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Supporting Information for:

Fabrication of amorphous TiO_2 hydrogen channels and graphene wrappers to enhance hydrogen storage properties of MgH_2 with extremely high cycle stability

*Fanqi Bu [a],Ali Wajid [b], Na Yang [a], Mengyue Gu [a], Xuewen Zhao [a], Lei Huang [a], Xin Ji [a], Shujiang Ding [b], Yonghong Cheng [a], Jinying Zhang [a] **

[a] State Key Laboratory of Electrical Insulation and Power Equipment, Center of Nanomaterials for Renewable Energy (CNRE), School of Electrical Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, PR China

[b] School of Chemistry, Xi'an Key Laboratory of Sustainable Energy Materials Chemistry, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China

** Corresponding author: Email：jinying.zhang@mail.xjtu.edu.cn*

Material characterizations

Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and elemental mapping were acquired by Lorenz Transmission Electron Microscope (Talos F200X). Scanning electron microscopy (SEM) images were recorded by Quanta 250FEG equipment. X-ray diffraction (XRD) patterns were obtained from a Bruker D2 PHASER using Cu/Kα radiation (λ =1.5418Å) at 40 kV and 30 mA. Ar plasma etching was obtained by NanoClean Model 1070 at 44.4 W for different times (40 s and 120 s). X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Thermo Fisher ESCALAB spectrometer. The hydrogen storage properties of MgH_2-based materials were tested using a homemade HPSA-auto apparatus.[1] About 50 mg of the sample was taken for dehydrogenation/cycling and 100 mg for rehydrogenation tests. Temperature programmed desorption (TPD) was tested from 100°C to 400°C at a rate of 3 °C/min. The isothermal desorption kinetic properties of the samples were tested at different temperatures (225, 250, 275, and 300°C) under starting hydrogen pressures below 0.05 bar. Similarly, the isothermal hydrogen absorption kinetic properties of the samples were tested at different temperatures (50, 100, 150, and 200°C) under 30 bar H_2. The isothermal dehydrogenation (0.05 bar H_2) and rehydrogenation (30 bar H_2) tests of the samples were performed repeatedly at 300°C for the cycling test.

