Improved Hydrogen Storage Performance of $Ca(BH_4)_2$: A Synergetic Effect of Porous Morphology and in Situ Formed TiO_2

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Supplementary information

Synthesis of $Ca(BH_4)_2$:

Anhydrous $CaCl_2$ and $NaBH_4$ in a molar ratio of 1 : 2 was firstly ball milled in a homemade stainless steel jar filled with THF for 24 h on a planetary ball mill (QM-3SP4, Nanjing) with a rotating speed of 300 rpm. The ball-to-powder weight ratio was 10 : 1. And then, the ball-milled suspension was filtered in a homemade filtration system to remove the precipitates of NaCl and unreacted chemicals. Subsequently, the clarified filtrate was introduced to a homemade distillation system, in which the solvent was removed from the filtrate at 55 °C with a dynamic vacuum until the product became a white solid, *viz.*, the as-prepared $Ca(BH_4)_2 \cdot 2THF$. This white solid was then ground with a mortar and pestle to powder, which was then transformed to a homemade desolvated apparatus. A treatment under dynamic vacuum at 170 °C for 16 h was further performed to remove the THF adduct from $Ca(BH_4)_2 \cdot 2THF$ much completely.

The calculation of the ratios of the evolved gases from the $Ca(BH_4)_2$+0.1Ti(OEt)$_4$ mixture during heat treatment:

The details of the calculation of the ratios of the evolved gases from the $Ca(BH_4)_2$+0.1Ti(OEt)$_4$ mixture upon heating to 160 °C for 1 h based on the data shown in Fig. 3 as the following:

The weight loss in the process can be obtained from the TG measurement (Fig. 3(b)), which is denoted as W_{TG} here. In this case, the evolved gases in the heating process is taken to be ideal gas mixture, and the total number of moles of the evolved gases of C_2H_6, C_2H_6O and H_2 can be obtained from the pressure change of the container with a fixed volume by the state function of $PV=(n_1+n_2+n_3)RT$, where n_1, n_2 and n_3 are denoted as the number of moles of C_2H_6, C_2H_6O and H_2, respectively, evolved from one mole of $Ca(BH_4)_2$+0.1$Ti(OEt)_4$. The total number of moles of the evolved gases after the heat treatment is obtained from Fig. 3(c), which is of 0.69 moles.

The correlations of the weights of the different gases evolved after the heat treatment and the original solid mixture of $Ca(BH_4)_2$+0.1$Ti(OEt)_4$, and the number of moles of the different gases are expressed as the following:

$$\begin{aligned} &M_1 * n_1 + M_2 * n_2 + M_3 * n_3 = W_{TG}(* M_{mix} 1 \\ &n_1 + n_2 + n_3 = 0.69 \end{aligned} \qquad (1)$$

where M_1, M_2, M_3, M_{mix} are denoted as the molecular weights of C_2H_6, C_2H_6O, H_2 and $Ca(BH_4)_2$+0.1$Ti(OEt)_4$ mixture, respectively. Combining the equivalent numbers of carbon atoms in the evolved gases and in the 0.1 mole of $Ti(OEt)_4$ in the mixture,

$$2 * n_1 + 2 * n_2 = 0.1 * 8 \qquad (2)$$

the number of moles of C_2H_6, C_2H_6O and H_2 (n_1, n_2 and n_3, respectively) evolved from one mole of $Ca(BH_4)_2$+0.1$Ti(OEt)_4$ mixture are calculated as 0.2, 0.2 and 0.3, as shown in eqn (4) of the main article.

