Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

The structural, energetic and dehydrogenation properties of pure and Ti-doped Mg(0001)/MgH_2(110) interfaces

Bo Han[1], Yuxiao Jia[2], Jianchuan Wang[1,*], Xuezhang Xiao[2], Lixin Chen[2], Lixian Sun[3], Yong Du[1]

1 State Key Laboratory of Powder Metallurgy, Central South University, 410083, Changsha, China

2 State Key Laboratory of Silicon and Advanced Semiconductor Materials, School of Materials Science and Engineering, Zhejiang University, 310027, Hangzhou, China

3 Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, 541004, Guilin, China

Surface model and properties

For MgH_2(110) surface, we considered three stoichiometric slabs with different termination (see Fig. S1): H1-terminated surface exposed by a H atomic layer, H2-terminated surface exposed by two atomic H layers and Mg/H-terminated surface exposed by a layer including Mg atoms and H atoms. A vacuum thickness of 15 Å along the c direction was added. By testing the surface energy with respect to atomic layer, we choose the MgH_2(110) surface and Mg(0001) surface with six H−Mg−H trilayers and six Mg layers, respectively. The first three layers of the slab were allowed to relax while the bottom three layers were kept fixed to the bulk positions.

Surface energy (σ) can be used to reflect the stability of surface, the smaller σ is, the more stable surface is. The σ_{Mg} and $\sigma_{\mathrm{MgH_2}}$ were calculated by Eq. (S1) and Eq. (S2), respectively:

$$\sigma_{\mathrm{Mg}} = \frac{1}{2A_{\mathrm{s}}}\left[E_{\mathrm{slab}}^{\mathrm{Mg}} - n\mu_{\mathrm{Mg}}\right] \quad \text{(S1)}$$

$$\sigma_{\mathrm{MgH_2}} = \frac{1}{2A_{\mathrm{s}}}\left(E_{\mathrm{slab}}^{\mathrm{MgH_2}} - n'\mu_{\mathrm{MgH_2}}\right) \quad \text{(S2)}$$

where $E_{\mathrm{slab}}^{\mathrm{Mg}}$ and $E_{\mathrm{slab}}^{\mathrm{MgH_2}}$ are the total energy of the Mg slab and MgH_2 slab, respectively. μ_{Mg} and $\mu_{\mathrm{MgH_2}}$ are chemical potential of Mg and MgH_2. n and n' are the number of Mg atoms and the number of MgH_2 formula unit in the surface slab, respectively, and A_{s} is the area of the surface. Equations (S1) and (S2) are applicable to the stoichiometric surface.

The calculated surface energies are 0.476, 1.858, and 1.860 J/m^2 for H1-terminated, H2-terminated and MgH-terminated MgH_2 (110) surface, respectively. Moreover, the surface energy of H1-terminated MgH_2(110) agrees well with the calculated value of 0.509 J/m^2 by Hao and Sholl[1]. Thus, the H1-terminated MgH_2(110) surface was the most stable MgH_2(110) surface and hence adopted to constructed the Mg/MgH_2 interface model. For Mg(0001), its surface energy is 0.55 J/m^2, which is in good accordance with the experimental value of 0.78 J/m^2 and other theoretical calculated value of 0.53 J/m^2 [2].

For Ti-doped MgH_2 slab, it is a nonstoichiometric surface. The surface energy of the Ti-doped MgH_2 slab $\sigma_{\mathrm{Ti-MgH_2}}$ is calculated by

$$\sigma_{\mathrm{Ti-MgH_2}} = \frac{1}{2A_s}(E_{\mathrm{slab}}^{\mathrm{Ti-MgH_2}} - n_{\mathrm{Mg}}\mu_{\mathrm{Mg}} - n_{\mathrm{H}}\mu_{\mathrm{H}} - n_{\mathrm{Ti}}\mu_{\mathrm{Ti}}) \quad \text{(S3)}$$

where $E_{\mathrm{slab}}^{\mathrm{Ti-MgH_2}}$ is the total energy of the Ti-doped MgH_2 slab, n_{Mg}, n_{H} and n_{Ti} are the number of Mg, H and Ti atoms in the surface slab, respectively, μ_{Mg}, μ_{H} and μ_{Ti} are the chemical potentials of Mg, H and Ti, respectively. Meanwhile, the chemical potential of Mg and H in equilibrium with bulk MgH_2 must hold that:

$$\mu_{\mathrm{MgH_2}}^{\mathrm{Bulk}} = \mu_{\mathrm{Mg}} + 2\mu_{\mathrm{H}} \quad \text{(S4)}$$

