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

$Ca(BH_4)_2$–$LiBH_4$–MgH_2: A Novel Ternary Hydrogen Storage System with Superior Long-Term Cycling Performance†

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Supplementary information

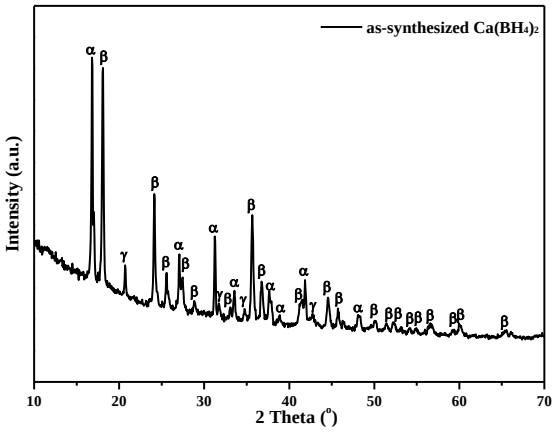

Fig. S1 XRD pattern of the as-synthesized $Ca(BH_4)_2$

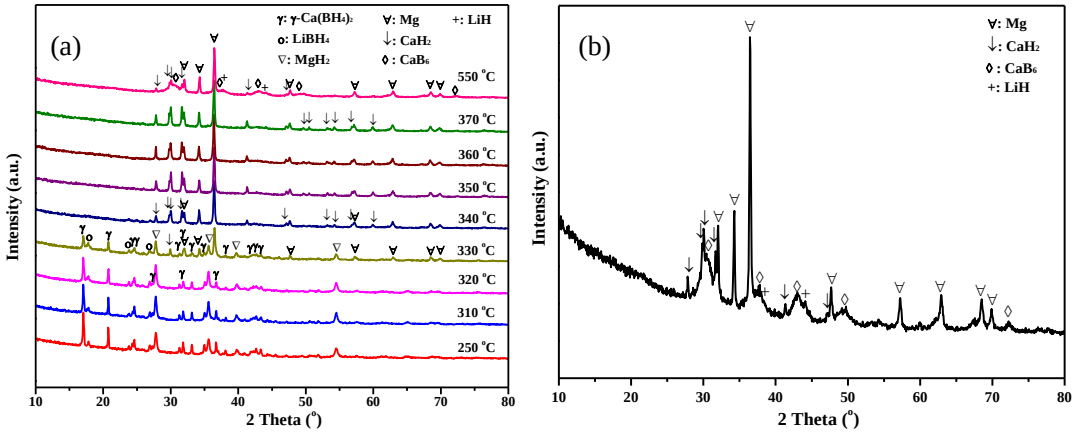

Fig. S2 XRD patterns of the dehydrogenation intermediates and product of the $Ca(BH_4)_2$+2$LiBH_4$+2MgH_2 ternary system at different dehydrogenation temperatures (a) and the amplified pattern of the dehydrogenated product at 550 °C (b).

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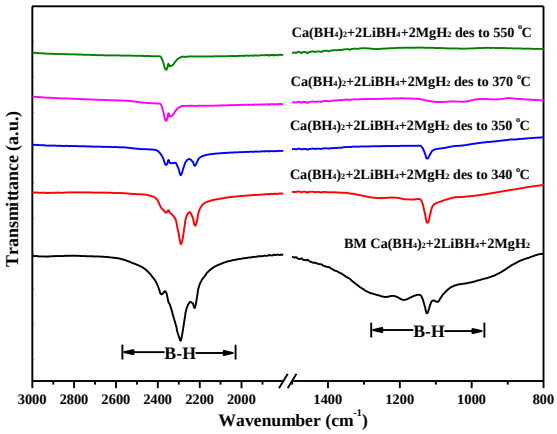

Fig. S3 FTIR spectra of the dehydrogenation intermediates and product of the $Ca(BH_4)_2$+2$LiBH_4$+2MgH_2 ternary system at different dehydrogenation temperatures.

