

Cite this: *Dalton Trans.*, 2020, 49, 3398Received 6th January 2020,
Accepted 21st February 2020

DOI: 10.1039/d0dt00050g

rsc.li/dalton

Effect of magnetic field on the hydrogen evolution activity using non-magnetic Weyl semimetal catalysts†

Uttam Gupta,^{a,b} Catherine R. Rajamathi,^a Nitesh Kumar,^a Guowei Li,^a Yan Sun,^a Chandra Shekhar,^a Claudia Felser^a and C. N. R. Rao^{a,b}

An external switch to control the kinetics of the reaction by manipulating the participating electrons could be interesting as it can alter the rate of the reaction without affecting the reaction pathway. The magnetic field, like a switch, is non-invasive, tunable, and clean; it can also alter the electrons in a material. We study the effect of an applied magnetic field on the hydrogen evolution activity of the NbP family of Weyl semimetals because of their extremely high mobility and large magnetoresistance at room temperature and good hydrogen evolution properties. We find that by applying a magnetic field of ~3500 G, the hydrogen evolution activity of NbP increases by up to 95%. The other members of this Weyl semimetal family (*viz.* TaP, NbAs, and TaAs) also exhibit increased hydrogen evolution activity. Thus, our observations suggest an interplay of electronic property, magnetic field, and catalytic activity in this class of compounds, providing evidence of manipulating the catalytic performance of topological materials through the application of a magnetic field.

Heterogeneous catalytic reactions such as hydrogen evolution are associated with the surface electronic states or surface atomic termination of catalysts.^{1,2} Catalysts with high carrier mobility and low hydrogen binding energy are desirable. For instance, two different polymorphs of molybdenum disulfide, namely semiconducting 2H-MoS₂ and metallic 1T-MoS₂, exhibit contrasting hydrogen evolution properties. The 1T-form has better conductivity which leads to a considerable hydrogen evolution reaction (HER) activity.^{3–5} In general, 2D-structures with high in-plane conductivity and exposed surface exhibit excellent catalytic activity.^{6,7} They also provide templates to grow other materials, which further enhances the

overall activity of catalysts.^{8,9} For example, the importance of the mobility of electrons in hydrogen evolution catalysts had also been proved earlier by using graphene as a medium for efficient transport of charge carriers, wherein linearly dispersing bands near the Dirac points of graphene are the source of the high mobility of charge carriers.^{10,11} Topological materials, such as topological insulators, Weyl semimetals or nodal line semimetals, are robust against surface modifications and defects derived from dangling bonds, vacancies, or doping which otherwise destroy surface states.^{12–15} Topological surface states (TSSs) are a result of the inversion of bulk bands, with the electron spin locked up with its momentum at the crystal surface in the presence of large spin-orbit coupling. Resultantly, backscattering is notably suppressed which otherwise dominates in materials that are constantly associated with surface defects to some extent.¹⁶ Topological materials are therefore good candidates as catalysts because they possess high conductivity, topologically protected surface states, and suitable carrier concentration around the Fermi level.^{12,13} Furthermore, owing to their rich and exotic physical properties, they provide a model platform to explore the interplay among surface states, electron transfer, and surface catalytic reactions.^{12,17}

It is now accepted that even an electron can act as a catalyst.^{18,19} Hence, altering the rate of a chemical reaction by manipulating the electrons on the catalyst surface would be an exciting way to control the kinetics of that reaction. Weyl semimetals are newly discovered quantum materials wherein the linearly dispersing bulk bands cross at Weyl points with finite chirality, with the total number of the positive chirality Weyl points being equal to that of the negative chirality.¹⁴ The discovery of Weyl semimetals has provided an ideal platform to test many previously unknown catalysts. The primary advantage of using Weyl semimetals as catalysts is their inherent property of very high charge mobility due to the linear crossing of bands at the Weyl points;¹⁴ besides, they contain special surface states that cannot be destroyed by breaking or scratching the surface because these states directly originate from the