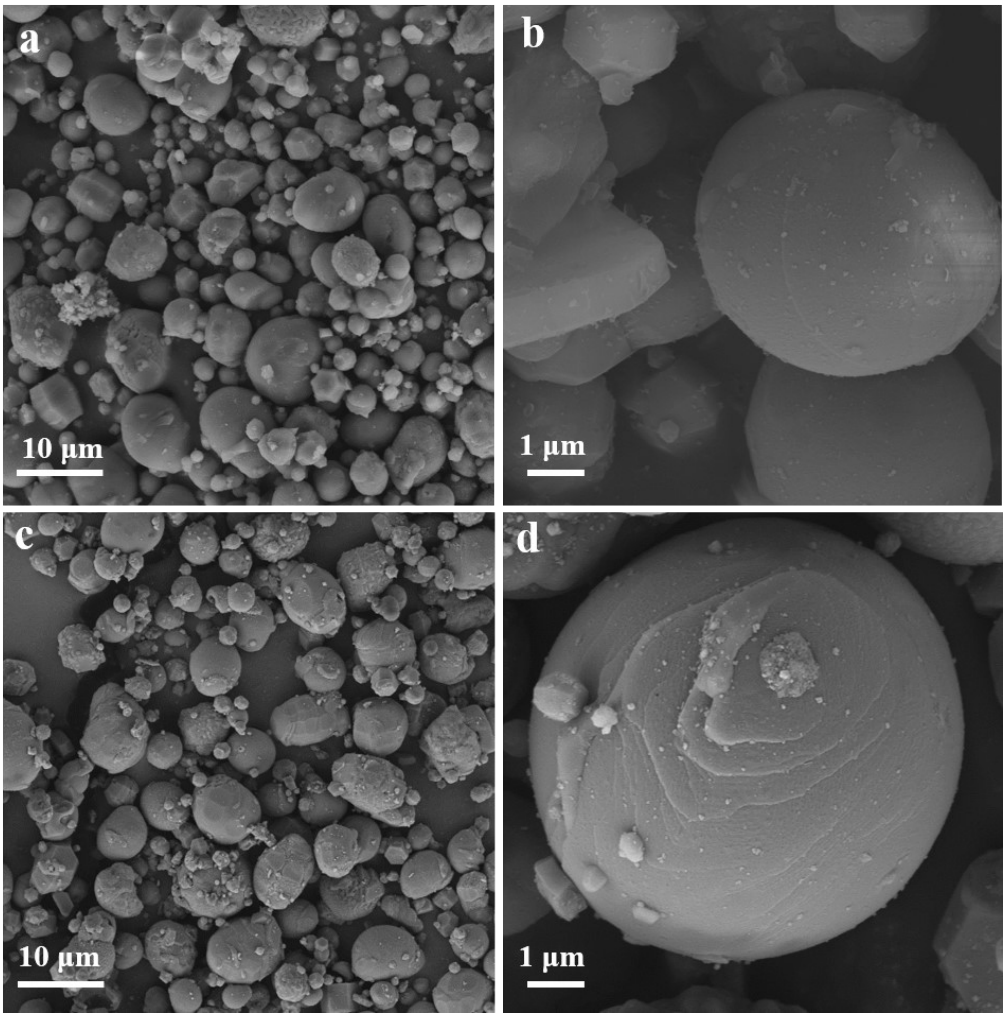

Figure S1. SEM images of (a, b) commercial MgH_2 and (c, d) MgH_2@10nmTiO_2 at different scales.

