Supporting Information

Structural inhomogeneity: A potential strategy to improve the hydrogen storage performance of metal hydrides

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1. Experimental Details

1.1 Sample preparation

The deposited substrate Ni was prepared by weakly acidic hydrolysis of Mg-Ni alloy. In a typical preparation, Mg-Ni alloy (0.5 g) was dispersed into deionized water (20 mL) via continuous stirring for about 30 min at room temperature. Then dilute hydrochloric acid (20 mL, 0.05 M) was added dropwise into the mixture. After the hydrolysis reaction, the black magnetic particles were collected, washed, and freeze-dried to obtain the deposited substrate Ni.

The nano-micro MNH was synthesized by a modified gas-solid reaction of hydriding chemical vapor deposition (HCVD). Approximately 30 mg of the deposited substrate Ni and an excess of Mg powder (~ 20 g) were separately placed into a reactor (Fig. S1). After adequate purification with Ar, low-pressure H_2 (~0.1 MPa) was introduced into the reactor. The reactor was first heated to 580 °C at a heating rate of 10 °C/min and then maintained at an isothermal state for 1 h under a 0.2 MPa H_2 pressure. During this process, the Mg atoms evaporated, migrated, and alloyed with the deposited substrate Ni, and $Mg_2Ni/MgNi_2$ was in situ generated. After the reactor was cooled to 340 °C, hydrogen pressure was increased to 2 MPa to hydrogenate the alloy, and the reactor was maintained at 340 °C for 1 h (Fig. S2a). Finally, the reactor was cooled to room temperature, and the nano-micro MNH was obtained. The detailed information of the chemicals is listed in Table S1.

As a comparative sample, Mg-Ni based hydride with large particle size (tens of micrometers) was also prepared by hydriding combustion synthesis (HCS) and noted

as HCS-Mg_2NiH_4. The synthesis parameters are shown in the schematic (Fig. S2b). Detailed synthesis process of HCS has been reported in our previous work. [1]

Table S1 Detailed information of the chemicals

Chemicals	Purity	Particles size	Company
Mg powder	≥99.7%	<44 μm	Weihao Magnesium Powder Co., Ltd.
Ni powder	≥99.9%	2-3 μm	Jiangyou Hebao Nanomaterials Co., Ltd.
Hydrochloric acid	37%		Lingfeng Chemical Reagent Co., Ltd.
H_2	99.999%		Nanjing Special Gas Co., Ltd.
Ar	99.999%		Nanjing Special Gas Co., Ltd.

1.2 Characterizations

Phase structure of all samples were analyzed by X-ray diffraction (XRD, ARL X'TRA, Cu-Kα radiation). The microscopic morphology and crystallographic information of all samples were measured by field emission scanning electron microscope (FESEM, Zeiss Merlin Compact) and high-resolution transmission electron microscope (HRTEM, FEI TF20). The Ni K-edge XANES measurements were carried out at the BL14W1 in Shanghai Synchrotron Radiation Facility, China. The dehydrogenation onset and peak temperature and hydrogen storage capacity of samples were tested through differential scanning calorimetry (DSC, TA Q2000) and temperature-programmed-desorption (TPD) under a heating rate of 10 °C/min. The isothermal de/hydrogenation kinetics properties of the samples were measured via a Sievert's type apparatus (GRC, Advanced Materials Co.) under 3 MPa initial hydrogen

pressure for absorption, and 0.005 MPa initial hydrogen pressure for desorption at various temperatures. To avoid oxidation of the samples, all operation was performed in a glovebox filled with Ar (99.999 %) and the oxygen/water concentrations below 0.01 ppm.

1.3 Calculations

Spin polarized DFT calculations were made in VASP 5.4.4 software package. [2] The projector augmented wave (PAW) potentials [3] with the kinetic energy cutoff of 520 eV were adopted during the calculation, and the Perdew-Burke-Ernzerhof (PBE) realization of generalized gradient approximation (GGA) was used to describe the exchange correlation between electrons. [4] The Brillouin zone integration is performed using a 3x3x1 k-mesh. The $MgNi_2$ (001) slab and Mg_2NiH_4 (1-1-1) slab were constructed and fully relaxed, and the energy and force convergence criteria were set to 10^{-5} eV and 0.02 eV/Å, respectively. Before the calculations of electronic structures, the slabs positions are chosen according to the lowest surface energy. A vacuum layer of 15 Å was added on the slab to avoid the influence between adjacent images.

