

Supporting Information

Synthesis of single-crystalline Ge₁Sb₂Te₄ nanoplates in solution phase

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Materials

All reagents in this work are analytical grade and commercially available. Antimony(III) chloride (SbCl_3 ; 99.99%), antimony(III) acetate ($\text{Sb}(\text{OAc})_3$; 99.99%),¹ tellurium powder (Te; 99.997%), germanium(IV) iodide (GeI_4 ; 99.99%), trioctylphosphine (TOP; 90%),² oleic acid (OA; 90%),² and oleylamine (OLA; 70%)² were purchased from Sigma-Aldrich corporation. Hexamethyldisilazane (HMDS; 98%)³ was purchased from Acros-Organics corporation.

Equipments used for electrical measurements and characterization

Powder X-ray diffraction pattern (XRD) analysis was performed on a Rigaku Ultima IV X-ray diffractometer using $\text{Cu K}\alpha$ radiation source ($\lambda = 1.54 \text{ \AA}$). Scanning electron microscopy (SEM) images were obtained by Hitachi SU8010 for observing the morphology and energy-dispersive x-ray spectroscopy was also done for the composition analysis. High resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) were obtained by JEOL ARM200F. Dual-Beam Focus-Ion-Beam (FIB) was performed by FEI (Nova 200) to deposit platinum line on a single GST-124 HP. Dual E-Gun Evaporation System was performed by ULVAC EBX-10C to deposit SiO_2 layer on a single GST-124 HP. And all electrical measurements were performed with HP 4145B semiconductor parameter analyzer and Agilent 8110A pulse generator.

Synthesis procedure of GST-124 hexagonal plates (HPs)

GST-124 HPs were synthesized in 50 ml three-neck flask connected to the Schlenk line system under a purified argon atmosphere. 8.24 mg Te and 5.58 mg Sb(Cl)₃ were dissolved separately in 0.5 ml TOP, the former was stirred at 130 °C and the latter was at room temperature (named A and B solution). Meanwhile, 15 mg GeI₄ were dissolved in 10 ml OLA and 1 ml OA, and were ultrasonicated for 20 min (named C solution). A, B, C solutions and 1 ml HMDS were then sequentially injected into 5 ml OLA preheated at 130 °C. As the mixture was heated back to 130 °C, it was held for 20 min to drive out the evaporating gas from HMDS. Then, system was slowly heated (2 °C / min) to 320 °C and aged for 4 hours. The resulting GST-124 HPs were washed by centrifugation at 8000 rpm with approximately 1:5 v/v toluene and ethanol for several times, and were dissolved and kept in toluene.

Fabrication process of SiN_x membrane devices for measuring the electrical characteristics of GST-124 HPs

GST-124 HPs was incorporated into a specialized-designed SiN_x membrane device to demonstrate the electrical properties of it. The SiN_x membrane device was prepared as reported¹. To prevent GST-124 HPs from aggregating on the SiN_x membrane, spin-coating method with 5 μdilute GeSbTe HPs solution at 2000 rpm for 15 sec was used. At low intensity (6.9-pA, 30kV), Ga⁺ ion FIB resources was operated to contact the opposite sides of single GST-124 HP with platinum precursors. Later, high intensity (30-pA, 30kV) Ga⁺ ion source was used to connect the pre-localized platinum line with electrode of SiN_x membrane device. Finally, a 40 nm SiO₂ layer was deposited by e-gun evaporation system to finish the fabrication process.