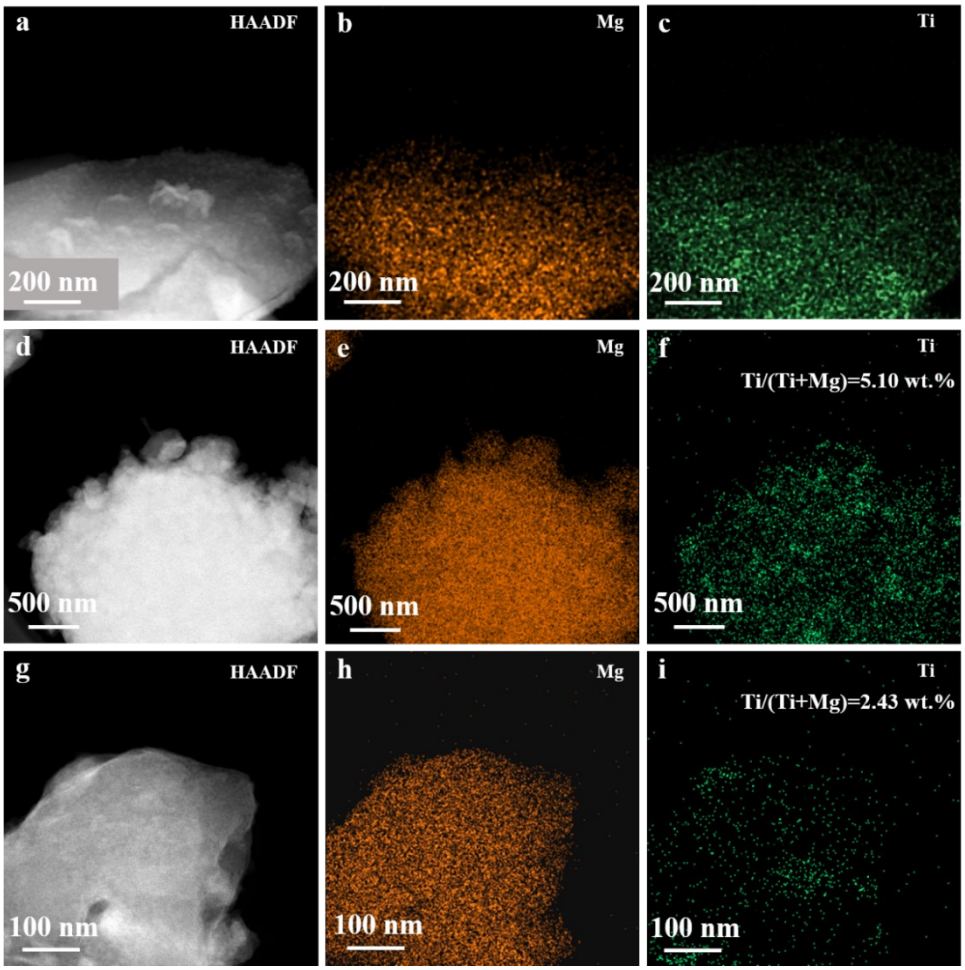

Figure S2. HAADF-STEM images and elemental mapping analysis of MgH_2-20nmTiO_2 (a-c) before and after (d-f) 40 s, and (g-i) 120 s of Ar plasma etching.

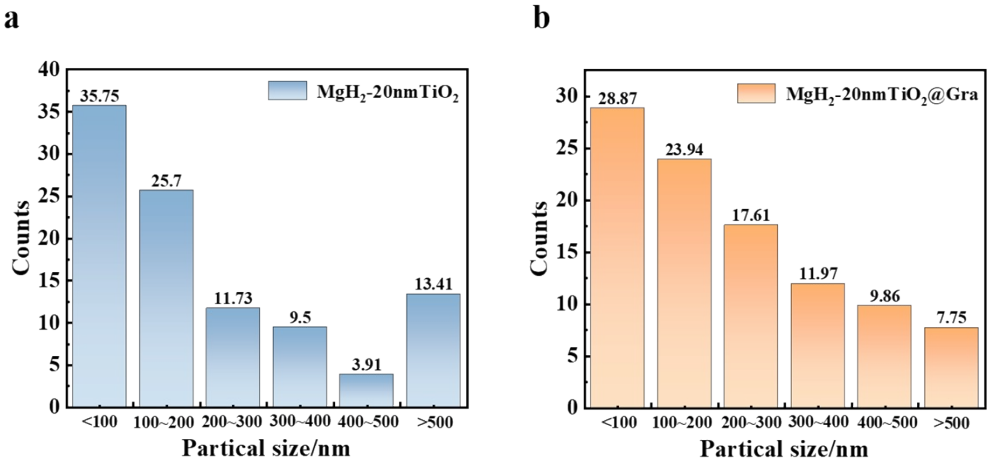

Figure S3. Partical size distribution of (a) MgH_2-20nmTiO_2 and (b) MgH_2-20nmTiO_2@Gra.

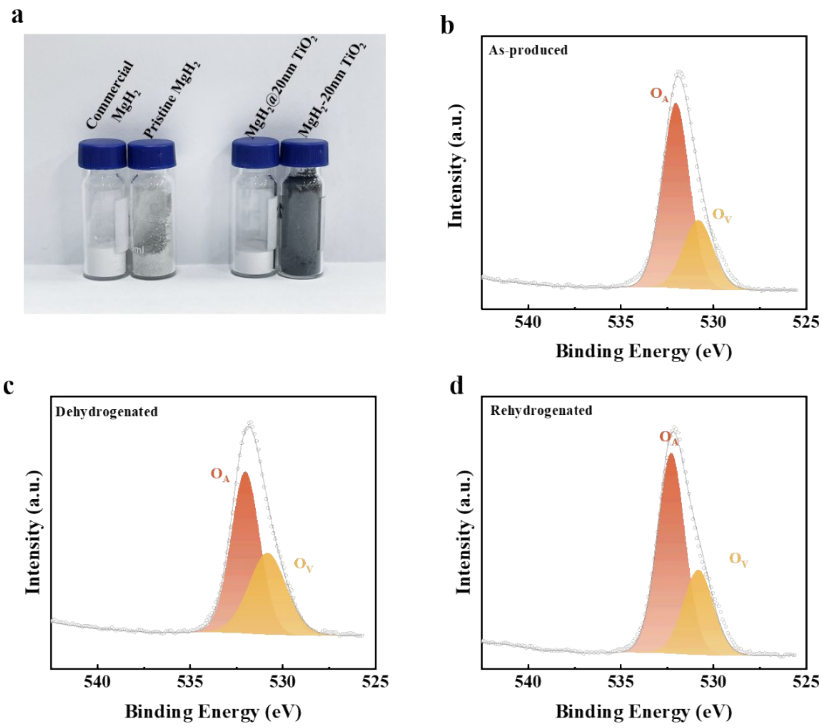

Figure S4. (a) Optical images of commercial MgH_2, pristine MgH_2, MgH_2@20nmTiO_2 and MgH_2-20nmTiO_2. High-resolution O 1*s* spectrum of the (b) as-produced, (c) dehydrogenated, and (d) rehydrogenated MgH_2-20nmTiO_2@Gra.

