Ambipolar Field Effect in Sb-Doped Bi$_2$Se$_3$ Nanoplates by Solvothermal Synthesis

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ABSTRACT: A topological insulator is a new phase of quantum matter with a bulk band gap and spin-polarized surface states, which might find use in applications ranging from electronics to energy conversion. Despite much exciting progress in the field, high-yield solution synthesis has not been widely used for the study of topological insulator behavior. Here, we demonstrate that solvothermally solution-synthesized Bi$_2$Se$_3$ nanoplates are attractive for topological insulator studies. The carrier concentration of these Bi$_2$Se$_3$ nanoplates is controlled by compensational Sb doping during the synthesis. In low-carrier-density, Sb-doped Bi$_2$Se$_3$ nanoplates, we observe pronounced ambipolar field effect that demonstrates the flexible manipulation of carrier type and concentration for these nanostructures. Solvothermal synthesis offers an affordable, facile approach to produce high-quality nanomaterials to explore the properties of topological insulators.

KEYWORDS: Topological insulator, solvothermal synthesis, Bi$_2$Se$_3$ nanoplate, ambipolar field effect, Sb doping, low carrier density

Topological insulators represent a novel class of semiconductors with spin-polarized metallic surface states which exhibit inherent robustness and unique electronic properties with potential applications in low-energy dissipation electronics, thermoelectric materials, catalysis, and near-infrared transparent electrodes. In most proposed applications, controlling bulk carriers of these materials with a bulk band gap and spin-polarized surface states is crucial. Here, we report a facile, electrostatically controlled approach to produce high-quality Bi$_2$Se$_3$ nanomaterials by solvothermal synthesis. In low-carrier-density, Sb-doped Bi$_2$Se$_3$ nanoplates, we observe pronounced ambipolar field effect that demonstrates the flexible manipulation of carrier type and concentration for these nanostructures. Solvothermal synthesis offers an affordable, facile approach to produce high-quality nanomaterials to explore the properties of topological insulators.
Synthesized nanoplates are characterized by transmission electron microscopy (TEM, FEI Tecnai F20 microscope operated at 200 kV). TEM samples are prepared by drop-casting the suspension onto lacey carbon films supported by Ni grids. Nanoplates lie flat on the membrane from the surface tension generated by evaporation of the ethanol. TEM analysis on nanoplates of pure and Sb-doped Bi$_2$Se$_3$ are summarized in Figure S1 and Figure 1B, respectively. As-grown nanoplates typically exhibit hexagonal morphology with 120° edge facets and lateral dimension in micrometers but typically less than 20 μm. The sharp diffraction pattern in selected area electron diffraction and clear lattice fringes in high-resolution TEM images (HRTEM) confirm the single-crystalline nature of these nanoplates. The lattice spacing in HRTEM is ∼0.21 nm, well matching the expected spacing of (11-20) planes. The compositions of individual nanoplates are determined by energy dispersive X-ray spectroscopy (EDS). An EDS spectrum from pure Bi$_2$Se$_3$ shows stoichiometry of Bi/Se ∼ 2/3, whereas the EDS spectrum from Sb-doped samples (Figure 1D) reveals identifiable Sb peak corresponding to an atomic percentage of ∼1%, which confirms that Sb is successfully incorporated into the nanoplates during the solvothermal reaction. Sb$_2$Se$_3$ naturally crystallizes in orthorhombic structure, whereas Bi$_2$Se$_3$ stabilizes in layered rhombohedral structure. Accordingly, Sb exhibits limited solubility in ternary rhombohedral (Bi$_2$Sb$_{2n-1}$)Te$_n$, in sharp contrast to the ternary (Bi$_2$Sb$_{2n-1}$)Te$_n$ system that crystallizes in rhombohedral for the entire composition range. We notice that the Sb percentage in solvothermally synthesized nanoplate is much lower than that of vapor-phase-synthesized nanoribbon (up to 7 at. %), likely due to the lower reaction temperature.

