Supporting Information

Synthesis, Structure and Dehydrogenation of Zirconium Borohydride Octaammoniate

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Experimental Section

Preparation

The starting materials, $LiBH_4$ (98%) and ammonia borane (99.9%) were purchased from Sigma-Aldrich. Anhydrous $ZrCl_4$ (> 99.5%) and ammonia were obtained from Alfa Aesar. All of the above materials were used as-received without further purification. NH_3 was purified using soda lime before use. $Zr(BH_4)_4$ was prepared by ball milling a mixture of $LiBH_4$ and $ZrCl_4$ in a molar ratio of 6:1 for 6 h at 300 rpm under an atmosphere of argon using a stainless steel sphere with a ball-to-powder ratio of 30:1 and at a temperature below 20 °C. The milling process was carried out by alternating 6 min of milling with 6 min of rest in order to avoid increasing the temperature of the powders in the vial, and thus solid-state $Zr(BH_4)_4$ crystals were obtained in the lid of vial directly. Then, a white powdery solid, $Zr(BH_4)_4 \cdot 8NH_3$, was fabricated by exposing the $Zr(BH_4)_4$ crystals under a atmosphere of anhydrous ammonia placed in an ice-water bath for at least 8 h. The whole experimental process and products are illustrated in Equation (1), (2) and Scheme 1. All handling was conducted in a glove box equipped with a recirculation and regeneration system, which maintained the oxygen and water concentrations below 1 ppm.

$$ZrCl_4 + 4LiBH_4 \rightarrow Zr(BH_4)_4\uparrow + 4LiCl \qquad (1)$$

$$Zr(BH_4)_4 + 8NH_3 \rightarrow Zr(BH_4)_4 \cdot 8NH_3 \qquad (2)$$

Gas evolution measurements

Hydrogen release property measurements were performed by a mass spectrometer (QMS 403) connected to a thermogravimeter (TG, STA 449 C) using an insulated capillary tube and a heating rate of 5 °C min^{-1}. Temperature-programmed desorption (TPD) for volumetric quantitative measurements was performed to measure the decomposition behavior of the samples on a semi-automatic Sievert's apparatus, connected to a reactor filled with sample (~ 0.1 g) under an atmosphere of argon (1 bar) at a heating rate of 5 °C min^{-1}. The amounts of H_2 and NH_3 in the emission gas were quantified using gravimetric and volumetric results. First, the mass percent (Wp) and moles per gram (Mp) of gas released from the sample were calculated from the weights of the samples and volumetric results, then the mole proportion of H_2 (C_{H2}) and NH_3 (C_{NH3}) were calculated using the following equations.

$$C_{H2} + C_{NH3} = 1 \qquad (3)$$

$$(C_{H2} * 2.02 + C_{NH3} * 17.03) * Mp = Wp \qquad (4)$$

Characterizations

Synchrotron powder diffraction data for sample of $Zr(BH_4)_4 \cdot 8NH_3$ was collected at a wavelength of 1.0329 Å by a Mythen-II detector on the powder diffraction beamline, Australian synchrotron. For phase identification and structure determination, the as-synthesized samples were loaded into pre-dried 0.7 mm glass capillaries inside a glove box under an atmosphere of argon and sealed with vacuum grease for X-ray diffraction measurements. *In-situ* heating XRD experiments were performed with a Cybostar hot air blower at a heating rate of 3 °C/min.

A complete chemical analysis was performed for $Zr(BH_4)_4 \cdot 8NH_3$ to confirm its composition. The content of Zr and B were determined by inductively coupled plasma atomic emission spectroscopic analysis (P-4010, with a 40.68 MHz rf generator, Hitachi). Powders with a certain weight were dissolved in HCl + HNO_3/H_2O solvent (10 %), and then diluted to around 10−100 μg/mL concentration. The Zr content was measured with a standard inert gas fusion method (TC-436AR, Leco-Co) and the nitrogen content was calculated accordingly the obtained the Zr content.