^aMax Planck Institute for Chemical Physics of Solids, 01187 Dresden, Germany.
E-mail: Kumar@cpfs.mpg.de, Felser@cpfs.mpg.de

^bNew Chemistry Unit, International Centre for Materials Science, Sheikh Saqr Laboratory, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore-560064, India. E-mail: cnrao@jncasr.ac.in

†Electronic supplementary information (ESI) available. See DOI: 10.1039/D0DT00050G



bulk electronic property.²⁰ Furthermore, Weyl semimetals exhibit many other unique properties, including chiral anomaly and photogalvanic effect, owing to the inherent chirality of their electrons.^{12,21,22} Moreover, they show a strong response to an applied magnetic field, which is manifested as large magnetoresistance (MR) and magnetic-field-induced metal-insulator-like transition.^{23,24} In general, the above-mentioned effects in Weyl semimetals have been observed at very low temperatures; however, in the case of the NbP family of Weyl semimetals, the considerably large MR effect and high electron mobility can be observed even at room temperature.^{21,23,25,26} Thus, studying the effect of an applied magnetic field on catalysis using this class of compounds is of great implication as we can observe the effect of change in electronic properties on the chemical reaction.

The hydrogen evolution reaction (HER) would be an ideal model catalytic reaction to study as it involves few intermediate steps and one product that is easy to monitor over the course of the reaction. Meanwhile, Weyl semimetals cannot perform self-sensitized hydrogen evolution. Therefore, Eosin Y assisted dye-sensitized photochemical hydrogen evolution was performed using NbP, TaP, NbAs, TaAs, and MoS₂ as catalysts. In the presence of light, EY gets actuated to the excited singlet state EY^{1*} followed by an inter-system crossing to the low-lying triplet state EY^{3*}. Then, EY^{3*} receives an electron from TEOA, transforming into a reducing species EY⁻, which then yields an electron to the catalyst surface where the HER takes place (Fig. 1).^{3,4} The role of the catalyst here is to accept the electron from the dye and transfer it to water for reduction. The rate of reaction is dependent on the electronic properties and the hydrogen binding energy of the catalyst. Since catalysts act as a channel for electrons from dye to water, the catalytic properties can be tuned by perturbing the electronic properties *via* an external field such as a magnetic field. Furthermore, we have performed a number of control experiments to conclude that

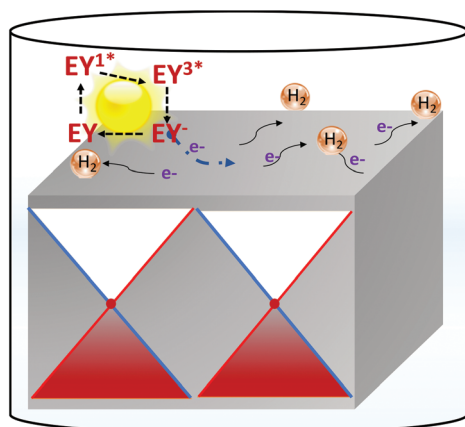


Fig. 1 Illustration of the photocatalytic hydrogen evolution process in the presence of Eosin Y (EY). The electron is transferred to the catalyst from the dye *via* a series of steps. The electron that is injected on the surface of the catalysts participates in the hydrogen evolution reaction.

the catalysts are hydrogen evolution sites and no other processes contribute to the HER (Table S1†).

Weyl semimetals can exhibit metallic conductivity along with considerably high electron mobility. Powdered forms of the single crystals of the compounds NbP, TaP, NbAs, and TaAs were characterized using X-ray powder diffraction and indexed (Fig. S1†). We first show the electronic properties of Weyl semimetal NbP and related compounds (TaP, NbAs, and TaAs) at room temperature. The transport properties of the single crystals of these compounds have recently been investigated in detail at cryogenic temperatures; however, in this study, we focus on properties relevant to our HER study at room temperature. The electron mobilities, resistivities, and MRs of the Weyl semimetals considered in our study at room temperature are listed in Table 1.