Bi$_2$Se$_3$ nanoplates can easily be identified in optical microscopy images. Certain substrates, such as the oxidized silicon with 300 nm thick SiO$_2$ layer used here, dramatically enhance the optical contrast to manifest thickness differences down to a single quintuple layer. Figure 2A is a typical optical image of an Sb-doped Bi$_2$Se$_3$ nanoplate on an oxidized silicon substrate (300 nm SiO$_2$/Si), showing thickness-dependent optical contrast. (B) Corresponding AFM image of the same nanoplate. The number of quintuple layers is marked in the image. This nanoplate has multiple quintuple layer steps suggesting a layer-by-layer growth solution process.

![Figure 1](image1.png)

Figure 1. (A) Layered rhombohedral crystal structure of Bi$_2$Se$_3$. Dashed green line indicates a Se(1)−Bi−Se(2)−Bi−Se(1) quintuple layer with thickness of ∼1 nm. (B) TEM characterization of solvothermally synthesized Bi$_2$Se$_3$ nanoplates on a nickel-grid-supported lacey carbon film. The high-resolution TEM image is taken along the [0001] direction, clearly revealing crystalline lattice fringes. The corresponding nanoplate is shown in the top-right inset. Sharp diffraction spots in the selected area diffraction pattern (left inset) further confirm the nanoplate is a high-quality crystal. (C) EDS spectrum of a pure Bi$_2$Se$_3$ nanoplate. (D) EDS spectrum of an Sb-doped Bi$_2$Se$_3$ nanoplate. Inset: stacked EDS spectra of the pure and Sb-doped nanoplates, showing the presence of Sb in the doped sample. The Sb peak in Sb-doped Bi$_2$Se$_3$ roughly corresponds to an atomic percentage of 1%.

![Figure 2](image2.png)

Figure 2. (A) An optical image of an Sb-doped Bi$_2$Se$_3$ nanoplate on an oxidized silicon substrate (300 nm SiO$_2$/Si) showing thickness-dependent optical contrast. (B) Corresponding AFM image of the same nanoplate. The number of quintuple layers is marked in the image. This nanoplate has multiple quintuple layer steps suggesting a layer-by-layer growth solution process.
crystal structure with high-energy edges and dangling bonds predominately distributed on the side surfaces that readily bind additional adatoms in planar growth. We note that AFM measurements are affected by residual PVP surfactant on the surface of the nanoplate. To unambiguously determine the actual thickness, we use Ar plasma etched, vapor-phase-synthesized Bi$_2$Se$_3$ nanoribbons establishing a correlation between optical contrast and sample thickness (Figure S2). Accordingly, optical imaging provides a facile gauge of the sample thickness. The thickness of residual surfactant coating on solvothermally synthesized nanoplates ranges from a few angstroms to $\sim$3 nm (Figures S3 and S4).