The chemical bonding in the species were identified using Fourier transform infrared spectroscopy (FT-IR, Nicolet Nexus 470) in the range of 500 cm^{-1} to 4000 cm^{-1}. The tested samples were pressed with potassium bromide (KBr) powder. During the IR measurement, samples were loaded into a closed tube with CaF_2 windows.

Solid-state ^{11}B nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer using a Doty CP-MAS probe with no probe background. The powder samples were spun at 12 kHz using 4 mm ZrO_2 rotors loaded in a purified argon atmosphere glove box.

Calculations

First-principles calculations based on density-functional theory (DFT) were performed by using Vienna ab initio simulation package (VASP) [1] with the ultrasoft pseudopotentials scheme [2] and the generalized-gradient approximation of Perdew-Burke-Ernzerhof [3, 4] for the electronic exchange-correlation functional. The energy cut-off for the plane wave expansion was set to 300 eV to ensure sufficient convergence (less than 1×10^{-4} eV/atom). 1×1×1 Monkhorst-Pack mesh [5] were used for unit cell of $Zr(BH_4)_4\cdot8NH_3$. The geometric optimization was performed using fixed lattice constants, while atomic positions of H in the unit cell were allowed to relax until the residual forces were less than 0.05 $eV\cdot Å^{-1}$.

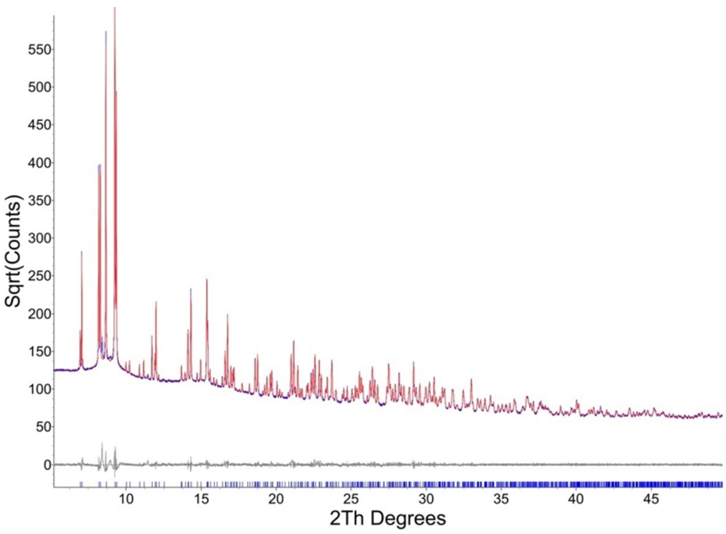

Fig. S1. Experimental (blue), fitted (red), and difference (grey line below observed and calculated patterns) synchrotron XRD profiles for $Zr(BH_4)_4 \cdot 8NH_3$. The vertical bars indicate the calculated positions of the Bragg peaks for $Zr(BH_4)_4 \cdot 8NH_3$ (blue). ($\lambda = 1.0329$ Å)

Table S1 Crystallographic and experimental details for $Zr(BH_4)_4 \cdot 8NH_3$ from Rietveld refinement.

Chemical formula	$Zr_1B_4N_8H_{40}$
Formula weight	286.5
Crystal system	Orthorhombic
Space group	*Pbca* (No. 61)
Unit cell dimensions	
a = 16.76181(28) Å	α=90°
b = 14.26414(26) Å	β=90°
c =13.65708(24)Å	γ=90°
Z	8
Density (calculated)	1.166(94) g/cm^3
Volume	3265.309(98) Å^3
R_B	4.41%
R_{wp}	6.62%
G_oF	1.329

Table S2 Calculated atomic coordination of $Zr(BH_4)_4 \cdot 8NH_3$.[a]

