Topological catalysis

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Over the past decade, heterogeneous catalysis and asymmetry synthesis have gained considerable attention. Topological materials exhibit symmetrically protected metallic surface states and massless high-mobility electrons, making them ideal materials for designing heterogeneous catalysts. However, there is limited information available on how topological materials with specific properties interact with reaction intermediates. Therefore, understanding the role of electrons and surface structures in topological materials is crucial for designing highly efficient heterogeneous catalysts for use in electrochemical water splitting and fuel cells. In this study, we used high-quality topological bulk single crystals to confirm the direct relationship between topological properties and surface redox reactions by experiments and theoretical analysis. It was observed that the catalytic reaction efficiency could be altered effectively by external fields such as magnetic and strain fields. We believe that manipulating the topological electronic structures would be highly useful for designing high-efficient catalysts, which can potentially be used in the future for asymmetric synthesis and for studying the origin of life.

Exploration of topological phase matter is, undoubtedly, the most exciting novel development of the past decade in the field of material science [1]. Theoretical and experimental observations have revealed their great potential applications in energy devices and quantum computing. Topology is a branch of mathematics that analyses the invariant properties of spaces undergoing constant deformation. In solid-state physics, the topology of a given material is determined from its band inversion in reciprocal space and characterized by topological invariants that remain unchanged during the deformation of the Hamiltonian. Z2 invariant and Chern number are two of the most commonly observed topological invariants.

The most known advantage of topological materials is their robust topologically non-trivial surface states (TSSs), which can withstand surface modifications such as defects and even slight oxidation. Besides, the electrons in topological materials can be expressed by the Dirac equation, while there exists a linearization between the relativistic energy and momentum of the topological materials, which results in extremely high mobility in the system and develops a variety of unusual transport properties.

Several research groups have confirmed that the number of topological materials is surprisingly higher than what was known. According to the Inorganic Crystal Structure Database, 27% of the materials are topological [2]. Although multiple state-of-the-art catalysts are known to be carriers of topological band structures such as Pt, Au, RuO_2, and IrO_2, their surface properties, derived from band inversion, have rarely been studied. Understanding the design of high-quality topological crystals that exhibit interesting physical properties, and most importantly, which crystal surface with a determined atomic layer should be exposed, is challenging.

1. Topological insulators

Over the past decade, Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 have been the most extensively studied three-dimensional topological insulators (TIs). Although the excited electrons have a long lifespan, which benefits the electron-hole separation efficiency in the photocatalysis reactions [3], surface states near the Fermi level can directly transfer electrons to and from the surface-adsorbed molecules, thus reducing the reaction barriers.

In addition to TIs being ideal catalysts, they can also promote reaction kinetics of a given catalyst by the synergistic effect. In this study, we demonstrated the potential of manipulating topological surface states to design high-performance electrocatalysts. We deposited 2H phase MoS_2 thin layers on Bi_2Te_3 films. It was observed that the combined MoS_2/Bi_2Te_3

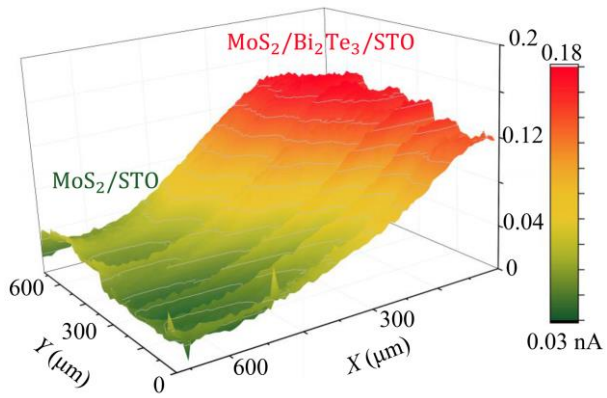

Fig. 1: Substrate generation/tip collection mode (HER activity) of the catalysts comprising MoS_2/STO and MoS_2/Bi_2Te_3/STO.

catalyst improved the hydrogen evolution reaction (HER) activities as to MoS_2 alone, as seen in Fig. 1. Furthermore, theoretical analysis showed that the enhanced catalytic activity originated from the charge redistribution at the interface between the Bi_2Te_3 TI substrate and MoS_2 films. The delocalized *sp*-derived topological surface states induced electrons being transferred to the MoS_2 layer, thereby activating the basal plane for the adsorption of hydrogen.