By substituting Eq. (S4) into Eq. (S3), the surface energy can be expressed as Eq. (S5):

$$\sigma_{\mathrm{Ti-MgH_2}} = \frac{1}{2A_s}(E_{\mathrm{slab}}^{\mathrm{Ti-MgH_2}} - n_{\mathrm{Mg}}\mu_{\mathrm{MgH_2}}^{\mathrm{Bulk}} + (2n_{\mathrm{Mg}} - n_{\mathrm{H}})\mu_{\mathrm{H}} - n_{\mathrm{Ti}}\mu_{\mathrm{Ti}}) \quad \text{(S5)}$$

In addition, the chemical potential of bulk MgH_2 can also be expressed as Eq. (S6):

$$\mu_{\mathrm{MgH_2}}^{\mathrm{Bulk}} = \mu_{\mathrm{Mg}}^{\mathrm{Bulk}} + 2\mu_{\mathrm{H}}^{\mathrm{Bulk}} + \Delta H_{\mathrm{f}}(\mathrm{MgH_2}) \quad \text{(S6)}$$

where $\Delta H_{\mathrm{f}}(\mathrm{MgH_2})$ is the formation energy of bulk MgH_2, which is calculated as -0.56 eV. It's worth noting that $\mu_{\mathrm{Mg}} - \mu_{\mathrm{Mg}}^{\mathrm{Bulk}} \leq 0$, $\mu_{\mathrm{H}} - \mu_{\mathrm{H}}^{\mathrm{Bulk}} \leq 0$. Combined with Eq. (S6), the range of $\Delta\mu_{\mathrm{H}}$ ($\mu_{\mathrm{H}} - \mu_{\mathrm{H}}^{\mathrm{Bulk}}$) can be obtained:

$$-0.28\ \mathrm{eV} \leq \Delta\mu_{\mathrm{H}} \leq 0 \quad \text{(S7)}$$

Table S1. The calculated lattice parameters for Mg and MgH_2.

	Mg		MgH_2	
	a (Å)	c/a	a (Å)	c (Å)
This work	3.206	1.60	4.487	2.994
Exp	3.209 or 3.203 [3,4]	1.624 or 1.624 [3,4]	4.501 [5]	3.010 [5]
Other DFT	3.175 or 3.177 [6,7]	1.623 or 1.622 [6,7]	4.460 [6]	2.987 [6]

Table S2 The hydrogen removal energy E_r(H) (eV) in the pure and Ti-doped Mg(0001)/MgH_2(110) interfaces. The serial number for H atoms are shown in Fig. 5(a).

H atom	E_{re} (eV)	
	Undoped interface	Ti-doped interface
H1	0.35	0.60
H2	0.47	0.58
H3	0.64	0.82
H4	1.08	1.09
H5	1.17	1.22
H6	1.14	1.23
H7	1.08	1.18

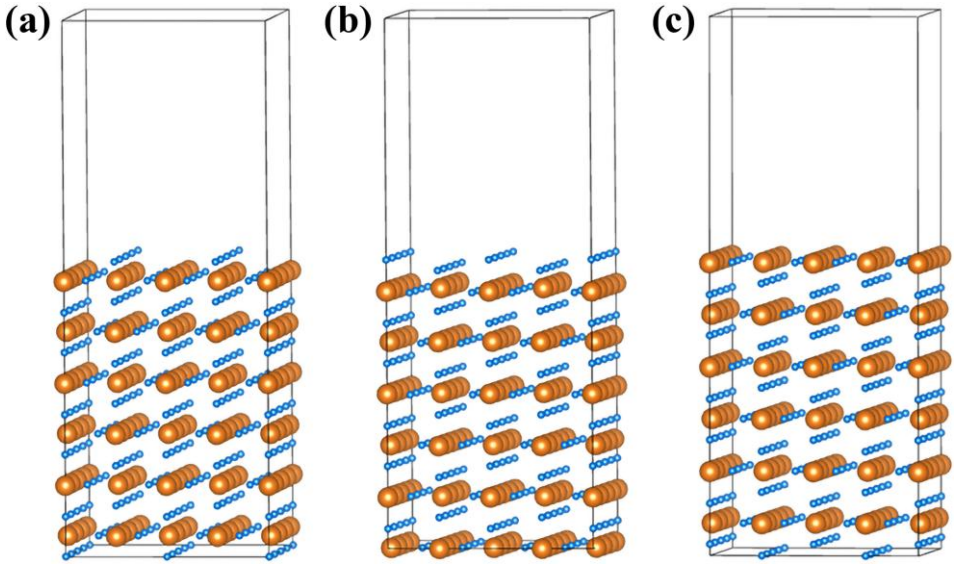

Fig. S1 The atomic structure of (a) H1-terminated (b) H2-terminated and (c) Mg-H terminated MgH_2 (110) slab. Orange and blue spheres represent Mg and H, respectively.

