

Heterogeneous catalysis at the surface of topological materials F

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ABSTRACT

Intriguing properties are frequently reported in various topologically non-trivial materials. They include robust metallic surface states, high carrier mobility, chiral fermions, and ultralong Fermi arcs. An exciting recent finding is that these properties are strongly related to adsorption and electron transfer in various heterogeneous catalysis reactions, such as hydrogen evolution, oxygen evolution, oxygen reduction, enantiospecific adsorption, and hydrometallation. Thus, we expect that the introduction of non-trivial symmetry-protected topological order will offer important freedom for designing high-performance heterogeneous catalysts. To uncover the contribution of the topologically non-trivial electronic structure to the heterogeneous reactions, *in situ* techniques are urgently needed to detect the interaction between surface states, topological electrons, and reaction intermediates.

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The establishment of a topological framework has revolutionized the field of condensed matter physics since the first experimental verification of quantum wells of HgTe.^{1,2} Exotic physical properties and electronic states were then rapidly realized in various topological phases, from topological insulators to the recently reported Weyl/Dirac semimetals, nodal line semimetals, and higher-order topological matter.³ These properties and states create a roadmap for the construction of next-generation quantum storage devices and even quantum computers. Even more strikingly, several research teams recently confirmed that the symmetry protected topological phase is surprisingly common, as more than 27% of the materials in the Inorganic Crystal Structure Database are topological in nature.^{4–6} Evidently, the contribution of this characteristic to the physical/chemical properties and applications of these materials is greatly underestimated.

The study and application of topological materials have made great progress recently although there are still gaps toward practical usage. The difficulties lie in the fact that it is very hard to distinguish topological surface states (TSSs) from bulk states. For example, thin films with precisely controlled thickness and ultrahigh quality are needed to form a truly insulating bulk for topological insulators. The quantum anomalous Hall effect, which is the theoretical basis of various devices, occurs only at extremely low temperatures and sometimes under high magnetic fields.^{7,8} Interestingly, topologically nontrivial electronic structures present new opportunities for chemists, especially

in the field of heterogeneous catalysis. In such reactions, all processes including mass adsorption, electron transfer, and desorption occur exactly at the catalyst surfaces and are strongly related to the surface properties.

The topological matter is characterized by linear energy-momentum dispersion around Fermi points as a result of bulk band inversion. Thus, electrons and holes can be described by Dirac or Weyl equations and are considered to be massless relativistic particles such as a 3D analog of graphene. For chemists and materials scientists, this unique band structure can be understood from an analysis of a chain with equally spaced H atoms based on the classic Hückel formulation, where the topology of the orbital interaction determines how a band runs.⁹ Interpretations of topology from the viewpoint of chemists can be found in excellent recent reviews.^{10–12} Materials that have a non-trivial topological electronic structure exhibit many interesting properties, such as a metallic surface without resistance, spin-momentum locking states of electrons involving anti-backscattering and Anderson localization, and Fermi arcs that resist disturbance by surface modification, defects, and changes in chemical potential. The detection of various interesting phenomena such as extremely high mobility, large magnetoresistance, and chiral magnetotransport is the result of the unique electron behavior.¹³ Thus, high-performance functional materials can be predicted and designed by tailoring these physical properties through band engineering (Fig. 1).

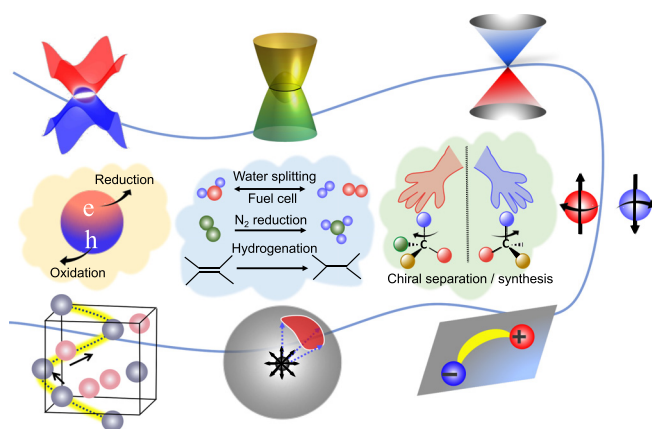


FIG. 1. The non-trivial topological electronic structure in functional materials endows them with unique physical properties such as high-mobility, robust surface states, chiral electrons, super-long Fermi arcs, and non-vanishing electronic Berry phases. They are favorable tools for chemists to control various heterogeneous catalysis processes such as photo/electrocatalysis, separation of enantiomers, and chiral synthesis.