2. Topological semimetals

Although TIs exhibit *sp*-orbital derived surface states, their poor conductivity and low chemical stability still limits their further catalytic applications. Topological semimetals such as Weyl semimetal, Dirac semimetal, and recently derived various nodal line semimetals, have gained wide attention due to their high electrical conductivity. Moreover, introducing of *d*-zone transition metals into the semimetals could promote the bonding and adsorption of molecules, resulting in significantly increased catalytic reactions kinetics.

$PtSn_4$ was the first Dirac nodal arc semimetal, where Dirac-like features and 'drumhead' surface states were confirmed experimentally. A large size $PtSn_4$ bulk single crystal was grown and exfoliated into the plate with a defined crystal surface and atomic termination. It was found that due to the presence of the intrinsic and stable surface states in the Pt layer of $PtSn_4$ [4], electrons were directly transferred from the occupied robust surface states to adsorbed hydrogen in the HER. Our results indicated that an ultra-low overpotential of 37 mV was required to deliver a current density of 10 mA cm^{-2} with a turnover frequency (TOF) of 1.54 H_2 s^{-1} at 100 mV, which sets $PtSn_4$ a benchmark catalyst for HER.

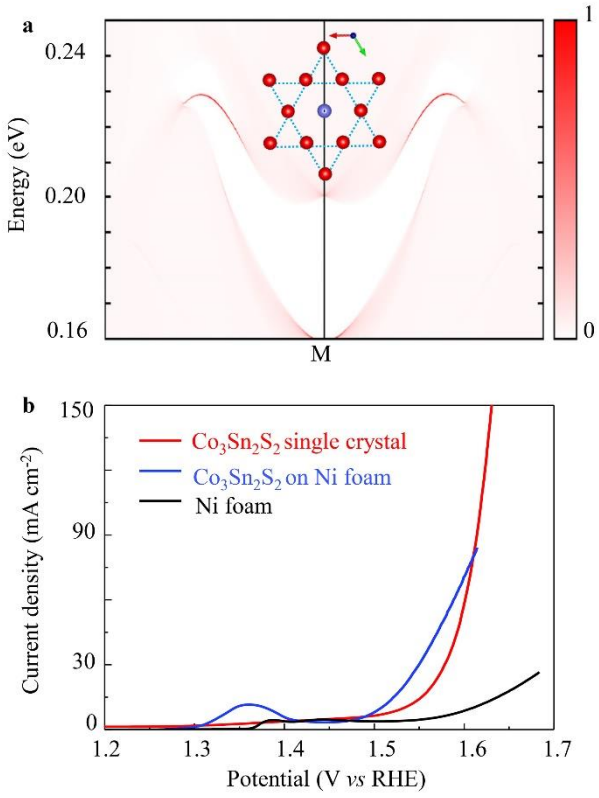

Fig. 2: a. Topological surface states of the topological semimetal $Co_3Sn_2S_2$ catalysts derived from the Co-Kagome lattices, and b. OER activities of the topological semimetal $Co_3Sn_2S_2$ catalysts.

Besides, surface states in semimetals can be tuned by manipulating their topological structure. In $Co_3Sn_2S_2$, a topological semimetal, a Co-derived topological surface state was observed in the naturally exfoliated Co Kagome lattice layer (Fig. 2a), which serves as catalytic center for the oxygen evolution process (OER), thereby resulting in efficient bonding and electron transfer due to the partially filled orbital (Fig. 2b). Although the surface area of $Co_3Sn_2S_2$ was much smaller than that of Co-based nanostructured catalysts, it exhibited an outstanding OER catalytic performance [5].