All the compounds exhibit metallic conductivity, *i.e.*, their resistivities decrease with decreasing temperature. As previously indicated, an important feature of these compounds is their large MR even at room temperature; MR is defined as the percentage increase in the resistivity of a material upon the application of a magnetic field. Fig. 2a shows the plot of MR as a function of an applied magnetic field. It is clear from the figure that the Weyl semimetal compounds considered in our study have a large MR value of 125–300% at room temperature, which is orders of magnitude higher than noble metals. Even at a low field of 0.5 T, the magnetoresistance is around 2–5% for these materials. Along with high mobility and large MR at room temperature, they also possess low hydrogen binding energy which would facilitate the rate of the reaction (Fig. 2b). Furthermore, photochemical hydrogen evolution with these

Table 1 Mobility, resistivity, and MR of Weyl semimetal catalysts considered in our study at room temperature

Catalyst	Mobility (cm ² V ⁻¹ s ⁻¹)	Resistivity (10 ⁻⁵ Ω cm)	MR (%)
NbP	275	6.30	253
TaP	849	2.53	279
NbAs	258	5.07	250
TaAs	385	4.75	129

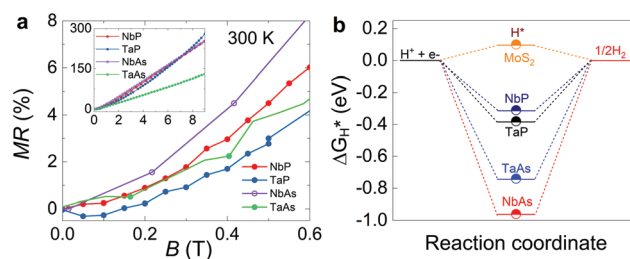


Fig. 2 (a). Magnetoresistance (MR) of Weyl semimetals NbP, TaP, NbAs, and TaAs at room temperature and 0.6 T magnetic field. The inset shows the MR of Weyl semimetals at room temperature till 9 T. (b) Calculated free energy for the hydrogen evolution reaction relative to the standard hydrogen electrode at pH 0 for Weyl semimetals and MoS₂. The values of Weyl semimetals and MoS₂ are taken from ref. 27 and 28 respectively.



materials previously studied show high HER activity due to metallic conductivity and high electron mobility.²⁷ Hence, NbP, TaP, NbAs, and TaAs are ideal candidates for observing the effect of an applied magnetic field on their catalytic hydrogen evolution activity.

Single crystals of the Weyl semimetals (NbP, TaP, NbAs, and TaAs) were powdered and characterized before conducting the hydrogen evolution studies. The particles are in the range of a few microns as inferred from FESEM images (Fig. S2†). The hydrogen evolution activity of these catalysts is recorded over the period and compared with MoS₂, a diamagnetic semiconductor, and a well-known hydrogen evolution catalyst (the XRD and SEM images of MoS₂ are shown in Fig. S1b and S4c†, respectively). In the case of MoS₂, the total amount of hydrogen gas evolved in 3 h was 652 $\mu\text{mol g}^{-1}$ and when a magnetic field is applied, there was a negligible change in the HER activity, with a yield of only 654 $\mu\text{mol g}^{-1}$ in 3 h (Fig. 3a). We use the same reaction mixture in the cases with and without the magnet, and the only difference is the additional injection of the dye in the case with the magnet. Furthermore, to rule out the possibility that the additional dye added in the case of the second reaction is contributing to the HER activity enhancement using NbP, we reverse the order of our HER reactions, *i.e.*, first, we perform the experiment with the magnet for 3 h, after which we remove the magnet and conduct the experiment again for 3 h. Upon removing the magnet, we observe an 88% decrease in the HER activity with NbP (Fig. 3b and c). When the field is applied later, the increment is 95% for the sample. Furthermore, to avoid any inconsistency, we performed all measurements for a particular sample on the same day at a constant temperature while keeping the location of the reaction vessel and lamp fixed throughout the experi-