The existence of nontrivial TSSs is considered the most promising characteristic of catalysis processes. Such TSSs are the result of band inversion between the bulk conduction and valence bands. Thus, they are robust and are protected against surface modification as long as the bulk band is preserved.^{14,15} Local perturbations such as light doping, defect creation, chemisorption of air molecules, or even slight oxidation under exposure to the ambient environment would not annihilate the TSSs.^{16–18} Such TSSs can facilitate the donation or acceptance of electrons from the adsorbates, thus enabling us to tailor the metal-adsorbate binding interactions.

The Bi_2Se_3 family of compounds is one of the most extensively studied 3D topological materials and the first prototype for probing the interaction between TSSs and adsorbates. The adsorption energy of small molecules and reaction intermediates such as CO , O_2 , and H^* could be enhanced in the presence of nontrivial TSSs.^{19,20} In contrast to the well-known adsorption mechanism based on the d -band theory, the TSSs are derived from the sp band rather than the d band for topologically trivial metal catalysts. The electrons are more delocalized for the sp band and thus decrease the diffusion and energy barriers of the adsorbed molecules.^{20,21} Direct bonding between the TSSs and adsorbates is not necessary. Even when a thin layer of a guest species is deposited on topological insulators, the TSSs will remain in the interface between the deposited film and topological insulators. This offers a possibility for optimizing the catalytic efficiency by introducing topological electrons into the investigated catalysts.^{22,23}

Note that the presence of metallic TSSs does not guarantee high activity of a catalyst. The strong ability to resist perturbation under surface modification is associated with a weak interaction between the TSSs and adsorbates, resulting in low species coverage and slow reaction kinetics.^{24–26} In addition, in various catalysis reactions, high electrical conductivity and mobilities are also required for fast electron transport to the interface between the electrolyte and catalyst surfaces. This can be addressed well by employing topological Weyl/Dirac semimetals that exhibit high conductivity and carrier mobilities. The ultra-high carrier mobility on the order of $10^6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is close

to that of graphene, has been observed in many topological systems.²⁷ This is highly important for many types of photocatalysis reactions, which require efficient electron-hole pair generation and recombination suppression. The high carrier mobilities and optimized reaction barrier energy facilitate fast electron transfer between the TSSs and surface adsorbates. Consequently, topological semimetal catalysts exhibit enhanced activity and even surpass the benchmark set by noble-metal-based catalysts.^{28–32}

Interestingly, the state-of-the-art catalysts for water and proton-exchange membrane fuel cells, Pt and IrO_2 , are characterized by a large spin Hall effect, which is closely related to the Berry phase of conduction electrons.^{33,34} This is not a coincidence but a result of the intrinsic band structure. Indeed, Dirac nodal lines/rings are observed in these compounds, and they are protected by mirror symmetry. The Berry curvatures are derived mainly from the nodal lines and contribute greatly to the strong spin Hall effect. The distribution of the projected Berry curvatures is determined by the band structure at the Fermi level, which in turn controls the chemical potential of the investigated material. This further determines the electron transfer process at the interface between the catalysts and reactants.

