Spontaneous hydrogen production using gadolinium telluride

Highlights

A simple approach for the generation of pure Hydrogen

A significant $H_2$ production enhancement was observed in GdTe crystal

The experimental finding supported by thermodynamic and DFT calculations

The non-uniform oxide layer boosts the hydrogen generation performance of GdTe
Spontaneous hydrogen production using gadolinium telluride

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SUMMARY
Developing materials for controlled hydrogen production through water splitting is one of the most promising ways to meet current energy demand. Here, we demonstrate spontaneous and green production of hydrogen at high evolution rate using gadolinium telluride (GdTe) under ambient conditions. The spent materials can be reused after melting, which regain the original activity of the pristine sample. The phase formation and reusability are supported by the thermodynamics calculations. The theoretical calculation reveals ultralow activation energy for hydrogen production using GdTe caused by charge transfer from Te to Gd. Production of highly pure and instantaneous hydrogen by GdTe could accelerate green and sustainable energy conversion technologies.

INTRODUCTION
Hydrogen is a vital ingredient in chemical (majorly in synthesis of ammonia), metallurgical, glass, semiconductor, and pharmaceuticals industries.1-3 The calculated demand for hydrogen in fossil fuels-free future is expected to increase to more than two gigaton per year.4 The majority of all hydrogen produced globally comes from natural gas (50%), primarily through steam methane reforming (reaction of steam and natural gas), and the rest is generated from oil (30%), coal (16%), and electrolysis of water (4%). The by-products of the major synthesis processes are complex mixtures of condensable hydrocarbons and CO2. This causes emission of 830 Mt of CO2 per year, which is detrimental to the environment. Therefore, the instantaneous hydrogen production from water splitting will be environmentally beneficial. There are a number of other methods to produce hydrogen, including water electrolysis, water splitting by photo-catalysis, fuel reforming, nuclear hydrogen generation, and linking the nuclear reactor and hydrogen production process is difficult. The purification issue is still being researched in laboratories for biomass-processing technologies. Unwavering efforts are made to investigate renewable, environmentally friendly, and high-efficiency hydrogen-generation methods in response to the drawbacks mentioned above.

Alkali metals like sodium, aluminum, magnesium, and potassium react with water to produce H2 gas.5-11 These reactions are highly exothermic and extremely difficult to control.6,7,9,12 Recently, several high-entropy alloys and metal-hydrides/carbides have been explored to generate H2 by controlled water splitting.13,14 However, most of these materials have high activation barriers for H2 production. On the other hand, the state-of-the-art electrocatalyst consists of platinum, palladium, and 2D materials hybrids that require external energy to overcome the activation barrier.15-26 Recently, it has been realized that atomically thin catalysts expose the highest number of active sites, maximize atom-utilization efficiency and reaction selectivity, and increase the electrocatalytic activity of a system.27-30 However, due to the poor structural stability, they can restrict the catalytic efficiency of the system. Today, the field necessitates new material with optimized activation energy barrier, for producing instantaneous yet controlled pure hydrogen.

Here we demonstrate instantaneous generation of highly pure hydrogen using gadolinium telluride (GdTe) crystal from water splitting (Figures 1A and 1B). The GdTe is produced by simple and easily scalable induction melting (see STAR Methods supplemental information). The material is recyclable without loss of any activity. Post-reaction analysis of materials confirms the formation of non-uniform oxide layers (Gd2O3), the activation barrier.15-26 Recently, it has been realized that atomically thin catalysts expose the highest
which assists the reaction. Theoretical calculations indicate that the charge transfer from Te to Gd enhances the chemical activity, which results in ultralow activation energy for instantaneous hydrogen generation.

RESULTS AND DISCUSSION

GdTe crystals produced by induction melting method (using Gd and Te in 1:1 atomic ratio; see supplemental information) crystallize in the well-known NaCl-type fcc structure (Fm-3m) (Figure 1C) with lattice parameters of \( a = b = c = 6.25 \, \text{Å} \) and \( \alpha = \beta = \gamma = 90^\circ \). This matches with the optimized lattice parameter of GdTe obtained from the density functional theory (DFT) calculations and previously reported values. \(^3\) This is further used to generate different close-packed surfaces as shown in Figure S1 related to DFT calculation. Synthesized sample shows four major peaks corresponding to \( E_1^g, A_g, B_2^g, \) and \( E_2^g \) modes in the Raman spectrum (Figure 1D), which confirms its purity. \(^3,23\) Also, energy-dispersive X-ray analysis (EDAX) shows the presence of Gd and Te after melting (Figure S2 related to synthesis of GdTe). Furthermore, scanning electron microscopy (SEM) images (inset of Figure 1C) reveal the smooth surface of the crystals.

To understand the chemical activity of produced GdTe crystal, its ability of splitting the water to generate hydrogen without external energy is demonstrated. A large number of hydrogen bubbles were generated immediately as GdTe reacts with water at room temperature (Figure 2A) and can be clearly seen in the provided video captured during the reaction (Video S1 related to Figure 2A). In the beginning, a steady HER rate of \( \sim 0.022 \, \mu \text{mol min}^{-1} \, \text{g}^{-1} \) was observed for 5 min, which then increases rapidly after 10 min where eventually \( \sim 1.0 \, \text{g} \) of GdTe produced more than \( \sim 1.87 \, \mu \text{mol} \) of \( \text{H}_2 \) within 30 min (Figure 2B and supplemental information). Along with water, GdTe also reacts with dry methanol to produce \( \text{H}_2 \) with slower rate (Figure S3A related to Figure 2A) where sudden increase in \( \text{H}_2 \) production is observed in gas chromatography data after 30 min (Figure S3B related to Figure 2B). Moreover, GdTe shows the most favorable onset potential when compared with state-of-the-art HER catalyst (Figure 2C). \(^34-40\)

