

# Opportunities in chemistry and materials science for topological insulators and their nanostructures

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Electrical charges on the boundaries of topological insulators favour forward motion over back-scattering at impurities, producing low-dissipation, metallic states that exist up to room temperature in ambient conditions. These states have the promise to impact a broad range of applications from electronics to the production of energy, which is one reason why topological insulators have become the rising star in condensed-matter physics. There are many challenges in the processing of these exotic materials to use the metallic states in functional devices, and they present great opportunities for the chemistry and materials science research communities.

Scattering and energy dissipation are common in charge-transport processes. A major discovery of condensed-matter physics in the 1980s, the quantum Hall effect, is realized in electrons confined in two dimensions in the presence of a strong magnetic field, in which dissipationless current flows along the sample's edge. In the past few years, topological insulators have been found to have similar metallic states that are also transported in a low-dissipation state. The existence of these remarkable electronic states is due to an intrinsic interaction in solids — spin-orbit coupling, instead of an external applied metallic field — which has the potential to impact multiple areas of applications.

In this Perspective, we introduce the basic concepts and interesting properties of topological insulators. After a brief overview of this rapidly developing field, we discuss the materials challenges and chemical issues encountered in current research. We conclude with potential applications of these remarkable materials and the possible influence on many other areas.

#### The physical basis of topological insulators

Topological insulators are insulators or semiconductors with metallic electronic states always present at their boundary with other insulating materials. The exotic metallic surface is a so-called helical metal, in which the electron spin is oriented perpendicularly to its orbital momentum. Topological insulators have a two-dimensional form as wire-like metallic edges wrapping around certain 2D materials (quantum wells or thin films), as shown in Fig. 1a. Along such edges, spin-up and spin-down electrons counter-propagate. Topological insulators can also be 3D, in the form of metallic surfaces covering the entire material. The spin texture on such surfaces is best illustrated in momentum space as a 'spin-resolved' band structure (Fig. 1b). At the chemical potential, each momentum has one spin polarization, which rotates as the momentum moves along the Fermi surface. Knowledge of the helical spin texture of the surface of a topological insulator is essential for understanding their unusual properties.

In ordinary materials, backscattering, in which electrons take a 'U-turn' owing to collisions with crystal defects, effectively degrades the current flow and increases the resistance. On the surface of topological insulators, such backscattering processes are completely suppressed, so charge transport is in a dissipationless or low-dissipation state. To understand this remarkable property, we will first review the charge transport in its predecessor — the quantum Hall

state (Fig. 1c). In a quantum Hall system, an intense magnetic field is applied perpendicularly to electrons confined two-dimensionally, thereby driving the electrons to circulate in quantized orbitals. As a result, the quantum Hall system becomes inert and insulating internally, but has electrons flowing along the sample edge. The unique property of this metallic edge is that it propagates the electronic charge in one direction only, making it unlikely to be reflected back or scattered, and is therefore dissipationless. This form of charge transport is extremely attractive for electronic devices. The requirement of a large magnetic field, however, strictly limits the potential applications of the quantum Hall effect. In topological insulators the spin-orbit coupling, an intrinsic interaction between electron's spin and its motion, causes moving electrons to be subject to a spin-dependent force, giving rise to a helical metal at the material's surface, even without an external magnetic field. On the surface of a topological insulator, if a forward-moving electron were to be reflected back by crystal defects, its spin would have to flip because the momentum changes sign (Fig. 1d; spin and momentum are 'locked' in helical metal). To abide by the law of conservation of angular momentum, however, magnetic impurities or an external magnetic field would be needed to flip the spin; surface electrons are thus prohibited from making a 'U-turn' in their absence. Accordingly, electrons in 2D topological insulators flow along the sample edges unimpeded, which is termed the quantum spin Hall effect. For 3D topological insulators, although surface electrons can be scattered in multiple directions, near-U-turn scatterings are much less than in ordinary metals, therefore charge transport on such surfaces is in a low-dissipation state. Further, the complete suppression of backscattering has a far-reaching consequence: in a normal metal, electrons may form insulating states when scattering is so strong that they become localized (Anderson localization)1. The surface states of a topological insulator do not undergo Anderson localization and are conductive even with strong crystal disorder<sup>2</sup>.