Atom	X	Y	Z
Zr1	0.60119	0.06677	0.22751
B11	0.85875	0.27313	0.72004
H11a	0.86229	0.21810	0.78894
H11b	0.86854	0.35271	0.75233
H11c	0.90766	0.25433	0.65586
H11d	0.79341	0.27004	0.68304
B12	0.42744	0.86730	0.44908
H12a	0.40172	0.80161	0.49713
H12b	0.39897	0.94179	0.47413
H12c	0.50019	0.86856	0.46670
H12d	0.41700	0.85683	0.36125
B13	0.23338	0.83341	0.44533
H13a	0.24761	0.76433	0.49095
H13b	0.24055	0.89865	0.49891
H13c	0.27817	0.83581	0.37776
H13d	0.16671	0.83059	0.41555
B14	0.63800	0.44904	0.38392
H14a	0.58789	0.44514	0.45120
H14b	0.62474	0.51763	0.33353
H14c	0.70391	0.45599	0.42323
H14d	0.63677	0.37810	0.33530
N21	0.71743	0.99298	0.18429
H21a	0.76350	1.03223	0.21511
H21b	0.72138	0.92943	0.21903
H21c	0.73432	-0.01237	0.10807
N22	0.29742	0.85998	0.65711
H22a	0.24963	0.90363	0.64216
H22b	0.31728	0.84057	0.58771
H22c	0.27184	0.80134	0.68885
N23	0.94985	0.04383	0.64018
H23a	0.92826	0.11068	0.65626
H23b	0.01225	0.04658	0.63474
H23c	0.92877	0.03189	0.56943
N24	0.00632	0.65123	0.11337
H24a	0.06386	0.64037	0.13825
H24b	0.00152	0.62365	0.04395
H24c	-0.00186	0.72277	0.10584
N25	0.60890	0.95969	0.35619
H25a	0.66033	0.91965	0.35812
H25b	0.61062	0.99911	0.42047

H25c	0.56255	0.91262	0.36668
N26	0.56345	0.27227	0.79207
H26a	0.50230	0.26160	0.78664
H26b	0.59210	0.21905	0.75486
H26c	0.57749	0.26518	0.86531
N27	0.48236	0.04657	0.32369
H27a	0.43629	0.09114	0.30171
H27b	0.45697	0.98060	0.32990
H27c	0.49481	0.06702	0.39509
N28	0.66211	0.16425	0.11400
H28a	0.63561	0.22811	0.09703
H28b	0.72022	0.18417	0.13249
H28c	0.66725	0.12979	0.04717

[a] The geometric optimization was performed using fixed lattice constants, while atomic positions of H in the unit cell were allowed to relax until the residual forces were less than 0.05 eV·Å^{-1}.

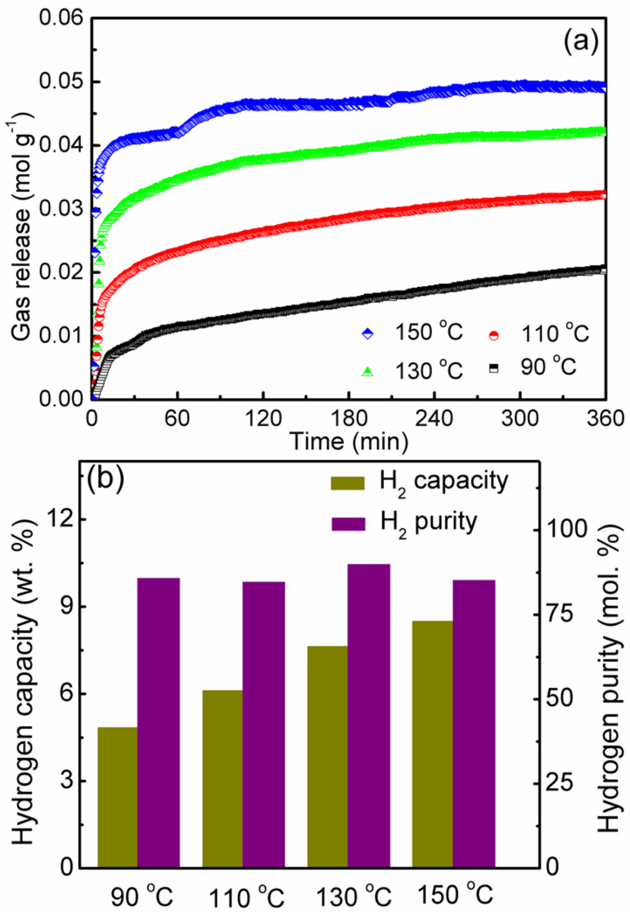

Fig. S2. (a) Isothermal dehydrogenation results for $Zr(BH_4)_4 \cdot 8NH_3$ at various temperature. (b) a summary of hydrogen release capacity and purity of part a.