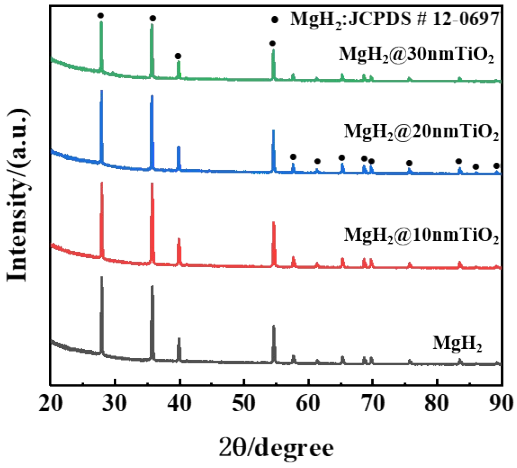

Figure S5. XRD patterns of MgH_2 and MgH_2@TiO_2.

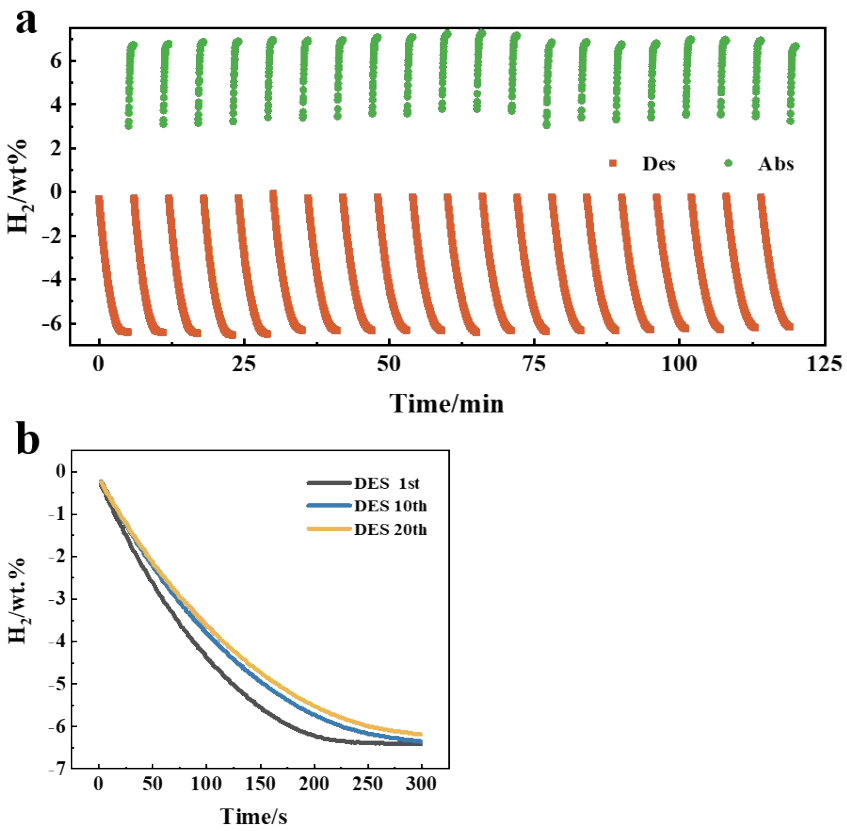

Figure S6. The isothermal hydrogen desorption (300°C/0.05 bar) and absorption (300°C/30 bar) cycling curves of MgH_2-20nmTiO_2.