Another attractive property of topological insulators is the inherent robustness of their metallic surface properties. First, consider the surface electronic states in a normal semiconductor. Dangling bonds and reconstructions are common on the surfaces of semiconductors, which may introduce surface states that have energy residing in the bandgap (Fig. 1e). These surface states are usually easily modified or even destroyed, because they depend on the bonding structures and adsorbates on the surface. On the contrary, surface

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states in topological insulators are robust against almost any type of surface modification (Fig. 1f). This robustness originates from a property called the topological invariant, which cannot change as long as the material remains insulating. As topological insulators have a different topological invariant from an ordinary insulator, the interface between the two has to be gapless for the invariant to change. The gapless surface states are an effect that occurs at the interfaces of topological insulators and insulating media and their existence is irrespective of local chemical bonding structures.

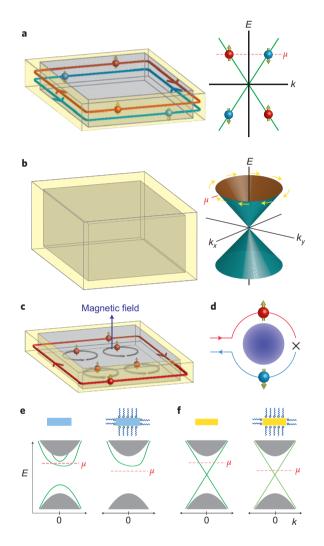


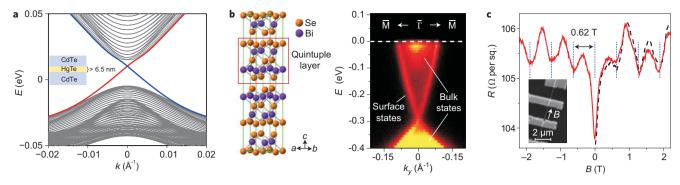
Figure 1 | Exotic electronic states in topological insulators. a, The metallic edge (shown in yellow) of a 2D topological insulator, in which spin-up and spin-down electrons counter-propagate (left), and the corresponding idealized spin-resolved band structure of the edge states (right). The pink line is the chemical potential  $\mu$ . **b**, The metallic surface of 3D topological insulators (left), and the corresponding idealized spin-resolved band structure of the surface states (right) revealing how the electron spin rotates as its momentum moves on the Fermi surface. **c**, The quantum Hall effect in a 2D electron system, with a dissipationless metallic edge. d, Any potential backscattering process on a topological insulator surface with a nonmagnetic impurity (purple circle) is prohibited, owing to the conservation of spin angular momentum. e, On the left, an ordinary semiconductor and corresponding band diagram with coexisting surface (green lines) and bulk states (grey area). After surface modification, both surface and bulk electronic properties are modified (right). In this particular case, surface states no longer contribute to the transport process (no states available at  $\mu$ ).  $\mathbf{f}$ , A topological insulator and the corresponding band structure (left). After surface functionalization, the surface states remain intact, whereas  $\mu$  shifts (right).

# A rapidly developing field

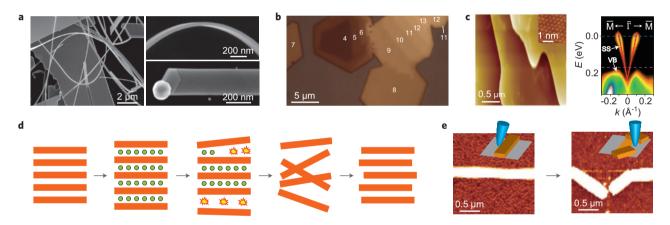
The history of topological insulators comprises a series of theoretical predictions validated by experimental evidence. In 2004, a simplified model of dissipationless transport in a 2D topological insulator was proposed<sup>3</sup>. Subsequent searches for valid material candidates predicted the (Hg,Cd)Te quantum well to be a 2D topological insulator<sup>4,5</sup> (Fig. 2a). In 2007, the quantum spin Hall effect was indeed observed in this system as quantized conductance<sup>6</sup>. Although realized only in a carefully engineered quantum well structure, the demonstration of dissipationless transport without using an external magnetic field was rather encouraging.

