Topological Quantum Materials for Heterogenous Catalysis

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The electronic structure plays a crucial role in determining the efficiency of heterogeneous catalysts. Topological quantum materials (TQMs), which exhibit intriguing electronic properties such as spin–orbital coupling and exotic spin/orbital angular momentum, offer new opportunities for linking solid-state topologies with catalysis. Over the past decade, the field of topological catalysis has emerged at the intersection of condensed matter physics and chemistry, exploiting the unique electronic properties of TQMs to drive catalytic reactions with enhanced activity and selectivity. Utilizing high-quality topological bulk single crystals, we have experimentally and theoretically confirmed a direct relationship between the topological quantum properties and heterogenous catalysis. Notably, we have demonstrated that the catalytic reaction efficiency can be effectively modulated by external stimuli such as magnetic fields and light. The manipulation of topological electronic structures holds great promise for designing high-efficiency catalysts, with potential implications as diverse as asymmetric synthesis and the origin of life.

Pt is a topological metal and the widely used catalyst for the hydrogen evolution reaction (HER). It is also the most efficient catalyst for the oxygen reduction reaction (ORR), offering high activity and selectivity. Similarly, the nodal line materials IrO_2 and RuO_2 are among the most efficient catalysts for the oxygen evolution reaction (OER) and exhibit high activity and stability. Is it merely a coincidence that the best catalysts are also topological materials? Efforts to answer this question led to what is now known as the field of topological catalysis. Over the past decade, there has been growing interest in the use of topological quantum materials (TQMs) for catalytic reactions such as the HER, OER, ORR, CO_2 reduction, and asymmetric catalysis. However, the interaction between the topological properties and catalytic reaction processes is still largely unknown. Further exploration of the topological properties is required from the perspectives of both chemistry and physics to uncover the relationship between topological band structures and catalysis and thus design of highly efficient heterogeneous catalysts.

Topological Quantum Materials for the HER

One of the most significant advantages of TQMs for the HER is their robust nontrivial topological surface states (TSSs). These TSSs are protected by topological invariants and offer highly active and stable sites for catalytic reactions. Using high-quality single crystals, distinct surfaces can be investigated by cutting the crystals to expose well-defined planes. This precise control over the surface structure facilitates the identification of those with a high density of surface states, and particularly topologically protected surface states. In addition, the high charge-carrier mobilities in TQMs promote electron transfer during catalysis, thereby boosting the catalytic activity.

Layered two-dimensional (2D) materials such as transition metal chalcogenides are promising electrocatalysts for the HER owing to their flexible compositions and distinct electronic structures. However, their active sites usually stem from the edge sites, whereas the basal planes, which have higher surface areas, are difficult to activate. We investigated the use of $AgRuO_3$, a

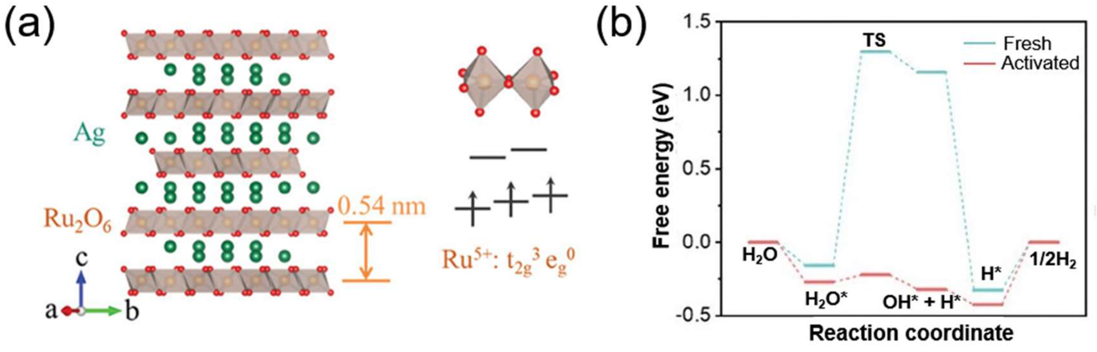

Fig. 1: (a) Crystal structure of layered $AgRuO_3$ and electronic configuration of distorted octahedral Ru sites. (b) Reaction energy profiles of fresh and activated $AgRuO_3$ for alkaline water splitting.

