Supplementary Information

Remarkably Improved Hydrogen Storage Performance of MgH_2 Catalyzed by Multivalence NbH_x Nanoparticles

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Table S1. Kinetic models examined in the isothermal desorption curves of nanoconfined samples

Symbol	Model	Integral $f(\alpha)$ form
D1	one-dimensional diffusion	α^2
D2	two-dimensional diffusion	$\alpha+(1-\alpha)\ln(1-\alpha)$
D3	three-dimensional diffusion (Jander equation)	$[1-(1-\alpha)^{1/3}]^2$
D4	three-dimensional diffusion (Ginstling-Braunshtein equation)	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
F1	First-order reaction	$-\ln(1-\alpha)$
R2	two-dimensional phase boundary	$1-(1-\alpha)^{1/2}$
R3	three-dimensional phase boundary	$1-(1-\alpha)^{1/3}$
A2	Avarami-Erofe'ev	$[-\ln(1-\alpha)]^{1/2}$
A3	Avarami-Erofe'ev	$[-\ln(1-\alpha)]^{1/3}$

Synthesis of NbH_x nanoparticles

Mechanochemical synthesis is a wide used technique that employs ion exchange reaction during ball milling.[1] This method has been used recently to synthesize AlH_3[2] and MgH_2[3,4]. Usually a reaction byproduct phase is also formed and added during milling to separate the desired reaction

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product and the variation in the microstructure of the synthesized product can be obtained as a function of the quantity of byproduct used as a reaction buffer. Thus, we apply this method to synthesis nano-sized NbH_x through iron exchange reaction during ball milling. Mass Spectrometry (MS) measurement of gas inside the jar after ball milling was carried out on a QIC-20 (HIDEN ANALYTICAL LTD) gas analysis system. The results are presented in Figure S1, which shows that only hydrogen is released. Also, the colour of the reagents turned from yellow to black after ball milling, indicating LiH and $NbCl_5$ reacted in the ball milling process. Furthermore, the mixture after ball milling was tested by XRD. Figure S2 reveals that NbH and LiCl were the only phases detected, indicating that LiH and $NbCl_5$ were completely reacted in the ball milling process. Moreover, Figure 1 shows that other Nb-based Hydride ($NbH_{2.7}$) formed in the ball milling process. Thus, the synthesis process was proceeding according to the following equation:

$$5LiH + NbCl_5 \rightarrow NbH_x + 5LiCl + 1/2(5-x)H_2$$

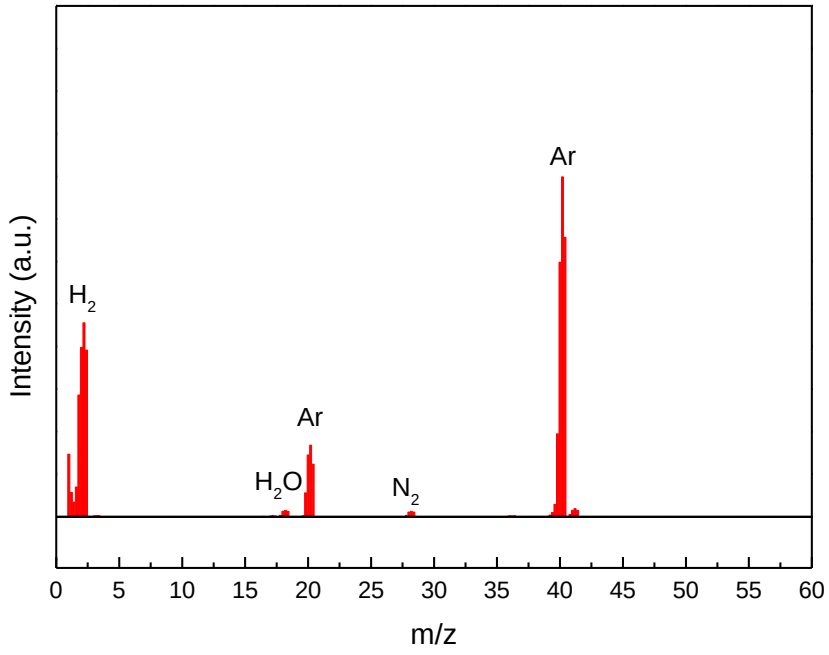

Figure S1. MS profile of gas inside the jar after ball milling LiH and $NbCl_5$ for 5h (Ar was the protecting gas and H_2O and N_2 were remaining gas inside the pipe of QIC-20).

