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# Graphene-Templated Synthesis of *c*-Axis Oriented Sb<sub>2</sub>Te<sub>3</sub> Nanoplates by the Microwave-Assisted Solvothermal Method

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**Supporting Information** 

**ABSTRACT:** The successful mechanical exfoliation and chemical synthesis of graphene has attracted considerable attention for the synthesis of other twodimensional materials on graphene template. Chalcogenide materials such as  $Sb_2Te_3$  are of interest due to the rhombohedral lattice structure with twodimensional hexagonally closed-packed atomic layers along the *c*-axis. Here we synthesized *c*-axis-oriented  $Sb_2Te_3$  nanoplates (NPs) on graphene substrates by the microwave-assisted solvothermal method. The microwave irradiation resulted in a higher temperature of graphene, compared with the synthesis solution, which was



revealed by the single-mode microwave experiments and an analytical model based on energy balance and convective heat transfer. Besides, the lattice mismatch between *c*-axis-oriented Sb<sub>2</sub>Te<sub>3</sub> and bridge sites of graphene was only 4%, which is also favorable for the graphene-templated Sb<sub>2</sub>Te<sub>3</sub> synthesis. *c*-Axis-oriented single-crystalline Sb<sub>2</sub>Te<sub>3</sub> NPs as large as 7  $\mu$ m could be successfully synthesized on graphene with negligible damage of the graphene template. Larger surface coverage could be obtained by merging Sb<sub>2</sub>Te<sub>3</sub> NPs. The merged Sb<sub>2</sub>Te<sub>3</sub> NPs were polycrystalline with rotated grain boundaries. This work provides a facile, rapid, and low-cost synthesis route of *c*-axis-oriented Sb<sub>2</sub>Te<sub>3</sub> NPs on graphene templates, which may be extended for the synthesis of various two-dimensional materials with hexagonally closed-packed atomic layers along the *c*-axis.

# INTRODUCTION

The successful mechanical exfoliation and chemical synthesis of graphene, single atomic layer of sp<sup>2</sup>-hybridized carbon atoms, has initiated tremendous research activities in two-dimensional (2D) materials.<sup>1,2</sup> The layered materials such as boron nitrides, transition-metal dichalcogenides, and chalcogenides exhibited unique mechanical, electrical, and optical properties.<sup>3,4</sup> Among them, chalcogenide materials (Bi<sub>2</sub>Te<sub>3</sub>, Sb<sub>2</sub>Te<sub>3</sub>, Bi<sub>2</sub>Se<sub>3</sub>, etc.) have attracted considerable attention as near room temperature thermoelectric materials and topological insulators comprising only one Dirac cone.<sup>5,6</sup>

High-quality chalcogenide thin films were typically synthesized by high-vacuum technologies such as molecular beam epitaxy (MBE), metal organic chemical vapor deposition, pulsed laser deposition, thermal evaporation, and sputtering.<sup>7–18</sup> Recently, chalcogenide thin films were also constructed on chemically inert graphene substrates using MBE as well as sputtering methods.<sup>19–22</sup> Especially, the simple sputtering method enabled the preferential *c*-axis orientation of Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> thin films on graphene templates possibly due to the hexagonal lattice structure, although the precise mechanism was not revealed.<sup>19</sup> Sb<sub>2</sub>Te<sub>3</sub> is a V<sub>2</sub>VI<sub>3</sub> pnictogen chalcogenide with a small band gap and belongs to the  $R\overline{3}m$  space group (rhombohedral structure) with 2D hexagonally closed-packed atomic layers along the *c*-axis.<sup>23</sup> One of the hurdles of these high-vacuum technologies is the scale-up synthesis at low cost. Besides, graphene was heavily damaged during the sputtering process due to the momentum of depositing atoms (~10 eV).  $^{19,24}$ 