Ab initio molecular dynamics (AIMD) calculations were carried out to study the migration of H atoms in $MgNi_2$ and Mg_2NiH_4. During the AIMD calculations, only gamma point was taken into consideration. The time step was set to 1 fs with the hydrogen mass set to 2 atomic mass units. The canonical NVT ensemble was established at 500 K by using a Nose-Hoover thermostat.
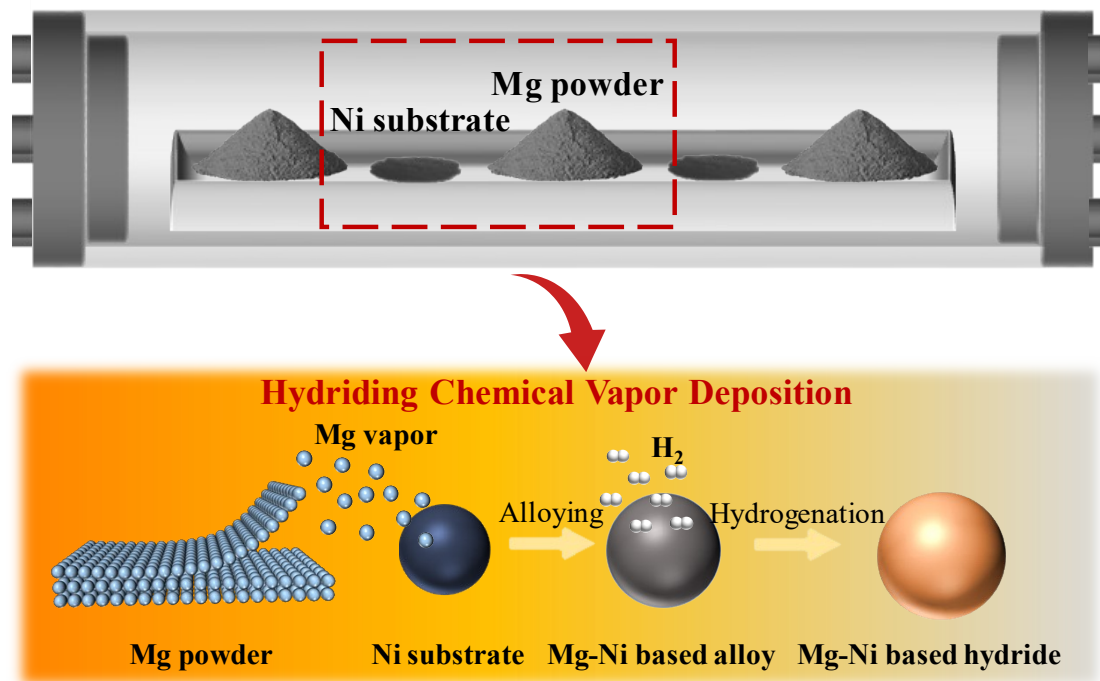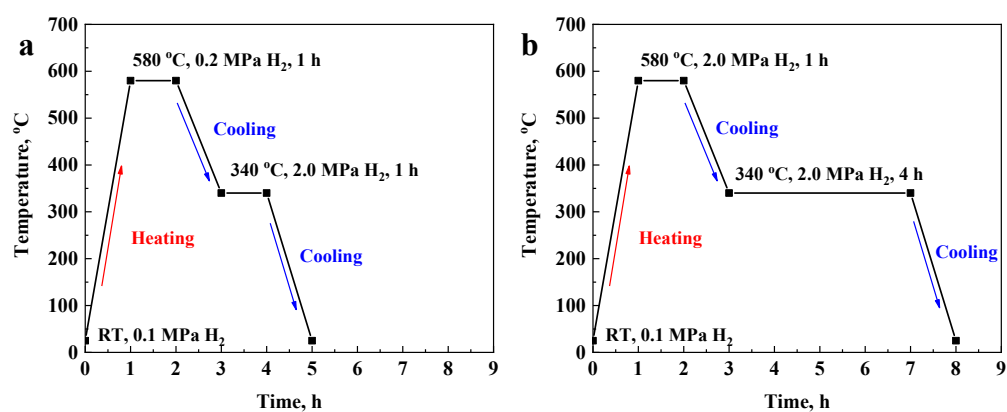
Fig. S1 Schematic diagram of HCVD.