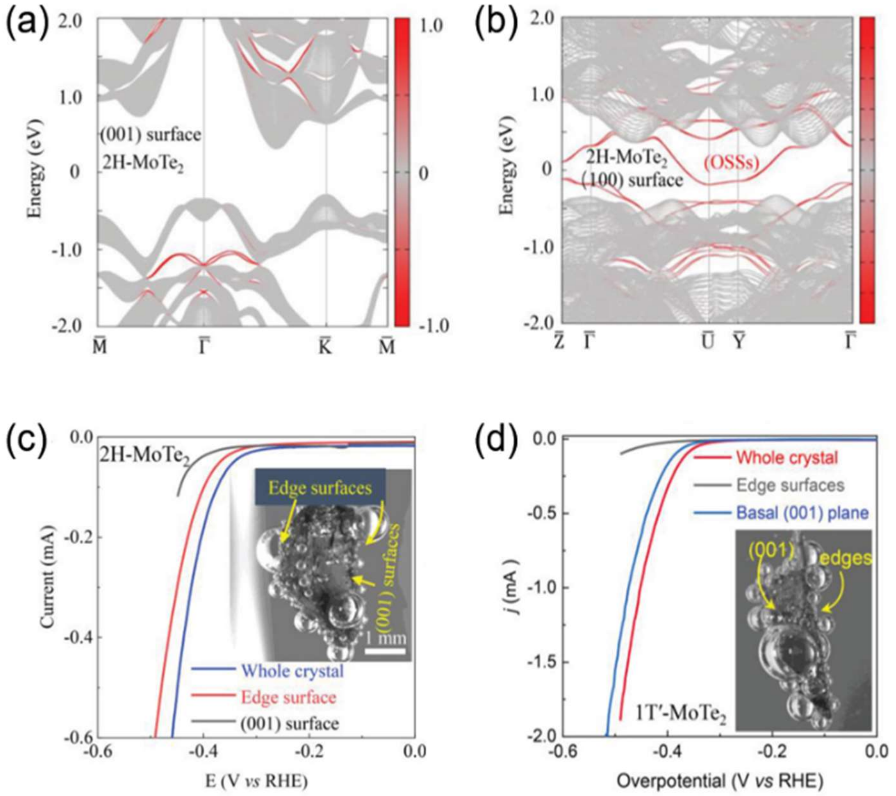

Fig. 2: Calculated obstructed surface states (OSSs) of 2H-MoTe$_2$ at the (a) (001) and (b) (100) surfaces. OSSs only exist at the edge sites, such as the (100) surface. The gray and red lines represent the bulk and surface bands, respectively. (c) Linear sweep voltammograms of 2H-MoTe$_2$ HER catalyst for the whole crystal, the (001) basal plane, and the edge surfaces. Almost all of the activity originates from the edge surfaces. Inset: Photograph of 2H-MoTe$_2$ bulk single crystal during the HER with a constant overpotential of −0.43 V vs. RHE. Hydrogen bubbles are generated on the edge surfaces but not the (001) basal plane. (d) Polarization curves of 1T′-MoTe$_2$ bulk crystal for the whole crystal, the (001) basal plane, and the edge surfaces. Almost all of the activity originates from the (001) basal plane. Inset: Photograph during the HER, showing hydrogen bubble production on the (001) basal plane.

quasi-2D layered compound with high electrical conductivity, for the HER in an alkaline environment [1]. Owing to its weak interlayer Ag–O bond strength, $AgRuO_3$ was easily activated and then split to expose more basal planes for the HER (Figure 1a). Partial interlayer Ag ions were reduced to Ag nanoparticles, accompanied by the formation of oxygen vacancies on the basal planes, whereas no metallic Ru was observed. This resulted in outstanding HER activity with a low overpotential (Figure 1b). The results shed light on the evolution of quasi-2D metal oxides during the HER and highlighted the active role of basal planes in alkaline water splitting.