The next important progress is the realization that the basic concepts of a 2D topological insulator can be extended to 3D<sup>7-9</sup>, which is the focus of current experiments, and of our discussion in this Perspective. The planar metallic surface of a 3D topological insulator can be studied by surface-sensitive probes. The first predicted material was a Bi<sub>x</sub>Sb<sub>1-x</sub> alloy<sup>10</sup>, whose surface electronic band structure was directly confirmed by angle-resolved photoemission spectroscopy (ARPES)11. In ARPES, electrons in the crystal are ejected by high-energy photons, whose energy and momentum are measured and used to obtain the electronic band structure. Although the surface bands of  $Bi_xSb_{1-x}$  are rather complicated, this work initialized the extensive search for further candidate materials. A key advance was the prediction and experimental confirmation of topological insulators in layered binary chalcogenides 12-14, including Bi, Se, Bi, Te, and Sb<sub>2</sub>Te<sub>3</sub> (Fig. 2b); their helical spin texture was later verified by spinresolved ARPES<sup>15</sup>. These topological insulators have become the materials of choice in experiments because they have several desirable properties. Their surface states have a linear relation between energy and momentum, termed a single Dirac cone, inside a relatively large bandgap (~0.2 to 0.3 eV), so the remarkable properties of the surface states are accessible up to room temperature. In these binary compounds, high-purity crystals with the appropriate stoichiometry and uniform composition are easier to achieve compared with alloys and multi-element compounds. Scanning tunnelling spectroscopy (STS) is also used to study the electronic properties of the surface states 16-20, and the interference patterns observed from defects or surface terraces confirm the complete suppression of backscattering processes. Several new families of materials have also now been proposed as topological insulators, such as thalliumbased ternary chalcogenides and Heusler compounds<sup>21-24</sup>, enriching the materials candidates for future study and applications.

Electron-transport measurements on the surface states of 3D topological insulators turn out to be much more challenging. Intuitively, if the chemical potential of the topological insulator lies in the bulk bandgap, surface carriers are expected to determine the transport properties. As a result of unintended doping from crystal imperfections, however, residual bulk carriers are always present in the actual samples and often dominate the total conductivity. Low-dimensional nanostructures, with a large surface-to-volume ratio, provide attractive systems for transport studies, because the contribution from surface carriers is much greater than that from bulk crystals, and are therefore most relevant to electronic device applications. Fieldeffect transistor devices can be fabricated on these nanostructures, and the chemical potential can then be electrically modulated using the gate voltage. Aharonov-Bohm interference observed in Bi<sub>2</sub>Se<sub>3</sub> nanoribbons provides evidence of surface transport in a 3D topological insulator<sup>25</sup> (Fig. 2c): in quasi-1D nanoribbons, the topological surface states form a tubular metallic system, on which the wave nature of electrons manifests as periodic magnetoresistance oscillations depending on the magnetic flux along the ribbon's axis. These interference experiments are powerful tools for probing tubular metallic structures, as demonstrated previously in a study on carbon nanotubes<sup>26</sup>. Aharonov-Bohm interference was later also observed in Bi<sub>2</sub>Te<sub>3</sub> nanoribbons<sup>27</sup>. Surface transport has also been revealed in bulk single crystals that have suppressed residual



