

## Topological materials as efficient catalysts for hydrogen evolution reaction

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Searching novel catalysts for efficient and cost-effective hydrogen evolution is one of the most important subjects in the area of catalysis. The traditional method for enhancing the activity of a catalyst is to increase the concentration of active sites and/or enhancing the metallicity. Our study proposes and demonstrates a different principle that goes beyond local site optimization by utilizing topological electronic states to enhance the catalytic activity. The band inversion in topological materials leads to numerous favourable physical properties such as robust surface states, extremely high conductivity, and high carrier mobility, which significantly influence the interfacial charge transfer and transport behaviour in the catalytic process. In addition, the topological surface states (TSS) can act as both electron acceptors or donators for small adsorbed molecules, consequently tailoring the adsorption energy and Gibbs free energy by choosing a topological phase with a specific electronic structure. We tested various topological materials such as Weyl semimetals, 1T'-MoTe<sub>2</sub>, NbP, TaP, NbAs, and TaAs; topological insulators (TI) Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>2</sub>Se, Bi<sub>2</sub>Te<sub>3</sub>, and Sb<sub>2</sub>Te<sub>3</sub>; triple-point metal MoP; and nodal line semimetal PtSn<sub>4</sub>. The MoTe<sub>2</sub> and TaAs family of Weyl semimetals were proved to be excellent catalysts in dye-sensitised visible-light photocatalytic hydrogen evolution experiments. Comparison of NbP with some typical catalysts demonstrated that the former works better than the semiconducting TiO<sub>2</sub> or metal catalysts such as Ni under similar experimental conditions. We also established for the first time that bismuth selenide and telluride TIs are active for hydrogen evolution catalysis, where the two-dimensional topological surface states play a crucial role. Moreover, topological MoP and PtSn<sub>4</sub> exhibit significantly small overpotentials in the electrocatalytic hydrogen evolution reaction. In a short span of time, we have demonstrated that the topological features of a material can be exploited as an effective tool to achieve high catalytic activity. Our long-term goal is to tune the catalytic reaction pathway by topological materials employing external parameters such as magnetic field.

Catalytic processes occurring on an electrode surface have been an important topic in chemistry and play an important role in our life. For example, the famous Haber–Bosch process is based on the conversion of hydrogen and nitrogen into ammoniac, which is then used as the central ingredient for fertilizers to sustain the world's food supply. Large-scale production and safe storage of hydrogen are among the most efficient solutions to our energy demands. Evolution of hydrogen from water splitting using conventional catalysts such as the semiconducting TiO<sub>2</sub> or highly expensive Pt metal has been known for few decades.

The traditional strategy for enhancing the activity of a catalyst involves increasing the density of active sites and/or enhancing the conductivity by nano-structuring, doping, straining, or edging. However, the electrocatalysts thus obtained are often highly complex with uncertain exposed crystal surfaces and a high density of defects. This can give rise to more problems such as difficulties in identifying and controlling the active sites, poor chemical stability, and unsatisfactory theoretical treatment. In addition, increasing the density of active sites by these strategies causes only a small degree of improvement in the electrocatalytic activity. It is suggested that the difference between a high-loading and low-loading catalyst might only be one to three

orders of magnitude, while this value might be 10 for a catalyst with high intrinsic activity.

Topological insulators (TI), Dirac/Weyl semimetals, and the recently identified nodal line semimetals are a new class of materials that are attracting increasing attention in physics and materials science. These materials have robust non-trivial surface states that are

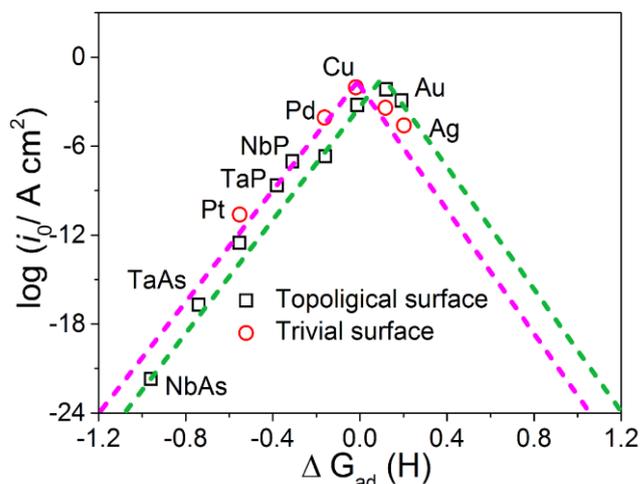


Fig.-1: Calculated activity of HER over the studied Au, Ag, Cu, Pt, and Pd clusters supported on TI Bi<sub>2</sub>Se<sub>3</sub> substrate. Solid and open points correspond to the activity of SOC (OFF) and SOC (ON), respectively.

protected from non-magnetic disorders due to the band structure topology [1]. As opposed to trivial surfaces such as dangling surface states or Shockley states, the topological surface state has a unique electronic structure and spin texture that not only allow us explore novel quantum phenomena such as ultrahigh magnetoresistance, conductivity, and intrinsic Hall effects, but also find application in surface chemistry, e.g., the hydrogen evolution reaction (HER).