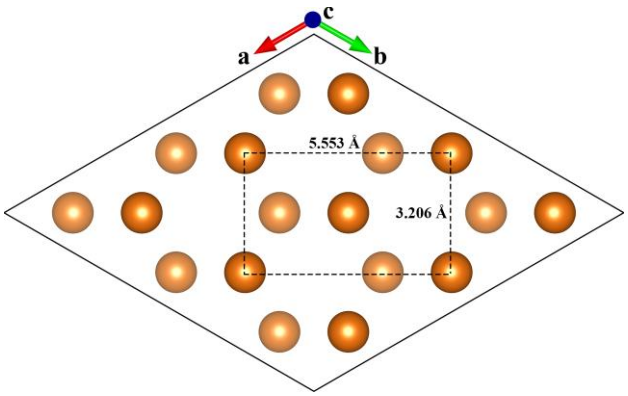

Fig. S2 Schematic diagram of hexagonal structure converted to orthorhombic structure of Mg(0001) surface.

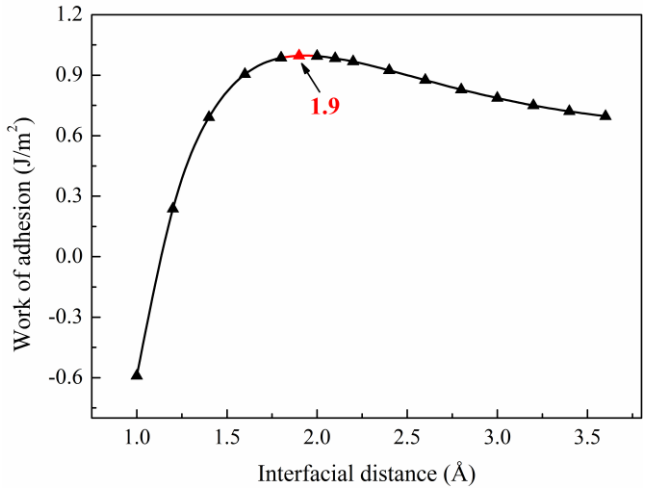

Fig. S3 The work of adhesion as a function of interfacial distance

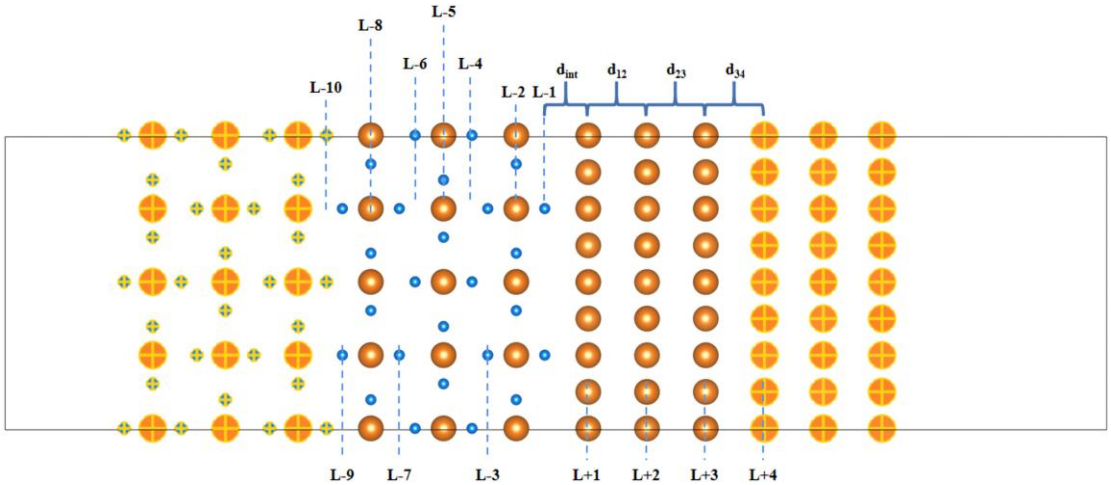

Fig. S4 The labels of atomic layers in the Mg(0001)/MgH_2(110) interface. The atoms with yellow crosses are fixed in the structural optimization.