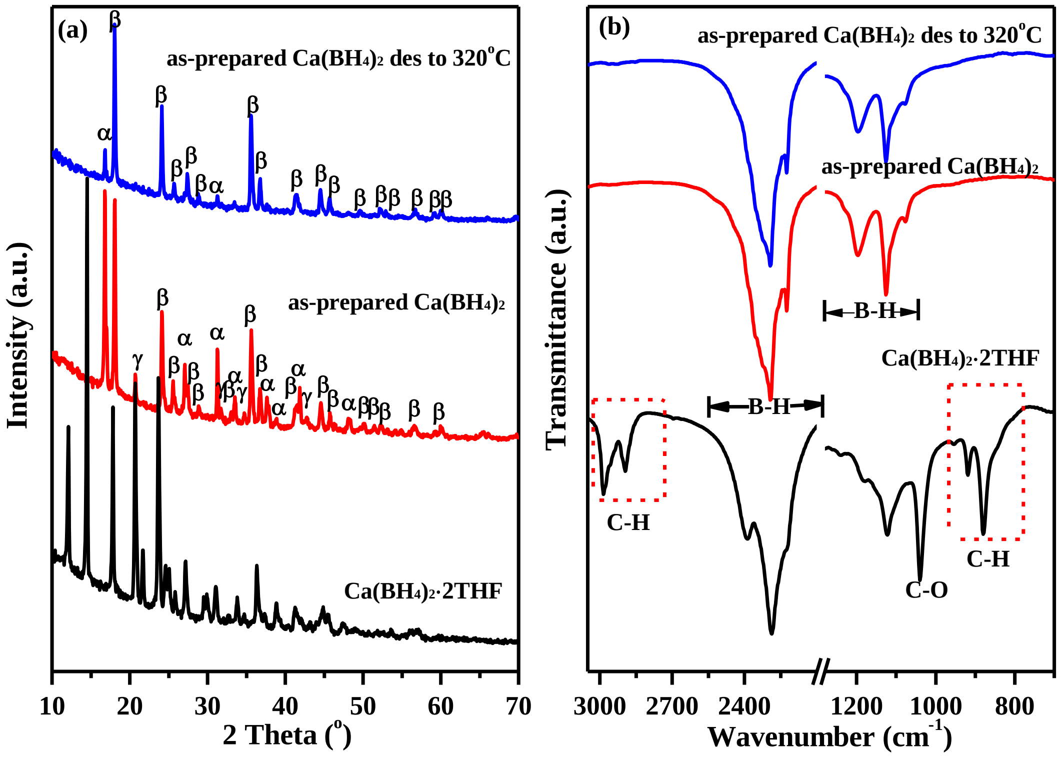

Fig. S1 XRD patterns (a) and FTIR spectra (b) of the as-prepared $Ca(BH_4)_2$·2THF, the as-prepared $Ca(BH_4)_2$ and the $Ca(BH_4)_2$ desorbed to 320 °C.