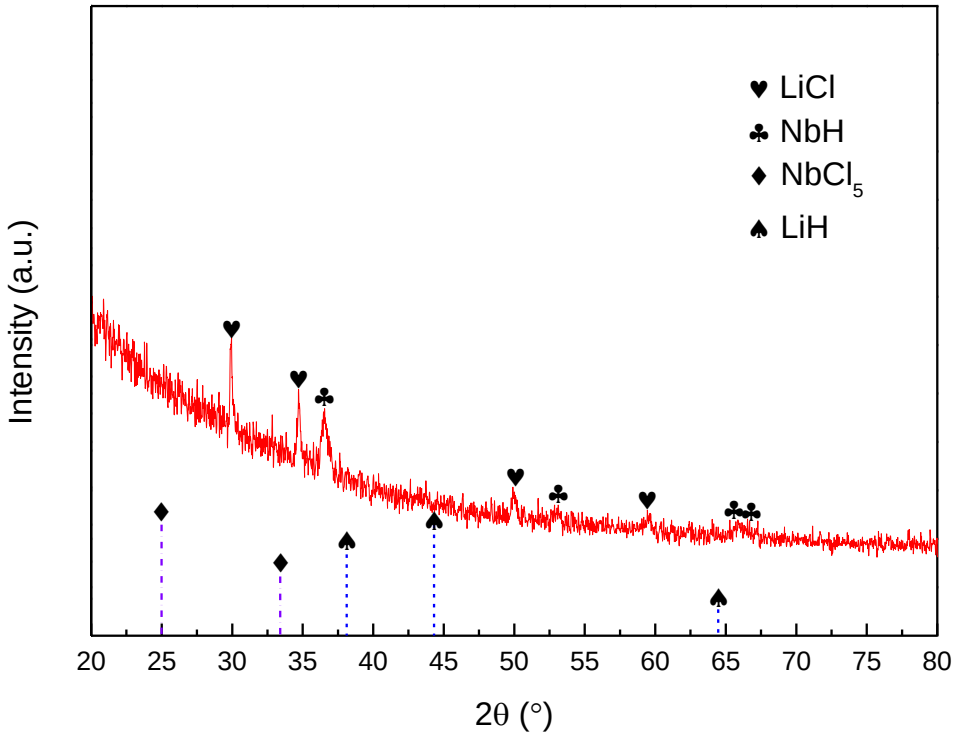

Figure S2. XRD of products inside the jar after ball milling LiH and $NbCl_5$ for 20h.