Chiral crystals began attracting attention owing to their superb topological electronic properties, which result from their structural chirality, lattice translation, and time-reversal symmetry. In the absence of operations such as inversion, mirror, or other rotoinversion symmetries, this family of compounds exhibits near-ideal topological electronic structures, for example, the largest possible Fermi arcs and wide nontrivial energy windows.^{35–38} These structures ensure a large density of states (DOS) of the topological surface electrons at the Fermi level, providing an abundant conduction electron bath for surface reactions. Another advantage of the topological non-trivial chiral compounds is the large band inversion between the inverted bands, which significantly increases the topological robustness under changes in the chemical potential. The observation of high selectivity as heterogeneous catalysts for methylation and hydrogenation may be related to the unique topological features.^{39,40}

In addition to the chiral structure, chiral electrons with specified spins have been observed. For electrons within a few nanometers of the surface of topological matter, the spin is locked to the transport direction, and the materials become electronically helical because the momentum and spin are correlated. In fact, we know that all the surface reactions such as adsorption and catalysis involve bond formation or electron transfer. Thus, both the spin and the charge should be transferred simultaneously. These chiral electrons were found to supply an inherent link between the catalysts and reactants and may even provide clues in the search for the origin of life. In the laboratory, scientists pay particular attention to highly selective enantiomer synthesis by carefully controlling the temperatures, solvents, catalysts, etc. However, nature has an amazing ability to preserve chirality persistently and precisely. Electrons with different spins have different electron transmission probabilities through molecules with distinct chirality, which is called the chiral-induced spin selectivity (CISS) effect.^{41,42} This homochirality, which was pointed out by Louis Pasteur in the mid-19th century, can also be realized by the earth's magnetic field at an early age, which could be traced in recent enantiomer separation experiments.⁴³ Such chiral spins and electrons are widely observed in topological insulators and Weyl semimetals or in Dirac semimetals and triple-point topological metals by breaking their

symmetries using a magnetic field.⁴⁴ The manipulation of spin shows promise for applications in the chiral synthesis and catalysis reactions.

Observations of non-trivial topological electronic structures in perovskite manganites and Heusler alloys shed light on the new principles underlying the development of new catalysts. These families of compounds exhibit diverse physical and chemical properties and can easily be tailored by elemental doping or by introducing strain and defects. These compounds are cost-effective alternatives to noble metal catalysts and are effective for catalyzing many reduction and oxidation reactions such as those of O₂, CO, and NO_x and water splitting.^{45,46} This provides a new degree of freedom for designing high-performance catalysts. For example, perovskite manganites show a larger bulk bandgap and higher resistivities, making the TSSs easier to observe than those of the Bi₂Se₃ family. Tunable magnetic properties and spin polarization can be obtained in Heusler alloys by regulating the composition of the compounds. This makes it possible to design ideal catalysts with the desired conductivity, spin structure, orbital filling and suitable SSs.

These recent developments illustrate that the use of topology has paved the way for a new class of catalysts for use in surface reactions. However, for a meaningful discussion in practice, the basic and difficult point is to make sure the existence of topological non-trivial electronic states during the heterogeneous catalysis processes. Surface reconstruction or even oxidation always happens at the catalyst surface, particularly in the redox reactions. Topological insulators such as Bi₂Te₃ and Bi₂Se₃ could provide itinerant and high-mobility electrons for chemical reactions but are accompanied by the surface oxidations.⁴⁷ The formation of such a native oxide could reduce the relative contribution of TSSs at the surface and degrade the electron transfer process, resulting in low catalytic performance.⁴⁸ It should be noted that the destroying of the topological electronic structure at the surface does not always mean a depressed catalytic efficiency. This is well confirmed in Dirac semimetals of layered noble metal dichalcogenides, with a significant improvement of the stability and catalytic activity when elemental vacancies are introduced.⁴⁹ However, the contribution and influence of TSSs must be carefully taken into consideration in this case.

For uncovering the relationship between the TSSs and surface chemical reactions, efforts can be made based on two aspects. Using high-quality bulk single crystals with well-defined surface termination is a key step. This not only helps the determination of the exact position where the heterogeneous reactions happen but also makes the theoretical treatment more reasonable. The *in situ* study of the interaction between the TSSs and reactants is another target. Angle-resolved photoemission spectroscopy (ARPES) can be extended to the study of surface adsorption and catalysis processes as they can characterize the electronic band structure and Fermi surface of crystals. Heterogeneous reactions involve the formation of bonding between the catalyst surface and surface adsorbates or reaction intermediates, which will inevitably modify the TSSs. This can be monitored from the shifting or passivation of the TSSs by ARPES.⁵⁰ Similarly, electrochemical scanning tunneling microscopy (ECSTM) could image the catalytic reactions at nanometer-scale resolution. This can be coupled with the ambient-pressure x-ray photoelectron spectroscopy to monitor the evolution of TSSs *in situ* in the reaction processes.