Such high activity was further quantified and compared by calculating the free energies of hydrogen evolution for different closed-packed planes of GdTe, namely (100), (110), (111), and (211) as shown in Figure S1 related to...
Figure 1C, found from the experimental XRD using computational hydrogen electrode (CHE) model by Petersen et al.\textsuperscript{41} Computed free energies of hydrogen evolution are compared in Figure 2D. H* intermediate is most strongly adsorbed on the Gd atom in the terrace site of (211) plane, with adsorption energy of $1.03 \text{ eV}$ where formation of $\text{H}_2$ is highly endothermic and promotes poisoning of the surface. However, low stability of the intermediate on Te atom of (110) surface with adsorption energy $1.78 \text{ eV}$ also decreases the reactivity of GdTe. Therefore, considering all possible different adsorption sites, H* is optimally stable on Gd atom of (100) plane having free energy of hydrogen adsorption, $\Delta G_0^\text{H} = 0.06 \text{ eV}$. This outperforms platinum (Pt), which otherwise showed prominent capability for HER with $\Delta G_0^\text{H} = 0.09 \text{ eV}$. Similarly, the Gd atoms in (110) plane and corner site of (211) plane have substantial potential for hydrogen evolution with $\Delta G_0^\text{H} = 0.14 \text{ eV}$ and 0.21 eV, respectively. Furthermore, according to calculated overall surface activities, (100) plane shows best potential for hydrogen evolution reaction followed by (110), (211), and (111) surface. Eventually this ensures uninterrupted formation of large number of $\text{H}_2$ as (100) plane has the lowest surface energy of 0.02 eV/Å\textsuperscript{2}.

After 30 min of the reaction, the $\text{H}_2$ generation reaches saturation (Figures 2A and 2B) and the color of the water changes from transparent to blackish brown (inset of Figure 2A and upper and lower panel of Figure S4A).
related to hydrogen production measurement. The reacted particles separated from the water after reaction saturation was found in the nanoscale range (a few nanometers) under high-resolution transmission electron microscopy (HRTEM) microscopic analyses. This surface reaction is shown by the in-site optical microscopy (Figure S5), time-interval optical microscopic images (Figures 2E and S6 related to Figure 2E), and 3D surface profile of GdTe surface (Figure 2F) during the reaction.

Furthermore, HRTEM images (right panel of Figure 3A) of the reacted particles separated from the water after 30 min show the formation of non-uniform amorphous oxide layer on the GdTe surface. Moreover, fast Fourier transform (FFT) patterns of two selected regions (inset) confirm formation of oxide layer and crystalline GdTe. EDAX also confirms the presence of Gd and Te (Figure 3B). The copper transmission electron...
microscopy (TEM) grid is the source of the copper found in EDAX. The final product of the reaction after 30 min was melted (denoted as GT-II sample), and its X-ray photoelectron spectroscopy (XPS) and XRD were analyzed. The powder XRD pattern of GT-II sample shows that the observed peaks correspond to cubic Gd$_2$O$_3$ and Gd$_2$Te$_3$, along with GdTe (Figures 3C and 3D). It was indexed based on the standard XRD pattern. The elemental compositions with their respective oxidation states of the GT-II sample were analyzed using de-convoluted XPS results (Figures 3E-3H) and full-scan XPS survey spectra (Figure S7A related to Figure 3A). The presence of elements was further confirmed with elemental mapping of the surface (Figure S7B related to Figure 3B). The high-resolution XPS spectra of Gd 4d, Gd 3d, O 1s, and Te 3d agree well with the previously reported values for pure metal and their oxidation states (Figures 3E-3H). The de-convoluted spectra of Gd 4d shows three sub-peaks at 141.1 eV, 143.1 eV, and 147.6 eV corresponding to Gd 5d$_{5/2}$, oxidation state of Gd, and Gd 5d$_{3/2}$, respectively. The core-level spectra of Gd 3d reveal its characteristics peaks at 1186.5 and 1218.6 eV by virtue of 3d$_{5/2}$ and 3d$_{3/2}$, respectively, which originate due to the spin-orbital coupling on a doublet. Absorption spectra also confirm the regeneration of GdTe after reaction and melting (Figures S8A and S8B related to Figure 3A). Therefore, due to the presence of GdTe in GT-II sample, it regained its ability to produce H$_2$ when reacted with water. The minute shift in binding energy indicates the reaction involves a charge transfer, although the amount of generated H$_2$ decreases from freshly prepared GdTe. Furthermore, the de-convoluted XPS profile of tellurium (Te 3d) can be assigned to Te$^0$ (572.9 eV), O–Te3d$_{3/2}$ (575.9 eV), C–Te3d$_{5/2}$ (583.3 eV), and O–Te3d$_{5/2}$ (586.2 eV) peaks (Figure 3H), indicating the formation of elemental Te and oxides of Te along with Gd$_2$O$_3$ and Gd$_2$Te$_3$.46,47