Like TSSs, obstructed surface states (OSSs) originate from the topologies of bulk electronic bands and can act as active sites for molecular adsorption. OSSs can exist in clean, large-gap, topologically trivial insulators, and are separated from the bulk states in the energy spectrum. Molybdenum dichalcogenides such as $MoTe_2$ exemplify the significance of OSSs for the HER (Figure 2a, b). The catalytic activity of $MoTe_2$ for the HER is strongly influenced by its structure, with its two primary polymorphs (the hexagonal 2H phase and topological trigonal 1T′ phase) each exhibiting distinct structural and electronic properties. In the 2H phase, the catalytic activity is primarily confined to the edges of the material, whereas the basal planes (the flat surfaces of the layers) remain largely inert and lack active sites for catalytic reactions. By contrast, the topological 1T phase exhibits metallic properties, wherein the basal planes become catalytically active (Figure 2c, d) [2].

We introduced a novel method for identifying the positions of active sites by searching for crystalline symmetry-protected obstructed atomic insulators with metallic surface states. The obstructed Wannier charge centers in obstructed atomic insulators are pinned by symmetries at some empty Wyckoff positions; consequently, surfaces that accommodate these sites are guaranteed to have metallic OSSs. OSSs have been confirmed to be the origin of the catalytic activity of crystalline materials. The theory on 2H-$MoTe_2$, 1T′-$MoTe_2$, and $NiPS_3$ bulk single crystals is verified, whose active sites are consistent with the calculations. Importantly, several high-efficiency catalysts have been successfully identified by just considering the number of obstructed Wannier charge centers and their symmetries. By applying this real-space-invariant theory to a database of 34,013 topologically trivial insulators, 1788 unique obstructed atomic insulators were identified, of which 465 were potential high-performance catalysts [3]. This methodology will facilitate the discovery of new catalysts for a wide range of heterogeneous redox reactions.

Topological Quantum Materials for Oxygen Catalysis

In contrast to the HER, oxygen catalysis (ORR and OER) involves the conversion of oxygen molecules in triplet states ($^3\Sigma_g^-$) (unpaired electrons in parallel) and water in singlet ground states ($^1\Delta$) (no unpaired electrons). Therefore, oxygen catalysis is a spin-dependent electron-transfer process.; However, it suffers from sluggish reaction kinetics and a large overpotential.

Spin–momentum locking, arising from strong spin–orbit coupling, ensures the presence of robust surface states that are protected by time-reversal symmetry. These surface states exhibit a Dirac-like dispersion and are spin-polarized (i.e., the direction of an electron's spin is intrinsically linked to its momentum). This unique property results in chiral electrons, which can profoundly influence catalytic processes. Spin-polarized surface states enhance reactivity by providing selective adsorption sites, stabilizing reaction intermediates, and facilitating charge transfer. Additionally, the chiral nature of these electrons can impart chiral information to catalytic reactions, reducing spin-flip scattering. Understanding and leveraging these effects is crucial for developing more efficient and selective catalysts, especially in applications where spin-dependent processes are integral to the reaction mechanism.

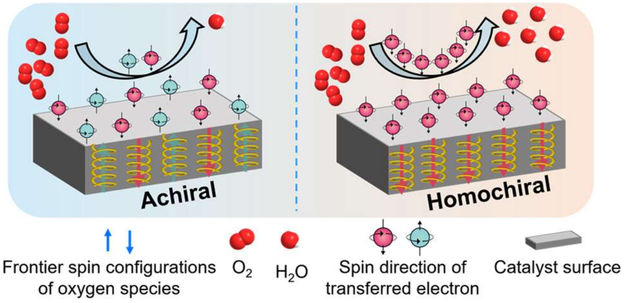

Fig. 3: Illustration of enhanced ORR activity on TH PdGa due to spin-polarized catalytic surface.

We demonstrated a topological homochiral (TH) PdGa crystal with a chiral catalytically active surface for the ORR (Figure 3). The spin polarization generated *in situ* at the electrode surface was studied by spin-resolved photoemission experiments and theoretical simulations. Both structural chirality and spin–orbit coupling are essential for the induction of spin polarization in TH PdGa. As a result, TH PdGa outperforms achiral PdGa by more than 100 times in terms of its kinetic current density at 0.85 V vs. the reversible hydrogen electrode (RHE). This work allowed us to elucidate the contributions of spin polarization to the enhanced acidic ORR activity [4].

Topological Quantum Materials for Asymmetric Catalysis

Biological homochirality is essential for life. However, the origin of chirality in organic compounds remains unclear. One proposed mechanism for the enantiomeric enrichment of organic compounds involves asymmetric synthesis and/or subsequent asymmetric adsorption on the surfaces of inorganic chiral crystals.