Here we synthesized *c*-axis-oriented Sb<sub>2</sub>Te<sub>3</sub> nanoplates (NPs) on graphene templates by the microwave-assisted solvothermal method. The microwave-induced temperature rise of the synthesis solution containing the graphene substrate was faster than the solution without graphene, which was investigated using a single-mode microwave reactor. An analytical model based on the energy balance and convective heat transfer between graphene and solution revealed a surface temperature of graphene 110 °C greater than that of the solution at a microwave power of 50 W. The lattice structure investigation also revealed that the lattice constant mismatch between c-axis-oriented Sb<sub>2</sub>Te<sub>3</sub> and bridge sites of graphene was only 4%. These are favorable for the solution-based synthesis of Sb<sub>2</sub>Te<sub>3</sub> on graphene substrates. *c*-Axis-oriented single-crystalline Sb<sub>2</sub>Te<sub>3</sub> NPs as large as 7  $\mu$ m could be successfully synthesized on graphene templates. The Sb<sub>2</sub>Te<sub>3</sub> thickness on graphene was tens of nanometers. The singlecrystalline Sb<sub>2</sub>Te<sub>3</sub> NPs could be merged during the synthesis, resulting in larger polycrystalline NPs with rotated grain boundaries. This solution-based synthesis of c-axis-oriented

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 $Sb_2Te_3$  NPs on graphene may enable scale-up synthesis at low cost with negligible damage of the graphene template.

# EXPERIMENTAL METHODS

**Synthesis and Transfer of Graphene.** Graphene was synthesized on a Cu substrate by the thermal chemical vapor deposition method similar to the previously published protocol.<sup>1,19,25,26</sup> Briefly, graphene was synthesized on an electropolished Cu substrate (The Nilaco Corporation, Tokyo, Japan) in a 2 in. quartz tube.<sup>26</sup> First, the copper substrate was heated to 1000 °C and kept constant for 30 min under H<sub>2</sub> flow. In the next step, H<sub>2</sub> and CH<sub>4</sub> were introduced at 1000 °C for 10 min to synthesize graphene. Finally, the Cu substrate was rapidly cooled to room temperature without any gas flow. The synthesized graphene film was transferred onto glass or SiO<sub>2</sub> (300 nm)/Si substrates by the poly(methyl methacrylate) (PMMA) coating (Sigma-Aldrich, St. Louis, No. 182265), copper etching (Transene, Danvers, MA, CE-100), and PMMA removal (acetone) process.<sup>1,19,25,26</sup>

Microwave-Assisted Solvothermal Synthesis of Sb<sub>2</sub>Te<sub>3</sub>. The microwave-assisted solvothermal synthesis of Sb<sub>2</sub>Te<sub>3</sub> NPs was published previously.<sup>27-30</sup> Here we modified the procedure to synthesize Sb<sub>2</sub>Te<sub>3</sub> NPs on graphene. The Sb<sub>2</sub>Te<sub>3</sub> NP synthesis was carried out using a multimode microwave reactor (CEM Co., Matthews, NC; MARS6). First, tellurium (Te, Sigma-Aldrich, 266418, 1 g) was dissolved in trioctyl phosphine (TOP, Sigma-Aldrich, 117854, 10 mL) in a microwave-heated autoclave (CEM Co.). The temperature was set at 220 °C for 2 min at a microwave power of 600 W followed by cooling to room temperature in 20 min. This resulted in yellow-colored ligated complex solution of Te-TOP.<sup>29</sup> Separately, SbCl<sub>3</sub> (Sigma-Aldrich, 117854, 1 g) was dissolved in 1,5-pentanediol (Sigma-Aldrich, P7703, 20 mL) by ultrasonication (490 W, 3 min). Finally, the two solutions were mixed and heated in a Teflon autoclave with and without the graphene on SiO<sub>2</sub>/Si wafer to synthesize Sb<sub>2</sub>Te<sub>3</sub> NPs. The reaction temperature was ramped to 220 °C in 45 s and kept constant for 10 s at a microwave power of 600 W. The mixture was cooled down to room temperature in 20 min. The Sb<sub>2</sub>Te<sub>3</sub> NPs synthesized on graphene was gently rinsed with acetone followed by drying at ambient air conditions. The Sb<sub>2</sub>Te<sub>3</sub> NPs synthesized in solution was vacuum-filtered, washed with acetone and isopropanol, and dried at ambient air conditions.