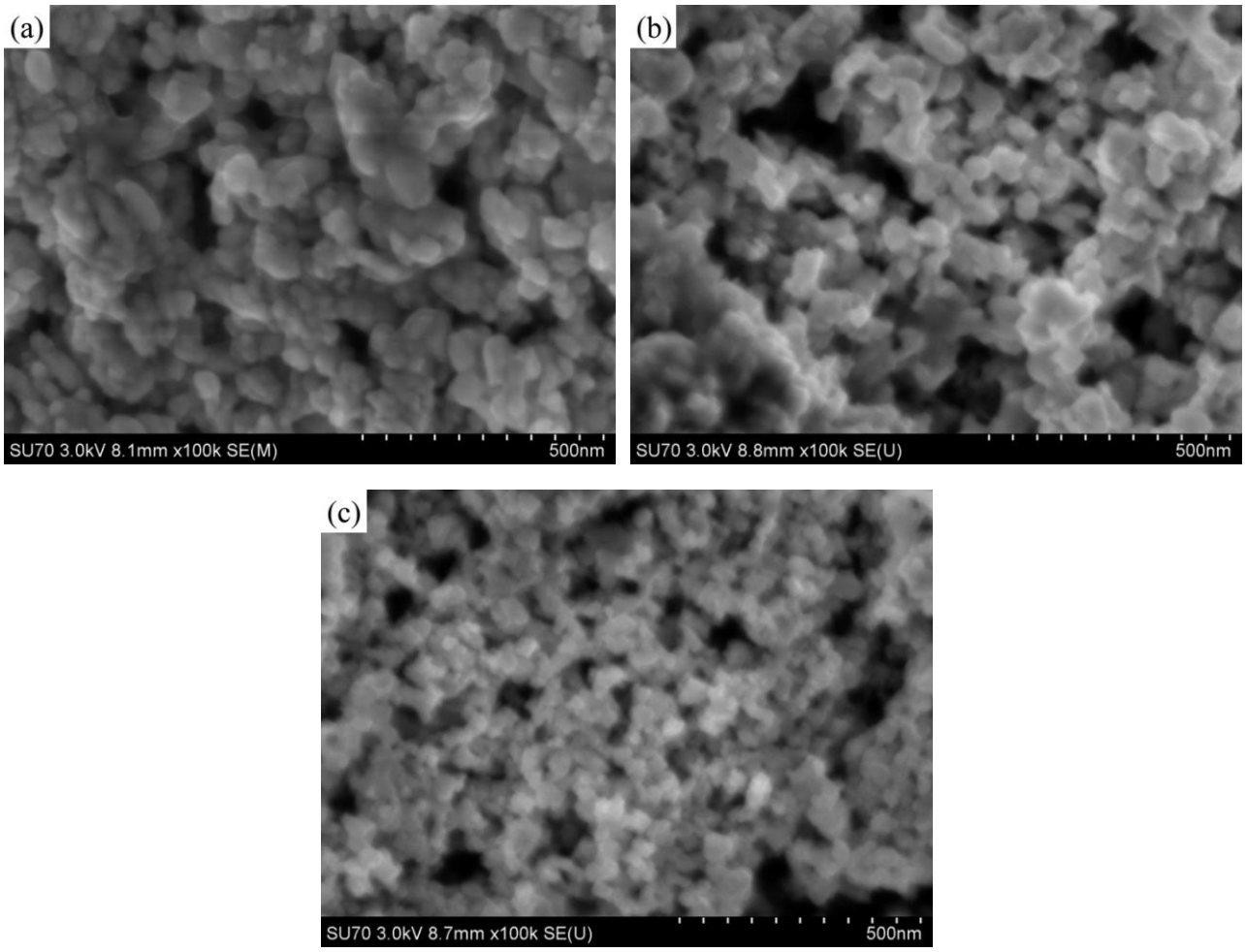

Figure S3. SEM images of (a) *a*-NbH_x, (b) *b*-NbH_x and (c) *c*-NbH_x powders.