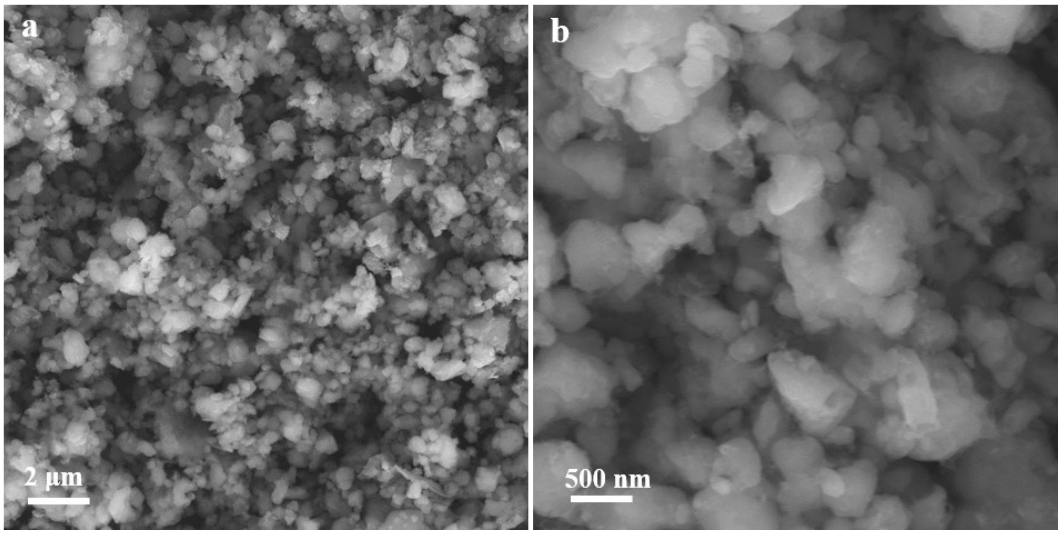

Figure S7. SEM images of MgH_2-20nmTiO_2@Gra after cycling at different scales.

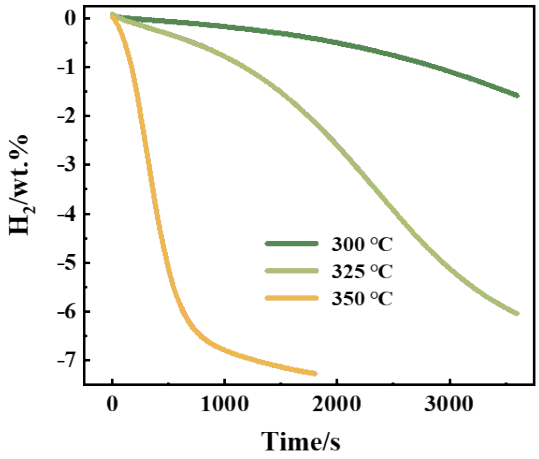

Figure S8. Isothermal dehydrogenation curves of MgH_2 at different temperatures.

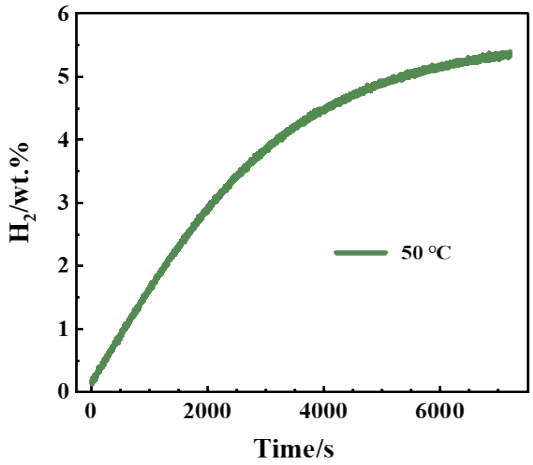

Figure S9. Isothermal hydrogen absorption curve of MgH_2-20nmTiO_2@Gra at 50°C, 30 bar H_2.