**Figure 2 | Evidence of topological insulators. a**, Calculated band diagram of a (Hg,Cd)Te quantum well with metallic edge states (red and blue traces) in the bulk bandgap<sup>50</sup>. The structure of the quantum well is shown in the inset. **b**, Layered crystal structure of 3D topological insulators in binary chalcogenide with Bi<sub>2</sub>Se<sub>3</sub> as an example (left). Each layer consists of five atomic sheets (a quintuple layer), which are bonded together by van der Waals interactions along the *c* axis. The electronic structure of Bi<sub>2</sub>Se<sub>3</sub> measured by spin-resolved ARPES (right), in which surface states form a quasi-linear, V-shape band inside the bulk bandgap (Dirac cone)<sup>13</sup>. The chemical potential of this crystal and many other as-grown samples lies in the bulk conduction band, indicating bulk carriers would dominate the charge-transport properties. Suppression of the bulk carrier density is thus required for topological insulators to make use of their attractive electric and optical properties. **c**, Magnetoresistance of a Bi<sub>2</sub>Se<sub>3</sub> nanoribbon in a radial magnetic field, where the periodic resistance oscillations come from the Aharonov-Bohm interference of the topological surface states<sup>25</sup>. Inset: a scanning electron microscope (SEM) image of the corresponding Bi<sub>2</sub>Se<sub>3</sub> nanoribbon device. The direction of the magnetic field (*B*) is indicated by an arrow. Figures reproduced from: **a**, ref. 50, © 2010 APS; **b** (left), **c**, ref. 25, © 2010 NPG; **b** (right), ref. 13 © 2009 NPG.



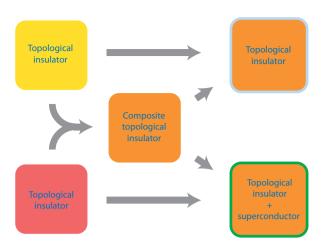
**Figure 3 | Nanostructures of topological insulators. a**, SEM images of Bi<sub>2</sub>Se<sub>3</sub> nanoribbons prepared by metal-catalysed chemical vapour deposition<sup>25</sup>. **b**, An optical microscope image of ultrathin Bi<sub>2</sub>Te<sub>3</sub> nanoplates grown on oxidized silicon reveals thickness-dependent colour and contrast. The number of quintuple layers is labelled on the image (a quintuple layer is about 1 nm thick)<sup>35</sup>. **c**, STM image of a 80-nm-thick Bi<sub>2</sub>Te<sub>3</sub> MBE film (left), and the corresponding band structure measured by *insitu* ARPES<sup>39</sup>, revealing surface states (SS) and the bulk valance band (VB) (right). Note that film has the chemical potential intrinsically lying in the bulk bandgap in the absence of compensation dopants. **d**, Schematic diagram of lithium (green circles) intercalation and exfoliation of layered topological insulators (orange). Lithiated crystals are exfoliated by the rapid release of hydrogen (indicated by the yellow symbols) in water. Exfoliated layers can restack back into crystals by controlled evaporation. **e**, Exfoliation of Bi<sub>2</sub>Se<sub>3</sub> nanoribbons using an AFM, in which multiple layers of the materials are 'knocked off' by the tip<sup>42</sup>. Figures reproduced from: **a**, ref. 25, © 2010 NPG; **b**, ref. 35, © 2010 ACS; **c**, ref. 39, © 2010 Wiley; **e**, ref. 42, © 2010 ACS.

bulk conductivity  $^{28,29};$  as expected, surface carriers show a very high mobility of  $\sim\!10,\!000$  cm  $^2$   $V^{-1}$  s  $^{-1}$  in some of these measurements  $^{29}.$ 

#### Materials development and challenges

Bulk single crystals of topological insulators are widely used in experiments. These crystals are usually grown by melting a mixture of powders of the elemental source materials. Fresh surfaces are created by cleaving the crystal along the natural cleavage plane. To access the remarkable properties of the surface carriers, it is necessary to controllably suppress the bulk conductivity by constraining the chemical potential to the bulk bandgap. Although doping of these materials has been investigated extensively for thermoelectric applications, the strategy cannot be directly adopted for quasi-insulating crystals owing to their different doping-level requirements (high-performance thermoelectric materials are typically doped to a high level to give metallic bulk conductivity). Progress has been made in growing very lightly doped crystals, either by using refined conditions or appropriate compensation doping (Sn for Bi<sub>2</sub>Te<sub>3</sub>; Ca, Sb and Mg for Bi<sub>2</sub>Se<sub>3</sub>)<sup>14,30-32</sup>.