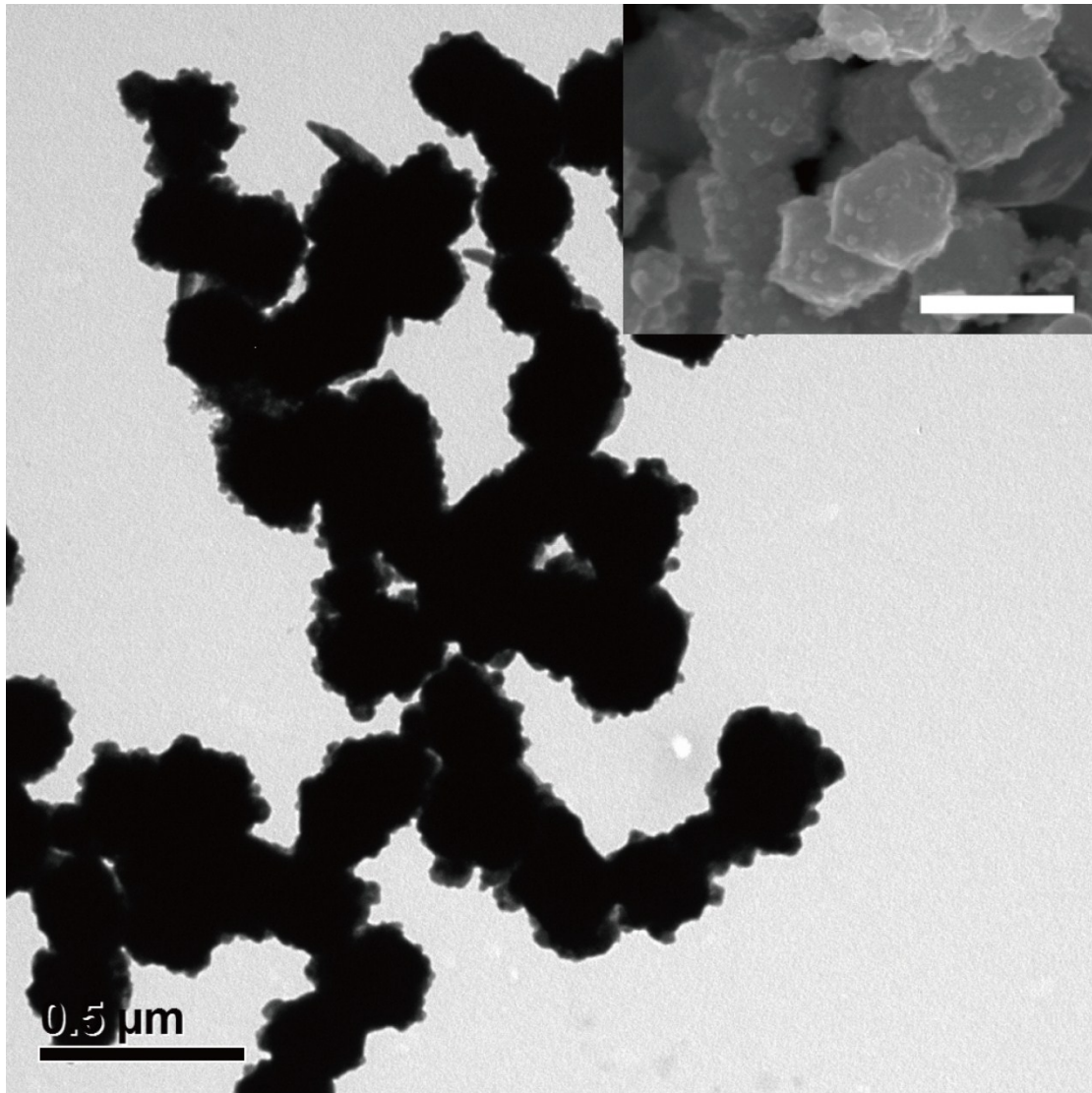


Fig. S.1. TEM image of as-prepared products using $\text{Sb}(\text{OAc})_3$ as Sb sources under 320 °C. Inset: SEM image of the same sample. Scale bar: 250 nm.

Table S.1. Statistical EDS quantitative analysis results from Fig. S.2

Sample No.	Elemental Atomic Ratio (%)			Normalized ratio compared to GST-124
	Ge	Sb	Te	
1	16.2	29.7	54.1	1.0 : 1.8 : 3.3
2	16.8	29.0	54.2	1.0 : 1.7 : 3.2
3	12.3	33.8	53.9	1.0 : 2.8 : 4.4
4	12.1	36.4	51.5	1.0 : 3.0 : 4.3
5	14.5	37.3	48.2	1.0 : 2.6 : 3.3
6	15.6	32.5	51.9	1.0 : 2.1 : 3.3
7	17.7	28.0	54.3	1.0 : 1.6 : 3.1
8	14.3	33.8	51.9	1.0 : 2.4 : 3.6
Average	14.9	32.6	52.5	1.0 : 2.2 : 3.5
Ideal GST-124	14.3	28.6	57.1	1.0 : 2.0 : 4.0

