Synthesis and Quantum Transport Properties of Bi\textsubscript{2}Se\textsubscript{3} Topological Insulator Nanostructures

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Bi\textsubscript{2}Se\textsubscript{3} nanocrystals with various morphologies, including nanotower, nanoplate, nanoflake, nanobeam and nanowire, have been synthesized. Well-distinguished Shubnikov-de Haas (SdH) oscillations were observed in Bi\textsubscript{2}Se\textsubscript{3} nanoplates and nanobeams. Careful analysis of the SdH oscillations suggests the existence of Berry’s phase $\gamma$, which confirms the quantum transport of the surface Dirac fermions in both Bi\textsubscript{2}Se\textsubscript{3} nanoplates and nanobeams without intended doping. The observation of the singular quantum transport of the topological surface states implies that the high-quality Bi\textsubscript{2}Se\textsubscript{3} nanostructures have superiorities for investigating the novel physical properties and developing the potential applications.

Topological insulators (TIs) are new emerging quantum materials with an insulating bulk and gapless surface states\textsuperscript{1–10}. Owing to the strong spin-orbit interaction, the conducting surface states are spin-polarized. The surface states are also immune to scattering by nonmagnetic impurities because of the preservation of time reversal symmetry and spin-momentum helical locking. These unique properties make TIs promising applications in spintronic devices. Recently, particular attention has been paid to three dimensional TIs such as Bi\textsubscript{2}Te\textsubscript{3} and Bi\textsubscript{2}Se\textsubscript{3}, which have a single massless Dirac cone for the surface state\textsuperscript{6–16}. Due to large surface-to-volume ratio of nanomaterials and enhanced surface contribution to conductivity, Bi\textsubscript{2}Se\textsubscript{3} nanostructures have more advantages for both fundamental investigations of the exotic surface states and potential applications in spintronics\textsuperscript{17–20}. Consequently, synthesis of high-quality Bi\textsubscript{2}Se\textsubscript{3} nanostructures is highly desirable. Various methods have been developed to fabricate Bi\textsubscript{2}Se\textsubscript{3} nanostructures, including mechanical exfoliation\textsuperscript{6,10}, molecular beam epitaxial (MBE)\textsuperscript{11–13}, sonochemical methods\textsuperscript{21}, solvothermal synthesis\textsuperscript{20,22}, metal-organic chemical vapor deposition\textsuperscript{23}, and chemical vapor deposition (CVD)\textsuperscript{17–19}. Nevertheless, synthesis of Bi\textsubscript{2}Se\textsubscript{3} nanostructures with a variety of morphologies is still a challenge.

On the other hand, magneto-transport properties of Bi\textsubscript{2}Se\textsubscript{3} nanostructures are very important for the potential applications in spintronic devices. The Aharonov-Bohm oscillations\textsuperscript{17}, two-dimensional transport\textsuperscript{19}, and Shubnikov-de Haas (SdH) oscillations\textsuperscript{24} related to the surface conduction of Bi\textsubscript{2}Se\textsubscript{3} nanoribbons are reported. The surface Dirac fermions can be detected via transport measurement of SdH oscillations, which demonstrate a Berry’s phase $\pi$\textsuperscript{24}. However, plotting the Landau level fan diagram using the resistance minima or maxima of the SdH oscillations to identify the index field $B_N$ will give opposite results. Therefore, the accurate determination of the index field $B_N$ is important to obtain the correct conclusion especially for the condition of existence of bulk conduction.

In this work, we have synthesized various Bi\textsubscript{2}Se\textsubscript{3} nanocrystals with various morphologies, including nanotower, nanoplate, nanoflake, nanobeam and nanowire, using a simple CVD method. To the best of our knowledge, our work reports the self-organized Bi\textsubscript{2}Se\textsubscript{3} nanostructures with the most abundant shapes. The bulk-quantity growth of Bi\textsubscript{2}Se\textsubscript{3} nanostructures is important for productive efficiency. These nanostructures were found to have high quality through systematical characterizations by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), transmission electron microscope (TEM), and selected area electron diffraction (SAED). The quantum transport properties of Bi\textsubscript{2}Se\textsubscript{3} nanoplates and nanobeams were studied at 1.5 K with magnetic field up to 14 T. Well-distinguished Shubnikov-de Haas (SdH) oscillations were observed. We found that the determination of the index field $B_N$ using the SdH oscillations in resistance $R_{xx}$ of the Bi\textsubscript{2}Se\textsubscript{3} nanoplates and nanobeams was different, that is, the $B_N$ was identified with...
minima in $R_{xx}$ for nanoplates, while with maxima in $R_{xx}$ for nanobeams. Careful analysis of the SdH oscillations suggests the existence of Berry’s phase $\pi$, which ambiguously demonstrates the quantum transport of the surface Dirac fermions.