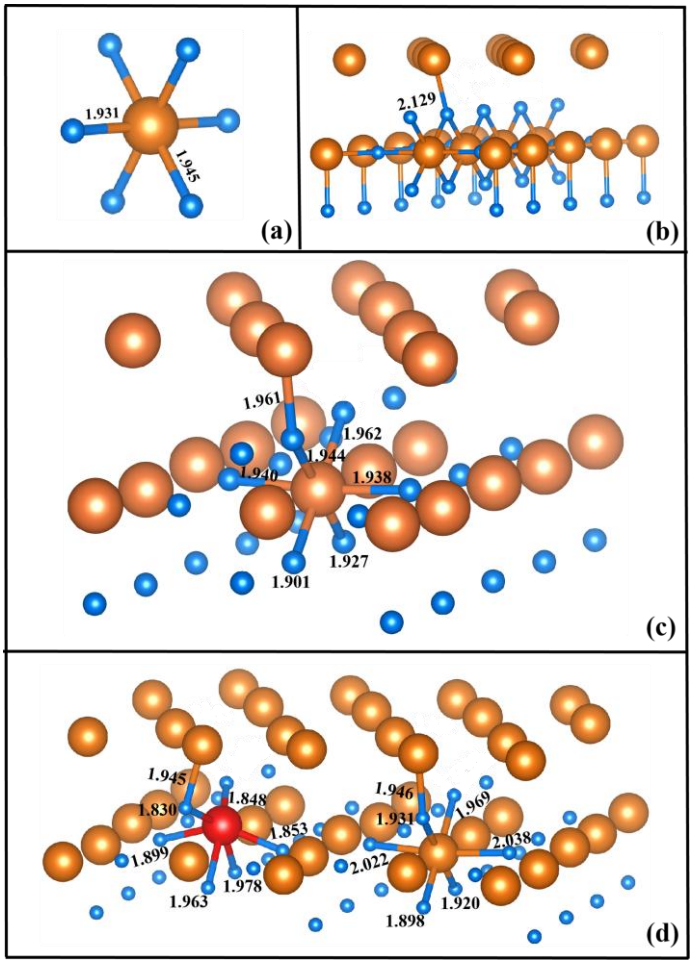

Fig. S5 Bond lengths (in Å) of Mg-H (or Ti-H) in (a) bulk MgH_2, (b) unrelaxed pure Mg(0001)/MgH_2(110) interface, (c) relaxed pure Mg(0001)/MgH_2(110) interface, (d) relaxed Ti-doped Mg(0001)/MgH_2(110) interface. Orange, blue and red balls represent Mg, H and Ti atoms, respectively.

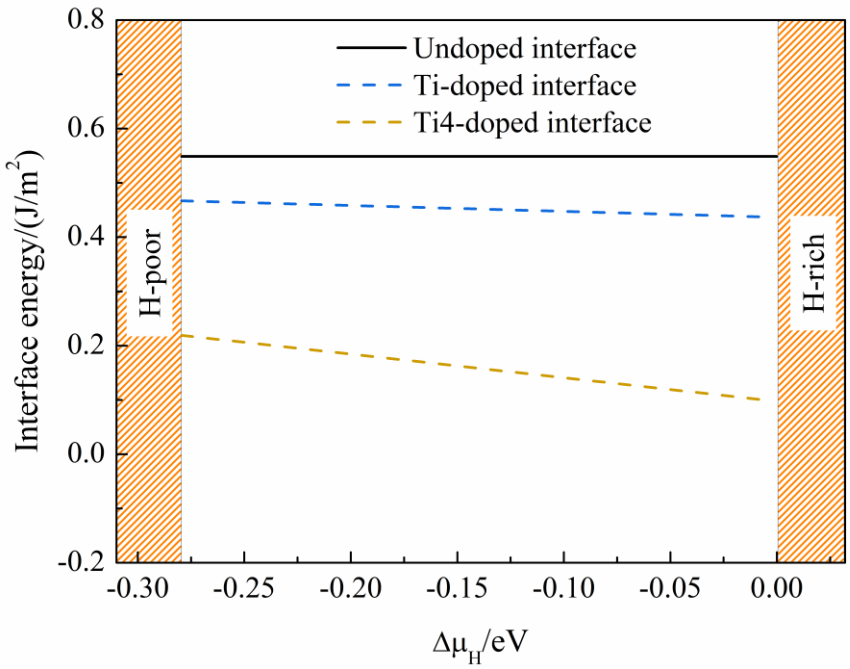

Fig. S6 The interfacial energy as a function of hydrogen chemical potential for the pure, single Ti-doped and four Ti-doped Mg(0001)/MgH_2(110) interfaces.