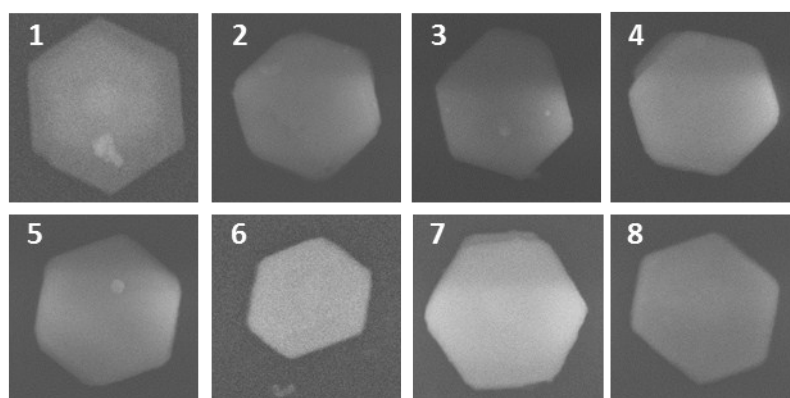


Fig. S.2. Eight GST-124 nanoplates with different diagonal lengths

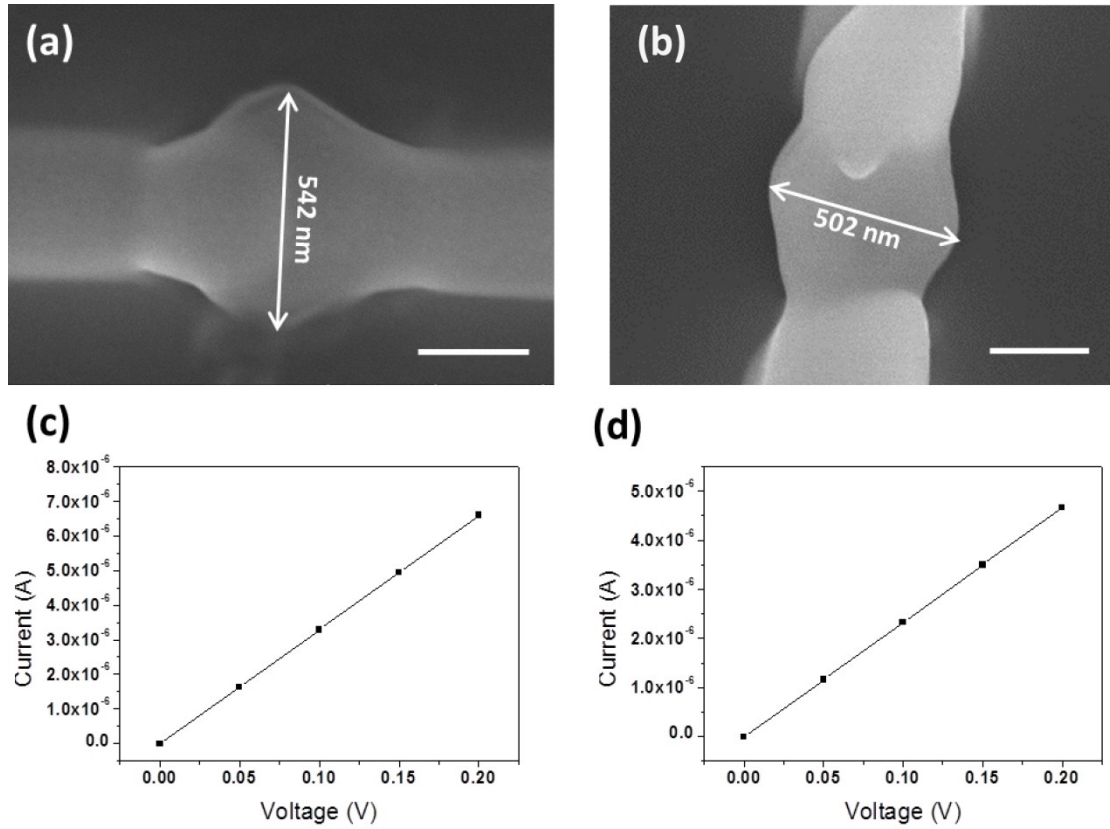


Fig. S.3. (a)-b) SEM images and (c)-(d) I-V curves of SiN_x membrane device with GST-124 nanoplates (Diagonal length = 542, 502 nm)