**Results**

The Bi$_2$Se$_3$ nanostructures were synthesized via a CVD method in a horizontal tube furnace using powder Bi$_2$Se$_3$ as evaporation source. Details of the growth were described in the Method section and Supporting Information Figure S1. Si substrates covered with a thin gold layer were placed downstream of the source to collect the products. The morphologies of the acquired Bi$_2$Se$_3$ nanostructures are shown by the SEM images in Figure 1. We find that the Bi$_2$Se$_3$ nanostructures with different morphologies can be obtained by changing the distance between the source and the Si substrate. When the Si substrate was placed close to the source ($\leq 5$ cm), there were prismoids (Figure 1(a)) with gold particle on the head (confirmed by EDS) formed on the Si substrate. The size and density of the prismoids also depend on the pressure inside the tube. Under nearly atmospheric pressure, only few isolated structures formed (Figure 1(a)). On the other side, under a low vacuum, the source is easier to be evaporated at the same temperature. Abundant source vapors quickly deposited and nucleated, resulting in denser and smaller structures (Figure 1(b)). The layered character of the as-grown Bi$_2$Se$_3$ nanostructures can be clearly seen in Figures 1(a, b). On the top of most structures there were obviously metal particles, indicating that the growth mechanism is dominant by the vapor-liquid-solid (VLS) mechanism along the c axis [0001].

When the Si substrate is 6–7 cm away from the source, the most visible resultants were chunk of nanoplates or nanoflakes with regular morphologies, as shown in the Figures 1(c–f). Under this condition, the temperature is lower and the self-catalytic mechanism may play an important role during the two-dimensional nucleation growth. The layered properties of the synthesized 2-D Bi$_2$Se$_3$ islands were further characterized by SEM and AFM measurements, as shown in the Supporting Information Figure S2. The formation of spirals was observed in the AFM images in Figures S2(b,c). From the AFM line profile analysis shown in Figure S2(d), the typical step height ($h$) is $\sim 1$ nm, which is well consistent with the thickness of one quintuple-layer of Bi$_2$Se$_3$. The typical terrace width ($\lambda$) is $\sim 800$ nm. The small nanoplate slope $1/800$ ($p = h/\lambda$) guarantees the two-dimensional growth mode. Recently, similar spirals were also observed during MBE epitaxy of Bi$_2$Se$_3$ on graphene/SiC$^{25}$.

When the substrate is about 9–10 cm away from the source, we generally get nanobelts, nanobeams, or nanowires (Figures 1(g, h)). The nanobelts range from tens of to one hundred micrometers in length, several micrometers in width, and hundred nanometers in thickness. The difference between the nanobelts and nanobeams is the width size, which is about hundreds of nanometers for the latter (Figure 1(g)). The nanowires are about one hundred nanometers in diameter and range from tens of to one hundred micrometers in length (Figure 1(h)). The cross-section shapes of the nanobelts and nanowires were further examined, and the SEM images are shown in Figure S3. The SEM characterization indicates that the cross-section shape of the nanobelts is rectangle. While for the so-called nanowire, the cross-section shape is not rectangle, as shown in Figure S3(e,f).

The detailed growth mechanisms were presented in Figure 2. Bi$_2$Se$_3$ was layered rhombohedral crystal structure along c axis, as illustrated in Figure 2(a). Here, the c axis [0001] of the hexagonal cell corresponds to Bi$_2$Se$_3$ [111] of the approximately cubic closest-packed layer crystal structure, where five atomic layers in sequence of –Se-Bi-Se-Bi-Se- form a basic unit, i.e. quintuple layer (QL). The interaction within the QLS is strong, but the adjacent QLSs are coupled by relatively weak van der Waals interaction. The binding energies are different for different surfaces, which suggests different growth rate along different directions. The catalyst particles serve as nucleation sites for the growth of Bi$_2$Se$_3$ nanostructures. Via slow pumping, the evaporated molecules can be transported by the carrier gas and the dynamic balance during the growth process can also be largely maintained. Under high temperatures, the source vapors have high energy that can overcome the binding energy of [0001] surface, resulting in the growth along c axis with growth rate $V_c > V_a = V_b$ ($V_a$, $V_b$, $V_c$ are the growth rates along a, b, c axis, respectively), as seen in the products in Figures 1(a, b) and the sketch in Figure 2(b). Under lower temperatures, the energy of the vapors may be insufficient to overcome the binding energy of [0001] surface. The growth along [10-10] or [01-10] directions becomes dominant and results in the

![Figure 1 | SEM image of the Bi$_2$Se$_3$ nanostructures.](image1)