Characterizations. Raman measurements were carried out using a Renishaw spectrometer. The excitation wavelength was 532 nm. The X-ray diffraction (XRD) data were obtained by a Rigaku X-ray diffractometer (Rigaku Smart Lab, Rigaku Corporation, Tokyo, Japan). All measurements were carried out under the identical parallel beam mode (Cu K $\alpha$  radiation at 45 kV and 200 mA). The joint committee for powder diffraction standards card number used for peak indexing was 71-393. The scanning electron microscopy (SEM, JEOL, Tokyo, Japan, JSM7600F), high-resolution transmission electron microscopy (HRTEM, JEOL, JEM2100F), and atomic force microscopy (AFM, Seiko Instruments, Chiba, Japan, SPA400) analyses were also carried out. For HRTEM measurements, Sb<sub>2</sub>Te<sub>3</sub> NPs grown on graphene were transferred to a lacey carbon grid using a drop of diluted hydrofluoric acid.

## RESULTS AND DISCUSSION

As shown in Figure 1a, the optical transmittance of graphene on a glass substrate was  ${\sim}97.7\%$  at 550 nm. There was a



Figure 1. (a) Raman spectrum of graphene on a  $SiO_2/Si$  substrate at an excitation wavelength of 532 nm. The transmittance of graphene on a glass substrate and an optical image are also shown. (b) Microwaveinduced heating of the synthesis solution with and without the graphene substrate. The temperature of graphene estimated by an analytical model is also shown.

negligible D mode with an intensity ratio of G-to-2D modes smaller than 0.5, indicating successful synthesis of high-quality monolayer graphene.<sup>1,31</sup> The microwave-induced heating of graphene was investigated using a single-mode microwave reactor (Korea Microwave Instrument Co., Seoul, Korea, 2.45 GHz, WR-340 waveguide), and a schematic of experimental setup is provided in Figure S1 of the Supporting Information.<sup>32</sup> The microwave power was set at 50 W since the solution temperature increased rapidly in a short period of time at a higher power. The single-mode microwave system generates periodic electromagnetic fields whereas a multimode microwave system produces random nonuniform field distribution.<sup>32,33</sup> As shown in Figure 1b, the microwave-induced temperature increase of the synthesis solution containing the transferred graphene on a SiO<sub>2</sub>/Si substrate ( $10 \times 10 \times 0.5 \text{ mm}^3$ ) was investigated as a function of time. As a control, the temperature

of synthesis solution with a bare SiO<sub>2</sub>/Si substrate was also monitored. Surprisingly, the temperature increase of the solution with graphene  $(T_w)$  was greater than that of the solution without graphene  $(T_{w/o})$ . The difference between  $T_w$  and  $T_{w/o}$  was due to the greater microwave-induced heating of graphene compared with the synthesis solution.

An analytical model based on energy balance was developed to estimate the microwave-heated temperature of graphene  $(T_g)$ . The energy difference between two solutions at  $T_w$  and  $T_{w/o}$  was equated with the heat transfer from graphene to the surrounding solution. A uniform temperature of the solution and negligible heat loss to the outside of the solution (i.e., solution container) was assumed.

$$\sum C_{\mathbf{p}_i} m_i (T_{\mathbf{w}} - T_{\mathbf{w}/\mathbf{o}}) = h A_{\mathbf{s}} (T_{\mathbf{g}} - T_{\mathbf{w}}) \Delta t \tag{1}$$

where  $C_p$  is the specific heat capacity  $[J/g \cdot K]$ , *m* is the mass [g], *h* is the heat-transfer coefficient between graphene and the surrounding medium,  $A_s$  is the heat-transfer surface area, and  $\Delta t$  is the heat-transfer duration. The subscript *i* designates each component in solution (1: 1,5-pentanediol; 2: SiO<sub>2</sub>/Si substrate; 3: tellurium; 4: SbCl<sub>3</sub>), and material properties are summarized in Table S1 of the Supporting Information. The liquid property was approximated using that of the major solvent 1,5-pentanediol. The mass of graphene was neglected since it was significantly smaller than other components.