TQMs are attractive compared with other inorganic chiral solids because of their unique combination of intrinsic structural and electronic chirality. This distinctive characteristic provides a platform for studying the enantiospecific interactions between reactants and catalysts. Furthermore, TQMs facilitate investigations into structural chirality, enabling an in-depth exploration of the intricate interplay between chirality and quantum properties.

Interestingly, such investigations have the potential to shed light on the origins of life [5]. For example, our research group proposed a potential explanation for the emergence of chirality in nature through an enantioselective pathway using pure inorganic PdGa crystals [6]. We studied enantiomers L- and D-3,4-dihydroxyphenylalanine (L- and D-DOPA, respectively), and measured their electrochemical oxidation currents (I_L and I_D, respectively) upon interaction with the surfaces of chiral PdGa-A and PdGa-B crystals. Notably, this interaction inverted the electrochemical oxidation currents (I_L/I_D ratios of 1.24 and 0.81 on PdGa-A and PdGa-B, respectively), indicating that the oxidation of L-DOPA was more favorable than that of D-DOPA on the PdGa-A surface, whereas PdGa-B showed higher activity for the oxidation of D-DOPA (Figure 4a, b). These findings indicate that the interaction between L- and D-DOPA was strongly dependent on the bulk chirality of PdGa.

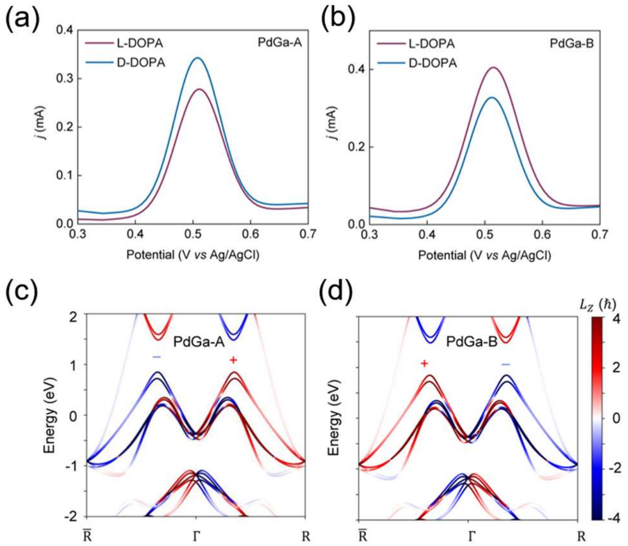

Fig. 4: Asymmetric catalysis on chiral crystals. Enantioselective oxidation of 3,4-dihydroxyphenylalanine (DOPA) on the surfaces of (a) PdGa-A and (b) PdGa-B crystals. Calculated orbital textures of (c) PdGa-A and (d) PdGa-B projected on the orbital polarization component (L_z). When spin–orbit coupling effects are considered, L_z exhibits opposite signs at $+k_y$ and $-k_y$, and the orbital angular momentum (OAM) polarization depends on the chirality of PdGa.

The differences in oxidation behavior were elucidated using classical thermodynamic adsorption theories. The binding energy of the L-DOPA/PdGa-B pair was 63 meV, which was higher than that of the D-DOPA/PdGa-B pair (112 meV). Thus, the adsorption energies of L- and D-DOPA on PdGa-B differed by 48 mV owing to chiral interactions. Furthermore, the momentum-space texture of the orbital angular momentum (OAM) around the Fermi level was examined. The spin-split branches indicated a parallel OAM between the orbital polarization and momentum, with the orbital polarization component (L_z) always bearing opposite signs at the $+k_y$ and $-k_y$ points (Figure 4c and 4d). Positive or negative magnetization in the [111] direction is expected depending on the chiral crystal structure of PdGa. This study highlighted the significance of OAM polarization as a driving force for enantiomeric recognition.