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REFERENCES

- 1M. König, S. Wiedmann, C. Brune, A. Roth, H. Buhmann, L. W. Molenkamp, X. L. Qi, and S. C. Zhang, *Science* **318**, 766 (2007).
- 2Y. L. Chen, J. G. Analytis, J. H. Chu, Z. K. Liu, S. K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z. X. Shen, *Science* **325**, 178 (2009).
- 3F. Schindler, Z. Wang, M. G. Vergniory, A. M. Cook, A. Murani, S. Sengupta, A. Y. Kasumov, R. Deblock, S. Jeon, I. Drozdov, H. Bouchiat, S. Gueron, A. Yazdani, B. A. Bernevig, and T. Neupert, *Nat. Phys.* **14**, 918 (2018).
- 4M. G. Vergniory, L. Elcoro, C. Felser, N. Regnault, B. A. Bernevig, and Z. Wang, *Nature* **566**, 480 (2019).
- 5T. Zhang, Y. Jiang, Z. Song, H. Huang, Y. He, Z. Fang, H. Weng, and C. Fang, *Nature* **566**, 475 (2019).
- 6F. Tang, H. C. Po, A. Vishwanath, and X. Wan, *Nature* **566**, 486 (2019).
- 7M. Götz, K. M. Fijalkowski, E. Pesel, M. Hartl, S. Schreyeck, M. Winnerlein, S. Grauer, H. Scherer, K. Brunner, C. Gould, F. J. Ahlers, and L. W. Molenkamp, *Appl. Phys. Lett.* **112**, 072102 (2018).
- 8C. Z. Chang, J. Zhang, X. Feng, J. Shen, Z. Zhang, M. Guo, K. Li, Y. Ou, P. Wei, L. L. Wang, Z. Q. Ji, Y. Feng, S. Ji, X. Chen, J. Jia, X. Dai, Z. Fang, S. C. Zhang, K. He, Y. Wang, L. Lu, X. C. Ma, and Q. K. Xue, *Science* **340**, 167 (2013).
- 9R. Hoffmann, *Angew. Chem. Int. Ed.* **26**, 846 (1987).
- 10L. Muchler, H. Zhang, S. Chadov, B. Yan, F. Casper, J. Kubler, S. C. Zhang, and C. Felser, *Angew. Chem.* **51**, 7221 (2012).
- 11L. M. Schoop, F. Pielhofer, and B. V. Lotsch, *Chem. Mater.* **30**, 3155 (2018).
- 12A. Martin Pendas, J. Contreras-Garcia, F. Pinilla, J. D. Mella, C. Cardenas, and F. Munoz, *Chem. Commun.* **55**, 12281 (2019).
- 13B. Yan and C. Felser, *Annu. Rev. Condens. Matter Phys.* **8**, 337 (2017).
- 14B. Yan and S. C. Zhang, “Reports on progress in physics,” *Phys. Soc.* **75**, 096501 (2012).