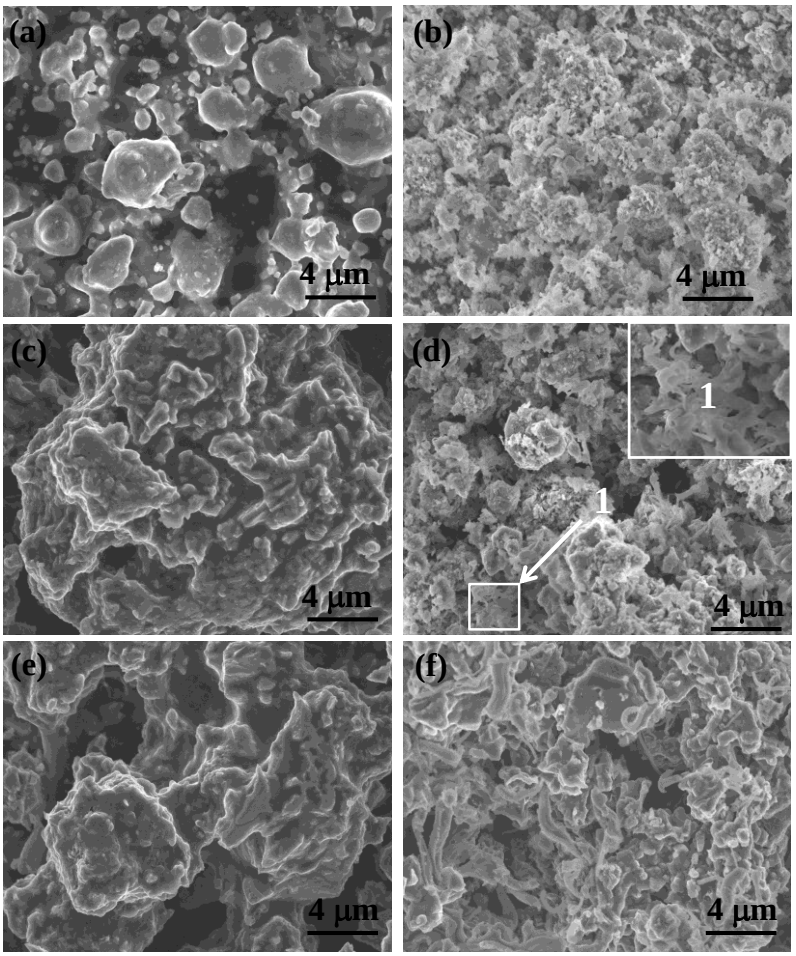

Fig. S4 SEM images of the as-milled $Ca(BH_4)_2$+2$LiBH_4$+2MgH_2 mixture (a), and the 1st dehydrogenation (b), 1st hydrogenation (c), 2nd dehydrogenation (d), 9th hydrogenation (e) and 10th dehydrogenation (f) products dehydrogenated at 370 °C for 30 min, and hydrogenated at 350 °C for 18 h.

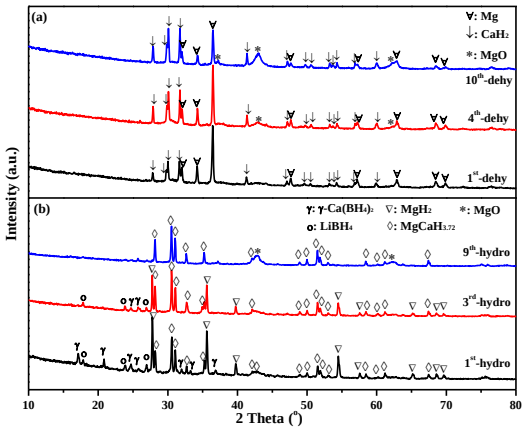

Fig. S5 XRD patterns of the dehydrogenation (a) and re-hydrogenation (b) products of the $Ca(BH_4)_2$+2$LiBH_4$+2MgH_2 system dehydrogenated at 370 °C for 30 min, and re-hydrogenated at 350 °C for 18 h for different cycles.

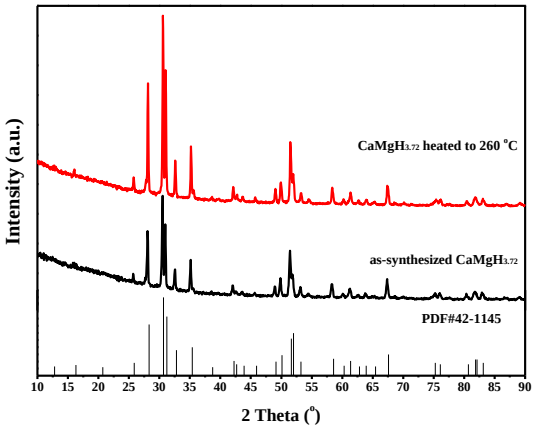

Fig. S6 XRD patterns of the present synthesized $CaMgH_{3.72}$ and its product heated to 260 °C.