Fig. S2 Schematic of the heating-cooling process of (a) HCVD and (b) HCS used in this work.
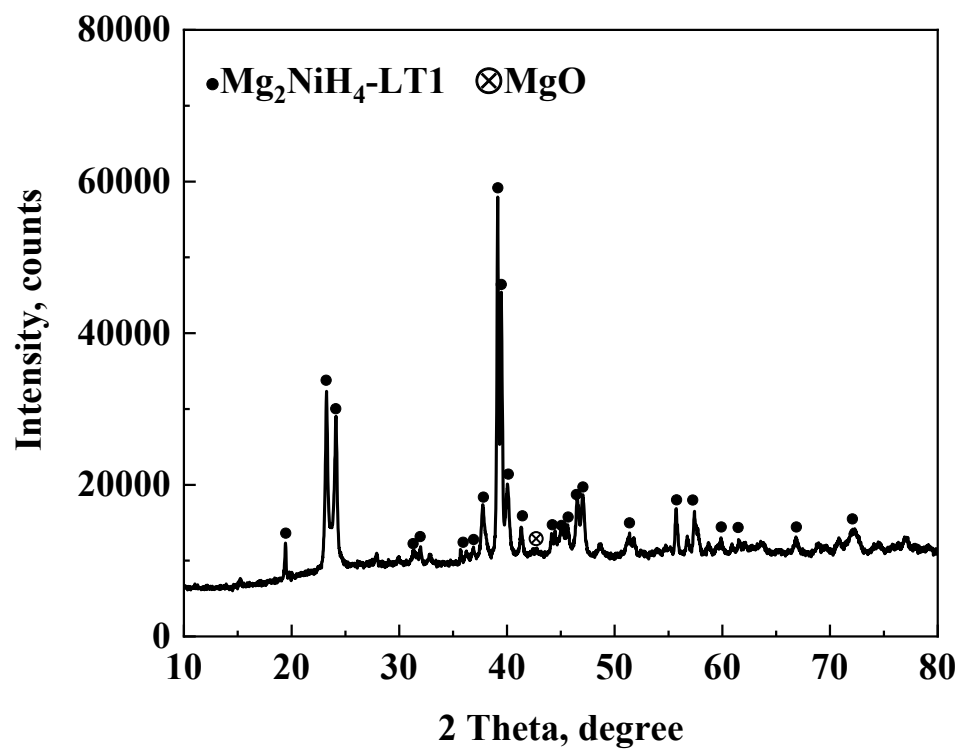
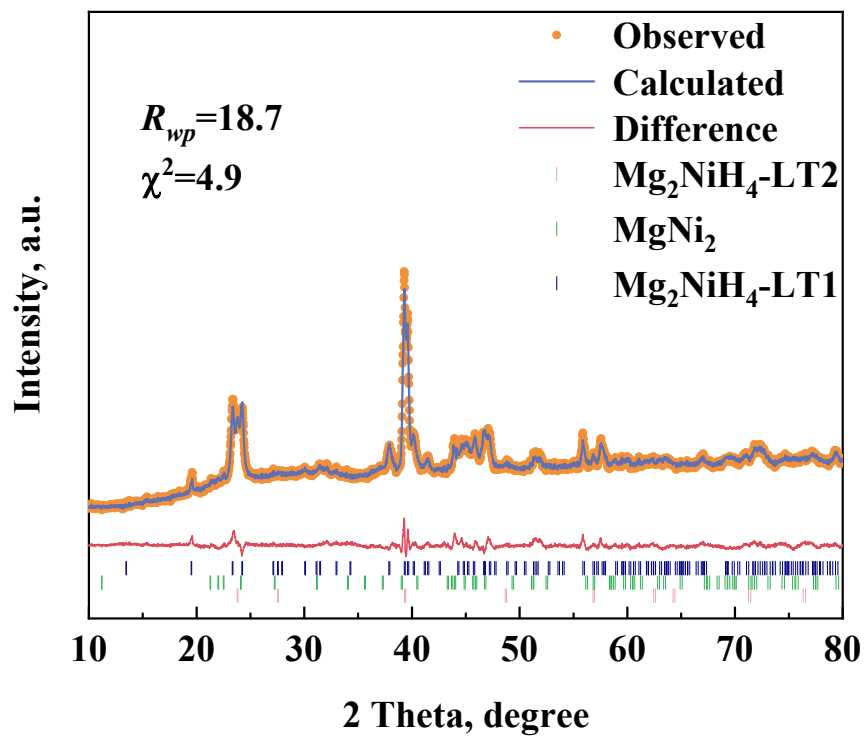Fig. S3 