To understand the role of produced by-product on the reaction kinetics of GdTe in water, thermodynamics calculations were performed at 25°C by varying the mole fraction of reacting reagents (Figures 3I and 3J). Both the production of H$_2$ and production of Gd$_2$O$_3$ increase with increase in mole fraction of Gd$_2$Te$_3$ that reacts with 1 mol of H$_2$O. However, their production saturates at around 0.66 mol fraction of GdTe where the amount of Gd$_2$Te$_3$ starts increasing. Furthermore, upon increasing mole fraction of H$_2$O that reacts with 1 mol of Gd$_2$Te$_3$, production of both H$_2$ and Gd$_2$O$_3$ increases. However, the GdTe is fully consumed at around 0.5 mol fraction H$_2$O, and the amount of Te starts increasing. The calculations suggest that the formation of Gd$_2$O$_3$ helps in H$_2$ evolution and drives the reaction. The ratio of mole fraction of GdTe and H$_2$O should be maintained far from 1, so as to generate optimum number of products (H$_2$ and Gd$_2$O$_3$) and waste (Gd$_2$Te$_3$ and Te). It is suggested that the reaction has happened in 3 possible stages: (i) after immersion, the water molecule diffuses into the crystal surface through the active site and reacts with GdTe to start a linear production of H$_2$; (ii) after that, Gd$_2$O$_3$ is formed over the surface, which opens more reaction sites progressively, and reaction rate increases rapidly; (iii) at the end, the production of Gd$_2$O$_3$ and H$_2$ reaches saturation and the amount of Gd$_2$Te$_3$ is increased. Recently, reusability of other metal alloy such as Al-Ga for H$_2$ generation was reported. Here, Ga metal removes the passive oxide layer on Al surface, which improves the reusability of the material in H$_2$ production.44 Chen et al. also reported that the bulk Al alloy containing Ga, In, and Sn shows hydrogen production without formation of oxide layers.49 The amorphous oxide layers on catalyst surface improve the overall catalytic performance by creating more active sites in our case also, the non-uniform amorphous oxide layers on GdTe surface improve the chemical reaction probably by increasing the surface porosity.

Thermodynamic calculations demonstrate that while Te does not produce hydrogen, Gd does, along with the formation of stable Gd$_2$O$_3$. Therefore, to differentiate the reactivity of Gd and Te and the contribution of Te to make GdTe as an active material for hydrogen production, the orbital overlap and d-band center model was considered. Gd atoms consist of higher amounts of states overlapping with the H states for (100) (Figure S9 related to Figure 2D), (110) (Figure S10 related to Figure 2D), and (211) (Figure S12 related to Figure 2D) surfaces and d-band center closer to Fermi level (pinned at 0 eV) (Figure 4A) (Tabel S1 related to DFT calculation) that increases the stability of H* intermediate in comparison with Te. This causes Gd atoms to react with water and form Gd$_2$O$_3$. However, 3-coordinated Te atom in (111) surface has better overlap with H states (Figure S11 related to Figure 2D) and hence more reactivity than 6-coordinated Gd atom that forms respective oxide. Furthermore, the reaction of Gd in water shows less activity (0.0011 µmol min$^{-1}$ gm$^{-1}$) for hydrogen evolution (Figure S13 related to Figure 4C) in comparison with GdTe as d-band center of Gd atom is at −0.35 eV for Gd (100) surface, which is less appropriate than...
the Gd atom on (100) surface of GdTe for the adsorption of hydrogen. Moreover, according to the density of states (DOS) plot of Gd (100), the filled states near fermi level are contributed by the filled d_{x^2-y^2} and d_{xy} orbital. However, in GdTe (100) surface, the filled states near fermi level are mainly contributed by the d_{xz} orbital (Figures 4B and 4C). This is because in GdTe the Gd atoms interact with the Te atoms by their d_{x^2-y^2} orbitals as confirmed by the electron-accumulated blue region around Te atoms that is spread along the bond (Figure 4D). Correspondingly, the electron density in the d_{x^2-y^2} orbital in Gd decreases as Te atoms being more electronegative pull electron density from Gd. Now, H atom approaching the surface from the z-direction interacts by its s-orbital with the orbitals of the surface atoms having more z-directed orientation (d_{xz}, d_{yz}, d_{z^2}). This in turn proves the superiority of GdTe bimetallic surface over Gd surface.

Here, we demonstrated the safe and controlled production of H_{2} along with the recyclability of GdTe. It interacts instantly without any external energy (potential/heat etc.) with water and produces H_{2} gas. The main innovation in this work is to tune the material property and reactivity for spontaneous yet controllable H_{2} production. In our case, the non-uniform amorphous oxide layers on GdTe surface improve the reaction probably by increasing the porosity during the electrochemical reaction. Therefore, GdTe can be used to

![Figure 4. DFT calculation for HER](image-url)

(A) Free energy of hydrogen adsorption and the d (Gd) or p (Te) band centers for different active sites. Density of states diagram of d-orbitals of Gd atoms on (B) (100) surface of GdTe and (C) (100) surface of Gd. (D) Charge distribution diagram on (100) surface of GdTe. Yellow region depicts charge-depleted region, and blue region depicts charge-accumulated region.
generate hydrogen instantly anywhere without necessitating any external energy sources, which has upper hand over widely considered hydrogen-generating reagents like alkali metals in terms of controllability. Furthermore, we provide fundamental insights into the structure-activity relationships of this material that can guide future materials design principles for related applications. So, we believe that this Gd-Te alloy system will be a good choice for industry applications in future.”

Conclusions
In conclusion, spontaneous water splitting without any external energy was observed. In first 30 min, one gram of GdTe crystal produced \(1.87 \mu\text{mol} \) of \(\text{H}_2\), after which the reaction rate saturates and continues to produce hydrogen until 23 hrs at the same rate. The GdTe crystals were produced by industrially scalable induction melting in argon atmosphere. The reaction produces nanostructures of \(\text{Gd}_2\text{O}_3\) on GdTe, which assists in continuous production of hydrogen by opening more reaction sites progressively. The spent materials can be reused after melting, which do not lose their chemical activity. The theoretical calculation reveals the ultralow activation energy barrier for hydrogen evolution on most stable (100) surface of GdTe as a reason of suitable orbital overlap and d-band center of Gd atom. Production of highly pure and instantaneous hydrogen using GdTe can be utilized in several next-generation sustainable energy conversion technologies.