![Figure 2 | Schematic diagram of the growth mechanisms.](image2)
polygon morphologies as shown the products in Figures 1(c–f) and the sketch in Figure 2(c), which are commonly present in epitaxial growth of Bi$_2$Se$_3$ nanoplates. Under much lower temperatures, the growth induced by catalyst along [11-20] direction breaks the crystal intrinsic symmetry and results in the one-dimensional preferential growth as presented in Figures 1(g, h) and Figure 2(d), respectively. Therefore, different kinds of morphologies of Bi$_2$Se$_3$ nanostructures can be synthesized through changing the distance between the source and the Si substrate which changes the temperature of the collection substrates and energy of the source vapor. Morphologies and good crystallinity of the synthesized samples have been verified by the TEM images, high resolution TEM (HRTEM) images, and SAED patterns, as shown in Figure 3. Furthermore, EDS spectrums (Figures 3(e, f)) collected from the head and the body of one nanobeam (Figure 3(c)) show the Au catalyst particle on the head and the compositions of Bi and Se in the body, which obviously verify the VLS growth mechanism.

Electrical transport properties of the synthesized Bi$_2$Se$_3$ nanostructures were also studied. The as-grown Bi$_2$Se$_3$ nanostructures were transferred onto an insulator substrate. Micro-Hall devices based on the nanoplates and four-probe devices based on the nanobeams were fabricated via the processes including electron beam lithography, metal deposition, and lift-off. Typical SEM images of the devices are shown in Figures 4(a, e). As shown in Figure S4, the SEM image of a nanobeam device viewed using a 52° tilted sample stage indicates the nanobeam with a rectangle cross-section and a flat top surface. The temperature dependences of resistance for Bi$_2$Se$_3$ nanoplate and nanobeam are shown in Figure S5. The resistances for both samples decrease with decreasing temperature from 300 K to 20 K, showing a metallic behavior. Below 20 K, the resistance tends to saturate, which may result from the surface conduction and the bulk residual conduction.

The magnetoresistance (MR) of the nanoplate and nanobeam devices measured at 1.5 K are shown in Figures 4(b, f), respectively. A large positive MR of $\sim$200% with no evidence of saturation was found at 14 T. Interestingly, there are also oscillations superposed on the linear MR at high magnetic field. Figures 4(c, g) show the SdH oscillations obtained by subtracting the positive MR background for the nanoplate and nanobeam, respectively. The well-resolved SdH oscillations indicate the high-quality of the samples and also offer a platform to study the special quantum properties of the topological insulators. To confirm the observed phenomenon, more than ten devices were measured and similar results were obtained.

We analyzed the SdH oscillations by plotting the Landau index versus the inverse of the magnetic field (1/B). Under a perpendicular magnetic field, the energy spectrum of the surface states are formed as Landau levels (LLs). As B is changed, the energy spacing between LLs and the degeneracy of each LL will change accordingly. When the Fermi energy is located between two LLs, the carriers are localized which results in the minima in conductance. Therefore, the value of $B_N$ can be indexed by the Landau index N (In the quantum Hall regime, it corresponds to the Hall platform). Due to the tensor relation, the conductance is expressed as $G_{xx} = R_{xx}/[R_{xx}^{1/2} + R_{xy}^{3/2}]$, where the Hall resistance $R_{xy} = -B/(n\epsilon^2d)$, n is the carrier concentration, $\epsilon$ is the charge element, and d is the sample thickness.

For the Bi$_2$Se$_3$ nanoplate devices, the Hall resistance ($R_{xy}$) was measured using the Hall bar structure. The Hall resistances of the nanoplate under various temperatures are shown in Figure S6(a). The sign of the Hall slope indicates the n-type carrier transport in the as-grown Bi$_2$Se$_3$ nanoparticles. By fitting the $R_{xy}$-B curves in the low magnetic field region, the Hall carrier concentration and Hall mobility were calculated. As shown in Figure S6(b), the Hall carrier concentration is about $10^{19}$ cm$^{-3}$, and slightly increases with increasing temperature. The Hall mobility is $\sim$6000 cm$^2$/V s at 1.4 K and changes little below 30 K. The conductance $G_{xx}$ was calculated and the $G_{xx}$-$B$ curve is presented Figure S7(a). Via subtracting the background, the oscillations in $G_{xx}$ at high magnetic field were clearly observed. To compare with the oscillations of $R_{xy}$, we plotted the $\Delta G_{xx}$ and $\Delta R_{xx}$ as a function of B in one figure, as shown in Figure S7(b). It is interesting to note that the minima in $G_{xx}$ are well consistent with the minima in $R_{xx}$ suggesting that the Bi$_2$Se$_3$ nanoparticles are of high quality and the surface conductance $G_{xx}$ is dominant for the Bi$_2$Se$_3$ nanolayer device at low temperatures. Therefore, we plotted the $1/B_{Ni}$ (where the minima in $R_{xx}$ appear) against N for the Bi$_2$Se$_3$ nanoplate devices, as shown in Figure 4d. The linear fitting gives an intercept of 1/2, indicating the SdH oscillations are originated from the surface states with Dirac fermions. From the fitted slope F of 44.3, the carrier concentration $n \sim 1.07 \times 10^{12}$ cm$^{-2}$ is also obtained.