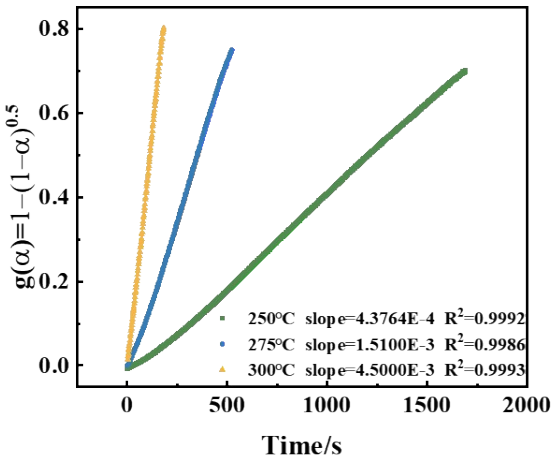

Figure S10. Time dependence of R2 modeling equation g(α) for MgH_2-20nmTiO_2@Gra at different temperatures.

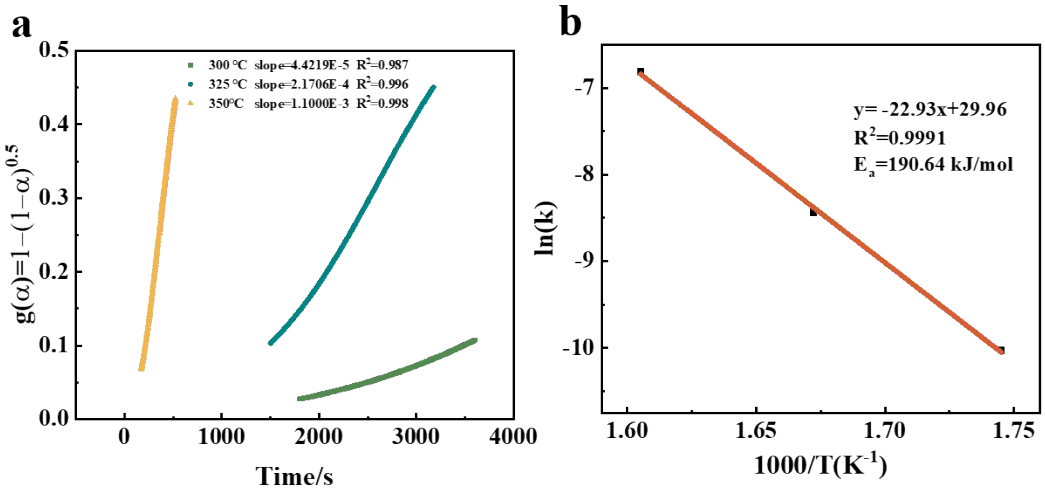

Figure S11. (a) Time dependence of R2 modeling equation g(α) for MgH_2 at different temperatures, and (b) Arrhenius plot for the dehydriding kinetics of MgH_2.

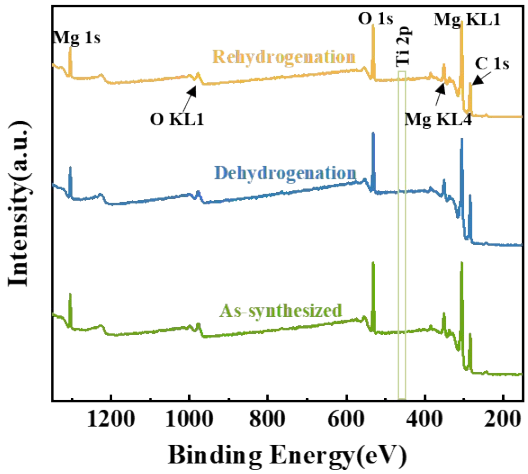

Figure S12. XPS spectra of MgH_2-20nmTiO_2@Gra at different states.

Table S1. Summary of hydrogen sorption properties for catalyst-enhanced MgH_2 composites.