Electrical properties of solvothermally grown Bi$_2$Se$_3$ nanoplates are studied in single nanoplate devices. As-grown nanoplates are drop-cast on oxidized silicon substrates with a prepatterned metal marker array. Nanoplates free of terraces are selected according to their optical contrast for transport studies to simplify data interpretation. We notice these nanoplates are mainly in the thinner range of the thickness distribution, suggesting additional terraces tend to nucleate and grow as the nanoplates get thicker. Electrodes are fabricated onto each nanoplate by standard e-beam lithography and thermal evaporation of Cr/Au films (10 nm/100 nm) with the six-terminal Hall bar geometry (schematic shown as the inset of Figure 3A). To ensure reliable ohmic contacts, a gentle Ar plasma etching process is performed in a sputtering chamber to remove residual PVP and EDTA on the nanoplates right before metal film deposition. All the transport measurements are carried out at 2 K inside an Oxford cryostat with a digital lock-in amplifier (Stanford Research Systems SR830), and the thickness of individual nanoplate is determined by the optical contrast and the AFM measurements (Supporting Information). The area carrier density and mobility values obtained from Hall measurements are summarized in Figures 3A and 3B, respectively. To compare the results with other synthetic approaches, we adopt the empirical curves of carrier density and mobility from Kim et al., shown as the green curves in Figure 3, obtained from their MBE films and bulk single crystals of pure Bi$_2$Se$_3$. Apparently, pure Bi$_2$Se$_3$ from solvothermal growth exhibits higher carrier density than the empirical values, presumably due to the low reaction temperature which favors the formation of Se vacancies. High-quality MBE films are typically grown at 190–250 °C and bulk crystals at 550–750 °C. The mobility values of pure Bi$_2$Se$_3$ nanoplates are also lower than MBE films. Sb doping effectively reduces the carrier density and enhances the mobility approaching the properties of MBE films, indicating significant improvement of the crystal quality. Notice that all the nanoplates measured here are thicker than the critical thickness of $\sim$6 nm for Bi$_2$Se$_3$, below which the surface states between the top and bottom surfaces of the nanoplate may hybridize to form a conventional semiconductor or 2D quantum spin Hall system. The effective carrier concentrations and Hall mobility values presented here have the contributions from both the bulk and surface carriers. The lack of distinctive signatures in magnetotransport prevents us from analyzing each components in a quantitative manner, so we limit our discussion to the effective carrier concentration and mobility.

The properties of Sb-doped nanoplates are further explored with backgate field effect transistor devices. Solvothermally synthesized nanoplates suspended and stored in ethanol are readily transferred onto various substrates by drop-casting. Here, we use a 300 nm thick SiO$_2$ dielectric layer on a degenerately doped n-type silicon substrate to apply a backgate voltage (device schematic shown as the inset of Figure 3A). The spread of carrier density of Sb-doped samples falls into an interesting range, allowing us to access distinctive gating behaviors. In Sb-doped nanoplates with low carrier density, we have observed a pronounced field effect (Figure 4A). Typical dependence of the resistance on the gate voltage, $R_{\text{eff}}$, exhibits a sharp peak that is 2 orders of magnitude higher than the resistance at large $V_G$. The Hall coefficient, $R_{\text{H}}$, also reverses its sign near the peak of the resistance, changing from the original n-type conductor to a p-type conductor through a mixed state with the coexistence of electrons and holes. Such an ambipolar field effect requires the effective suppression of bulk carriers, a characteristic behavior for low-density topological insulator nanoplates, which is also previously observed in graphene—a another material with gapless two-dimensional Dirac fermions. In nanoplates with moderate carrier density (Figure 4B), a strong field effect is still observed, where $R$ and $R_{\text{H}}$ increase a few times by applying large negative voltage. Although the nanoplate cannot be fully inverted into p-type within the limit of gate voltage, the clear response by electrostatic gating corresponds to effective carrier depletion. In nanoplates with high carrier density, however, the changes of $R$ and $|R_{\text{H}}|$ by applying a backgate voltage are much smaller, suggesting the dominance of excessive bulk carriers in the charge transport process irrespective of the external electric field. Apparently, the initial carrier density largely determines the behaviors of electrostatic gating for Bi$_2$Se$_3$ nanoplates, and
compensational Sb doping is therefore critical to enhance the electrical field effect by reducing the intrinsic carrier density.

This work provides a systematic study of Sb-doped Bi2Se3 nanoplates synthesized by a solvothermal reaction in the context of topological insulators. Sb doping allows access of nanoplates with low carrier density, which can be further suppressed by electrostatic gating. A pronounced ambipolar field effect is observed in certain Sb-doped nanoplate transistor devices, demonstrating the flexible manipulation of carrier type and density in these nanostructures. Solution derived nanocrystals afford an alternative approach to access high-quality topological insulator materials.

ASSOCIATED CONTENT

Supporting Information
Additional TEM characterization, optical images, AFM measurements, and volume carrier density versus nanoplate thickness. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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