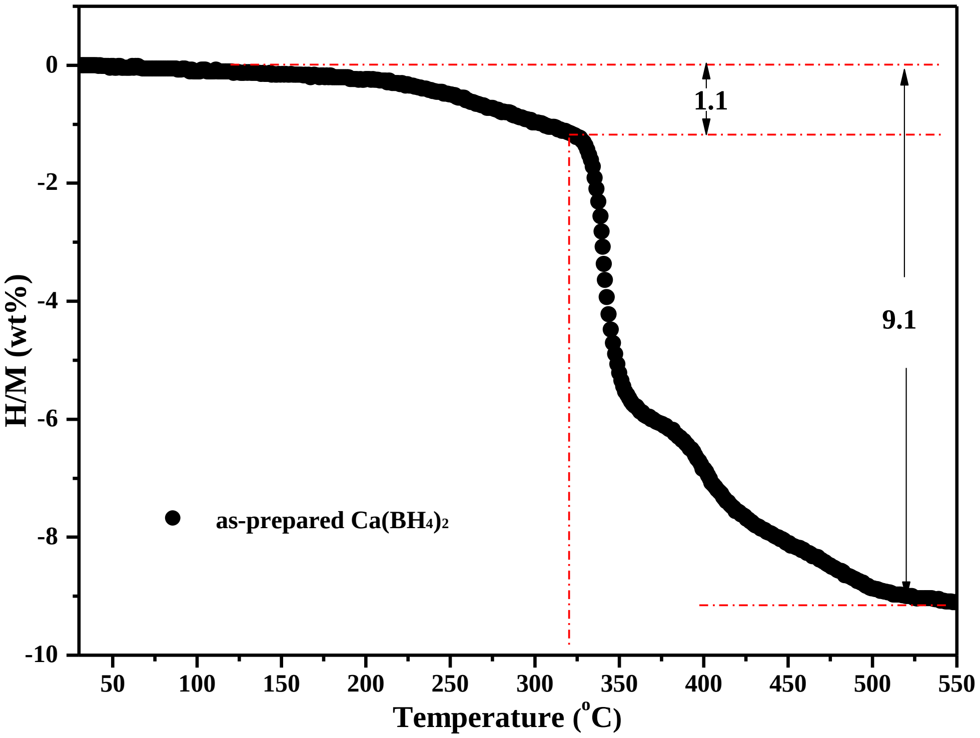

Fig. S2 Hydrogen desorption curve of the as-prepared $Ca(BH_4)_2$. The heating rate is 2 °C min^{-1}.

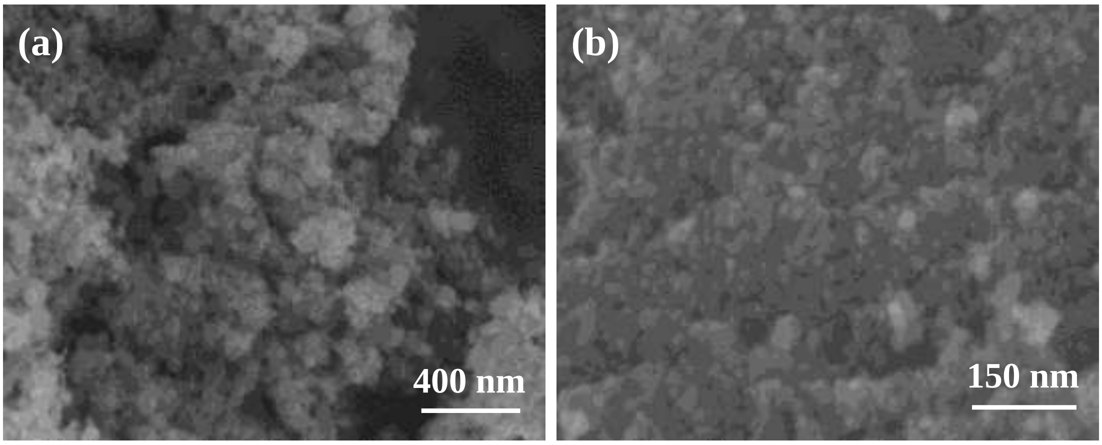

Fig. S3 SEM images of the commercial TiO_2 (a) and home-made TiO_2 derived from $Ti(OEt)_4$ (b).