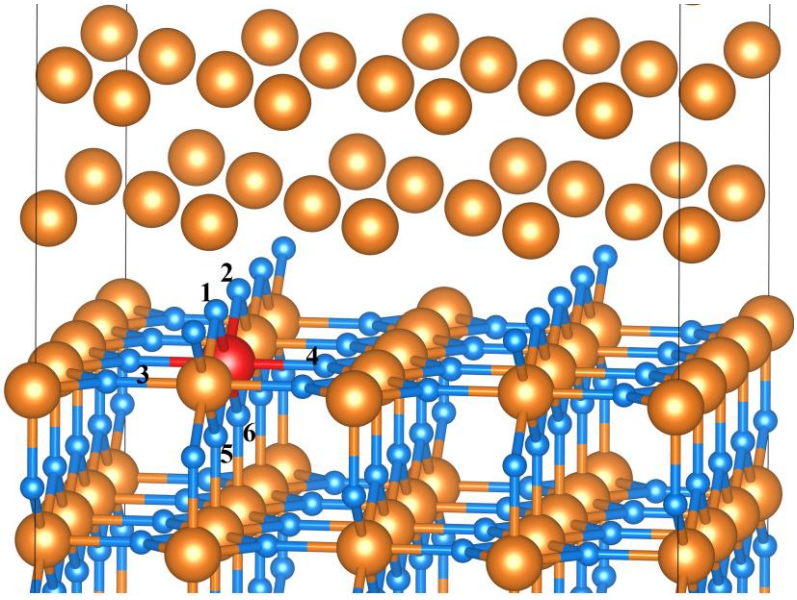

Fig. S7 Three group H atoms (H_1: H1 and H2; H_2: H3 and H4; H_3: H5 and H6) used to the analysis of PDOS.

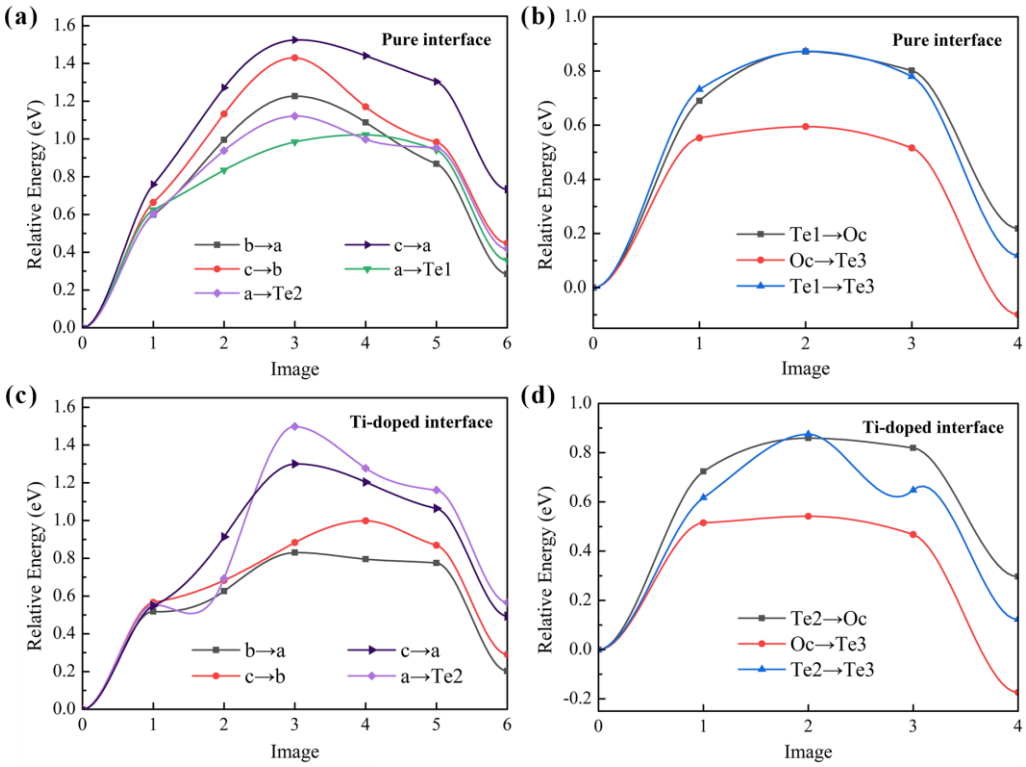

Fig. S8 The diffusion barriers of H along the diffusion paths shown in Fig. 6 in the pure (a and b) and Ti-doped (c and d) Mg(0001)/MgH_2(110) interfaces.

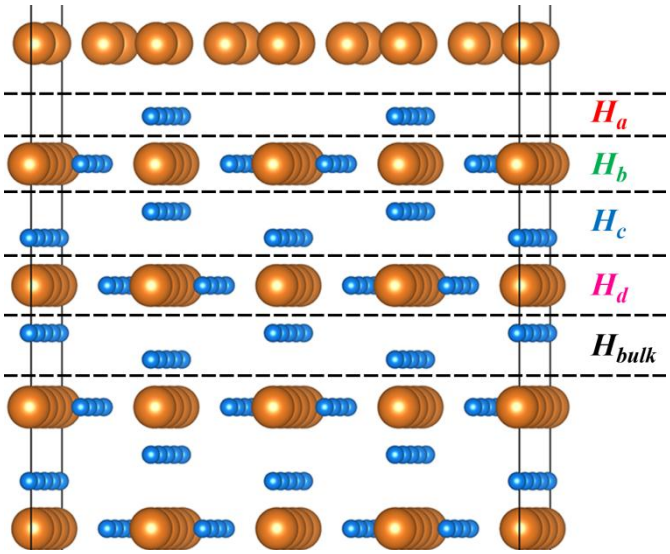

Fig. S9 The classification of H atoms close to the interface. We indicated five groups of these H atoms with H_a, H_b, H_c, H_d and H_{bulk}. Orange and blue spheres represent Mg and H, respectively.