We look at the problem of catalysis through the lens of topology. Our approach is much distinct from the conventional method of maximizing the number of surface sites to increase the efficiency of a catalyst. We show that in topological materials, the robust surface states and well-enhanced mobility due to the special electronic structure can lead to high efficiency for the catalytic HER. We chose a variety of topological materials, including Weyl semimetals  $1T'$ -MoTe<sub>2</sub>, NbP, TaP, NbAs and TaAs; TIs Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>2</sub>Se, Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub>; the triple-point metal MoP; and the nodal line semimetal PtSn<sub>4</sub>.

### Tailoring hydrogen adsorption by topological surface states

Generally, the trends in catalytic activity are rationalised by the *d*-band theory, which assumes that the nature of metal–adsorbate interactions is determined by the hybridization of the metal *d*-band with the bonding  $\sigma$ -orbital of the adsorbate. This is the basis for (electro)catalytic reactions following volcano plot. Our previous work indicates that the topological surface states could be used to tailor the adsorption energy of hydrogen on the catalyst surfaces [2]. The stability of all the transition metal clusters (Au, Ag, Cu, Pt, and Pd) studied can be increased by supporting them on the topological Bi<sub>2</sub>Se<sub>3</sub> crystal surface, due to the increasing in adsorption energy (Figure 1). The effective volcano plots for the catalytic reactions are always shifted toward the metals with weak reactivity due to the TSSs effect. Thanks to the robust surface states of the TIs, electrical charges favour forward motion over backscattering on the boundaries of impurities, resulting in low dissipation and excellent performance in terms of electrical conductivity.

### Robust surface states in topological Weyl semimetal for HER

In contrast to TIs that are metallic at the surface but insulating in the bulk, topological Weyl semimetals have pairs of Dirac cones in the bulk and exhibit unusual surface states with open Fermi arcs (Figure 2a).

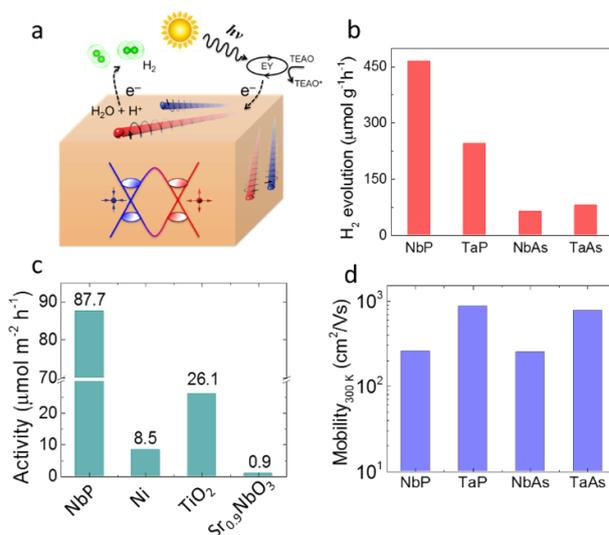


Fig.-2: (a) Schematic of visible-light HER on the surface of a Weyl semimetal. (b) Photocatalytic HER activity of various Weyl semimetals of the TaAs family, (c) Photocatalytic HER activity per unit surface area of Weyl semimetal NbP compared to some traditional catalysts. (d) Electron mobility of various Weyl semimetals of the TaAs family at room temperature.

We studied the photocatalytic HER performance of a series of topological Weyl semimetals such as  $1T'$ -MoTe<sub>2</sub>, TaAs, NbAs, TaP, and NbP [3]. We find that the topological two-dimensional dichalcogenide MoTe<sub>2</sub> is more efficient for dye-sensitised visible-light photocatalytic hydrogen evolution experiments as compared to the non-topological metal TaS<sub>2</sub>. Furthermore, the TaAs family of Weyl semimetals are excellent catalysts for HER, where phosphides generally perform better than arsenides (Figure 2b). The high room-temperature carrier mobility, robust topological surface states, and high metallicity make NbP a superior catalyst compared to the conventional semiconducting TiO<sub>2</sub> or metal catalysts such as Ni, in terms of activity per unit surface area (Figure 2c). Our transport measurements indicate large electronic mobility at room temperature (Figure 2d), which facilitates the rapid transfer of carriers for the catalytic reactions, thereby enhancing the kinetics of the HER.