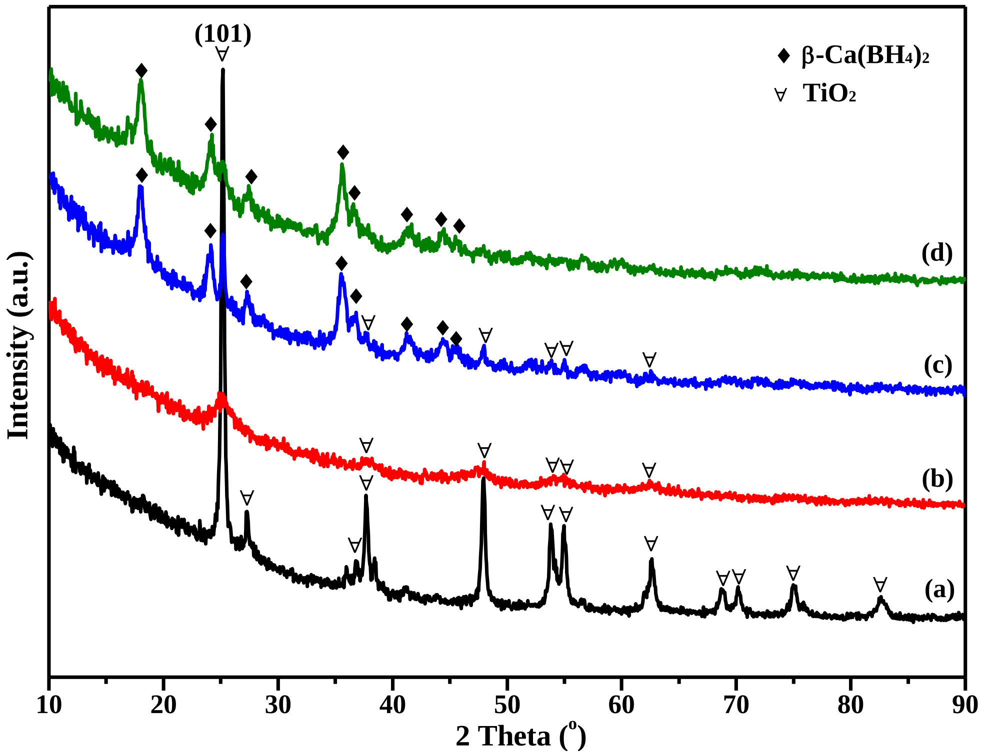

Fig. S4 XRD patterns of the commercial TiO_2 (a), home-made TiO_2 (b), the mixtures of $Ca(BH_4)_2$+0.1TiO_2 (commercial) (c) and $Ca(BH_4)_2$+0.1TiO_2 (home-made) (d).

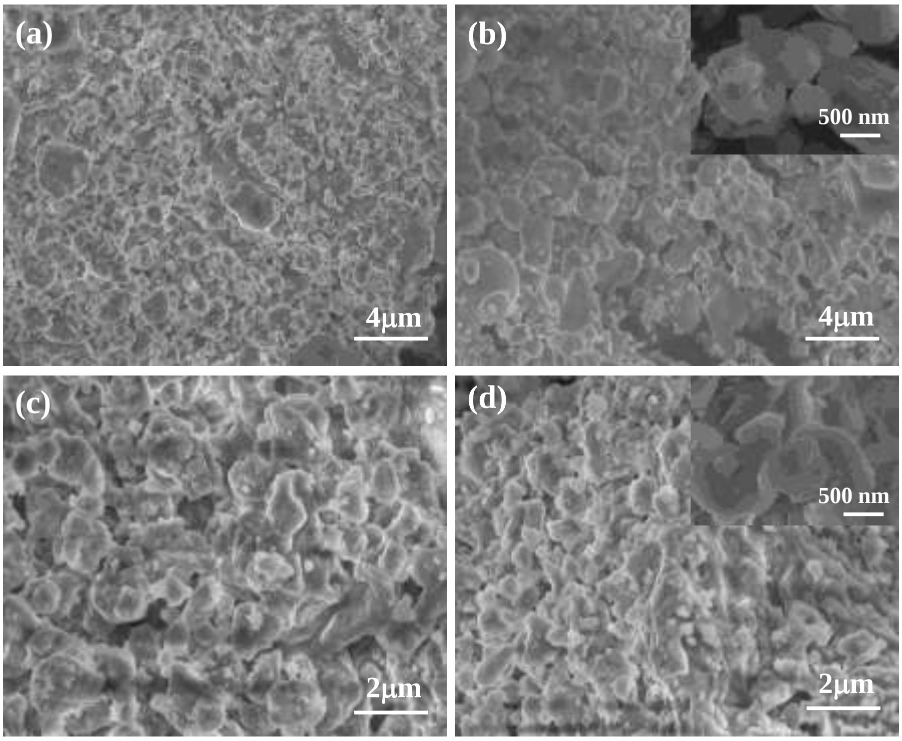

Fig. S5 SEM images of the $Ca(BH_4)_2$+$0.1TiO_2$ (commercial) (a) and $Ca(BH_4)_2$+$0.1TiO_2$ (home-made) (b) heated at 160 °C for 1 h; the $Ca(BH_4)_2$+$0.1TiO_2$ (commercial) (c) and $Ca(BH_4)_2$+$0.1TiO_2$ (home-made) (d) desorbed to 420 °C for 1 h (d).