The natural convection heat-transfer coefficient of a horizontal plate under a laminar flow regime was employed for the calculation.<sup>34</sup>

$$h = \frac{0.54k \left(\frac{g\beta(T_{g} - T_{w})L_{c}^{3}}{\nu^{2}}Pr\right)^{1/4}}{L_{c}}$$
(2)

where *k* is the thermal conductivity of the fluid  $[W/m \cdot K]$ , *g* is the local acceleration due to gravity  $[m/s^2]$ ,  $\beta$  is the volume expansion coefficient [1/K],  $L_c$  is the characteristic length [m],  $\nu$  is the kinematic viscosity of the fluid  $[m^2/s]$ , and *Pr* is the Prandtl number.  $L_c$  was obtained by the area-to-periphery ratio of graphene. Finally, eqs 3 and 4 were obtained by combining eqs 1 and 2.

$$\sum C_{p_i} m_i (T_{\rm w} - T_{\rm w/o}) = \frac{0.54k \left(\frac{g\beta L_c^3}{\nu^2} Pr\right)^{1/4}}{L_c} A_s (T_{\rm g} - T_{\rm w})^{5/4} \Delta t$$
(3)

$$T_{g} = T_{w} + \left[ \sum_{p_{i}} C_{p_{i}} m_{i} (T_{w} - T_{w/o}) / \frac{0.54k \left(\frac{g\beta L_{c}^{3}}{v^{2}} Pr\right)^{1/4}}{L_{c}} A_{s} \Delta t \right]^{4/5}$$
(4)

The calculated  $T_g$  using eq 4 is shown in Figure 1b. The experimentally measured solution temperatures were first fitted using third-order polynomial equations as shown in Figure S2 of the Supporting Information. The fitted data were used for the model since a small fluctuation in the solution temperature resulted in a large variation in  $T_g$ . The graphene temperature increased rapidly in Regime 1 as the microwave irradiation time increased. The temperature difference between graphene and solution was as large as 110 °C, demonstrating a significantly

larger microwave absorption cross section of graphene compared with the synthesis solution. The high temperature of graphene is favorable for the solution-based synthesis of  $Sb_2Te_3$ . However, the temperature of graphene decreased in Regime 2 even with the continuous microwave irradiation. This could be due to the heat loss to the solution container. The heat loss to the container is no longer negligible as the solution temperature increased beyond 74 °C, leading to underestimation of graphene temperature.

The  $Sb_2Te_3$  NP synthesis study was carried out at a greater microwave power (600 W) using a multimode microwaveassisted solvothermal reactor (MARS6) as shown in Figure 2a.



**Figure 2.** (a) Schematic of the synthesis process. (b) SEM image of  $Sb_2Te_3$  NPs synthesized in solution. (c) SEM image of  $Sb_2Te_3$  NPs synthesized on graphene. An SEM image of a bare  $SiO_2/Si$  wafer after synthesis of  $Sb_2Te_3$  NPs is provided in the inset. (d) Raman spectra of pure  $Sb_2Te_3$  NPs and  $Sb_2Te_3$  NPs on graphene. (e) Comparison of the D-mode of graphene after synthesis of  $Sb_2Te_3$  by sputtering or microwave-assisted solvothermal methods. The spectrum of the  $Sb_2Te_3$ –graphene bilayer synthesized by sputtering was reproduced from a literature for comparison.<sup>19</sup>

The synthesis temperature was optimized at 220 °C (see Figure S3 of the Supporting Information). A greater synthesis temperature produced more  $Sb_2Te_3$  NPs. However, it was difficult to investigate *c*-axis-aligned  $Sb_2Te_3$  NPs on graphene due to the vigorous out-of-plane growth of  $Sb_2Te_3$ .