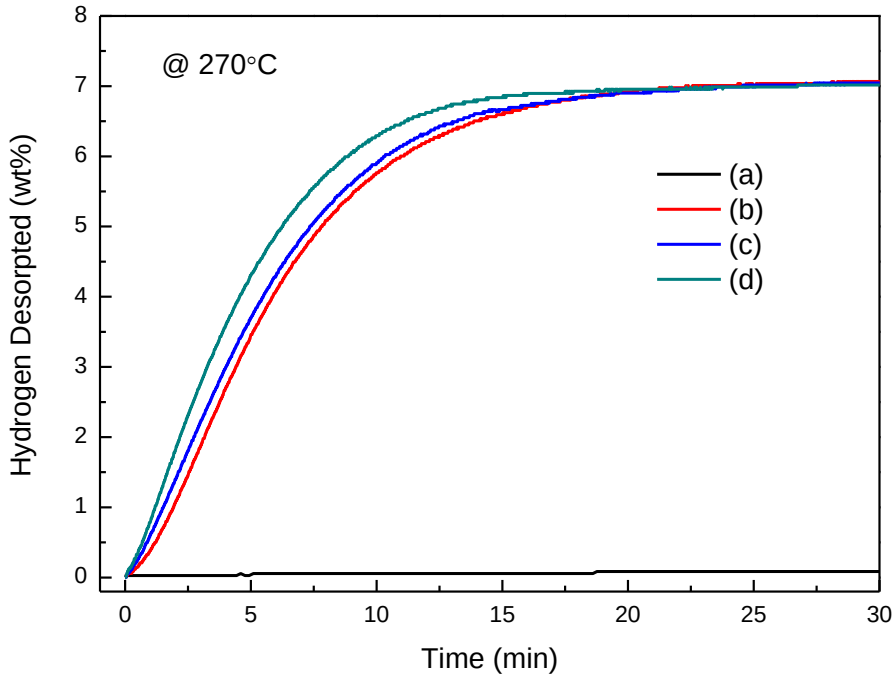

Figure S4. Isothermal desorption curves of (a) BM MgH_2, (b) MgH_2/*a*-NbH_x, (c) MgH_2/*b*-NbH_x and (d) MgH_2/*c*-NbH_x samples under 3 kPa hydrogen back pressure at 270 ℃.

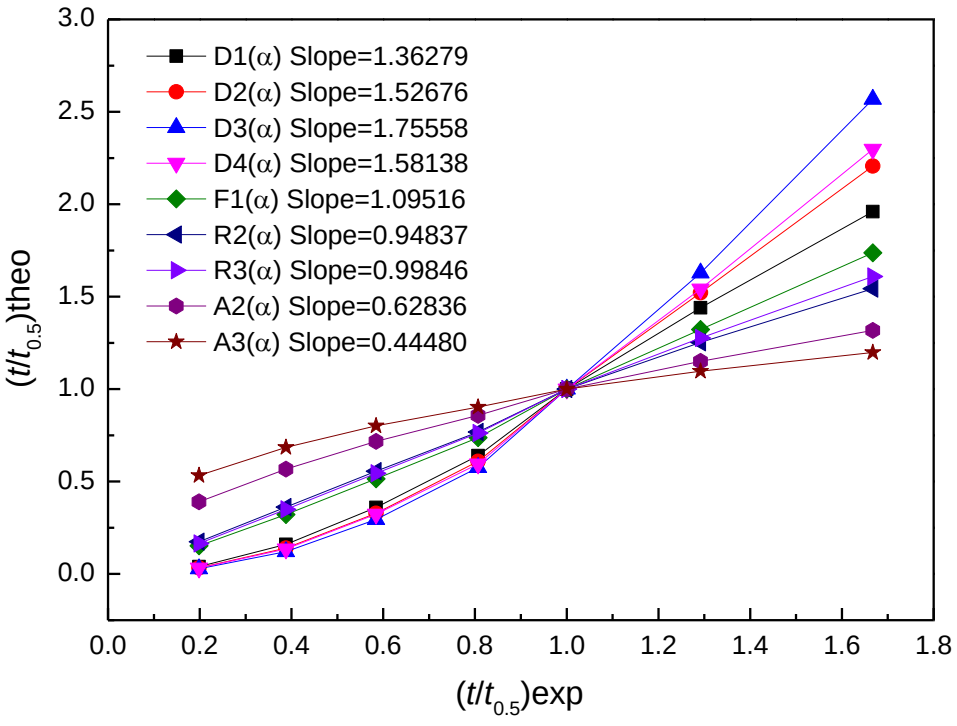

Figure S5. $(t/t_{0.5})_{theo}$ vs $(t/t_{0.5})_{exp}$ of MgH_2/*c*-NbH_x composite for various kinetic models.