XRD pattern of as-prepared HCS-Mg$_2$NiH$_4$.
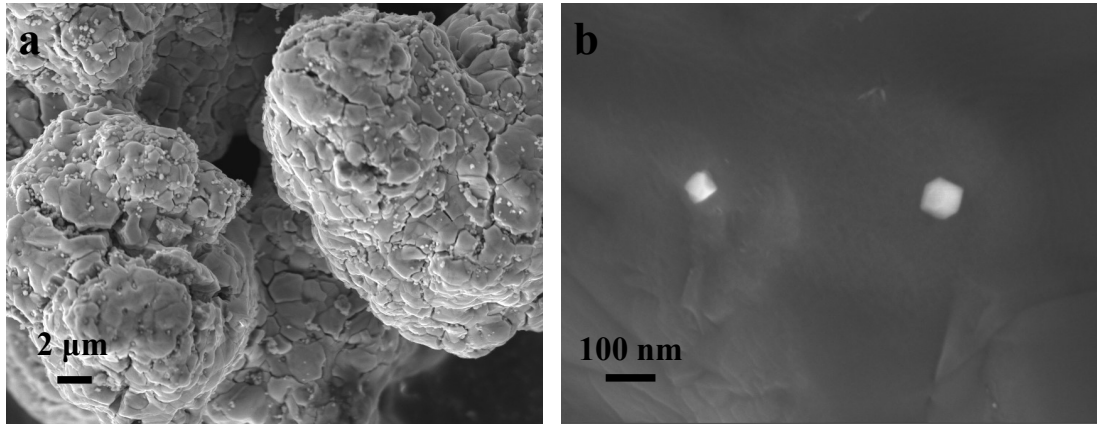
Fig. S4 Rietveld refinement of nano-micro MNH.