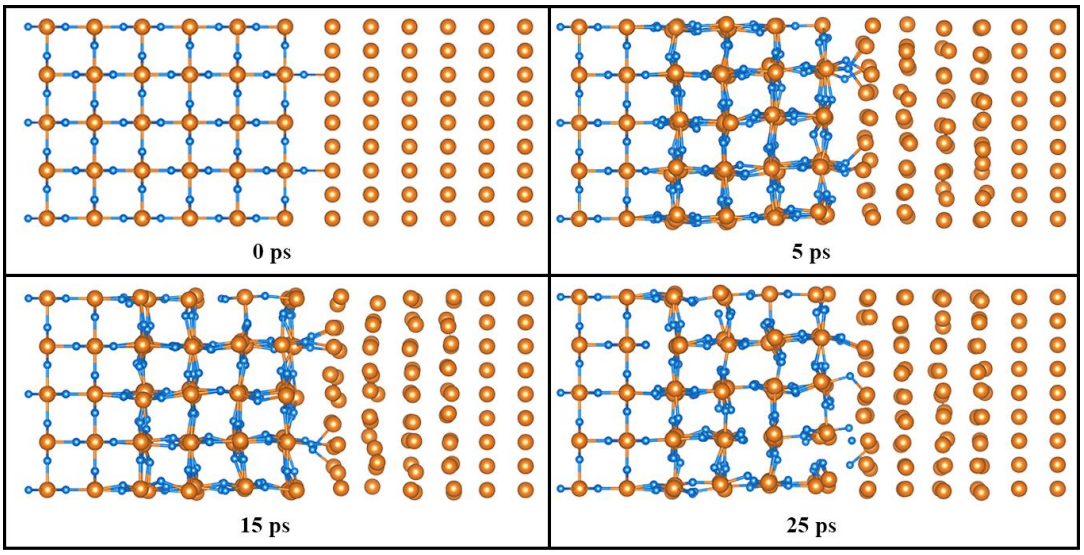

Fig. S10 Snapshots of the pure Mg(0001)/MgH_2(110) interface for T = 600 K at 0 ps, 5 ps, 15 ps and 25 ps. Orange, blue and red spheres denote Mg, H and Ti, respectively.