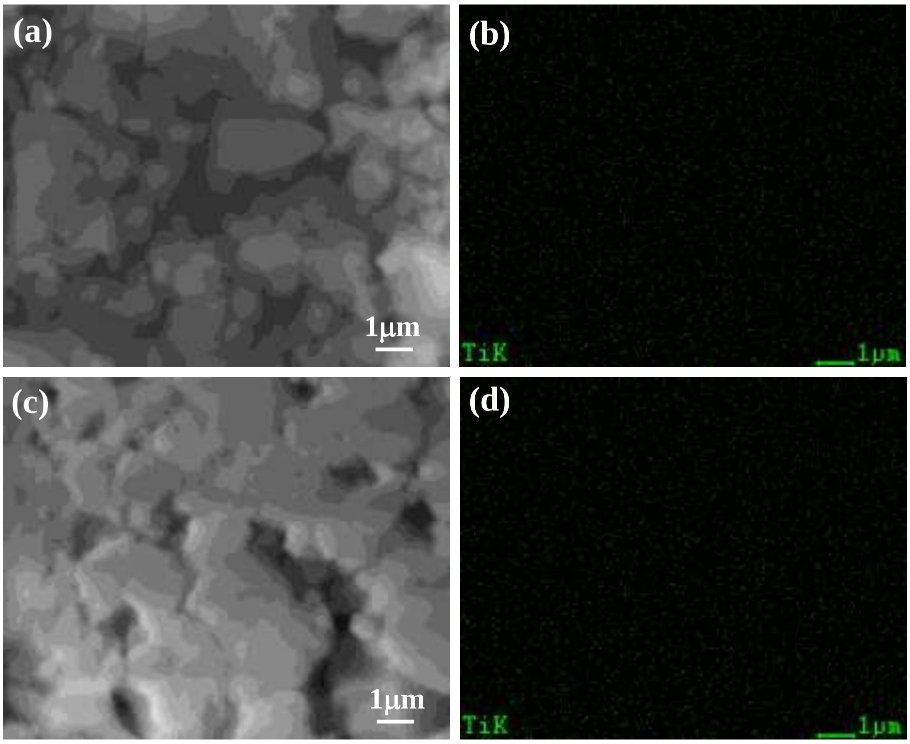

Fig. S6 SEM images (a, c) and the corresponding EDS mapping of Ti (b, d) for the porous $CaB_2H_7/0.1TiO_2$ (a, b) and $Ca(BH_4)_2$+$0.1TiO_2$ (home-made) (c, d).

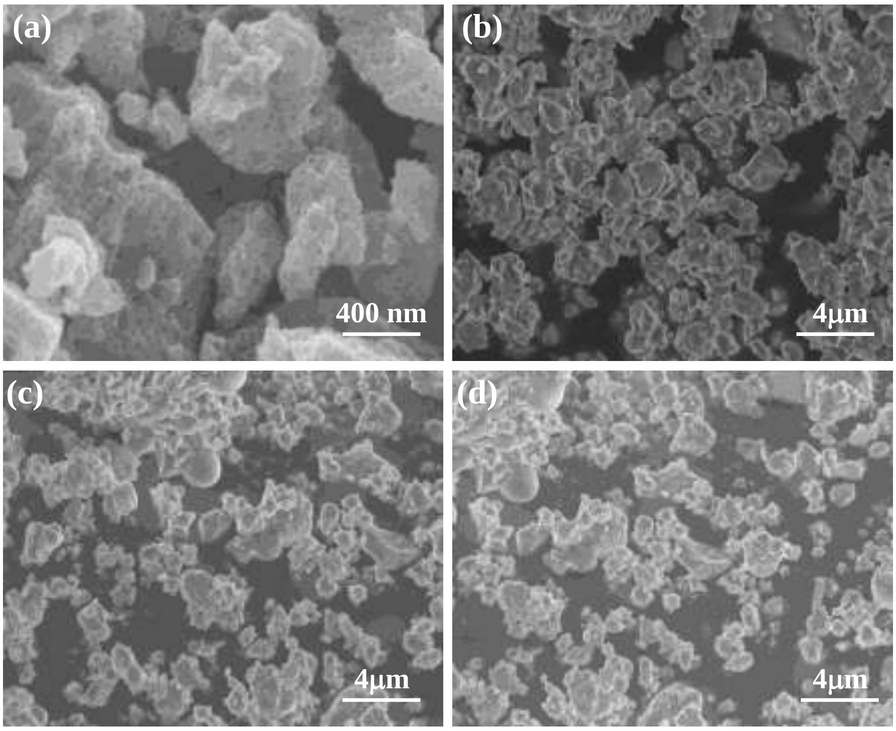

Fig. S7 SEM images of the $Ca(BH_4)_2$+0.1Ti(OEt)$_4$ mixture desorbed to 280 °C (a), the as-milled $Ca(BH_4)_2$ (b), $Ca(BH_4)_2$+0.1TiO_2(commercial) (c) and $Ca(BH_4)_2$+0.1TiO_2 (home-made) (d).