### Topological insulators for photochemical water splitting

Rhombohedral Bi<sub>2</sub>Se<sub>3</sub> and Bi<sub>2</sub>Te<sub>3</sub> are the first two of the most extensively studied TIs because of their simple Dirac-type surface states and large bulk gap. The topological surface states for these crystals are extremely simple and well confirmed by angle-resolved photoemission spectroscopy (ARPES) experiments. On the surface, the electron spin is in a lock-up state with

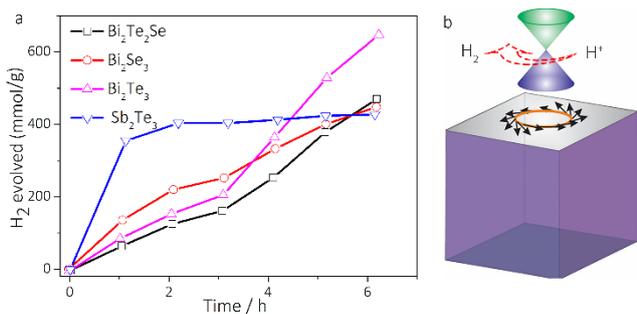


Fig.-3: (a) Catalytic behaviour of the topological insulators under study. Bi<sub>2</sub>Te<sub>3</sub> is the most active in the series. (b) Illustration of surface states of a topological insulator.

the momentum due to intrinsic interactions, the spin-orbit coupling (SOC) forming a vortex-like spin texture. Thus, the forward- and backward-moving states carry opposite spin polarizations and cannot be scattered into each other. This scenario provides ideal conducting channels for fast electron transport. Our measurements on topologically non-trivial compounds such as Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub>, and Bi<sub>2</sub>Te<sub>2</sub>Se, and topologically trivial Sb<sub>2</sub>Te<sub>2</sub>Se showed that the topological phases could significantly improve the photocatalytic activity (Figure 3a) [4]. Because of the time-reversal symmetry protection, the excited electrons stay for a longer time on the surface of the TI than on the surface of the dye molecules. Thus, the electrons from the surface states can populate the conduction band, so that electrons are readily supplied to H<sup>+</sup> ions for the HER (Figure 3b).

### Structuring topological semimetal for large exchange current density in HER

Although we proved that TIs and topological semimetals are efficient catalysts, their low chemical stability and small surface area hinder their performance for long-time and large-scale hydrogen production. We address this problem by interface engineering [5]. Very recently, pairs of Weyl points, three-component fermions, and superconductivity have been theoretically and experimentally verified in the bulk electronic structure of MoP crystals (Figure 4a). Our group revealed that MoP has low resistivity (8.2 μΩ at 300 K) and a promising charge carrier density (~1.1 × 10<sup>23</sup> cm<sup>-3</sup> at 300 K). Such surface properties are advantageous for electrochemical reactions occurring on the electrocatalyst surfaces. Thus, MoP encapsulated in a Mo and P co-doped carbon layer (MoP@C) structure was synthesized, which exhibited outstanding electrocatalytic HER performance, with an extremely low overpotential of 49 mV at a current density of 10 mA/cm<sup>2</sup> and a Tafel slope of 54 mV/dec in an alkaline

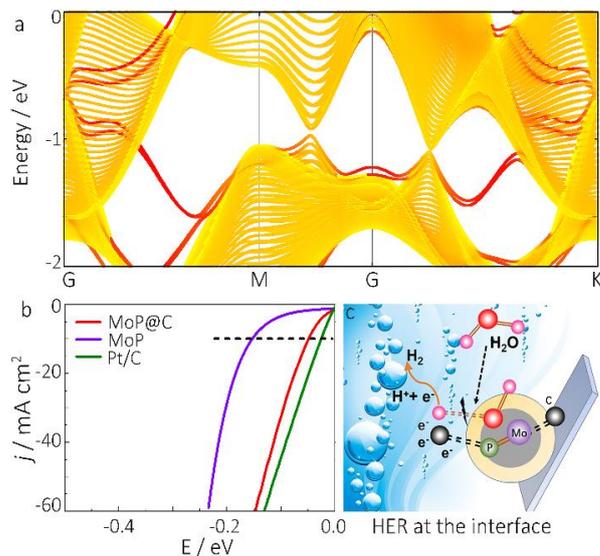


Fig.-4: (a) Band structure of MoP based on slab structure with 60 unit cell layers (red: surface state bands; yellow: bulk state bands). (b) Polarization curve for the prepared electrocatalysts. (c) Illustration of high-efficiency HER process by carbon doping.

solution (Figure 4b). The exchange current density surpassed that of the Pt/C electrocatalyst. In addition, electron transport analysis indicated that the topological semimetal MoP has high conductivity and mobility due to the topologically protected triple-point fermions and complex Fermi surface. Furthermore, the presence of P-C and Mo-C bonds at the interface between the carbon layer and the MoP particles modulated the band structure of MoP@C and facilitated fast transfer, accumulation, and delocalization of electrons, which in turn led to the excellent HER activity of this material (Figure 4c).