Figure 2b shows an SEM image of  $Sb_2Te_3$  NPs homogeneously nucleated in solution. Hexagonal and truncated-triangular NPs could be observed similar to the particles previously synthesized by the microwave-assisted solvothermal method.<sup>27–30</sup> Energy-dispersed X-ray analysis confirmed the near-stoichiometry of Sb<sub>2</sub>Te<sub>3</sub> NPs as shown in Figure S4 of the Supporting Information. The Te-to-Sb ratio was 1.485. Figure 2c shows Sb<sub>2</sub>Te<sub>3</sub> NPs synthesized on graphene. Most NPs were flat whereas some NPs were grown in the out-of-plane direction of graphene. The greater surface temperature as well as hexagonal lattice structure of graphene contributed to the synthesis of Sb<sub>2</sub>Te<sub>3</sub> NPs on graphene as will be discussed shortly. As a control, a bare SiO<sub>2</sub>/Si wafer was inserted in the solution, and Sb<sub>2</sub>Te<sub>3</sub> synthesis was carried out using an identical condition. However, no Sb<sub>2</sub>Te<sub>3</sub> NPs could be observed on the surface of the SiO<sub>2</sub>/Si wafer as shown in the inset of Figure 2c. The Sb<sub>2</sub>Te<sub>3</sub> NPs could not also be observed by an optical image taken at a lower magnification (see Figure S5 of the Supporting Information). Figure 2d shows Raman spectra of pure Sb<sub>2</sub>Te<sub>3</sub> NPs and Sb<sub>2</sub>Te<sub>3</sub> NPs synthesized on graphene. The peak at 117 cm<sup>-1</sup> corresponds to the in-plane vibrational mode  $(E_{g}(2))$  of rhombohedral Sb<sub>2</sub>Te<sub>3</sub>.<sup>35</sup> The sample with  $Sb_2Te_3$  NPs synthesized on graphene shows peaks related to both  $Sb_2Te_3$  and graphene.<sup>31,35</sup> The D, G, and 2D modes of graphene are magnified in Figure 2e. The increase in D mode around 1300 cm<sup>-1</sup> was very small, indicating minimal damage of graphene substrate during the microwave-assisted solvothermal synthesis. We previously investigated Sb<sub>2</sub>Te<sub>3</sub>graphene bilayers by the sputtering method. There was a large D mode, indicating severe damage of graphene due to the momentum of depositing atoms (~10 eV).<sup>19,24</sup> In contrast, the pristine sp<sup>2</sup>-hybridized carbon structure of graphene could be conserved during the microwave-assisted solvothermal synthesis process.

Figure 3a,b shows schematics of the lattice structures of rhombohedral  $Sb_2Te_3$  NPs on (0 0 1), (0 1 0), and (1 0 0)



**Figure 3.** Blue atoms, Sb; pink atoms, Te. (a)  $(0\ 0\ 1)$  plane of Sb<sub>2</sub>Te<sub>3</sub>. The unit cell is shown by the red line and shaded region. (b)  $(0\ 1\ 0)$  and  $(1\ 0\ 0)$  planes of Sb<sub>2</sub>Te<sub>3</sub>. (c, d) The Sb<sub>2</sub>Te<sub>3</sub> unit cell on the  $(0\ 0\ 1)$  plane was overlaid on the bridge sites of graphene. The lattice constant of Sb<sub>2</sub>Te<sub>3</sub> (S) was 4.260 Å. The distance between bridge sites of graphene (G) was 4.440 Å, resulting in a lattice mismatch of ~4%.

planes. The lattice structures of distinct major planes of  $Sb_2Te_3$  crystal ((1 1 0), (1 0 1 0), (0 1 5), and (2 0 5) planes) are also provided in Figure S6 of the Supporting Information. The hexagonal lattice structure could be observed only on the (0 0 l) plane with a lattice constant of 4.260 Å.<sup>23</sup> The  $Sb_2Te_3$  unit cell on the (0 0 1) plane was overlaid on the lattice of graphene as shown in Figure 3c,d. The first-principle band calculation based on density functional theory revealed that the most stable adsorption site for nonmetallic elements is the bridge site of graphene lattice.<sup>36</sup> The distance between bridge sites of graphene was 4.440 Å, as shown in the magnified diagram

(Figure 3d).<sup>37</sup> The lattice mismatch between the lattice constant of Sb<sub>2</sub>Te<sub>3</sub> (S = 4.260 Å) and the distance between bridge sites of graphene (G = 4.440 Å) was only ~4%. The small mismatch in lattice constants is favorable for the synthesis of *c*-axis-aligned Sb<sub>2</sub>Te<sub>3</sub> NPs on graphene. The Sb<sub>2</sub>Te<sub>3</sub> NPs could not be synthesized on the bare SiO<sub>2</sub>/Si substrate by the microwave-assisted solvothermal method probably because of the abscence of lattice similarity (Figure 2c inset).