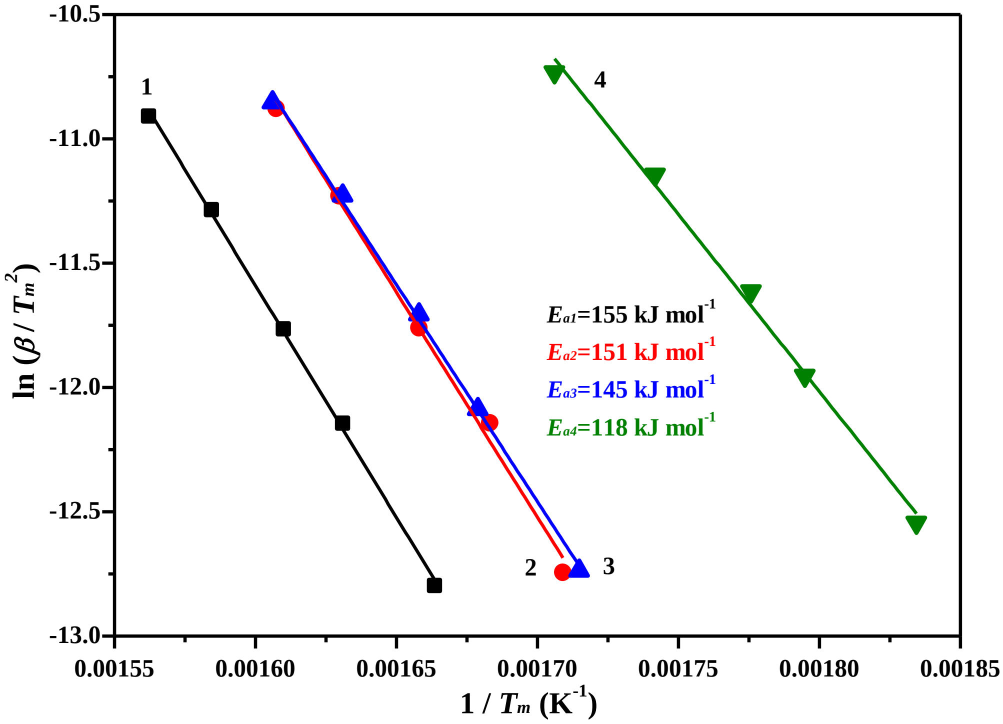

Fig. S8 Kissinger's plots of of the as-milled $Ca(BH_4)_2$ (1), $Ca(BH_4)_2$ with TiO_2 (commercial (2) and home-made (3)) externally added, and the porous CaB_2H_7/0.1TiO_2 system (4).