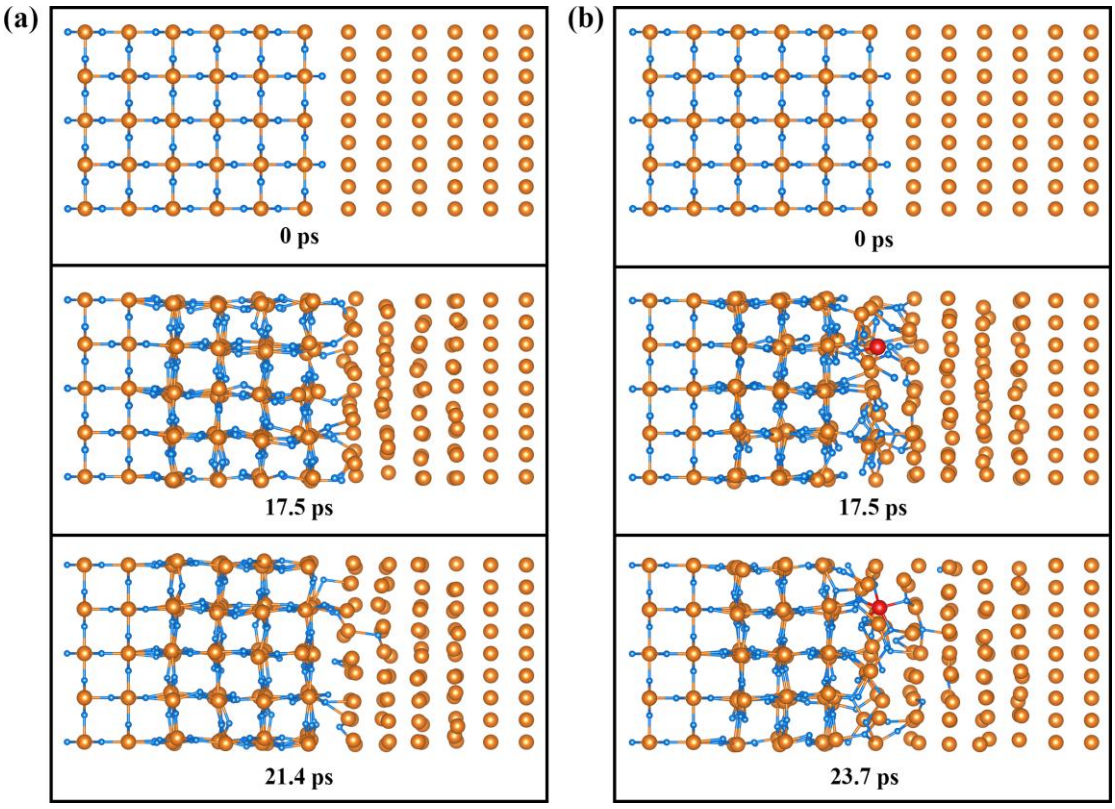

Fig. S11 (a) Snapshots of the pure Mg(0001)/MgH_2(110) interface for T = 800 K at 0 ps, 17.5 ps, and 21.4 ps. (b) Snapshots of the Ti-doped Mg(0001)/MgH_2(110) interface for T = 800 K at 0 ps, 17.5 ps, and 23.7 ps. Orange, blue and red balls denote Mg, H and Ti, respectively.

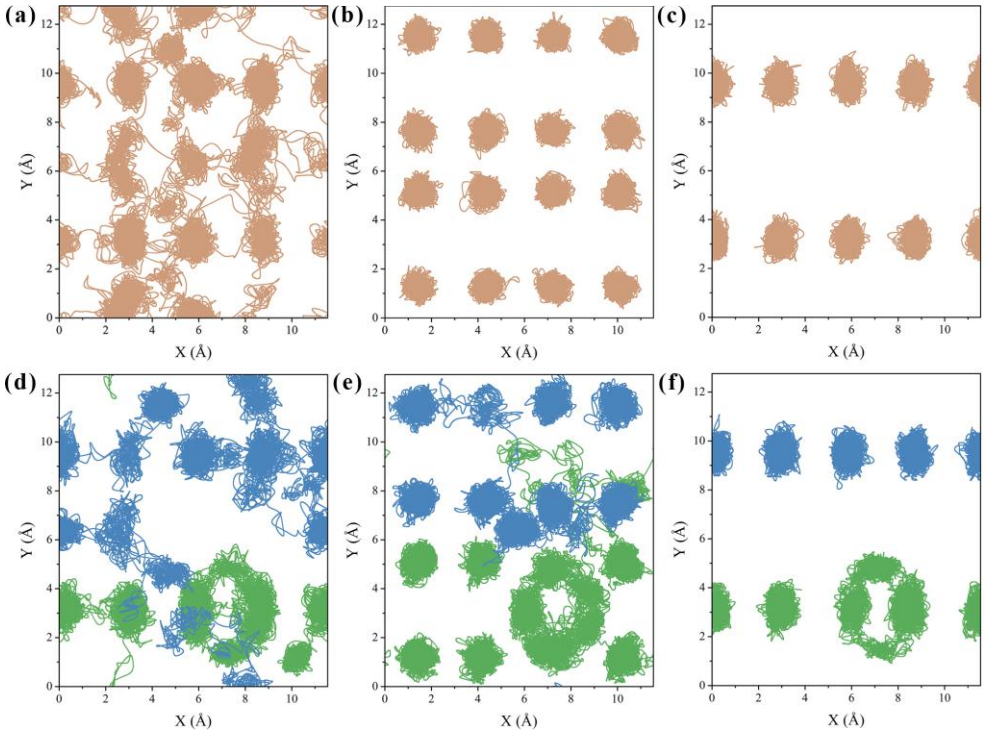

Fig. S12 Two-dimensional trajectories of the three layers of H atoms in the interface plane in (a-c) pure interface and (d-f) Ti-doped interface at 700 K. (a), (b) and (c) represent the trajectories (orange line) of H atoms of the first layer, second layer and third layer, respectively. (d-f) similar to (a-c), but in each layer, the H atoms are divided into two groups based on their distance to Ti atom. Green lines and blue lines show the trajectories of H atoms that are closer to Ti and that are further away from Ti, respectively.