Some  $Sb_2Te_3$  NPs on graphene were grown in the out-ofplane direction of graphene as shown in Figure 2c. These NPs could be removed by controlled sonication (500 W, 5 min) as shown in Figure 4a. Only flat  $Sb_2Te_3$  NPs grown in the in-plane



Figure 4. (a) SEM images of  $Sb_2Te_3$  NPs on graphene after sonication. Selected area electron diffraction analysis of a singlecrystalline  $Sb_2Te_3$  NP is also shown. (b) XRD analysis of randomly oriented pure  $Sb_2Te_3$  powders,  $Sb_2Te_3$  NPs on graphene, and  $Sb_2Te_3$ NPs on graphene after sonication.

direction of graphene could be observed after sonication. The size of single hexagonal NPs was as large as 7  $\mu$ m. The selected area electron diffraction (SAED) analysis revealed the singlecrystalline structure of Sb<sub>2</sub>Te<sub>3</sub> NPs. Symmetric hexagonal diffraction spots could be observed with a calculated interplanar distance of 0.214 nm, which corresponds to the reflection from the  $(11\overline{2}0)$  plane of rhombohedral Sb<sub>2</sub>Te<sub>3</sub> with a [0001] zone axis.<sup>29,30</sup> The X-ray diffraction (XRD) data of pure randomly oriented Sb<sub>2</sub>Te<sub>3</sub> powders, Sb<sub>2</sub>Te<sub>3</sub> NPs on graphene, and Sb<sub>2</sub>Te<sub>3</sub> NPs on graphene after sonication are compared in Figure 4b. The pure Sb<sub>2</sub>Te<sub>3</sub> powders showed characteristic peaks of randomly oriented  $Sb_2Te_3$  indexed to the rhombohedral  $Sb_2Te_3$ crystal structure. Surprisingly, as-grown Sb<sub>2</sub>Te<sub>3</sub> NPs on graphene exhibited strong preferential (0 0 l) orientation with a small  $(0\ 1\ 5)$  peak. The  $(0\ 1\ 5)$  was the strongest mode of randomly oriented Sb<sub>2</sub>Te<sub>3</sub> powders which was also observed

on the sputtered  $Sb_2Te_3$  film on graphene.<sup>19</sup> This (0 1 5) peak could come from the small number of  $Sb_2Te_3$  NPs synthesized in the out-of-plane direction of graphene as shown in Figure 2c. As shown in Figure S7 of the Supporting Information, the intensity of (0 1 5) and non-(0 0 1) peaks increased for asgrown  $Sb_2Te_3$  NPs on graphene as the synthesis duration increased from 45 to 150 s at 220 °C. More randomly oriented  $Sb_2Te_3$  NPs could be observed on graphene from SEM and XRD analysis. As shown in Figure 4b, only (0 0 1) peaks could be observed for  $Sb_2Te_3$  NPs on graphene after sonication, demonstrating a complete *c*-axis orientation. This is also consistent with the SEM observation (Figure 4a).

Figure 5a,b shows SEM and HRTEM images of merged  $Sb_2Te_3$  NPs on graphene. As shown in the magnified HRTEM



**Figure 5.** SEM (a) and HRTEM (b) images of merged  $Sb_2Te_3$  NPs on graphene. (c) Magnified HRTEM image of the square area shown in (b). (d) SAED analysis of the square area shown in (c).

image, dislocation could be observed at the seam of merged NPs (Figure 5c). The spacing between adjacent lattice fringes turned out to be 0.214 nm, which corresponds to the (11 $\overline{2}0$ ) plane of Sb<sub>2</sub>Te<sub>3</sub>. The SAED analysis performed on the seam revealed azimuthally rotated symmetric hexagonal diffraction spots (Figure 5d). This indicates the merging of two single-crystalline Sb<sub>2</sub>Te<sub>3</sub> NPs with rotated grain boundaries, demonstrating a polycrystalline nature. The calculated interplanar distance was 0.214 nm from SAED analysis, which is consistent with the spacing between the lattice fringes shown in Figure 5c. The diffraction spots correspond to the [0001] zone axis projection of reciprocal lattice of Sb<sub>2</sub>Te<sub>3</sub>.<sup>29,30</sup>