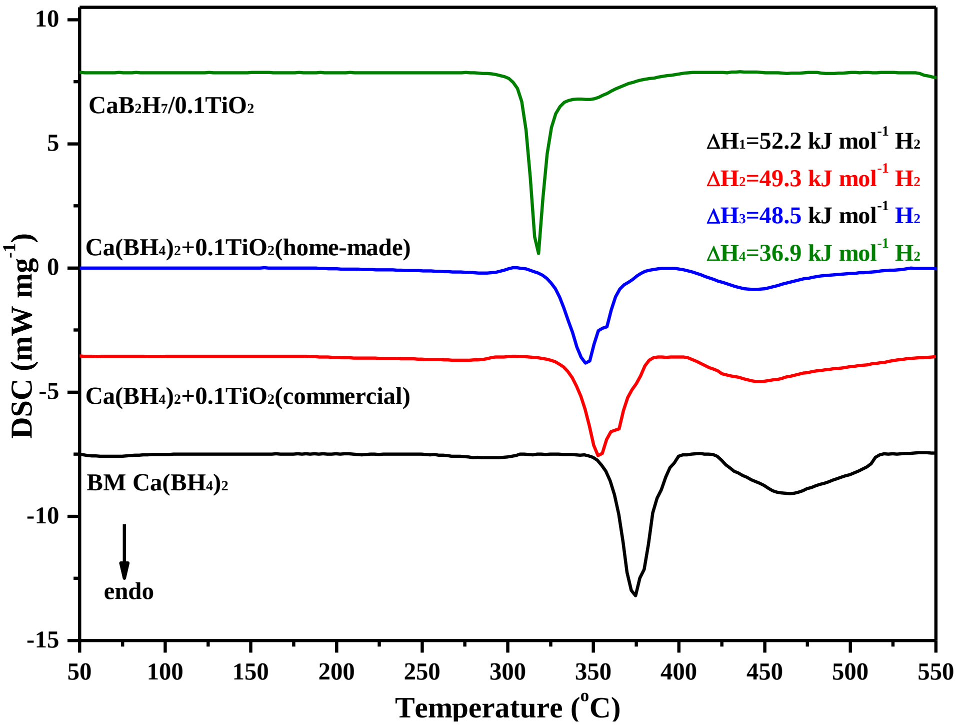

Fig. S9 DSC curves of the as-milled $Ca(BH_4)_2$, $Ca(BH_4)_2$ with TiO_2 (commercial or home-made) externally added, and the porous $CaB_2H_7/0.1TiO_2$ system.

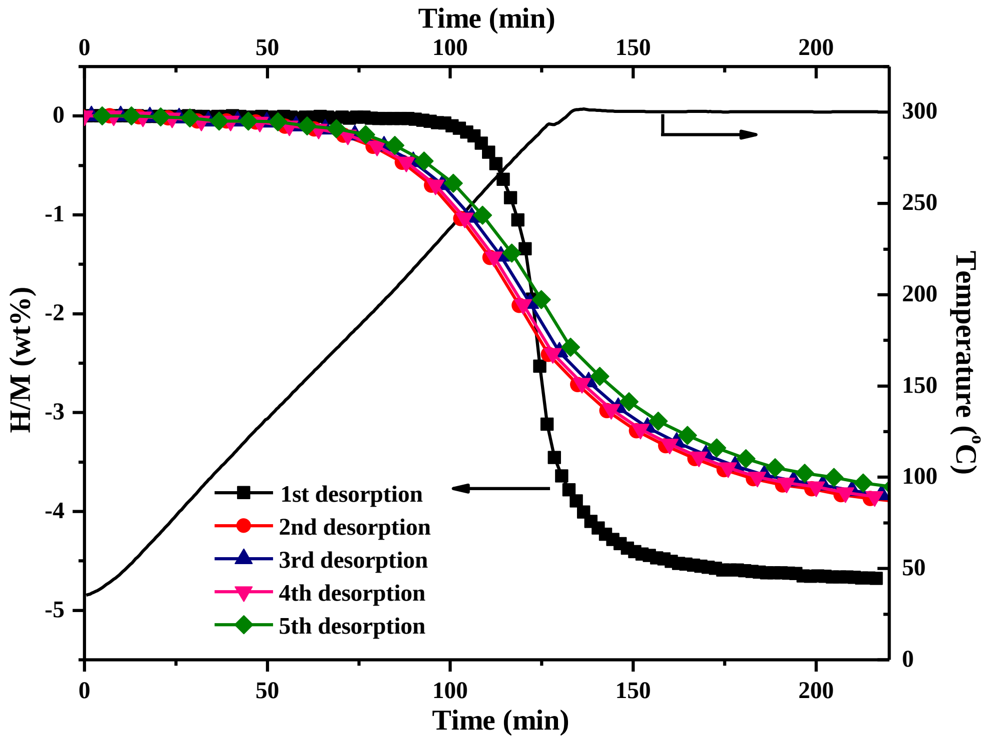

Fig. S10 Desorption curves of the first 5 desorption/absorption cycles of the porous $CaB_2H_7/0.1TiO_2$ system dehydrogenated at 300 °C for 1 h and hydrogenated at 350 °C and 90 bar H_2 pressure for 1 h.