ment. The amount of hydrogen gas evolved for Weyl semimetals in 3 h is 333, 64, 88, and 81 $\mu\text{mol g}^{-1}$ for NbP, TaP, NbAs, and TaAs without the magnetic field, respectively, whereas it increased to 652, 113, 98 and 110 $\mu\text{mol g}^{-1}$ (Fig. S2a-d†) with the application of the magnetic field, which corresponds to an increase of 95, 77.4, 11.3, and 36.5%, respectively (Fig. 3d). We had checked the stability of the compounds after hydrogen evolution before and after exposure to the magnetic field for both MoS₂ and NbP. We find no change in their morphology and chemical composition, indicating that the variation in the rate of the reaction is due to the manipulation of the electronic properties of the material by the magnet (Fig. S4†). Furthermore, the hydrogen evolution reaction is a complex process involving multiple steps and interplay between electronic surface states, electron transfer, and surface mass transfer reactions on the surface. The enhancement in the HER activity of the Weyl semimetals by the magnetic field shows that we can alter the rate of a chemical reaction by manipulating the participating electrons.

Based on our observations, it is clear that a magnetic field affects the HER activity when diamagnetic Weyl semimetals are used as catalysts; this effect is of interest considering that nonmagnetic materials were used for these experiments. Nevertheless, our results are consistent with the idea that the electronic properties of Weyl semimetals can be manipulated using a magnetic field. In this regard, nonmagnetic Weyl semimetals have earlier been shown to exhibit a negative MR induced by electron transport between two Weyl nodes of opposite chirality even at room temperature.²⁹ Electrons in metals, including topological Weyl semimetals, get localized upon the application of a magnetic field, which can also be understood in terms of the circular motion of electrons in a plane perpendicular to the direction of the applied magnetic field (Fig. 4).

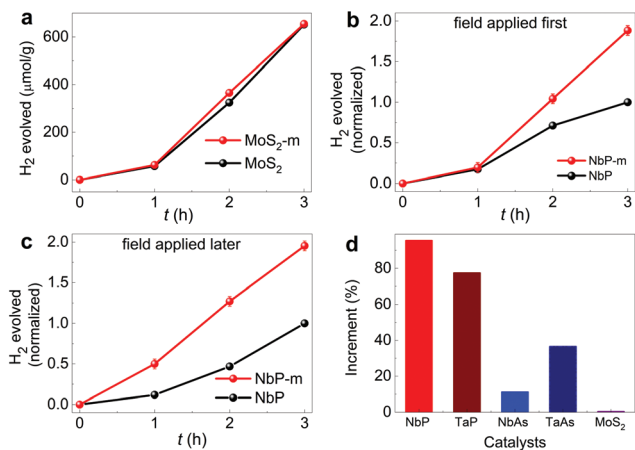


Fig. 3 (a) Comparative hydrogen evolution for MoS₂ over the period of time in the presence of the magnetic field (m) and absence. Normalized hydrogen evolution of NbP with (m) and without magnetic field for cases (b) magnetic field applied first, (c) magnetic field applied later. (d) The comparison of the increment in the magnetic field for Weyl semimetals and MoS₂. The hydrogen evolution graphs over the period are shown in Fig. S3.† The applied magnetic field is 3500 G. The same part of the crystal was used for the studies.