Figure 6a shows an SEM image of randomly oriented Sb<sub>2</sub>Te<sub>3</sub> NPs synthesized in solution. Figure 6b shows an AFM image of a single-crystalline Sb<sub>2</sub>Te<sub>3</sub> NP on graphene with a thickness of 50 nm. The AFM image of merged Sb<sub>2</sub>Te<sub>3</sub> NPs on graphene is shown in Figure 6c. The height of each NP was different, resulting in a step. The height profile and AFM image of other merged NPs are also provided in Figure S8 of the Supporting Information. The step height between merged NPs could be clearly observed. This indicated that single-crystalline Sb<sub>2</sub>Te<sub>3</sub> NPs were first separately synthesized on graphene followed by merging of NPs as the growth continued. Although a large surface coverage could be obtained by merging Sb<sub>2</sub>Te<sub>3</sub> NPs, single crystallinity of the merged NPs could not be obtained (Figure 5d). As shown in Figure 6d, the average thickness of Sb<sub>2</sub>Te<sub>3</sub> NPs synthesized on graphene was ~40 nm. This was



Figure 6. (a) SEM image of randomly oriented Sb<sub>2</sub>Te<sub>3</sub> NPs synthesized in solution. (b, c) AFM image of an Sb<sub>2</sub>Te<sub>3</sub> NP and merged Sb<sub>2</sub>Te<sub>3</sub> NPs synthesized on graphene. The scale bar is 500 nm. (d) Histogram of thickness of randomly oriented Sb<sub>2</sub>Te<sub>3</sub> NPs synthesized in solution (average ~100 nm) and Sb<sub>2</sub>Te<sub>3</sub> NPs synthesized on graphene (average ~40 nm). The scanned area on graphene was  $20 \times 20 \ \mu m^2$ .

smaller than that of the randomly oriented  $Sb_2Te_3$  NPs synthesized in solution (~100 nm). It is possible that the mass transport of reactants was limited due to the graphene substrate compared with the  $Sb_2Te_3$  NPs synthesized in solution, which have the reactant supply from both sides of NPs.

Graphene is an excellent substrate to synthesize layered materials with similar crystal structures since the strong bonding of carbon atoms provides chemical inertness.<sup>21</sup> This results in an atomically sharp interface between Sb<sub>2</sub>Te<sub>3</sub> and graphene by suppressing interfacial chemical reaction. The unique properties achieved in this study are discussed below. First, the solvothermal synthesis method constructed c-axisaligned Sb<sub>2</sub>Te<sub>3</sub> NPs on graphene due to the lattice similarity (Figure 4a). The spin coating or drop casting of solution synthesized Sb<sub>2</sub>Te<sub>3</sub> NPs on graphene resulted in randomly oriented aggregates of Sb<sub>2</sub>Te<sub>3</sub> NPs on graphene (see Figure S9 of the Supporting Information). Graphene has highly anisotropic thermal and electronic transport properties.<sup>19,3</sup> Therefore, the preferred c-axis orientation of Sb<sub>2</sub>Te<sub>3</sub> NPs is important for studying anisotropic thermal and electric transport properties of two-dimensional graphene/Sb<sub>2</sub>Te<sub>3</sub> heterostructures.

Second, Ohmic contact was realized between the graphene and  $\mathrm{Sb}_2\mathrm{Te}_3$  NPs synthesized on graphene as shown in Figure 7. The applied voltage was normalized with the thickness of  $\mathrm{Sb}_2\mathrm{Te}_3$  NPs to compare the induced current at the identical electric field strength (voltage/thickness). The current linearly increased with the applied voltage, quickly reaching an instrument compliance (100 mA). The  $\mathrm{Sb}_2\mathrm{Te}_3$  NPs with different thickness resulted in similar current-electric field behavior. The current–voltage characteristics were obtained in ambient atmosphere by contact mode (2 nN loading force) conductive atomic force microscopy (C-AFM). The platinum-coated silicon cantilever with a force constant of 0.2 N/m was used for the scan, and graphene was grounded.<sup>39–41</sup> Most