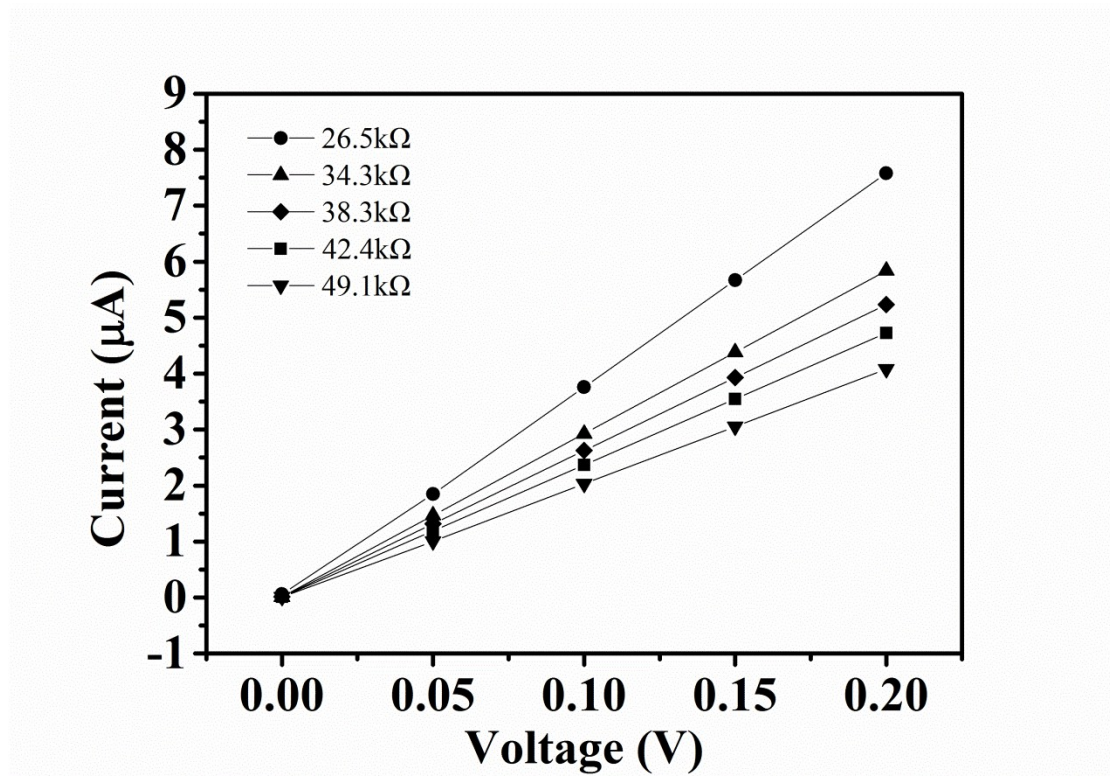
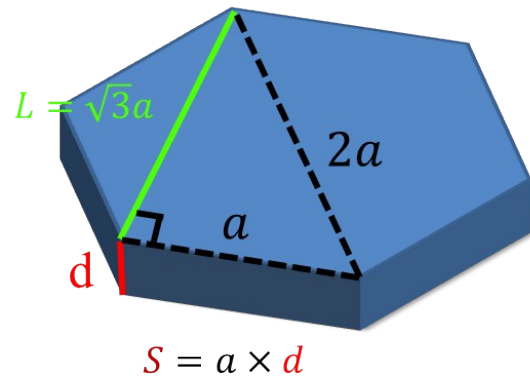