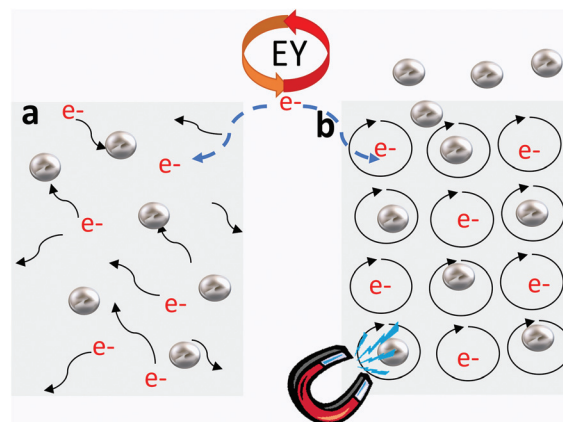


Fig. 4 The electron is transferred to the catalyst from the dye via a series of steps. The electron that is injected on the surface of the catalysts participates in the hydrogen evolution reaction. The movement of electrons in the (a) absence and (b) presence of a magnetic field. The electron in the magnetic field gets localized and moves in a circular pattern, while in the absence of the field the direction of flow is random.



The high mobility of electrons in Weyl semimetals ensures that such motion can persist for a considerable time before they are scattered (*i.e.*, long scattering time). These states are expected to be readily available for catalytic processes, leading to an increase in the HER activity under a magnetic field. However, further understanding of the mechanism of catalytic activity under a magnetic field and the manner in which it is related to the Berry curvature of topological Weyl semimetals are important topics for future research.

Conclusions

We observed a large enhancement in the hydrogen evolution catalytic activity of nonmagnetic Weyl semimetals of the NbP family upon the application of a magnetic field. The magnetic field almost doubled the HER activity of NbP; in addition, significant increases in the HER activity were also noted for other catalysts of this family. Such large variations in the catalytic activity of these semimetals indicate a drastic evolution of the bulk and surface electronic properties upon the application of a magnetic field, which is also reflected as a large MR effect at room temperature. The slight application of a magnetic field can alter the rate of the reaction significantly. It would be interesting to study the effect on catalysis by varying the magnetic field and understanding the exact mechanism *via in situ* experiments. Manipulation of electronic properties of catalysts may serve as an alternative route to change the rate of the reaction without affecting the reaction pathway which can be further explored for other chemical reactions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the ERC Advanced Grant No. 742068 'TOPMAT'. Dr U. Burkhardt for the SEM measurements. Open Access funding provided by the Max Planck Society.