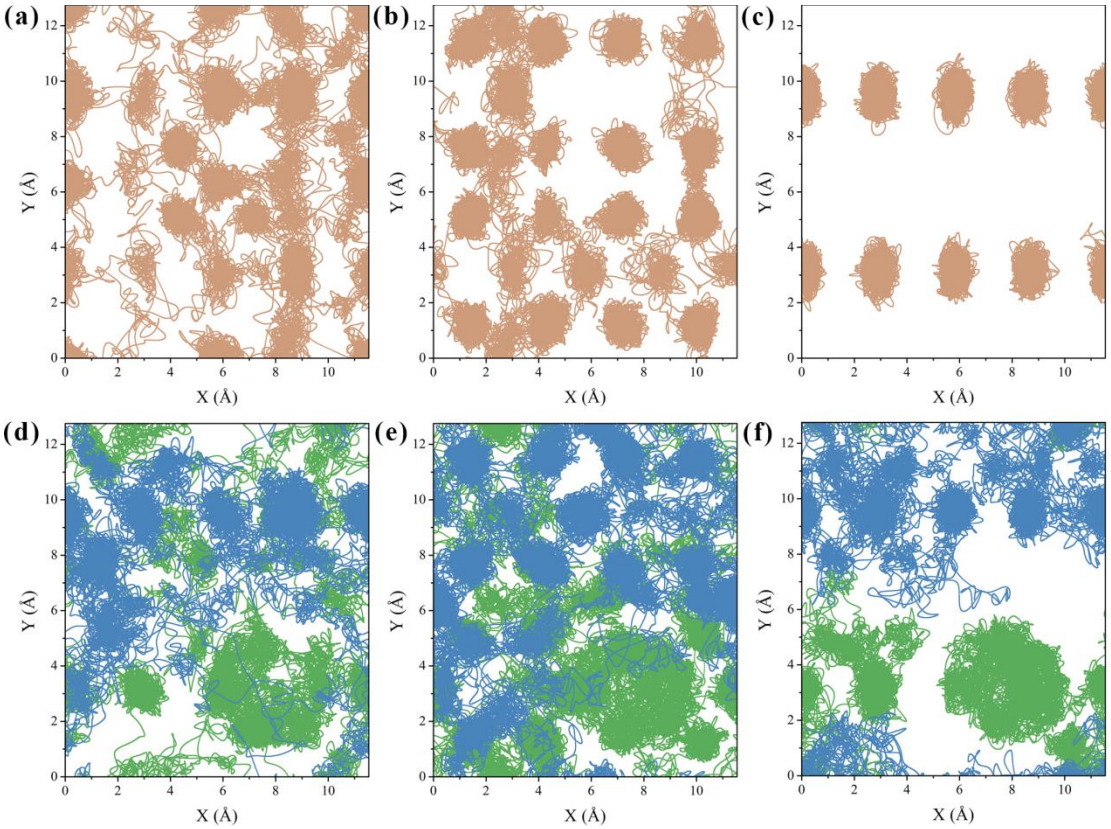

Fig. S13 Two-dimensional trajectories of the three layers of H atoms in the interface plane in (a-c) the pure interface and (d-f) Ti-doped interface at 800 K. (a), (b) and (c) represent the trajectories (orange line) of H atoms of the first layer, second layer and third layer, respectively. (d-f) similar to (a-c), but in each layer, the H atoms are divided into two groups according to their distance to Ti atom. Green lines and blue lines show the trajectories of H atoms that are closer to Ti and that are further away from Ti, respectively.

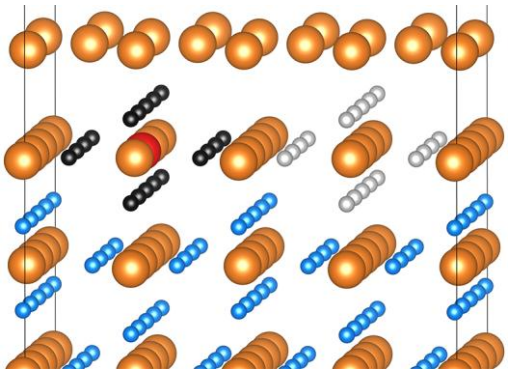

Fig. S14 The classification of the three layers of H atoms at the interface. The black and grey small balls represent the H atoms closer to Ti and further away from Ti, respectively. Orange, red and blue balls denote Mg, Ti and H in other layers, respectively.

References

1 S. Hao and D. S. Sholl, *J. Phys. Chem. C*, 2012, **116**, 2045-2050.

2 E. Zuo, X. Dou, Y. Chen, W. Zhu, G. Jiang, A. Mao and J. Du, *Surface Science*, 2021, **712**, 121880.

3 G. B. Walker and M. Marezio, *Acta Metall.*, 1959, **7**, 769-773.

4 M. E. Straumanis, *J. Appl. Phys.*, 1949, **20**, 726-734.

5 M. Bortz, B. Bertheville, G. Böttger and K. Yvon, *J. Alloys Compd.*, 1999, **287**, L4-L6.

6 S. A. Shevlin and Z. X. Guo, *J. Phys. Chem. C*, 2013, **117**, 10883-10891.

7 B.-C. Zhou, S.-L. Shang, Y. Wang and Z.-K. Liu, *Acta Mater.*, 2016, **103**, 573-586.