Limitations of the study
In the current work, some \(\text{Gd}_2\text{Te}_3\) and \(\text{Gd}_2\text{O}_3\) nanoparticles also develop as a result of chemical reaction. These materials rarely could have completely lost their bulk. The GdTe’s effectiveness is further decreased by the generated \(\text{Gd}_2\text{O}_3\). Also, there is relatively little usage of God in the realm of study. As a result, the price of the material is somewhat higher. But, with more synthesis process improvement, we may develop a more economical method of producing pure hydrogen from GdTe in the future.

STAR METHODS
Detailed methods are provided in the online version of this paper and include the following:

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SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.isci.2023.106510.

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AUTHOR CONTRIBUTIONS
P.K., C.S.T., S.S., A.R.S.G., S.R., and S.D. conceived and designed the project. P.K. and S.D. performed the experiments. A.P. and M.P. carried out the theoretical investigation. P.K., A.P., S.D., R.B., and S.R. analyzed
the results. P.K., A.P., and S.D wrote the original draft. P.M.A, S.S., A.K.S., and C.S.T supervised the project and edited the manuscript. All authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

INCLUSION AND DIVERSITY
We worked to ensure gender balance in the recruitment of human subjects. We worked to ensure ethnic or other types of diversity in the recruitment of human subjects. We worked to ensure that the study questionnaires were prepared in an inclusive way. We worked to ensure sex balance in the selection of non-human subjects. We worked to ensure diversity in experimental samples through the selection of the cell lines. We worked to ensure diversity in experimental samples through the selection of the genomic datasets. One or more of the authors of this paper self-identifies as an underrepresented ethnic minority in their field of research or within their geographical location. One or more of the authors of this paper self-identifies as a gender minority in their field of research. One or more of the authors of this paper self-identifies as a member of the LGBTQIA+ community. One or more of the authors of this paper self-identifies as living with a disability. One or more of the authors of this paper received support from a program designed to increase minority representation in their field of research. While citing references scientifically relevant for this work, we also actively worked to promote gender balance in our reference list.

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REFERENCES
1. Lubitz, W., and Tumas, W. (2007). Hydrogen: an overview. Chem. Rev. 107, 3900–3903. https://doi.org/10.1021/cr050200z.
2. Derycke, V., Soukiassian, P.G., Amy, F., Chabal, Y.J., D’angelo, M.D., Enriquez, H.B., and Silly, M.G. (2003). Nanochemistry at the atomic scale revealed in hydrogen-induced semiconductor surface metallization. Nat. Mater. 2, 253–258. https://doi.org/10.1038/nmat833.
3. Ohsawa, I., Ishikawa, M., Takahashi, K., Watanabe, M., Nishimaki, K., Yamagata, K., Katsura, K.I., Katayama, Y., Asoh, S., and Ohta, S. (2007). Hydrogen acts as a therapeutic antioxidant by selectively reducing cytotoxic oxygen radicals. Nat. Med. 13, 688–694. https://doi.org/10.1038/nm1577.
4. Oliveira, A.M., Beswick, R.R., and Yan, Y. (2021). A green hydrogen economy for a renewable energy society. Curr. Opin. Chem. Eng. 33, 100701. https://doi.org/10.1016/j.coech.2021.100701.
5. Xu, S., Zhao, X., and Lu, J. (2018). Liquid metal activated aluminum-water reaction for direct hydrogen generation at room temperature. Renew. Sustain. Energy Rev. 92, 12–37. https://doi.org/10.1016/j.rser.2018.04.052.
6. Mason, P.E., Uhlig, F., Vanek, V., Buttersack, T., Bauerecker, S., and Jungwirth, P. (2015). Coulomb explosion during the early stages of the reaction of alkali metals with water. Nat. Chem. 7, 250–254. https://doi.org/10.1038/nchem.2161.
7. Roach, P.J., Woodward, W.H., Castleman, A.W., Reber, A.C., and Khanna, S.N. (2009). Complementary active sites cause size-selective reactivity of aluminum cluster anions with water. Science 323, 492–495. https://doi.org/10.1126/science.1165884.
8. Deel, B.E., and Svec, H.J. (1953). Metal—water reactions. Il. Kinetics of the reaction between lithium and water vapor. J. Am. Chem. Soc. 75, 6173–6175. https://doi.org/10.1021/ja0120a019.
9. Shimoojo, F., Ohmura, S., Kalia, R.K., Nakano, A., and Vashishtha, P. (2010). Molecular dynamics simulations of rapid hydrogen production from water using aluminum clusters as catalysts. Phys. Rev. Lett. 104, 126102. https://doi.org/10.1103/PhysRevLett.104.126102.
10. Xu, S., and Liu, J. (2019). Metal-based direct hydrogen generation as unconventional high density energy. Front. Energy 13, 27–53. https://doi.org/10.3389/fenrg.2018.00630.
11. Reber, A.C., Khanna, S.N., Roach, P.J., Woodward, W.H., and Castleman, A.W. (2010). Reactivity of aluminum cluster anions with water: origins of reactivity and mechanisms for H2 release. J. Phys. Chem. A 114, 6071–6081. https://doi.org/10.1021/jp911136z.
12. Jaramillo, T.F., Jergensen, K.P., Bonde, J., Nielsen, J.H., Horch, S., and Chorkendorff, I. (2007). Identification of active edge sites for electrochemical H2 evolution from MoS2 nanocatalysts. Science 317, 100–102. https://doi.org/10.1126/science.1141483.
13. Sun, Y., and Dai, S. (2021). High-entropy materials for catalysis: a new frontier. Sci. Adv. 7, eabg1600. https://doi.org/10.1126/sciadv.abg1600.
14. Kim, J., Kim, H.J., Ruqia, B., Kim, M.J., Jang, Y.J., Jo, T.H., Baik, H., Oh, H.S., Chung, H.S., Baek, K., et al. (2021). Crystal phase transition creates a highly active and stable RuC5 nanosurface for hydrogen evolution reaction in alkaline media. Adv. Mater. 33, 2105248. https://doi.org/10.1002/adma.202105248.
15. Zhang, J., Zhao, Y., Guo, X., Chen, C., Dong, C.-L., Liu, R.-S., Han, C.-P., Li, Y., Gogotsi, Y., and Wang, G. (2018). Single platinum atoms immobilized on an Mxene as an efficient catalyst for the hydrogen evolution reaction. Nat. Catal. 1, 985–992. https://doi.org/10.1038/s41929-018-0195-1.
16. Chhetri, M., Rana, M., Loukya, B., Patil, P.K., Datta, R., and Gautam, U.K. (2015). Mechnanochemical synthesis of free-standing platinum nanosheets and their electrocatalytic properties. Adv. Mater. 27, 4430–4437. https://doi.org/10.1002/adma.201501056.
17. Liu, D., Li, X., Chen, S., Yan, H., Wang, C., Wu, C., Haleem, Y.A., Duan, S., Lu, J., Ge, B., et al. (2019). Atomically dispersed platinum supported on curved carbon supports for efficient electrocatalytic hydrogen evolution. Nat. Energy 4, 512–518. https://doi.org/10.1038/s41560-019-0402-6.
18. Zhu, Z., Yin, H., He, C.T., Al-Mamun, M., Liu, P., Jiang, L., Zhao, Y., Wang, Y., Yang, H.G., Tang, Z., et al. (2018). Ultrathin transition metal dichalcogenide/3d metal hydroxide
hybridized nanosheets to enhance hydrogen evolution activity. Adv. Mater. 30, 1801171. https://doi.org/10.1002/adma.201801171.