### Topological nodal line semimetals PtSn<sub>4</sub>: a promising candidate to replace Pt

One possible bottleneck in the effective utilization of TIs or Dirac/Weyl semimetals as catalysts is the much lower carrier density around the Fermi level due to the weak strength of electrostatic screening. For Dirac nodal line (DNL) semimetals, the band crossing points around the Fermi level form a closed loop at the Fermi level in the momentum space (Figure 5a). DNL semimetals also have a characteristic surface state, the drumhead-like state, which is topologically non-trivial and generally accompanied by high carrier density at the Fermi level. A newly approved DNL semimetal showed excellent stability with an overpotential of 37 mV at a current density of 10 mA/cm<sup>2</sup> in 1 M KOH (electrolyte), which is comparable to the result for platinum based structures and recently reported advanced electrocatalysts (Figure 5b) [6]. The linear

band crossing in the semimetal leads to large room-temperature carrier mobility, which is possibly attributed to the high Fermi velocity of massless Dirac states. This facilitates rapid charger transfer in the catalytic process, thereby accelerating the HER kinetics. The present study indicates that manipulating the robust surface states (Figure 5c and d), as well as high conductivity and mobility, would be a better approach than the traditional method of creating active sites by nanosizing, doping, straining, and edging, thus providing a new guide for searching high-performance catalysts.

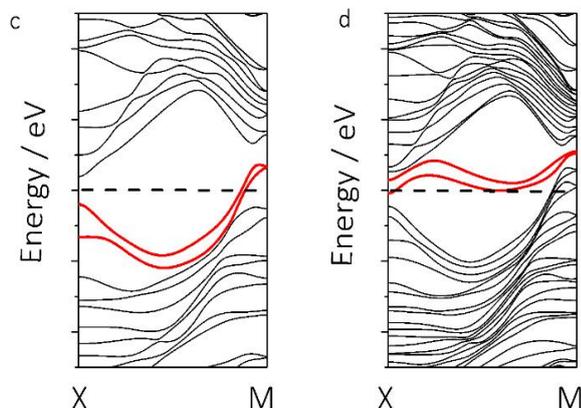
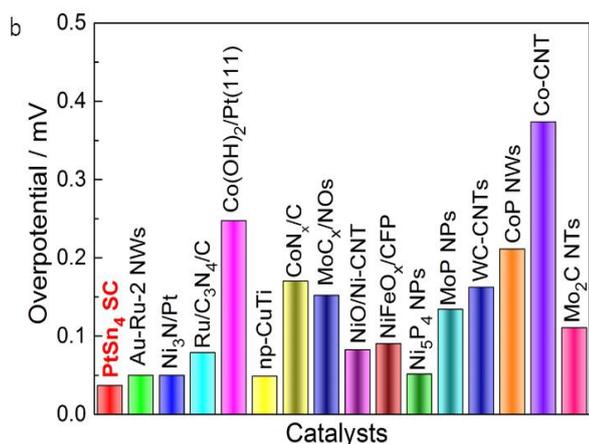
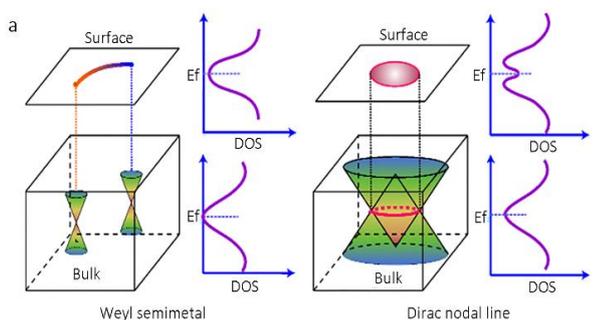


Fig.-5: (a) Schematics of momentum space diagrams and density of states of TWs and DNLs. (b) Catalytic performance of different catalysts. (c) Robust surface states before and after hydrogen adsorption.

## Conclusions

The field of topological materials, despite rapid progress, is still in its infancy, especially in terms of their influence and potential applications in chemistry. The various topological phases give rise to exotic physical properties such as robust surface states, chiral anomaly, high conductivity, and excellent mobility, but these features do not necessarily indicate good catalytic activity. The task of chemists is to develop solid materials that combine the advantages of the topological phases and working principles for a good catalyst. Our investigation indicates that by designing topological materials having distinct electronic properties via different strategies (such as doping or exposing a unique crystal surface), we can engineer topological materials into highly efficient catalysts for application to hydrogen evolution and beyond. The scope of our strategy will further be expanded to tune the catalytic reaction pathway by topological materials employing external parameters such as magnetic field.

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