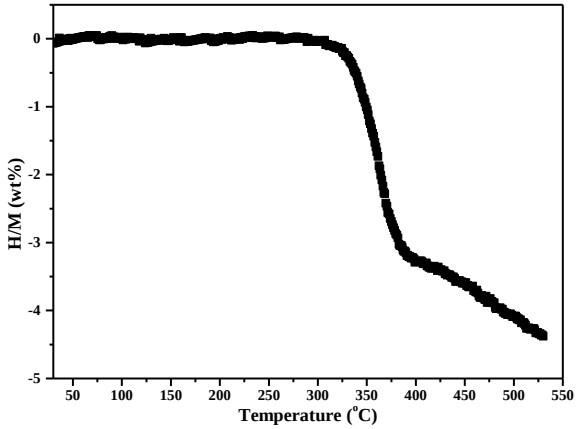

Fig. S7 Dehydrogenation curve of the present synthesized $CaMgH_{3.72}$.

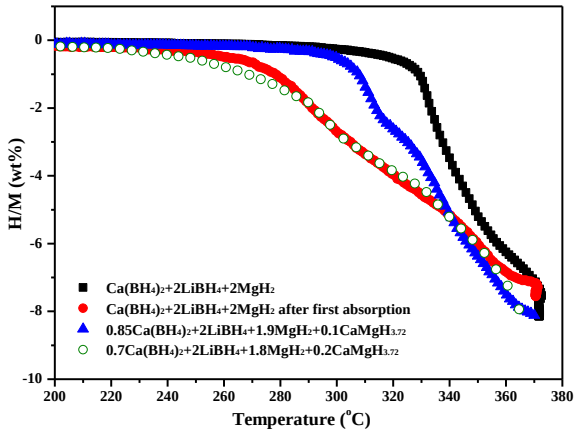

Fig. S8 Dehydrogenation curves of the $Ca(BH_4)_2$+2$LiBH_4$+2MgH_2 system of the 1st and the 2nd rounds, and the initial dehydrogenation curves of the 0.85$Ca(BH_4)_2$+2$LiBH_4$+1.9MgH_2+0.1$CaMgH_{3.72}$ and 0.7$Ca(BH_4)_2$+2$LiBH_4$+1.8MgH_2+0.2$CaMgH_{3.72}$ systems.

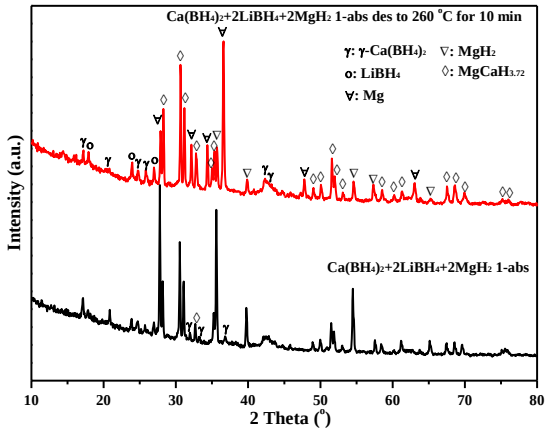

Fig. S9 XRD patterns of the product of the 1st round hydrogenated product of the ternary system heated to 260 °C and dwelling for 10 min as well as the original hydrogenated product.

Table S1 Desorption rates of the main desorption stages of the different systems

System	Desorption rate (wt% H_2 min^{-1})
$Ca(BH_4)_2$+2$LiBH_4$+2MgH_2	0.336
$Ca(BH_4)_2$	0.178
$Ca(BH_4)_2$+MgH_2	0.141
$Ca(BH_4)_2$+2$LiBH_4$	0.018
2$LiBH_4$+MgH_2	0.013

Table S2 The apparent activation energy (E_a) of dehydrogenation and the dehydrogenation reaction enthalpy ($\triangle H$) of the different systems

System	E_a (kJ mol^{-1})			$\triangle H$ (kJ mol^{-1} H_2)
	1st-step	2nd-step	3rd-step	overall
$Ca(BH_4)_2$+2$LiBH_4$+2MgH_2	162	147	143	40.3
BM $Ca(BH_4)_2$	155	209	–––	52.2
$Ca(BH_4)_2$+MgH_2	158	191	–––	45.5
2$LiBH_4$+MgH_2	169	168	–––	44.6