Fig. S.4. DC I-V sweep of five different GST-124 nanoplates



$$R = \rho \frac{L}{S} = \rho \frac{\sqrt{3}a}{a \times d} = \frac{\sqrt{3}\rho}{d} = \frac{\sqrt{3}(1 \times 10^{-3})}{50 \times 10^{-7}} \cong 350 \text{ (Ohm)}$$

Fig. S.5. Schematic diagram of a single GST-124 nanoplate and the approximated calculation of the electrical resistance of that with the crystal size as reported here. R : electrical resistance, ρ : resistivity, about 1 mOhm cm, L : length of the path which current goes through, S : cross-sectional area which current goes through, d : thickness, about 50 nm

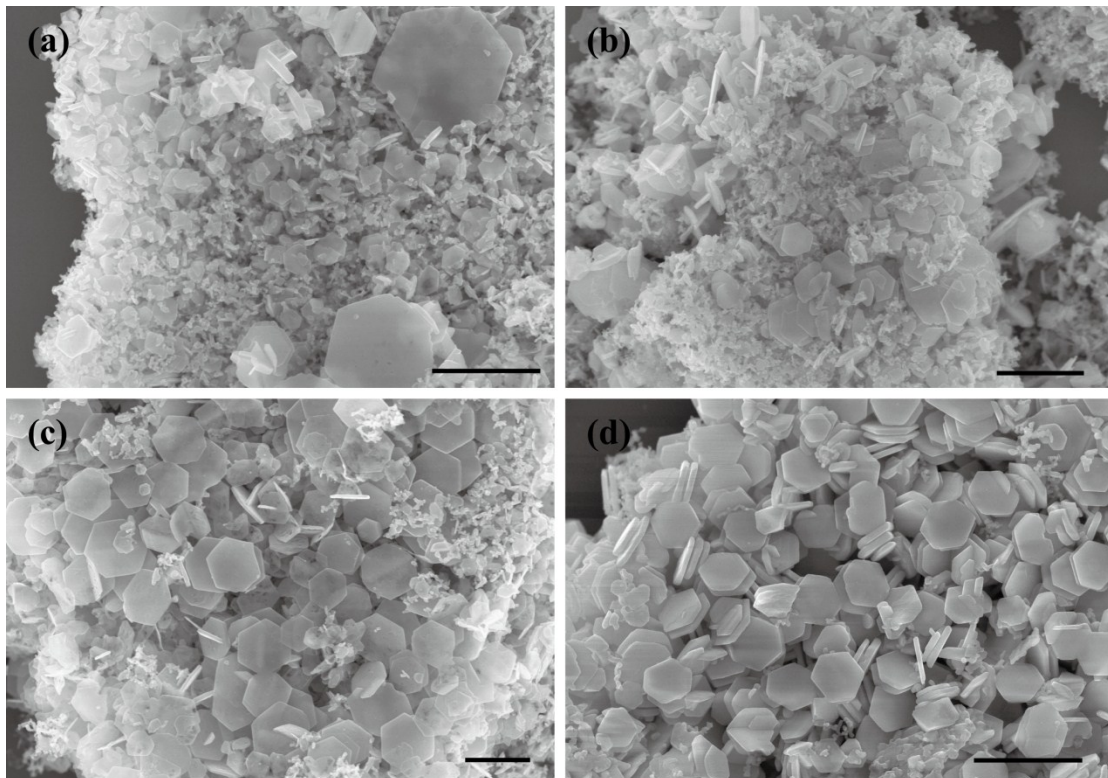


Fig. S.6. SEM images of GST-124 synthesized with different reaction temperatures and times (a)300 °C, 2 hr (b)300 °C, 4 hr (c)320 °C, 2 hr (d)320 °C, 4 hr (scale bar : 1 μm).

References :

1. W. Li, L. Luo, H. Yamashita, J. A. Labinger, and M. E. Davis, *Microporous Mesoporous Mater.*, 2000, **37**, 57-65.
2. W. Luan, H. Yang, N. Fan, and S.-T. Tu, *Nanoscale Res. Lett.*, 2008, **3**, 134 - 139.
3. D. D. Vaughn, J. F. Bondi, and R. E. Schaak, *Chem. Mater.*, 2010, **22**, 6103-6108.