19. Wu, Z., Wang, J., Xiao, K., Lei, W., Liu, X., and Wang, D. (2018). MoS2–MoP heterostructured nanosheets on polymer-derived carbon as an electrocatalyst for hydrogen evolution reaction. J. Mater. Chem. A 6, 616–622. https://doi.org/10.1039/C7TA09307A.

20. Cao, D., Ye, K., Moses, O.A., Xu, W., Liu, D., Song, P., Wu, C., Wang, C., Ding, S., Chen, S., et al. (2019). Engineering the in-plane structure of metallic phase molybdenum disulfide via Co and O dopants toward efficient alkaline hydrogen evolution. ACS Nano 13, 11733–11740. https://doi.org/10.1021/acs.nano.9b05714.

21. Benck, J.D., Hellstern, T.R., Kibsgaard, J., Chakhchouk, P., and Jaramillo, T.F. (2014). Catalyzing the hydrogen evolution reaction (HER) with molybdenum sulfide nanomaterials. ACS Catal. 4, 9573–9571. https://doi.org/10.1021/cs500923c.

22. Xie, J., Zhang, H., Li, S., Wang, R., Sun, X., Zhou, M., Zhu, W., Lou, X.W.D., and Xie, Y. (2013). Defect-rich MoS2 MoP ultrathin nanosheets with additional active edge sites for enhanced electrocatalytic hydrogen evolution. Adv. Mater. 25, 3807–3813. https://doi.org/10.1002/adma.201302685.

23. Fang, Y., Liu, Y., Qi, L., Xue, Y., and Li, Y. (2022). 2D graphene: an emerging carbon material. Chem. Rev. 51, 2681–2709. https://doi.org/10.1021/acs.csrv.5c00952.

24. Huang, C., Li, Y., Wang, N., Xue, Y., Zuo, Z., Liu, H., and Li, Y. (2018). Progress in research into 2D graphdiyne-based materials. Chem. Rev. 118, 7744–7803. https://doi.org/10.1021/acs.chemrev.b602086c.

25. Zheng, X., Xue, Y., Zhang, C., and Li, Y. (2022). Controlled growth of multidimensional interface for high-selectivity ammonia production. CCS Chem. 1–5. https://doi.org/10.1016/j.ccschem.2022.02189.

26. He, F., Gou, Y., Wu, X., Xia, Y., Yang, L., Wu, C., Li, P., Zhang, R., Fang, R., Li, N., and Xie, Y. (2022). Advances on theory and experiments of the energy applications in graphdiyne. CCS Chemistry, 1–15. https://doi.org/10.1016/j.ccschem.2022.020328.

27. Yu, H., Xue, Y., Huang, B., Hui, L., Zhang, C., Fang, Y., Liu, Y., Zhao, T., Li, Y., Liu, H., and Li, Y. (2019). Ultrathin nanosheet of graphdiyne-supported palladium atom catalyst for efficient hydrogen production. iScience 11, 31–41. https://doi.org/10.1016/j.isci.2018.12.006.

28. Jin, H., Gu, Q., Chen, B., Tang, C., Zheng, Y., Zhang, H., Jaroniec, M., and Qiao, S.-Z. (2020). MoS2 ultrathin nanosheets with direct synthesis of 2D layered transition-metal nitrides for efficient hydrogen evolution. Chem 6, 2382–2394. https://doi.org/10.1002/chem.202006037.

29. Zhao, X., Shi, S., Yang, J., Gong, W., Sun, J., Chen, B., Guo, K., Chen, B., Zhu, Z., Cui, D., et al. (2020). Perovskite microcrystals with intercalated monolayer MoS2 nanosheets as advanced photocatalyst for solar-powered hydrogen generation. Matter 20, 935–949. https://doi.org/10.1016/j.matter.2020.07.004.