Perspective of Topological Catalysis

Topological catalysis leverages the interplay of spin, orbital, and topological properties in TQMs to enhance catalytic processes through unconventional quantum phenomena. The unique TSSs, protected by time-reversal symmetry, exhibit robust electronic properties that are resistant to defects and impurities. These TSSs are characterized by strong spin-orbital coupling, leading to a locked relationship between the electron's spin and momentum, which can be harnessed to control catalytic reactions such as HER, OER, and ORR with high precision. The Berry phase, arising from the geometrical properties of the electronic wavefunctions, influences the charge carriers' dynamics, enhancing their mobility and reactivity on the catalyst surface. Additionally, the OAM of the electrons, coupled with their spin, can be manipulated to induce chiral currents, leading to a chiral anomaly that used for the asymmetric syntheses. This intricate dance of spin, orbital, and topological features offers a pathway to design catalysts with unprecedented activity and selectivity, opening new frontiers in quantum-enhanced catalytic processes.

Moreover, the TQMs are distinguished by their strong responsiveness to external stimuli such as strain, magnetic fields, and light. Mechanical strain can induce changes in the band structure, affecting the Berry curvature and thereby altering charge and spin transport properties, which are crucial for catalytic processes. For example, tensile or compressive strain can upshift or downshift the *d*-band center of electrocatalysts, tuning the adsorption energy of intermediates. The modulation of lattice strain can be achieved by misfit layered compounds (MLCs) (e.g., $(SnSe)_{1.16}(NbSe_2)$ and $(PbSe)_{1.14}(NbSe_2)$). MLCs exhibit lattice mismatch between layers, leading to the formation of Moiré patterns or strain-induced alterations in their electronic structures. These materials are represented by the general formula $[(MX)_{(1+\delta)}]_m[(TX_2)_n]$, where m and n can equal 1, 2, or 3; T is a transition metal element; M is a post-transition metal or rare-earth element; and X is a chalcogen. Significant charge transfer occurs from the MX layers to the TX_2 layers of MLCs, resulting in a variety of intriguing physical phenomena that can potentially be used for catalysis.

Recently, it was found that twisted moiré structures act as artificial chiral layered materials. The construction of moiré lattices facilitates the formation of chiral structures and surface configurations and diversifies the electronic states. This makes them an ideal platform for modulating structural and electronic properties. Some quantum properties such as chiral anomalies can even be induced at room temperature. The chirality of electronic structures can be induced by artificially manipulating chiral electronic states in crystals, such as chiral charge density waves and spin structures, often in the presence of magnetic or optical field modulations. Thus, in materials lacking structural chirality,

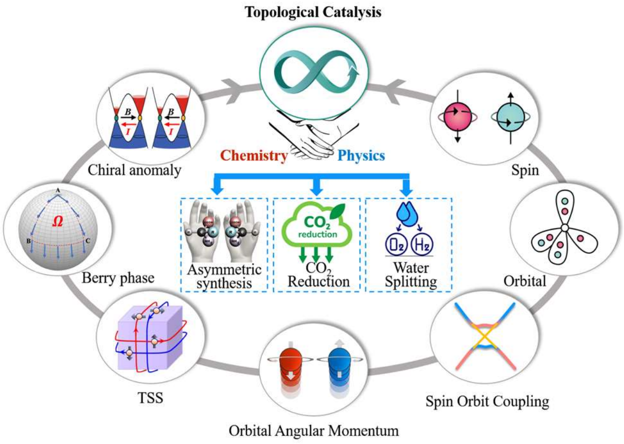

Fig. 5: Topological quantum properties provide a powerful tool for the controlling of electro/photocatalysis, chiral synthesis, and even to understand the origin of life.

the ordered chiral states of the electrons can dominate the electron transport process during reactions and serve as chiral carriers.

When the TQMs are subjected to an electric or magnetic field, the TSSs can experience shifts in their energy levels or modifications in their spin texture, leading to enhanced catalytic activity or selectivity for CO_2 reduction and OER. In doing so, we hope to be able to identify intrinsic physical properties such as anomalous hall effect (AHE) that can be tuned for catalysis. Eventually, we want to achieve a comprehensive understanding of the correlation between magnetic fields and catalytic performance. This responsiveness allows for real-time control over the catalytic activity, enabling the design of smart catalysts that adapt their behavior dynamically in response to changing environmental conditions. Such tunability not only optimizes reaction pathways but also paves the way for developing catalysts that can operate efficiently under a wide range of conditions, making topological catalysis a promising avenue for advanced and adaptable catalytic systems.

External Cooperation Partner

Xinliang Feng (Max Planck Institute of Microstructure Physics, Halle; and TU Dresden); Benjamin List (Max Planck Institut für Kohlenforschung, Mülheim an der Ruhr).

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