Fig. S5 FESEM images of nano-micron MNH at different magnification.
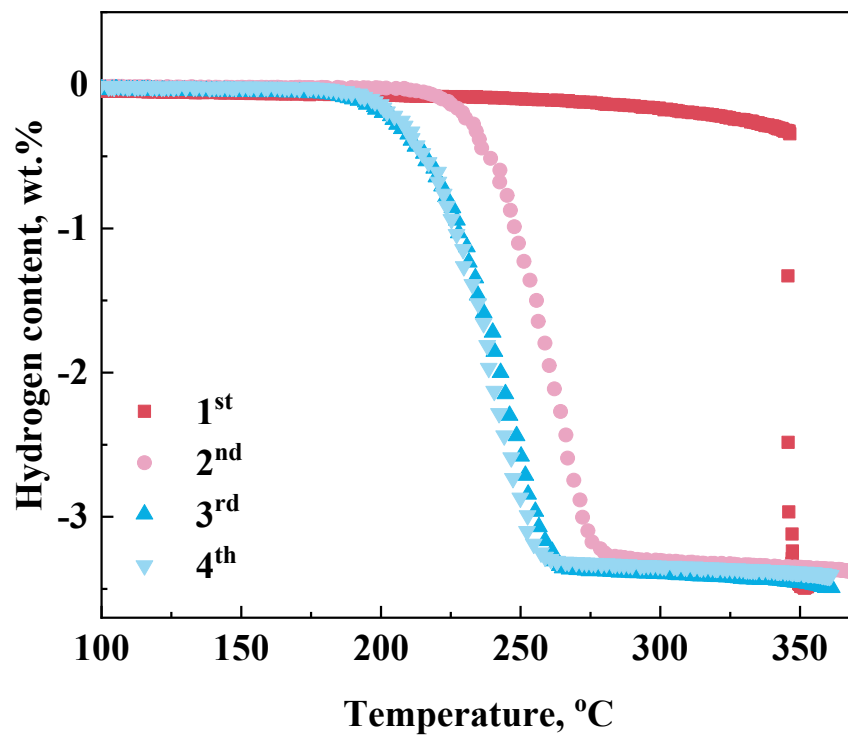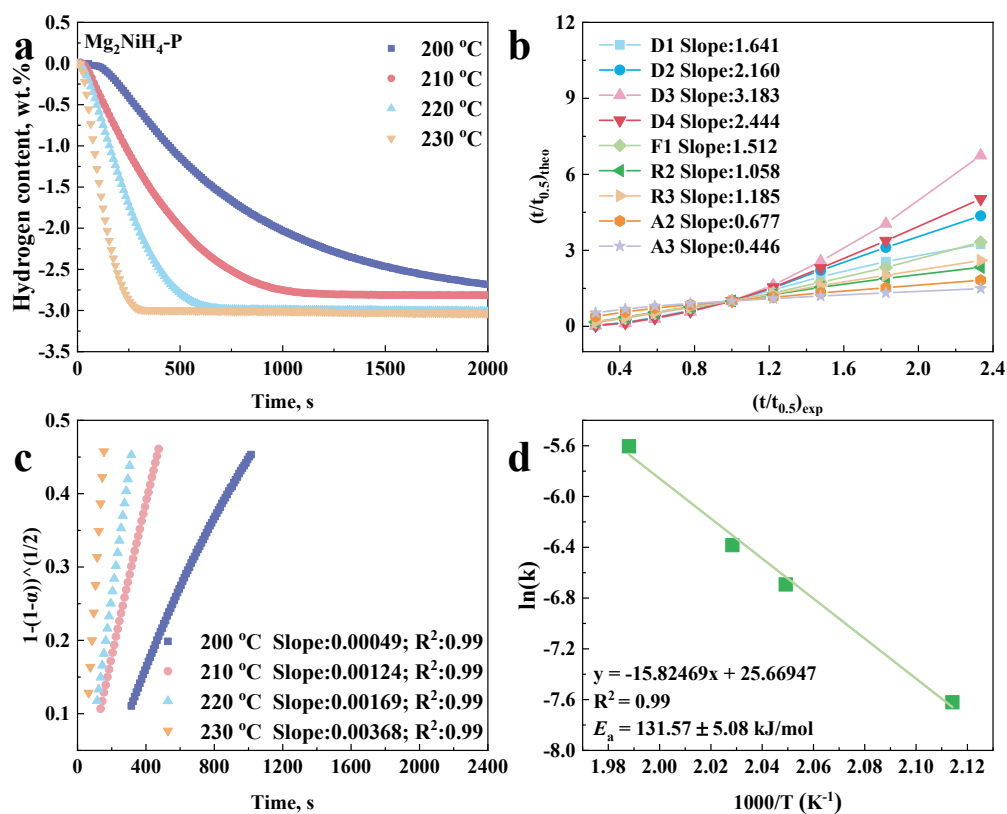
Fig. S6 TPD curves of HCS- Mg_2NiH_4.