- 15D. Kong and Y. Cui, *Nat. Chem.* **3**, 845 (2011).
- 16X. Wang, G. Bian, T. Miller, and T. C. Chiang, *Phys. Rev. Lett.* **108**, 096404 (2012).
- 17C. Chen, S. He, H. Weng, W. Zhang, L. Zhao, H. Liu, X. Jia, D. Mou, S. Liu, J. He, Y. Peng, Y. Feng, Z. Xie, G. Liu, X. Dong, J. Zhang, X. Wang, Q. Peng, Z. Wang, S. Zhang, F. Yang, C. Chen, Z. Xu, X. Dai, Z. Fang, and X. J. Zhou, *Proc. Natl. Acad. Sci. U. S. A.* **109**, 3694 (2012).
- 18L. Plucinski, G. Mussler, J. Krumrain, A. Herdt, S. Suga, D. Grützmacher, and C. M. Schneider, *Appl. Phys. Lett.* **98**, 222503 (2011).
- 19C. R. Rajamathi, U. Gupta, K. Pal, N. Kumar, H. Yang, Y. Sun, C. Shekhar, B. Yan, S. Parkin, U. V. Waghmare, C. Felser, and C. N. R. Rao, *ChemPhysChem* **18**, 2322 (2017).
- 20H. Chen, W. Zhu, D. Xiao, and Z. Zhang, *Phys. Rev. Lett.* **107**, 056804 (2011).
- 21N. Memmel and E. Bertel, *Phys. Rev. Lett.* **75**, 485 (1995).
- 22L. Li, J. Zeng, W. Qin, P. Cui, and Z. Zhang, *Nano Energy* **58**, 40 (2019).
- 23J. Xiao, L. Kou, C.-Y. Yam, T. Frauenheim, and B. Yan, *ACS Catal.* **5**, 7063 (2015).
- 24Q. Qu, B. Liu, J. Liang, D. Pan, and I. K. Sou, *arXiv:1807.09957* [physics.chem-ph].
- 25S. Sarkar, J. Yang, L. Z. Tan, A. M. Rappe, and L. Kronik, *Chem. Mater.* **30**, 1849 (2018).
- 26A. Politano, G. Chiarello, C.-N. Kuo, C. S. Lue, R. Edla, P. Torelli, V. Pellegrini, and D. W. Boukhvalov, *Adv. Funct. Mater.* **28**, 1706504 (2018).
- 27C. Shekhar, A. K. Nayak, Y. Sun, M. Schmidt, M. Nicklas, I. Leermakers, U. Zeitler, Y. Skourski, J. Wosnitza, Z. Liu, Y. Chen, W. Schnelle, H. Borrmann, Y. Grin, C. Felser, and B. Yan, *Nat. Phys.* **11**, 645 (2015).
- 28C. R. Rajamathi, U. Gupta, N. Kumar, H. Yang, Y. Sun, V. Süß, C. Shekhar, M. Schmidt, B. Yan, S. Parkin, C. Felser, and C. N. R. Rao, *Adv. Mater.* **29**, 1606202 (2017).
- 29Y. He, D. Yan, L. R. Ng, L. Shi, S. Wang, H. Lin, S.-H. Lin, H. Luo, and K. Yan, *Mater. Chem. Front.* **3**, 2184 (2019).