References

- 1 T. Banerjee, F. Haase, G. Savasci, K. Gottschling, C. Ochsenfeld and B. V. Lotsch, *J. Am. Chem. Soc.*, 2017, **139**, 16228–16234.
- 2 Y. Jing and T. Heine, *J. Mater. Chem. A*, 2018, **6**, 23495–23501.
- 3 U. Maitra, U. Gupta, M. De, R. Datta, A. Govindaraj and C. N. R. Rao, *Angew. Chem., Int. Ed.*, 2013, **52**, 13057–13061.
- 4 U. Gupta, B. S. Naidu, U. Maitra, A. Singh, S. N. Shirodkar, U. V. Waghmare and C. N. R. Rao, *APL Mater.*, 2014, **2**, 092802.
- 5 D. Voiry, M. Salehi, R. Silva, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy, G. Eda and M. Chhowalla, *Nano Lett.*, 2013, **13**, 6222–6227.
- 6 X. Ren, J. Zhou, X. Qi, Y. Liu, Z. Huang, Z. Li, Y. Ge, S. C. Dhanabalan, J. S. Ponraj, S. Wang, J. Zhong and H. Zhang, *Adv. Energy Mater.*, 2017, **7**, 1700396.
- 7 Q. Jiang, L. Xu, N. Chen, H. Zhang, L. Dai and S. Wang, *Angew. Chem.*, 2016, **128**, 14053.
- 8 W. Han, C. Zang, Z. Huang, H. Zhang, L. Ren, X. Qi and J. Zhong, *Int. J. Hydrogen Energy*, 2014, **39**, 19502–19512.
- 9 Z. Zhang, Y. Liu, L. Ren, H. Zhang, Z. Huang, X. Qi, X. Wei and J. Zhong, *Electrochim. Acta*, 2016, **200**, 142–151.
- 10 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183.
- 11 C. Huang, C. Li and G. Shi, *Energy Environ. Sci.*, 2012, **5**, 8848–8868.
- 12 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.*, 2019, **5**, eaaw9867.
- 13 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, *Angew. Chem., Int. Ed.*, 2019, **58**, 13107–13112.
- 14 B. Yan and C. Felser, *Annu. Rev. Condens. Matter Phys.*, 2017, **8**, 337–354.
- 15 L. Muechler, H. Zhang, S. Chadov, B. Yan, F. Casper, J. Kübler, S.-C. Zhang and C. Felser, *Angew. Chem., Int. Ed.*, 2012, **51**, 7221–7225.
- 16 L. M. Schoop, F. Pielnhofer and B. V. Lotsch, *Chem. Mater.*, 2018, **30**, 3155–3176.
- 17 M. Z. Hasan, S.-Y. Xu, I. Belopolski and S.-M. Huang, *Annu. Rev. Condens. Matter Phys.*, 2017, **8**, 289–309.
- 18 A. Studer and D. P. Curran, *Nat. Chem.*, 2014, **6**, 765.
- 19 K. N. Houk and B. List, *Acc. Chem. Res.*, 2004, **37**, 487–487.
- 20 X. Wan, A. M. Turner, A. Vishwanath and S. Y. Savrasov, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 205101.
- 21 X. Huang, L. Zhao, Y. Long, P. Wang, D. Chen, Z. Yang, H. Liang, M. Xue, H. Weng, Z. Fang, X. Dai and G. Chen, *Phys. Rev. X*, 2015, **5**, 031023.
- 22 Q. Ma, S.-Y. Xu, C.-K. Chan, C.-L. Zhang, G. Chang, Y. Lin, W. Xie, T. Palacios, H. Lin, S. Jia, P. A. Lee, P. Jarillo-Herrero and N. Gedik, *Nat. Phys.*, 2017, **13**, 842.
- 23 C. 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.*, 2015, **11**, 645.
- 24 M. N. Ali, J. Xiong, S. Flynn, J. Tao, Q. D. Gibson, L. M. Schoop, T. Liang, N. Haldolaarachchige, M. Hirschberger, N. P. Ong and R. Cava, *Nature*, 2014, **514**, 205.



- 25 N. J. Ghimire, Y. Luo, M. Neupane, D. J. Williams, E. D. Bauer and F. Ronning, *J. Phys.: Condens. Matter*, 2015, **27**, 152201.
- 26 F. Arnold, C. Shekhar, S.-C. Wu, Y. Sun, R. D. dos Reis, N. Kumar, M. Naumann, M. O. Ajeesh, M. Schmidt, A. G. Grushin, J. H. Bardarson, M. Baenitz, D. Sokolov, H. Borrmann, M. Nicklas, C. Felser, E. Hassinger and B. Yan, *Nat. Commun.*, 2016, **7**, 11615.
- 27 C. R. Rajamathi, U. Gupta, N. Kumar, H. Yang, Y. Sun, V. Süß, C. Shekhar, M. Schmidt, H. Blumtritt, P. Werner, B. Yan, S. Parkin, C. Felser and C. N. R. Rao, *Adv. Mater.*, 2017, **29**, 1606202.
- 28 B. Hinnemann, P. G. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Horch, I. Chorkendorff and J. K. Nørskov, *J. Am. Chem. Soc.*, 2005, **127**, 5308–5309.
- 29 A. C. Niemann, J. Gooth, S.-C. Wu, S. Bäßler, P. Sergeius, R. Hühne, B. Rellinghaus, C. Shekhar, V. Süß, M. Schmidt, C. Felser, B. Yan and K. Nielsch, *Sci. Rep.*, 2017, **7**, 43394.