30. Sun, J., Li, S., Zhao, Q., Huang, C., Wu, Q., Chen, W., Xu, Q., and Yao, W. (2021). Atomically confined calcium in nitrogen-doped graphene as an efficient heterogeneous catalyst for hydrogen evolution. iScience 24, 102728. https://doi.org/10.1016/j.isci.2021.102728.

31. Zvornik-Walters, C.E., Heathman, S., and Kimczuk, T. (2013). Pressure-induced phase transitions in LaTe (Ln=La, Gd, Ho, Yb) and AmTe. J. Phys. Condens. Matter 25, 265401. https://doi.org/10.1088/0953-8984/25/26/265401.

32. Treindl, A., and Wachter, P. (1977). Raman Spectra of GdS, GdSe, GdTe and LaTe: Phonon Density of States in Fcc Metals. Phys. Lett. 64, 147–150. https://doi.org/10.1016/0031-9163(77)90559-X.

33. Lei, S., Lin, J., Zhang, G., Mapp, A., Farahi, G., Klemens, S., Gao, T., Rodolakis, F., McChesney, J.L., et al. (2020). High mobility in a van der Waals layered antiferromagnetic metal. Sci. Adv. 6, eaay4607. https://doi.org/10.1126/sciadv.aay4607.

34. Mahmood, J., Li, F., Jung, S.-M., Okay, M.S., Ahmad, I., Kim, S.-J., Park, N., Jeong, H.Y., and Baek, J.-H. (2017). Atomically confined calcium in nitrogen-doped graphene as a universal ruthenium-based catalyst for the hydrogen evolution reaction. Nat. Nanotechnol. 12, 441–446. https://doi.org/10.1038/nnano.2016.304.

35. Li, Z., Zhang, H.Y., Ren, L.L., Lu, Q.B., Ren, X., Zhang, C.H., Wang, Y.F., Lin, S.H., Zhang, X.A., Li, J., et al. (2021). Phosphorus-modified ruthenium-tellurium dendritic nanotubes outperform platinum for alkaline hydrogen evolution. Nat. Commun. 12, 5026–5032. https://doi.org/10.1038/s41467-020-17008-9.

36. Subbaraman, R., Tripkovic, D., Strmcnik, D., Chang, K.-C., Uchimura, M., Paulikas, A.P., Stamencev, V., and Markovic, N.M. (2011). Enhancing hydrogen evolution activity in water splitting by tailoring Li +/Ni(OH)4- Pt interfaces. Science 334, 1256–1260. https://doi.org/10.1126/science.1211934.

37. Franceschina, E.A., Lacconi, G.I., and Corti, H.R. (2015). Kinetics of the hydrogen evolution on nickel in alkaline solution: new insight from rotating disk electrode and impedence spectroscopy analysis. Electrochim. Acta 159, 210–218. https://doi.org/10.1016/j.electacta.2015.01.110.

38. Oh, A., Sa, J.Y., Hwang, H., Baik, H., Kim, J., Kim, B., Joo, S.H., and Lee, K. (2016). Rational design of Pt–N–Co ternary alloy nanoframe electrocatalysts for cobalt reduction reaction in dye-sensitized solar cells. Nano Energy 30, 867–876. https://doi.org/10.1016/j.nanoen.2016.09.001.

39. Amberger, A., Lopez, I., Ehlke, B., Barnett, J., Zhao, Y.K., Allen, A., and Oliver, S.R.J. (2022). Aluminum nanoparticles from a Ga-Al composite for water splitting and hydrogen generation. ACS Appl. Nano Mater. 5, 2636–2643. https://doi.org/10.1021/acsanm.1c04331.

40. Wang, W., Zhao, X.M., Chen, D.M., and Yang, K. (2012). Insight into the reactivity of Al-Ga-in-Sn alloy with water. Int. J. Hydrogen Energy 37, 2187–2194. https://doi.org/10.1016/j.ijhydene.2011.10.058.

41. Kwon, J., Han, H., Jo, S., Choi, S., Chung, K.Y., Ali, G., Park, K., Paik, U., and Song, T. (2021). Amorphous nickel–iron borophosphate for a robust and efficient oxygen evolution
51. Wang, B., Zhou, L.-L., Huang, Z.-Q., Pan, D.-S., Guo, Z.-H., and Song, J.-L. (2021). In situ construction of N-doped amorphous CoFe selenites toward efficient electrocatalytic water oxidation. J. Power Sources 483, 229196. https://doi.org/10.1016/j.jpowsour.2020.229196.

52. Bale, C.W., Bélisle, E., Chartrand, P., Decterov, S.A., Eriksson, G., Gheribi, A.E., Hack, K., Jung, I.-H., Kang, Y.-B., Melançon, J., et al. (2016). FactSage thermochemical software and databases, 2010–2016. Calphad 54, 35–53. https://doi.org/10.1016/j.calphad.2016.05.002.

53. Kresse, G., and Hafner, J. (1993). Ab-initio molecular dynamics for liquid metals. Phys. Rev. B 47, 558–561. https://doi.org/10.1103/PhysRevB.47.558.

54. Perdew, J.-P., Burke, K., and Ernzerhof, M. (1996). Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868. https://doi.org/10.1103/PhysRevLett.77.3865.

55. Jain, A., Ong, S.-P., Hautier, G., Chen, W., Richards, W.-D., Dacek, S., Cholia, S., Gunter, D., Skinner, D., Ceder, G., and Persson, K.-A. (2013). The materials project: a materials genome approach to accelerating materials innovation. Apl. Mater. 1, 011002. https://doi.org/10.1063/1.4812323.

56. Kumar, R., Das, D., and Singh, A.-K. (2018). C2N/WS2 van der Waals type-II heterostructure as a promising water splitting photocatalyst. J. Catal. 359, 143–150. https://doi.org/10.1016/j.jcat.2018.01.005.