3. Relation between topology and chirality in catalysis

Apart from the well-developed topological phases mentioned above, chiral fermions observed in topological semimetals are a ground-breaking concept as compared to Dirac and Weyl fermions in semimetals and have become popular in the field of quantum matter. Recent studies found that B20 intermetallic crystal compounds such as PdGa, CoSi, and PtGa exhibit chiral Fermi arc edge states that span throughout the Brillouin zone. The chiral fermions in these compounds are enforced at the center or to the corner of the bulk Brillouin zone owing to the crystal symmetry, resulting in a single pair of chiral nodes with long surface Fermi arcs, which can be used to tailor molecule adsorption and transformation in catalysis.

We studied the application of high-quality chiral crystals, such as PtAl, PtGa, PdGa, and RhSi, as HER catalysts [6]. It was observed that PtGa and PtAl could catalyse HER effectively with extremely low overpotentials of 13.3 and 14 mV, respectively, at a current density of 10 mA cm^{-2}. At an exceptionally high current density of 600 mA cm^{-2}, PtGa and PtAl exhibited remarkably low overpotentials of 113 and 151 mV, respectively. Our theoretical analysis verified

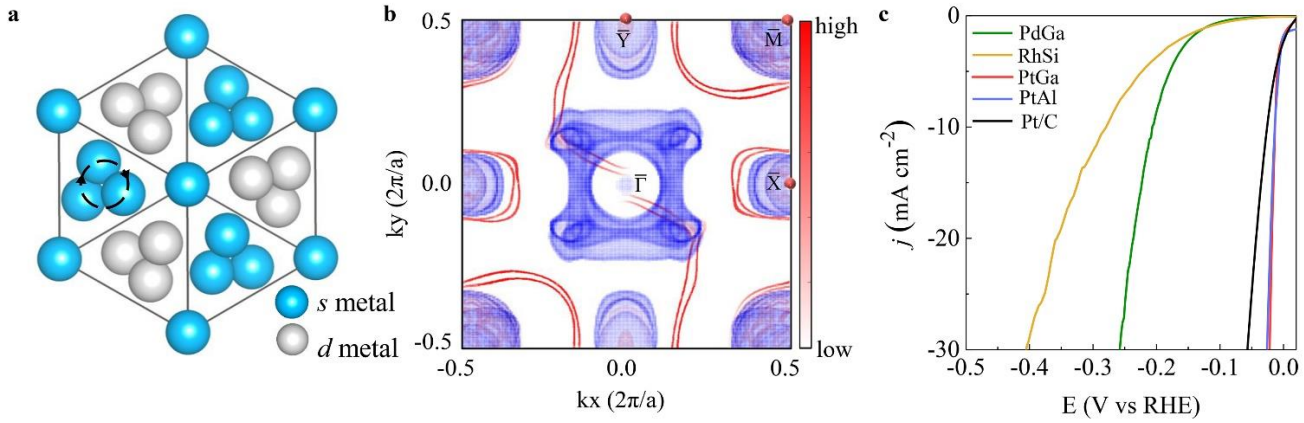

Fig. 3: a. Crystal structure of the B20 topological chiral crystal, b. Surface Fermi arcs of PtAl (001)-H with a chemical potential at charge neutral point, and c. HER performance of the B20 bulk single crystals.

the existence of super long Fermi arcs and large non-trivial energy window in the crystal, which are robust against H adsorption. Thus, the topologically protected surface states of the *d* orbitals of the transition metal atoms (Pt, Co, Pd…) could weaken H adsorption, which could significantly increase the HER kinetics (Fig. 3).

Additionally, the long surface Fermi arcs of B20 chiral crystals can determine the catalytic behavior of transition metals. We found that the H adsorption on transition metals (Mo, W, Ru, Rh, Pd, Pt, Ni, Co, and Fe) is significantly improved when deposited on the surface of a chiral crystal, such as PdGa. This is because the transfer of electrons from the transition metal atoms to the surface states of the PdGa substrate alters the *d* band structure of transition metals, which weakens the hydrogen bonding. Moreover, W/PdGa is considered a good HER catalyst with a nearly zero Gibbs free energy (0.2 eV), which was confirmed from the exchange current density and turnover frequency values of Pt-like activity when W atoms were deposited on the surface of the PdGa nanostructure.