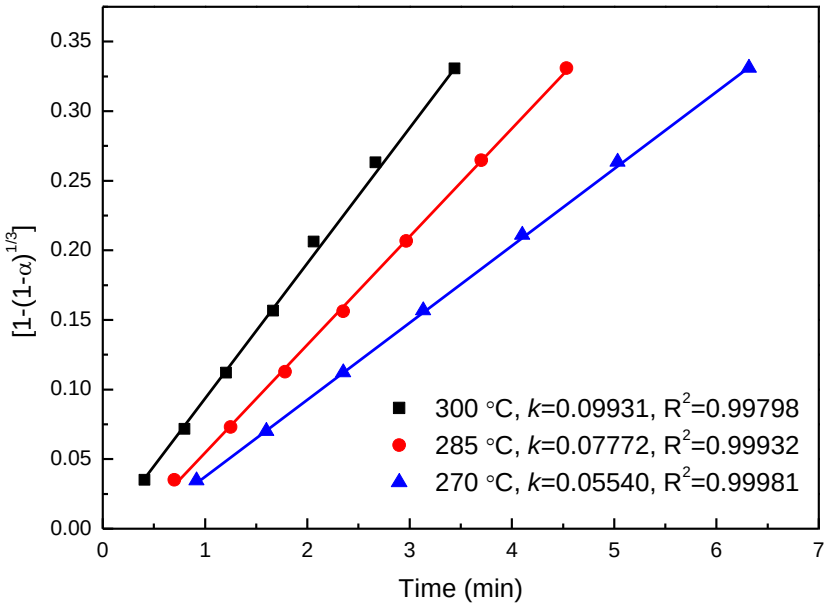

Figure S6. Time dependence of $f(\alpha)$ of MgH_2/*c*-NbH_x composite for various temperatures.

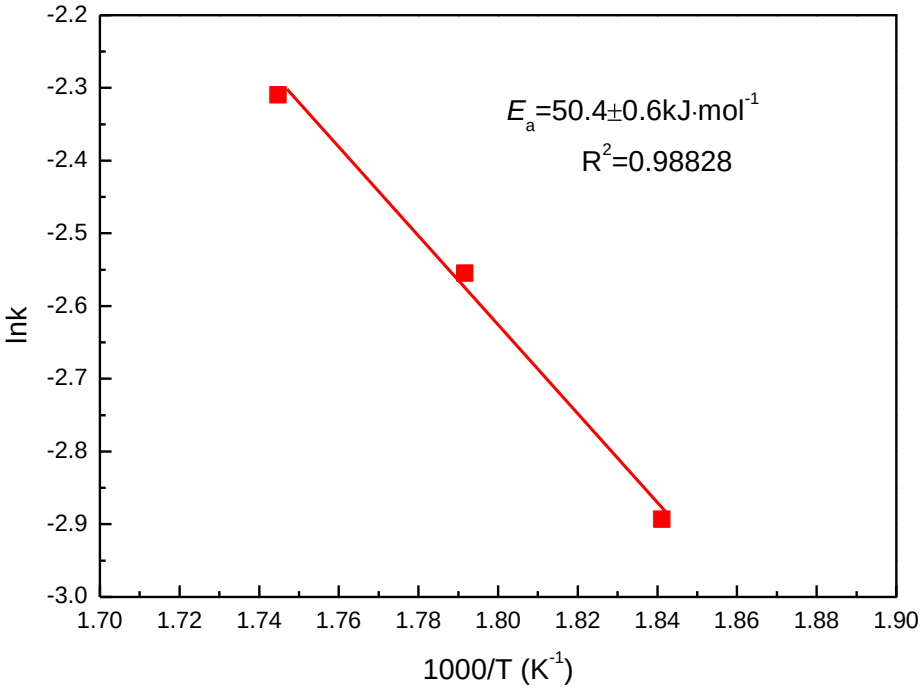

Figure S7. Arrhenius plots for the dehydrogenation of MgH_2/*c*-NbH_x composite.