57. Hinnemann, B., Moses, P.-G., Bonde, J., Jørgensen, K.P., Nielsen, J.-H., Horch, S., Chorkendorff, I., and Nørskov, J.K. (2005). Biomimetic hydrogen evolution: MoS2 nanoparticles as catalyst for hydrogen evolution. J. Am. Chem. Soc. 127, 5308–5309. https://doi.org/10.1021/ja0504690.

58. Medford, A.-J., Vojvodic, A., Hummelshøj, J.S., Voss, J., Abild-Pedersen, F., Studt, F., Bligaard, T., Nilsson, A., and Nørskov, J.K. (2015). From the sabatier principle to a predictive theory of transition-metal heterogeneous catalysis. J. Catal. 328, 36–42. https://doi.org/10.1016/j.jcat.2014.12.033.

59. Hammer, B., and Norskov, J.K. (1995). Why gold is the noblest of all the metals. Nature 376, 238–240. https://doi.org/10.1038/376238a0.
STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCES | SOURCE | IDENTIFIER |
|----------------------|--------|------------|
| **Chemicals, Peptides, and Recombinant Proteins** | | |
| Gd | Sigma-Aldrich | 7440-54-2 |
| Te | Sigma-Aldrich | 13494-80-9 |
| **Software and algorithms** | | |
| Vienna Ab-initio Simulation Package (VASP) | Vasp software GmBH, http://www.vasp.at/ | Version 5.4.4 |
| d-band center | Vaspkit(http://vaspkit.com/) | Key 503 |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Chandra S. Tiwary (chandra.tiwary@metal.iitkgp.ac.in).

Materials availability
This study did not generate new unique reagents.

Data and code availability
All data reported in this paper will be shared by the lead contact upon request. This study does not generate a new code. Any additional information required to reanalyze the data reported in this study is available from the lead contact upon request.

METHOD DETAILS

Synthesis of GdTe
GdTe was obtained via the vacuum induction melting route. Stoichiometric amounts of 99.99% pure gadolinium and tellurium were taken in a quartz tube. The metals were melted at a temperature of 1500°C under vacuum conditions and cooled by quenching to room temperature using Argon. Although the melting point of GdTe is 1825°C, a lower temperature was sufficient because the high vacuum conditions of 1 x 10^-5 mbar inside the furnace reduces the melting point of the metals and the compound. Hydrogen evolution reaction started immediately after contact with the atmosphere. Thus, the samples were stored under a vacuum. While handling the samples, they were immersed in ethanol to reduce interaction with ambient water vapor.

Characterization
The GdTe polycrystals obtained were powdered and XRD patterns were obtained using a Bruker D8 Advance Diffractometer with Cu-Kα (λ = 1.5406 Å) radiation and characterized based on the Pearson’s Crystal Database. Room temperature Raman spectroscopy was done using WITec UHTS Raman Spectrometer (UHTS 300 VIS, Germany) at a laser excitation wavelength of 532 nm. UV-Visible Spectroscopy was used to study the optical absorbance.

Hydrogen production measurement
The material was enclosed in a glass vial, and gas inside the vial was taken as a blank gas sample. Deionized water (1 ml) was added to the glass vial, and gas evolution was analyzed in a specified time interval. GdTe reacted with water immediately at room temperature and produced gas bubbles on the surface of the GdTe sample in the glass vial. Quantitative analyses of the product were carried out to corroborate the hypothesis of Hydrogen production and to determine the number of moles of gas produced. High precision gas-tight syringe was used to transfer the evolved gases into a gas chromatograph (GC; Dhrueva CIC Baroda) during the experiment. Thermal Conductivity Detector (TCD) was used for H₂ detection and quantification. The Standard gas mixture was used for GC Calibration. 1 gm of GdTe produced more than 1.87 μmol of Hydrogen within 30 minutes. The H₂ generation reaches saturation within 30 min, whereas
for Gd in water, Hydrogen production occur but comparatively very less to GdTe and didn’t attend saturation even after 1380 minutes (23 hours) of experiment.

We also note at the early stage, around ~5 min, during which the H₂ evolution rate is linearly increased. We observed a steady H₂ evolution rate of ~0.02205 μmol min⁻¹gm⁻¹ for GdTe and 0.0011 μmol min⁻¹gm⁻¹ for Gd in water.

**Thermodynamic calculation**

In order to ascertain the reactivity of GdTe with water, thermodynamic calculations were performed using FactSage 8.1 thermodynamic software. FactPS and FT helium databases were selected for the calculations which contain the optimized Gibbs energy parameters for the pure stoichiometric phases (Gd, Te, GdTe, Gd₂Te₃, Gd₂O₃), gas and aqueous phases. In the calculations, 1 mole of GdTe was reacted with varying H₂O and the reaction products were plotted as a function of varying H₂O. Similarly, 1 mol of water was reacted with varying GdTe and the reaction products were plotted as well. Both these sets of calculations aided in deducing the reaction products formed during the reaction of GdTe with water.

**DFT calculation**

Density functional theory (DFT) were done with Vienna ab initio simulations (VASP) package. The electron-ion interactions were described using all-electron projector augmented wave pseudopotentials, and Perdew-Bruke-Enzehof (PBE) generalized gradient approximation (GGA) was used to approximate the electronic exchange and correlations. The plane-wave kinetic energy cut off of 520 eV was used. All the structures were optimized using a conjugate gradient scheme until the energies, and the components of forces reached 10⁻⁶ eV and 0.001 eV Å⁻¹ for bulk GdTe and 10⁻⁵ and 0.01 eV Å⁻¹ for all the surfaces respectively. A vacuum region of 10 Å was added in the z-direction to prevent interactions between the periodic images. The Brillouin zone of bulk GdTe, (100), (110), (111), and (211) planes were sampled with 7 x 7 x 7 Monkhorst-Pack.