Figure 7. Current-electric field characteristics measured by C-AFM. Two  $Sb_2Te_3$  NPs synthesized on graphene (thickness = 32 and 54 nm) are compared with two  $Sb_2Te_3$  NPs spin-deposited on graphene (thickness = 60 and 133 nm). Representative AFM images are provided, and the scale bar is 500 nm. The current-electric field characteristics of spin-deposited  $Sb_2Te_3$  NPs on graphene are magnified in the inset plot.

 $Sb_2Te_3$  NPs deposited by spin coating were aggregated with random orientation (Figure S9 of the Supporting Information). Only a few *c*-axis-aligned  $Sb_2Te_3$  NPs were observed from the entire graphene substrate  $(1 \times 1 \text{ cm}^2)$  after the spin deposition. However, solid electrical contact with graphene was not realized, resulting in negligible current (Figure 7). The difference in thickness between the synthesized and spindeposited  $Sb_2Te_3$  NPs was as large as 4.15 times. However, the difference in current was much greater due to the poor contact between spin-deposited  $Sb_2Te_3$  NPs and graphene.

The significantly increased carrier mobility and electrical conductivity of graphene/Sb<sub>2</sub>Te<sub>3</sub> bilayer films were previously reported, compared with those of the pure Sb<sub>2</sub>Te<sub>3</sub> film, because of the high mobility  $(2.34 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$  and electrical conductivity (23 164 S cm<sup>-1</sup>) of graphene.<sup>19</sup> Such graphene/Sb<sub>2</sub>Te<sub>3</sub> bilayers were previously constructed using MBE or sputtering methods.<sup>19,20,22</sup> The MBE method requires ultrahigh-vacuum conditions, which is costly, and sputtering severely damaged the graphene substrate during the deposition.<sup>19,20,22</sup> Here, we obtained *c*-axis-aligned Sb<sub>2</sub>Te<sub>3</sub> NPs in Ohmic contact with graphene by a simple solution method without damaging the graphene is necessary to realize high mobility and electrical conductivity of the graphene/Sb<sub>2</sub>Te<sub>3</sub> NP heterostructure. The precise transport measurement of the graphene/Sb<sub>2</sub>Te<sub>3</sub> NP heterostructure needs to be carried out in the future.

Finally, the thickness of  $Sb_2Te_3$  NPs could be modulated by graphene (10–100 nm) as shown in Figure 6d. Further control of thickness may be useful for the study of Fermi level tuning or Landau quantization in the future.<sup>20,22</sup>

#### CONCLUSION

In summary, graphene was employed as a template for the solution-based synthesis of  $Sb_2Te_3$  NPs. The microwave irradiation resulted in a higher temperature of graphene, compared with the synthesis solution, which was revealed by the single-mode microwave experiments and an analytical model based on the energy balance and convective heat

transfer. Besides, the small lattice mismatch (4%) between *c*-axis-oriented Sb<sub>2</sub>Te<sub>3</sub> NPs and the distance between bridge sites of graphene facilitated the synthesis of Sb<sub>2</sub>Te<sub>3</sub> NPs on graphene. The synthesized Sb<sub>2</sub>Te<sub>3</sub> NPs on graphene were aligned along the *c*-axis. Each Sb<sub>2</sub>Te<sub>3</sub> NP was single-crystalline whereas merged NPs were polycrystalline with rotated grain boundaries. The size of single-crystalline Sb<sub>2</sub>Te<sub>3</sub> NP was as large as 7  $\mu$ m. This graphene-templated solvothermal method may be extended for the *c*-axis-oriented synthesis of various 2D materials with rhombohedral structures for the study of Dirac Fermions and thermoelectrics in the future.

# ASSOCIATED CONTENT

# **Supporting Information**

Schematic of the single-mode microwave reactor, material properties, microwave-induced heating of graphene, microwave-assisted solvothermal synthesis conditions, energy-dispersive X-ray analysis, optical microscopy, lattice analysis, XRD analysis, AFM, and SEM analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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