Topological insulator nanostructures stand out as excellent candidates for studying the exotic surface states and making functional devices. Methods for producing topological insulator nanomaterials can generally be categorized as bottom-up synthesis, top-down exfoliation, or a combination of both. As a bottom-up approach, topological insulator nanoribbons are made by metal-catalysed chemical vapour deposition in a tube furnace<sup>25,33</sup> (Fig. 3a). Doping can be achieved by introducing the dopants into the catalysts, which diffuse into the nanoribbons during their synthesis<sup>25,34</sup>. For example, Sn is an effective compensation dopant for reducing residual bulk conductivity in Bi<sub>2</sub>Se<sub>3</sub> nanoribbons, allowing experimental observation of the Aharonov-Bohm interference with the surface states<sup>25</sup>. Additional effective dopants and alternative doping approaches for the nanostructures, however, are yet to be explored. To enhance the tunability of the chemical potential in field-effect-transistor-like devices, ultrathin nanoplates down to a few nanometres in thickness are grown, with a recipe similar to that for nanoribbons but without a seed catalyst<sup>35</sup>. Interestingly, these nanoplates are semitransparent on oxidized silicon substrates



**Figure 4 | Heterostructures of topological insulators.** Composite topological insulators, made up of various topological insulators from the same family, offer the opportunity to engineer the bulk properties but preserve the topological surface states. Functional topological insulators are expected to be covered by an encapsulation layer, protecting the surface states from environmental contamination. Novel particles and phases may be created at the interface between topological insulators and other exotic materials, such as superconductors, to expand the application areas of these remarkable materials.

with thickness-dependent colour and contrast (Fig. 3b), similar to graphene. Graphene also serves as an ideal substrate for growing high-quality Bi<sub>2</sub>Se<sub>3</sub> via van der Waals epitaxy<sup>36</sup>. Furthermore, thin films of topological insulator materials and their superlattices are grown by metal–organic chemical vapour deposition and molecular beam epitaxy (MBE)<sup>37–39</sup>. Using carefully tuned conditions, MBE films — which intrinsically have the chemical potential residing in the bulk bandgap without additional compensation dopants — have been obtained by quasi defect-free growth<sup>39</sup> (Fig. 3c). Wet synthesis of many topological insulator materials has been extensively studied in the past. Recently, solvothermally synthesized Bi<sub>2</sub>Te<sub>3</sub> nanoribbons have been shown to be promising candidates for studying topological insulators<sup>27</sup>.

As a top-down approach, layered topological insulators are bonded together by weak van der Waals forces, so they can be mechanically exfoliated into thin flakes by the so-called Scotch-tape method<sup>40</sup> that is frequently used to produce graphene from graphite. Lithium intercalations and liquid-phase exfoliations is another generic way of producing thin films of layered materials that is applicable to topological insulators<sup>41</sup> (Fig. 3d). Lithium is initially intercalated between the layers and then oxidized by rinsing the lithiated crystals in water; hydrogen is rapidly released, which separates the layers into a colloidal suspension. Exfoliated flakes can restack back into the crystal form by controlled evaporation, which opens the opportunity to create composite topological insulators from multiple source materials. As a demonstration of the combination of bottom-up and top-down approaches, as-grown Bi<sub>2</sub>Se<sub>3</sub> nanoribbons are further thinned down to several nanometres using an atomic force microscope tip to 'knock' off the extra layers42 (Fig. 3e).

The chemistry at the surface of materials is crucial, but has not drawn sufficient attention in the topological insulator research community so far. Knowledge of topological insulator surfaces is frequently acquired by *in situ* measurements, such as ARPES or STM, with sample surfaces never exposed to ambient conditions. Although surface states of topological insulators are inherently robust against almost any surface modifications, these materials are prone to various surface chemical reactions. For example, amorphous native oxides may grow on chalcogenides exposed to the ambient environment, creating additional defect states and dangling bonds<sup>43</sup>. Observed by ARPES, the chemical potential on the surface of Bi<sub>2</sub>Se<sub>3</sub> changes dramatically after

exposure to air<sup>31</sup>. The ageing effects of surface-transport properties in air has also been observed in recent measurements<sup>28</sup>. These issues present a great need and opportunity for surface chemical modifications. A possible strategy is to grow a protective layer on the fresh surfaces, for example a self-assembled monolayer or by using inorganic encapsulation. Extra benefits may be the passivation of surface defects on as-grown crystals and further improvement of the transport properties for topological surface states, if appropriate chemicals are used.