Density of states (DOS) calculations for planes were performed by sampling the Brillouin zone with 7 x 7 x 7 Monkhorst-Pack. Band center was calculated by considering the first moment of d-states for Gd atoms and p-states for Te atoms. All the calculations were spin-polarized.

Posterior to the electronic and lattice optimization of the bulk GdTe structure, taken from Materials Project database: mp-574283, different surfaces, namely (100), (110), (111) and (211) were created each of them having 4 layers. Afterward, 2 x 2 x 1 supercell of each considered surfaces was created followed by electronic optimization. (100), (110), and (111) surfaces can adsorb H on either Gd or Te atom. However, for (211) surface, it can allow H to adsorb on 5 different positions, namely Gd and Te atoms on step, terrace and only Gd atom on corner site as adsorbed H on Te atom diffuses on top of Gd atom after optimization.

HER consist of two elementary steps:

\[ \text{H}^+ + \text{e}^- \rightarrow \text{H} \]  
\[ \text{H}^+ + \text{H} + \text{e}^- \rightarrow \text{H}_2 \]

The adsorption energy of the H⁺ intermediate involved in HER was calculated from the DFT using the following expression:

\[ \Delta E_{\text{ads}} = E_{\text{H}^+} - E_i - \frac{1}{2}E_{\text{H}_2} \]  

where, * represents a pristine GdTe surface, and the * superscript denotes that hydrogen is adsorbed on the GdTe surface. The intermediate adsorption energy was converted into Gibb’s free energy of adsorption using the following:

\[ \Delta G_{\text{ads}} = \Delta E_{\text{ads}} + \Delta \text{ZPE} - T \Delta S - \Delta G_U \]  

where, ∆ZPE is the difference in zero-point energies, ∆S is the change in entropy due to vibrational contributions, and ∆G_U = -e_U, where U is the applied electrode potential. The values of (∆ZPE-T∆S) for the reference molecule (H₂ gas) is 0.1328 eV. Calculated values of adsorption energies, (∆ZPE-T∆S), free energies of hydrogen adsorption are given in Table S1.
The goal is to find optimal stability of H* on the surface that agrees with the Sabatier principle. Hinnemann et al. confirmed that $\Delta G_0^0 = 0$ is a good descriptor for materials acting as material for hydrogen evolution. $^{28}$

The overall surface activity is given by $\frac{\sum \Delta G_0^0(n)}{n}$, where $\sum \Delta G_0^0(n)$ is the total free energy of hydrogen adsorption in (n) number of different sites for a particular surface.

Band center and DOS have already been established to be good descriptors for correlating materials and their HER catalytic activity. As the number of states of a particular adsorption site increases in the energy range of H states, interaction between them rises and consequently, adsorption energy increases.

The d-band center model has been used extensively to understand the role of d-electrons in bonding with the adsorbates by Norskov et al. $^{39}$ According to this model, the d-band center of the adsorbent being in close in energy with respect to the Fermi energy enhances the bond stability with adsorbate, having more electrons in the bonding state and less electrons in the bonding state the antibonding state, as shown in Table S1.

**QUANTIFICATION AND STATISTICAL ANALYSIS**

**Calculation of hydrogen production**

Quantitative analysis of the product (number of moles of gas produced) was carried out to corroborate the hypothesis of Hydrogen production by calibration with standard mixture of gas. Amount of hydrogen generated in headspace, and the gas was injected in Gas Chromatography instrument, no. of moles is given corresponding to 1 mL of injected gas.

**Calculation of number of moles**

1 mL of the calibration standard gas of different concentration was injected in TCD equipped with Gas Chromatography instrument and the areas of different peaks of the gases were noted and Calibration curve was plotted w.r.t. their corresponding no. of moles. These values were used to find out the moles of gas of our injected gas of interest (Hydrogen in this case).

1 mL of the standard mixture was injected.

| PV = nRT | P = 1 atm, T = 298 K |
|----------|----------------------|
| 1 x V = 1 x .0821 x 298 | $R = 0.0821 \text{ Latm/molK (universal gas constant)}$ |
| V = 24.45 L | $n =$ no. of mole |

So total no. of moles in 24.45 L is 1 mole

Or, no. of moles in 1 ml is $4.089 \times 10^{-5}$

A Calibration plot was plotted for different known concentration, and by fitting with linear curve a calibration equation was obtained. The calibration equation was used to calculate the moles of unknown concentration.

e.g., standard mixture contains 2 % of H$_2$ gas, i.e. 20,000 ppm

So, Total no. of moles of H$_2$ in 1ml = total no. of moles in 1ml $\times$ 20000 $\times$ 10$^{-6}$

$= 8.178 \times 10^{-7}$ mole

The area corresponding to Standard is defined as $A_{calib}$.

So, no. of moles of experiment ($A_{exp}$) can be calculated by putting unknown gas area in the linear equation.

Similarly, The rate of hydrogen production:
The rate of hydrogen production / minute gram of GdTe was calculated from initial data taken from linear fitting curve of calculated mole of Hydrogen vs time. Slope of the curve was rate of reaction, i.e. 0.022 μmol min\(^{-1}\) gm\(^{-1}\).

Total no. of moles of H\(_2\) in 0.5ml = total no. of moles in 0.5ml × 100000 × 10\(^{-6}\)

= 0.0000204367 × 100000 × 10\(^{-6}\) = 20.4367 × 10\(^{-6}\)

= 2.04367 micro moles

So total moles of H\(_2\) produced is = 11386737 × 2.04367 / 7257359

= 3.206501539 μmol.