4. Magnetism in topological catalysis

The relationship between spin polarization and electron transfer can be determined from the catalytic behavior of the transition-metal dichalcogenide, MoS_2. The edge sites in MoS_2 are known to be the catalytically active center due to room-temperature ferromagnetism, from amorphous to crystalline samples. Considering a non-collinear antiferromagnet Mn_3Pt for example, we confirmed that the hydrogen adsorption on Mn_3Pt can be modified depending on the spin polarization of the Mn atoms [7]. When spin polarization at the Mn sites is taken into consideration, the Gibbs free energy for hydrogen adsorption is modified significantly (Fig. 4). Interestingly, a similar Gibbs free energy for hydrogen adsorption was obtained between the Mn-Mn hollow sites and Pt sites based on the above strategy, that is, additional actives sites were created beyond Pt.

This is further verified using high-quality crystals of Heusler compounds that are characterized by pre-determined magnetic structures. The comparison of the OER activities of a series of Co based Heusler compounds depicts a strong correlation with the e_g orbital filling of reactive Co sites. The optimal catalytic activity was achieved as the e_g orbital filling approached unity. This study not only explores the potential of Heusler compounds as novel OER electrocatalysts but also demonstrates the optimization of catalysts by precisely regulating the configuration of electrons and spin polarisation [8].

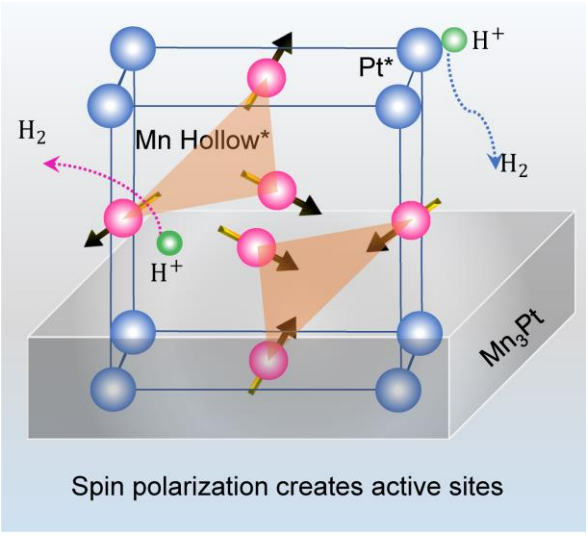

Fig. 4: Spin polarization and molecular adsorption on the surface of magnetic materials.

Further scope of topological catalysis

The electron spin in topological materials is locked to the momentum of the electron. However, the presence of external fields such as magnetic and strain fields can break the time-reversal symmetry and induce new properties, which enables scientists to control electrons and band structures to manipulate the desired catalytic reaction kinetics (Fig. 5).

Lattice straining can highly improve the performance of catalysts. Tensile or compressive strain can upshift or downshift the *d*-band center of electrocatalysts, thus altering the adsorption energy of intermediates. Lattice strain can be modulated by depositing thin catalyst films on piezoelectric substrates whose lattice parameters are in-situ tuned using an applied external voltage. As a result, the lattice structure of the thin films responds to the tension of substrates.

The magnetic field can induce electron spin polarization, resulting in changes in the reaction kinetics and selectivity. Besides, multiple topological materials have large magnetoresistances and high mobility of electrons or holes, which can be influenced by the magnetic field. Therefore, in the future, we intend to manipulate the spin states of intermediate species by inducing a magnetic field to generate triplet oxygen and decrease the overpotential of OER. Secondly, we intend to study the influence of magnetic fields on the transport properties of topological materials, to present an enhanced understanding of the correlation between the magnetic field and the catalytic performance.

Recently, photocatalysis, a process wherein small molecules (H_2O, CO_2, etc.) are converted into solar fuels, has gained wide attention. Heusler alloys are considered potential candidates for photocatalysis, because their band structure can be easily altered, and the charge carrier density and mobility can be controlled simultaneously, which can be significant in the separation and transfer of photoelectrons and holes.