- ³⁰G. Li, Q. Xu, W. Shi, C. Fu, L. Jiao, M. E. Kamminga, M. Yu, H. Tuysuz, N. Kumar, V. Suss, R. Saha, A. K. Srivastava, S. Wirth, G. Aufermann, J. Gooth, S. Parkin, Y. Sun, E. Liu, and C. Felser, *Sci. Adv.* **5**, eaaw9867 (2019).
- ³¹G. Li, C. Fu, W. Shi, L. Jiao, J. Wu, Q. Yang, R. Saha, M. E. Kamminga, A. K. Srivastava, E. Liu, A. N. Yazdani, N. Kumar, J. Zhang, G. R. Blake, X. Liu, M. Fahlman, S. Wirth, G. Aufermann, J. Gooth, S. Parkin, V. Madhavan, X. Feng, Y. Sun, and C. Felser, *Angew. Chem.* **58**, 13107 (2019).
- ³²J. Li, H. Ma, Q. Xie, S. Feng, S. Ullah, R. Li, J. Dong, D. Li, Y. Li, and X.-Q. Chen, *Sci. China. Mater.* **61**, 23 (2018).
- ³³B. Yan, B. Stadtmüller, N. Haag, S. Jakobs, J. Seidel, D. Jungkenn, S. Mathias, M. Cinchetti, M. Aeschlimann, and C. Felser, *Nat. Commun.* **6**, 10167 (2015).
- ³⁴J. N. Nelson, J. P. Ruf, Y. Lee, C. Zeledon, J. K. Kawasaki, S. Moser, C. Jozwiak, E. Rotenberg, A. Bostwick, D. G. Schlom, K. M. Shen, and L. Moreschini, *Phys. Rev. Mater.* **3**, 064205 (2019).
- ³⁵D. Rees, K. Manna, B. Lu, T. Morimoto, H. Borrmann, C. Felser, J. Moore, D. H. Torchinsky, and J. Orenstein, *arXiv:1902.03230* (2019).
- ³⁶N. B. Schröter, D. Pei, M. G. Vergniory, Y. Sun, K. Manna, F. de Juan, J. A. Krieger, V. Süß, M. Schmidt, and P. Dudin, *Nat. Phys.* **15**, 759 (2019).
- ³⁷N. Schröter, S. Stolz, K. Manna, F. de Juan, M. G. Vergniory, J. A. Krieger, D. Pei, P. Dudin, T. K. Kim, and C. Cacho, preprint *arXiv:1907.08723* (2019).
- ³⁸D. S. Sanchez, I. Belopolski, T. A. Cochran, X. Xu, J. X. Yin, G. Chang, W. Xie, K. Manna, V. Suss, C. Y. Huang, N. Alidoust, D. Multer, S. S. Zhang, N. Shumiya, X. Wang, G. Q. Wang, T. R. Chang, C. Felser, S. Y. Xu, S. Jia, H. Lin, and M. Z. Hasan, *Nature* **567**, 500 (2019).
- ³⁹X. Su, W. Lin, H. Cheng, C. Zhang, Y. Li, T. Liu, B. Zhang, Q. Wu, X. Yu, and F. Zhao, *RSC Adv.* **6**, 103650 (2016).
- ⁴⁰J. Prinz, C. A. Pignedoli, Q. S. Stockl, M. Armbruster, H. Brune, O. Groning, R. Widmer, and D. Passerone, *J. Am. Chem. Soc.* **136**, 11792 (2014).
- ⁴¹R. Naaman, D. H. Waldeck, and Y. Paltiel, *Appl. Phys. Lett.* **115**, 133701 (2019).
- ⁴²R. Naaman and D. H. Waldeck, *Annu. Rev. Phys. Chem.* **66**, 263 (2015).
- ⁴³K. Banerjee-Ghosh, O. Ben Dor, F. Tassinari, E. Capua, S. Yochelis, A. Capua, S. H. Yang, S. S. P. Parkin, S. Sarkar, L. Kronik, L. T. Baczewski, R. Naaman, and Y. Paltiel, *Science* **360**, 1331 (2018).
- ⁴⁴C. Shekhar, *Nat. Mater.* **17**, 953 (2018).
- ⁴⁵J. Hwang, R. R. Rao, L. Giordano, Y. Katayama, Y. Yu, and Y. Shao-Horn, *Science* **358**, 751 (2017).
- ⁴⁶T. Kojima, S. Kameoka, S. Fujii, S. Ueda, and A. P. Tsai, *Sci. Adv.* **4**, eaat6063 (2018).
- ⁴⁷K. Yin, Z. D. Cui, X. R. Zheng, X. J. Yang, S. L. Zhu, Z. Y. Li, and Y. Q. Liang, *J. Mater. Chem. A* **3**, 22770 (2015).
- ⁴⁸D. S. Kong, J. J. Cha, K. J. Lai, H. L. Peng, J. G. Analytis, S. Meister, Y. L. Chen, H. J. Zhang, I. R. Fisher, Z. X. Shen, and Y. Cui, *ACS Nano* **5**, 4698 (2011).
- ⁴⁹H. Huang, X. Fan, D. J. Singh, and W. Zheng, *ACS Omega* **3**, 10058 (2018).
- ⁵⁰S. Jakobs, A. Narayan, B. Stadtmüller, A. Droghetti, I. Rungger, Y. S. Hor, S. Klyatskaya, D. Jungkenn, J. Stöckl, M. Laux, O. L. A. Monti, M. Aeschlimann, R. J. Cava, M. Ruben, S. Mathias, S. Sanvito, and M. Cinchetti, *Nano Lett.* **15**, 6022 (2015).