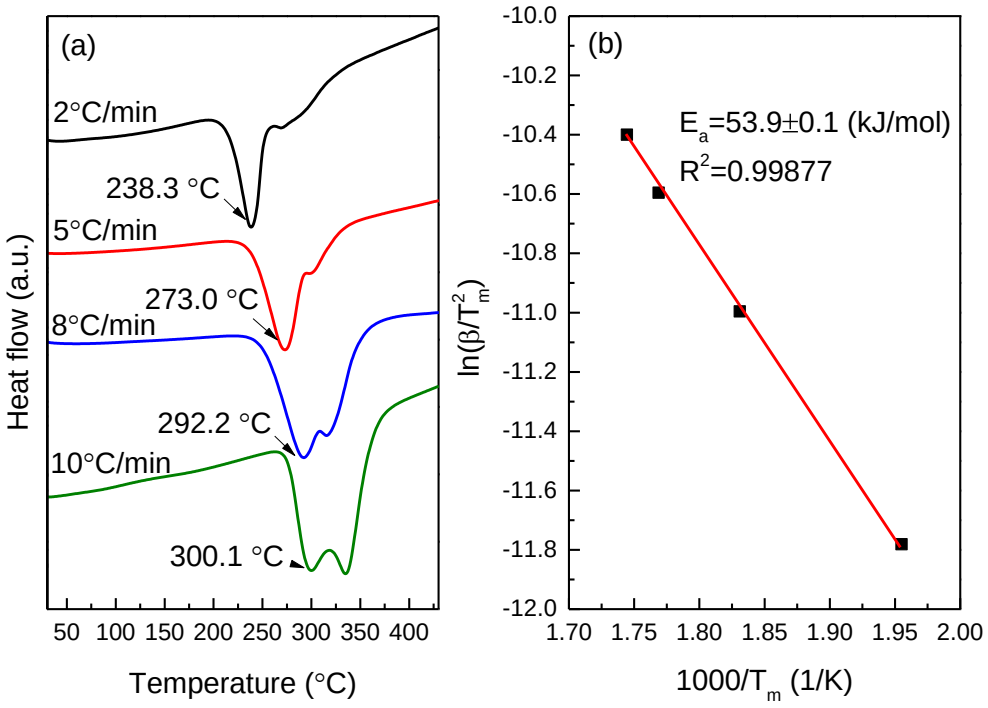

Figure S8. DSC curves (a) of MgH_2/*c*-NbH_x composite at various heating rates and the corresponding Estimation of the apparent activation energy (b) using Kissinger's method with the parameters obtained from DSC measurements.

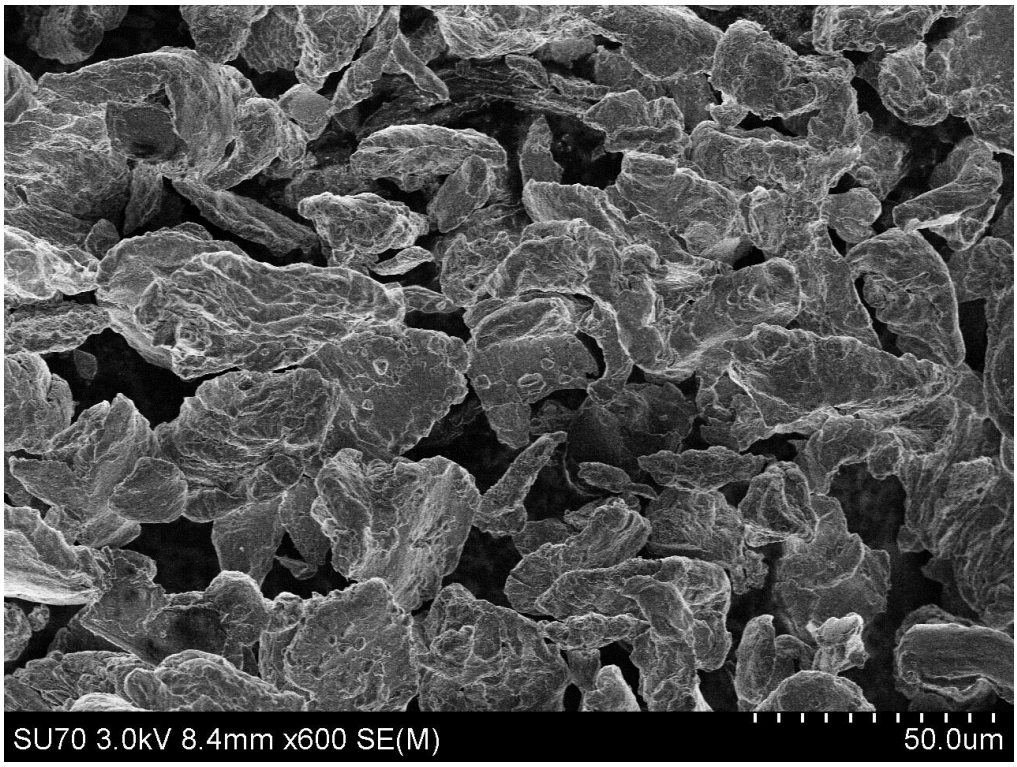

Figure S9. SEM image of as-received MgH_2.

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