Fig. S7 (a) isothermal dehydrogenation curves of HCS- Mg_2NiH_4 measured at 200, 210, 220 and 230 °C; (b) $(t/t_{0.5})_{theo}$ vs. $(t/t_{0.5})_{exp}$ of HCS- Mg_2NiH_4 at 220 °C for various kinetic models; (c) time dependence of kinetic modeling equation g(α) for HCS- Mg_2NiH_4 with 0.2<α<0.7 at different temperatures, and (d) Arrhenius plot for the dehydriding kinetics of HCS- Mg_2NiH_4.
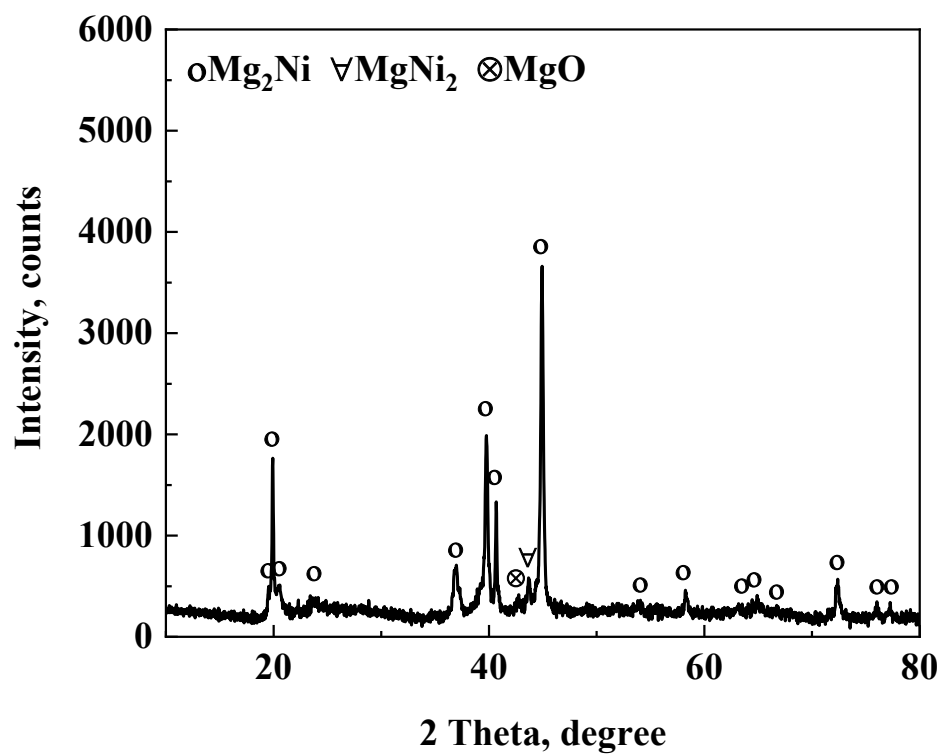
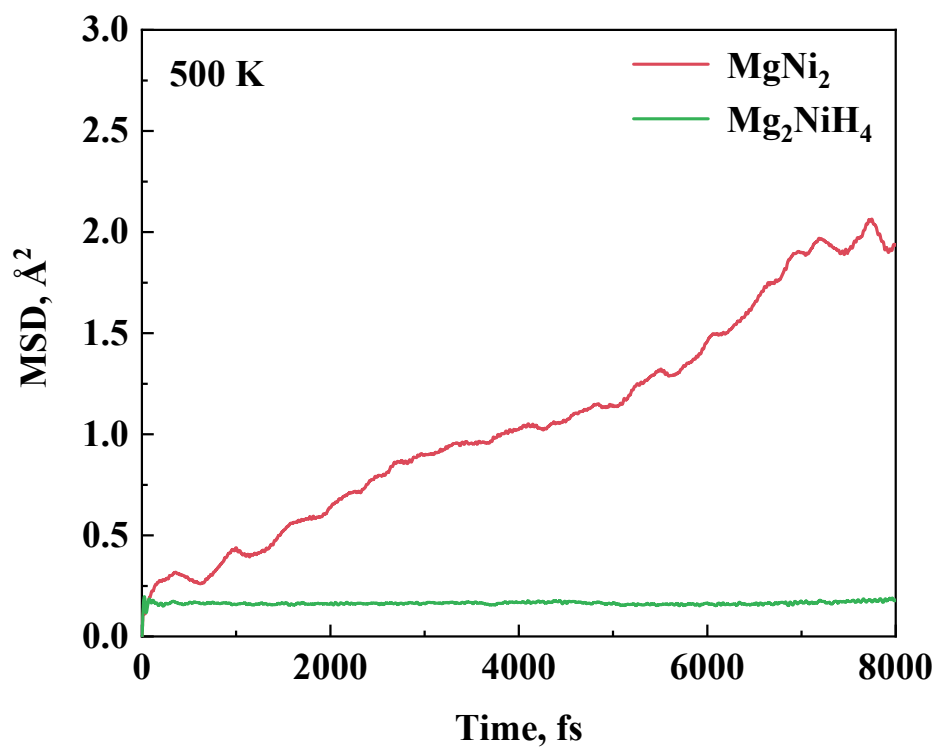Fig. S8 XRD pattern of dehydrogenated nano-micro MNH.

Fig. S9 MSD profiles of H diffusion in $MgNi_2$ and Mg_2NiH_4 at 500K

References

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