The next major material development in topological insulators may come from heterostructures (see Fig. 4). Encapsulated within protection layers, topological insulators are expected to form coreshell structures, with the surface states buried inside. Bulk properties of topological insulators can also be engineered with a composite materials approach. For such topological insulators made from a family of materials having the same topological invariant, additional surface states will not be created at the interfaces, whereas bulk electronic properties can be tailored. Each material is therefore the building-block for a multifunctional composite topological insulator. Currently, many groups are also evaluating the feasibility for generating exotic particles and phases at the interface between topological insulators and other materials, such as superconductors, possibly extending the application areas into quantum computing<sup>44</sup>.

# Potential applications and impacts

Electronics and optoelectronics are among the most important applications of tolological insulators. The suppression of backscattering of the surface states corresponds to exceptional transport mobility and reduced energy consumption, which is extremely attractive for semiconductor devices. The observation of Aharonov-Bohm interference from the high-mobility surface carriers in nanoribbons indeed confirms the remarkable transport properties are accessible via low-cost synthesis approaches such as chemical vapour deposition and solvothermal synthesis<sup>25,27</sup>. Another possible application of topological insulators is in spintronics — owing to the unique spin texture, the charge current on the surface of the topological insulators naturally supplies a net spin-density, which would be useful in memory or spin-torque devices<sup>45</sup>. Optoelectronics is an emerging area for topological insulators: the excellent transport properties and the linear relation between energy and momentum in some topological insulators make them competitors with graphene photonics and optoelectronics, for applications such as transparent conductors and wideband photodetectors<sup>46</sup>.

It is intriguing to note that almost all the proposed topological insulators are also thermoelectric materials. This is not a coincidence. Advanced thermoelectric materials have an optimized efficiency through low thermal conductivity and excellent electrical conductivity. Consequently, heavy-element compounds tend to have a better performance, because a large atomic mass reduces the thermal conductivity. Moreover, the optimal bandgap of semiconductors for thermoelectric applications is typically one order of magnitude higher than the thermal energy of the operation temperature, so room-temperature thermoelectric materials are usually narrow-gap semiconductors<sup>47</sup>. For topological insulators, spin-orbit coupling must be strong enough to modify the electronic structure — as spin-orbit coupling strength increases with atomic mass, this indicates that narrow-bandgap compounds consisting of heavy elements are the most promising candidates. It is therefore natural to explore the potential impact of the surface states of topological insulators on thermoelectricity, for example, in nanostructurally engineered high-performance thermoelectric materials. In composite materials consisting of topological insulators and ordinary semiconductors, the interfaces between the two constituents would scatter phonons and reduce the thermal conductivity, whereas the presence of topological surface states ensures excellent electrical conductivity across the interface, which may be the key to engineering such composite thermoelectric materials.

Many phase-change-memory materials are now being discovered to be topological insulators<sup>48</sup>. Phase-change memory makes use of the

resistivity differences between amorphous and polycrystalline phases of certain chalcogenides to record information; these phases are reversibly switched with the application of heat produced by passing an electric current through. In addition to pure phases, a partially crystalline state, in which crystallites precipitate out in an amorphous phase, is also achievable and important for multibit recording technology. The contribution from topological insulator surfaces may be essential to determine the electrical properties of these intermediate phases.

Another potential application of topological insulators is in catalytic chemistry. Thin flakes of layered topological insulators have a very large surface area, and so could serve as supports for various catalysts. Practically, recipes for mass-producing these flakes are available for many materials, such as the aforementioned liquid-phase exfoliations of crystals. The robust topological surface states provide a stable electron bath for effecting surface reactions. A recent theoretical study predicts that noble-metal-covered topological insulator flakes would exhibit enhanced catalytic activity in certain reactions<sup>49</sup>.

### **Concluding remarks**

Topological insulators have become the rising star in condensedmatter physics, and provide many challenges and opportunities for input from chemists and materials scientists. The scope covered in this Perspective is only the very tip of the iceberg; however, the remarkable properties of topological insulators discussed here may attract the attentions of a broad research community, with the potential for exciting breakthroughs and a wide range of applications.

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# **Additional information**

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