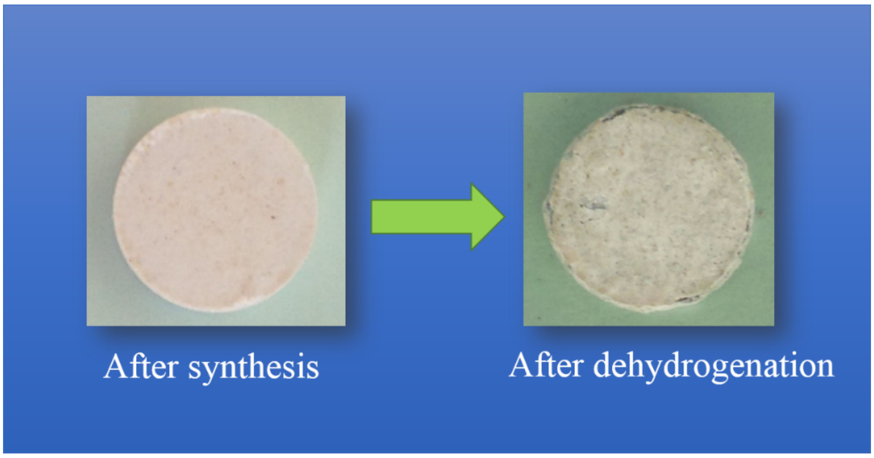

Fig. S3. Photograph of the $Zr(BH_4)_4 \cdot 8NH_3$ before and after dehydrogenation. They show that no foaming or expansion was present after dehydrogenation.

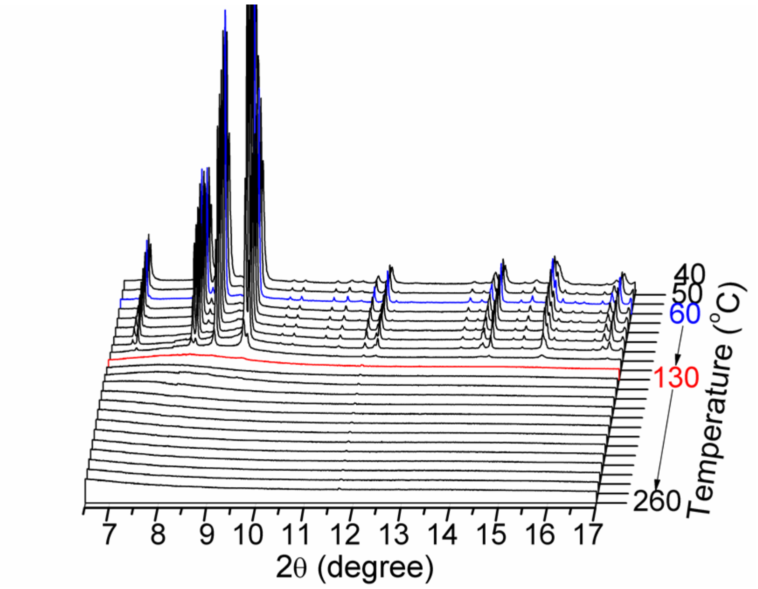

Fig. S4. The high-resolution *in-situ* XRD patterns for $Zr(BH_4)_4 \cdot 8NH_3$ from 40 to 260 °C were measured every 10 °C with a heating rate of 3 °C min^{-1} under an atmosphere of argon. ($\lambda = 1.0329$ Å)

References

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