For the Bi$_2$Se$_3$ nanobeams, it is very hard to determine the $B_N$ using the minima or maxima in $R_{xx}$ without Hall data. We are aware that recently Fang et al. assigned the maxima in $R_{xx}$ SdH oscillations to

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**Figure 3 | Microstructures and component analysis of the Bi$_2$Se$_3$ nanostructures.** (a–d) TEM images of different Bi$_2$Se$_3$ nanostructures. The insets show the corresponding HRTEM images and selected area electron diffraction patterns. (e, f) EDS spectra collected from the head and body of the Bi$_2$Se$_3$ nanoribbon in panel (c), respectively.
**Discussion**

The dimensionality of the SdH oscillations can be further checked by tilted magnetic field measurements. The magnetoresistance measured at temperature of 1.5 K with different angles between the normal direction of the substrate plane and the direction of the magnetic field was shown in Figure S8. The SdH oscillations in resistance are only related to the vertical component of the magnetic field, indicating two-dimensional transport properties. We noticed that the 2D-like magneto-transport in highly doped Bi$_2$Se$_3$ from bulk carriers was recently reported. In Ref. 27, the $R_{xx}$ minima of the SdH oscillations were labeled with $N$, because the $G_{xx}$ was all from the bulk carriers and the surface conduction can be neglected in such highly doped system. The authors of Ref. 27 thus obtained a zero intercept in the Landau level fan diagram. However, in our low doped Bi$_2$Se$_3$ nanoplates, surface conduction dominates the transport at low temperatures, which is the reason why we also assigned the valley positions in resistance to $N$ in Figure 4(d).

In conclusion, Bi$_2$Se$_3$ nanostructures with different morphologies have been synthesized and characterized through the methods including SEM, EDS, AFM, TEM and SAED. The as-grown Bi$_2$Se$_3$ samples are n-type doped and display metallic behaviors, which are attributed to the existence of intrinsic selenium vacancies. Transport properties of two typical Bi$_2$Se$_3$ nanostructures (nanoplates and nanobeams) were studied. The topological surface states behave as Dirac fermions due to the existence of a Berry’s phase. The observation of the singular quantum transport of the topological surface states implies that the high-quality Bi$_2$Se$_3$ nanostructures have superiorities for investigating the novel physical properties and developing the potential applications.

**Methods**

**Synthesis.** The Bi$_2$Se$_3$ nanostructures have been synthesized by a simple chemical vapor deposition method in a horizontal tube furnace. Commercial grade Bi$_2$Se$_3$ powders (Alfa Aesar, 99.999% purity) were placed in the center of the tube and used as source materials. Single-crystalline silicon substrates with electron beam evaporated gold thin layer, which acted as catalyst, were placed downstream of the source in order to collect the products. At first, the system was purged by a mechanical roughing pump and flushed by Argon more than three times to get rid of the oxygen. Then the system temperature was elevated to 700°C at a rate of 20°C min$^{-1}$. After stabilizing the temperature, argon carrier gas was introduced into the system at a flow rate of 30 sccm, not only to transport the sublimated vapors to cooler regions of the furnace, but also to control the proper environmental pressure for growth. The system was held at those conditions for about 0.5 hour and then cooled naturally to room temperature. In order to gather more source vapors, the substrates were placed in the tube furnace with an angle of 30 degrees to the horizontal.

**Device fabrication and measurements.** Bi$_2$Se$_3$ nanostructures were transferred to a Si substrate with 300 nm SiO$_2$ layer. Using a standard e-beam lithography technique, six-terminal Hall bar structure was patterned on individual Bi$_2$Se$_3$ nanoplates and multi-terminal electrodes were patterned on individual Bi$_2$Se$_3$ nanobeams. Via e-beam evaporation of Cr/Au (50/100 nm) and lift-off processes, the fabricated devices allowed us to measure the transport properties via four-probe method or Hall bar configuration. Transport measurements were performed in an Oxford Instrument with variable temperature insert (VTI). The electrical signals were measured using low-frequency lock-in techniques. The magnetic field up to 14 T was applied perpendicular to the substrate plane.
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**Author contributions**

Z.M.L. conceived and designed the study. Y.Y. performed the experiments. Y.B.Z., Y.Q.B., J.J.C., J.M. helped to do the experiments. D.P.Y. and X.S.W. gave scientific advice. Z.M.L. wrote the manuscript. H.C.W. commented on the manuscript. All authors contributed to discussion and reviewed the manuscript.

**Additional information**

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**Competing financial interests:** The authors declare no competing financial interests.

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