. The synthesis was performed inside a horizontal single-zone tubular furnace with a heating chamber 1 in. in diameter and 12 in. in length. A quartz process tube was used to contain the process. Experiments were done under a constant gas flow of 3% H<sub>2</sub> in Ar.

**Synthetic Procedures.** There are multiple crystalline phases of iron telluride that form based on synthesis temperature and precursor stoichiometry.<sup>3,41</sup> The marcasite structured  $\epsilon$ -phase has been reported to have a homogeneity range from 66.1 to 67.4% tellurium and an accepted peritectic formation temperature of 649 °C.<sup>41–43</sup> The  $\epsilon$ -FeTe<sub>2</sub> also forms from a eutectoid reaction at temperatures ranging from 514 to 517 °C.<sup>42</sup>

Scheme 1 presents the experimental setup for the chemical vapor deposition of FeTe<sub>2</sub>. FeCl<sub>2</sub> and Te powders were obtained and used without further purification. They were placed in a single alumina crucible with a molar ratio of 1 mole FeCl<sub>2</sub>/3 moles Te. The powder precursor masses were separated from each other by 3 cm to control their respective temperatures during the reaction. The crucible was placed in the furnace with the Te directly above the heating element and the FeCl<sub>2</sub> powder 3 cm upstream. Placing the FeCl<sub>2</sub> at a greater distance from the deposition substrate was done to lower the ratio of iron that reached the substrate compared to tellurium and to induce a 1:2 deposition stoichiometry on the substrate.

The substrate was removed from a sealed plastic sleeve and placed vertically at an angle inside a smaller crucible, with its polished face directed upstream. This crucible was placed, so the substrate was 8.5 cm downstream from the heating element. Crucible placement was designed to induce temperatures of 545, 550, and 520 °C on the FeCl<sub>2</sub>, Te, and substrate, respectively, based on the measured temperature gradient using an external thermocouple since the result of synthesis is sensitive to the temperature of precursors and substrate. These temperatures were chosen based on precursor vaporization rates and the formation temperature for FeTe<sub>2</sub>. The ends of the furnace's quartz tube were then closed, and the chamber flushed with 3% hydrogen balance argon carrier gas for 10 min prior to the start of the chemical vapor deposition reaction.

The chemical vapor deposition was performed under a constant carrier gas flow rate of 50 cubic centimeters per minute. The furnace was heated to a peak temperature of 550 °C from room temperature over 15 min at a rate of about 35 °C min<sup>-1</sup>. This temperature was maintained for 30 min to induce precursor vaporization and deposition on the substrate, as well as the nucleation and growth of FeTe<sub>2</sub> crystals. After 30 min, the furnace was shut off and the system cooled under a constant gas flow. The furnace cooled naturally from 550 to 170 °C, at which point the furnace casing was opened for more rapid cooling. The substrates were removed from the furnace once it reached room temperature and placed in a glovebox to prevent oxidation. This entire process was completed over the course of approximately 4 h.

**Characterization Methods.** X-ray diffraction data was obtained using a Rigaku Miniflex with Cu K $\alpha$  ( $\lambda = 0.15418$  nm) radiation. The obtained diffraction pattern was analyzed using Rietica software. Scanning electron microscopy and energy-dispersive X-ray spectroscopy data were obtained using a JEOL JSM-7600F scanning electron microscope.

An Asylum Research MFP 3D operated using noncontact AC Air topography mode was used to take atomic force microscopy images and measure the surface topology of the sample. No sample treatment was necessary prior to the measurement for this experiment.

Raman experiments for single-selected point Raman spectrum acquisition and 2D Raman spectral imaging were performed using a WITec confocal Raman microscope alpha 300 equipped with a solid-state laser ( $\lambda = 532$  nm), an electron multiplying CCD detector, and a 100 $\times$ /0.9NA objective lens. Unpolarized Raman scattered light was focused onto a multimode fiber and monochromator with an 1800 line/mm grating. Instrument calibration was verified by checking the position of Si at 520.7 cm<sup>-1</sup>.

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### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

TMDC, transition-metal dichalcogenide; vdW, van der Waals; Fe, iron; Te, tellurium; FM, ferromagnetic; MCA, magneto-crystalline anisotropy; MTe<sub>2</sub>, metal ditelluride; FeSe<sub>2</sub>, iron diselenide; H<sub>2</sub>, hydrogen; FeCl<sub>2</sub>, iron(II) chloride; EDS, energy-dispersive X-ray spectroscopy; SEM, scanning electron microscope; AFM, atomic force microscopy

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