System component	Dehydrogenation	Rehydrogenation	Ref.
MgH_2-TiO_2@rGO	300°C, 6 min, 6.0 wt.%; 275°C, 12 min, 5.8wt.%	200°C /30 bar H_2, 2 min, 5.9 wt.%	[2]
MgH_2/TiO_2	300°C, 5 min, 2.35 wt.%; 275°C, 10 min, 2.85wt.%	100°C /30 bar H_2, 30 min, 2.5 wt.%; 150°C /30 bar H_2, 10 min, 2.5 wt.%	[3]
MgH_2-TiO_2@Graphene	300°C, 30 min, 5.8 wt.%;	300°C /15 bar H_2, 1.5 min, 5.7 wt.%;	[4]
MgH_2-TiH_2@Graphene	300°C, 30 min, 6.5 wt.%;	300°C /15 bar H_2, 2.5 min, 6.0 wt.%;	[4]

MgH_2-$Na_2Ti_3O_7$ NT	300°C, 3.75 min, 5.5 wt.%; 250°C, 30 min, 1.7 wt.%	50°C /30 bar H_2, 30 min, 1.5 wt.%; 150°C /30 bar H_2, 30 min, 5.0 wt.%	[5]
MgH_2-Ti	275°C, 10 min, 5.75 wt.%; 250°C, 20 min, 5 wt.%	225°C /20 bar H_2, 15 min, 5.8 wt.%; 275°C /20 bar H_2, 10 min, 6 wt.%	[6]
MgH_2+N-Na_2TiO_3	300°C, 4 min, 6 wt.%; 275°C, 11 min, 6 wt.%	Room temperature/50 bar H_2, 3.8h, 4 wt.%; Room temperature/30 bar H_2, 10 h, 3.4 wt.%	[7]
MgH_2-Gra-Ni	250°C, 30 min, 5.2 wt.%; 300°C, 18 min, 6 wt.%	100°C /30 bar H_2, 15 min, 5.3 wt.%; 150°C /30 bar H_2, 8 min, 5.4 wt.%	[8]
MgH_2-Ti_3C_2	275°C, 30 min, 6.2 wt.%; 300°C, 20 min, 6.6 wt.%	100°C /30 bar H_2, 20 min, 2.6 wt.%; 150°C /30 bar H_2, 20 min, 5 wt.%;	[9]
MgH_2-Ni/TiO_2	275°C, 10 min, 5.85 wt.%; 300°C, 5 min, 5.94 wt.%	100°C /35 bar H_2, 30 min, 5.9 wt.%; 75°C /35 bar H_2,	[10]

		60 min, 6 wt.%	
MgH_2-(Ni-V_2O_3)@C	250°C, 100 min, 5.99 wt.%; 300°C, 5 min, 6.02 wt.%	50°C /35 bar H_2, 3 h, 5.07 wt.%; 150°C /35 bar H_2, 9 min, 6 wt.%	[11]
MgH_2-Ni@Pt	——	150°C /15 bar H_2, 1 h, 4.8 wt.%; 202°C /15 bar H_2, 10 min, 5.5 wt.%	[12]
MgH_2-Ti_2VC_2	275C, 10 min, 6.1 wt.%; 300°C, 5 min, 6.2 wt.%	150°C /30 bar H_2, 10 min, 5.7 wt.%;	[13]
MgH_2-20nmTiO_2@Gra	225°C, 2h, 3.29 wt.%; 250°C, 30 min, 5.82 wt.% 275°C, 10 min, 6.04 wt.%; 300°C, 2.5 min, 5.6 wt.%	50°C /30 bar H_2, 2 h, 5.39 wt.%; 100°C /30 bar H_2, 0.5 h, 6.17 wt.%; 150°C /30 bar H_2, 15 s, 5.41 wt.%; 200°C /30 bar H_2, 15 s, 5.75 wt.%	This work

Table S2. Comparison of dehydrogenation activation energy E_a with reported MgH_2 based composites

System component	Dehydrogenation activation energy E_a(kJ/mol)	Ref.
Bulk MgH_2	180.41	[5]
MgH_2-Co MOF	151.3 ± 9.4	[14]
MgH_2-Fe MOF	142.3 ± 6.5	[14]
Mg-CeF_3	155.3	[15]
MgH_2	154.9 ± 16.2	[16]
MgH_2-$CoMoO_4$/rGo	123.46 ± 7.8	[16]
MgH_2	161.3	[17]

MgH_2-TiN	144.7	[17]
MgH_2-TiO_2	118.9	[17]
MgH_2@Gra	142.17	[18]
MgH_2@CNT	133.77	[18]
pristine MgH_2	190.64	This work
MgH_2-20nmTiO_2@Gra	116.10	This work

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