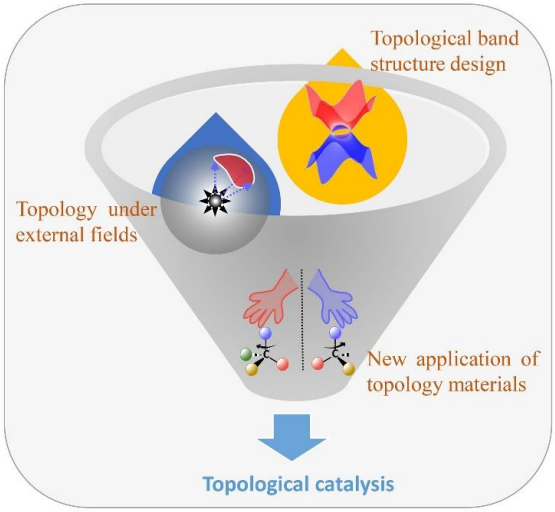

Fig. 5: The future of topological catalysis

External Cooperation Partners

Harun Tüysüz (Max-Planck-Institut für Kohlenforschung); Stuart Parkin (Max Planck Institute of Microstructure Physics).

References

[1] *Topological Materials: Weyl Semimetals, B. Yan and C. Felser, Annu. Rev. Condens. Matter Phys.* ***8*** *(2016) 337, doi.org/10.1146/annurev-conmatphys-031016-025458*

[2]* *A complete catalogue of high-quality topological materials, M. G. Vergniory, L. Elcoro, C. Felser, N. Regnault, B. A. Bernevig, and Z. Wang, Nature* ***566*** *(2019) 480, doi.org/10.1038/s41586-019-0954-4*

[3] *Photochemical water splitting by bismuth chalcogenide topological insulators, C. 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*** *(2017) 2322, doi.org/10.1002/cphc.201700344*

[4]* *Dirac Nodal Arc Semimetal $PtSn_4$: An Ideal Platform for Understanding Surface Properties and Catalysis for Hydrogen Evolution, G. 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. Auffermann, J. Gooth, S. Parkin, V. Madhavan, X. Feng, Y. Sun, and C. Felser, Angewandte Chemie* ***58*** *(2019) 2, doi.org/10.1002/anie.201906109*

[5]* *Surface states in bulk single crystal of topological semimetal $Co_3Sn_2S_2$ toward water oxidation, G. Li, Q. Xu, W. Shi, C. Fu, L. Jiao, M. E. Kamminga, M. Yu, H. Tüysüz, N. Kumar, V. Süß, R. Saha, A. K. Srivastava, S. Wirth, G. Auffermann, J. Gooth, S. Parkin, Y. Sun, E. Liu, and C. Felser, Sci. Adv.* ***5*** *(2019) eaaw9867.*

[6]* *Topological engineering of Pt-group-metal-based chiral crystals toward high-efficiency hydrogen evolution catalysts, Q. Yang, G. Li, K. Manna, F. Fan, C. Felser, and Y. Sun, Adv. Mater.* ***32*** *(2020) e1908518, doi.org/10.1002/adma.201908518.*

[7]* *Optimization of catalytic active sites in non-collinear antiferromagnetic Mn_3Pt bulk single-crystal, G. Li, Q. Yang, K. Manna, C. Fu, H. Deniz, J. Jena, F. Li, S. Parkin, G. Auffermann, Y. Sun, and C. Felser, Mater. Today Phys.* ***10*** *(2019) 100137, doi.org/10.1016/j.mtphys.2019.100137*

[8]* *Tunable e_g orbital occupancy in Heusler compounds for oxygen evolution reaction, M. Yu, G. Li, C. Fu, E. Liu, K. Manna, E. Budiyanto, Q. Yang, C. Felser, and H. Tuysuz, Angewandte Chemie* ***60*** *(2021) 5800, doi.org/10.1002/anie.202013610*

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