

## *Supporting information*

### **A novel method for the synthesis of solvent-free $\text{Mg}(\text{B}_3\text{H}_8)_2$**

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## Experimental

Mg<sub>2</sub>NiH<sub>4</sub> was obtained by reactive ball milling of Mg and Ni powers (2:1 ratio) under 7.5 MPa of hydrogen pressure.<sup>1</sup> Reaction yield was 83%, being MgO (13 wt.%) and Ni (4 wt%) the detected impurities by XRD (Fig. S1). The occurrence of MgO is attributed to unavoidable surface oxidation of the starting Mg powder (44 micron size, Cerac 99.6 % purity metal basis) either in the glove-box or from the supplier. Ni residual results from mass-balance of 2:1 (Mg:Ni) ratio, as MgO impurity is inert during the milling process. Initial Ni powder is 44 micron size, Cerac 99.9%.

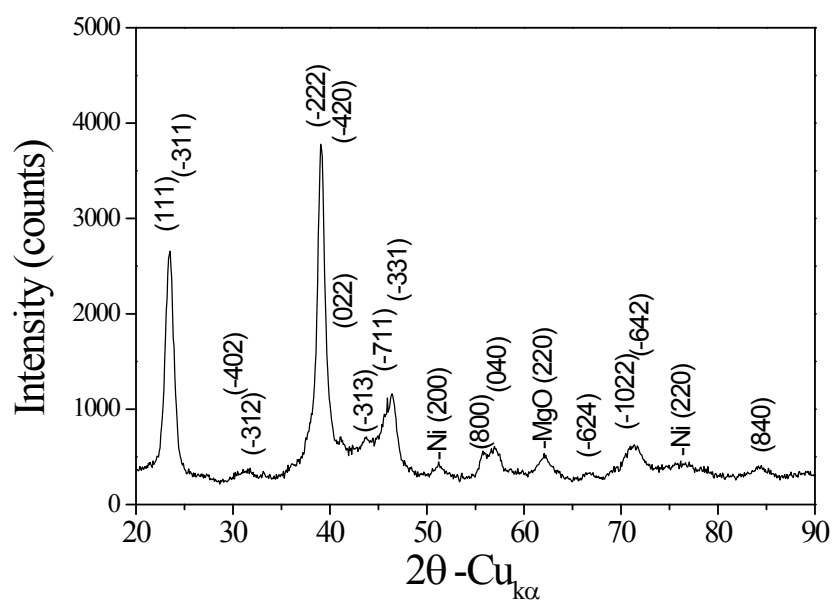
Carbon aerogel with average pore size of 10 nm was synthesized through resorcinol-formaldehyde condensation.<sup>2</sup> Resorcinol (Sigma Aldrich 99%, 8.65 g, 79 mmol), formaldehyde (Fisher chemical, analytical reagent 37-41%, stabilized by 12% methanol, 12.89 g, 158 mmol) and sodium carbonate (Across organics, anhydrous pure, 0.017 g, 0.16 mmol) were dissolved in deionized water. After curing (1 day at room temperature, 1 day at 60 °C and 3 days at 90 °C), the obtained gel was cooled, powdered and subsequently washed with acetone. The gel was pyrolyzed in a tubular oven at 800 °C for 10 hours in an Ar flow and stored in an Ar purified glovebox (MBraun Labmaster) after cooling to room temperature.

The mixture of Mg<sub>2</sub>NiH<sub>4</sub> and carbon with mass ratio of 1 to 9 was prepared by high-energy ball milling (spex8000) for 2 h. The purpose of adding carbon here is to avoid the agglomeration of ductile Mg<sub>2</sub>NiH<sub>4</sub> during the ball milling process under B<sub>2</sub>H<sub>6</sub> atmosphere. Ball milling under B<sub>2</sub>H<sub>6</sub> was carried out using a custom-made system.<sup>3</sup> NaZn(BH<sub>4</sub>)<sub>3</sub> was used as a diborane desorption source which was prepared according to literature.<sup>4</sup> 500 mg Mg<sub>2</sub>NiH<sub>4</sub>/C was filled in a milling vessel of 50 ml connected to the diborane source. The whole system was evacuated and purged with hydrogen at least 3 times. Subsequently, the diborane source was heated to 150 °C to fill the system with a B<sub>2</sub>H<sub>6</sub>/H<sub>2</sub> (1: 1) atmosphere with the pressure of 10 bar. The vessel containing Mg<sub>2</sub>NiH<sub>4</sub> was ball-milled under B<sub>2</sub>H<sub>6</sub>/H<sub>2</sub> at room temperature for 6 h and 24 h, respectively.

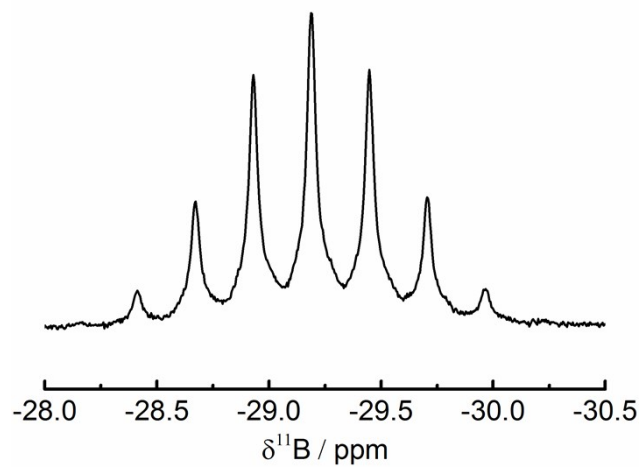
Solution-state nuclear magnetic resonance (NMR) experiments with dimethyl sulfoxide (DMSO-d<sub>6</sub>) as the solvent were carried out on a Bruker Avance-400 NMR spectrometer using a 5 mm inverse broad band probe at 25 °C. The relaxation was delayed by 60 s. <sup>11</sup>B NMR chemical shifts were reported in parts per million (ppm) externally referenced to a 1 M B(OH)<sub>3</sub> aqueous solution at 19.6 ppm as an external standard sample. For each measurement, amounts of ≈ 30 mg solid samples and about 5 mL of DMSO were weighed into tight vials and the suspensions were stirred on a shaker (KS 250, JANKE & KUNKEL, IKALabortechnik) for at least 30 min to facilitate dissolution. Undissolved solids were removed by filtration of the suspensions over Celite. The intensities of the NMR resonances were normalized according to the sample amount and the number of scans.

X-ray diffraction (XRD) measurements were performed using a Bruker D8 diffractometer equipped with a Goebel mirror selecting Cu K $\alpha$  radiation ( $\lambda=1.5418$ ) and a linear detector system (Vantec). Samples for XRD measurements were filled and sealed under an argon atmosphere into glass capillaries (diameter 0.7 mm, wall thickness 0.01mm).

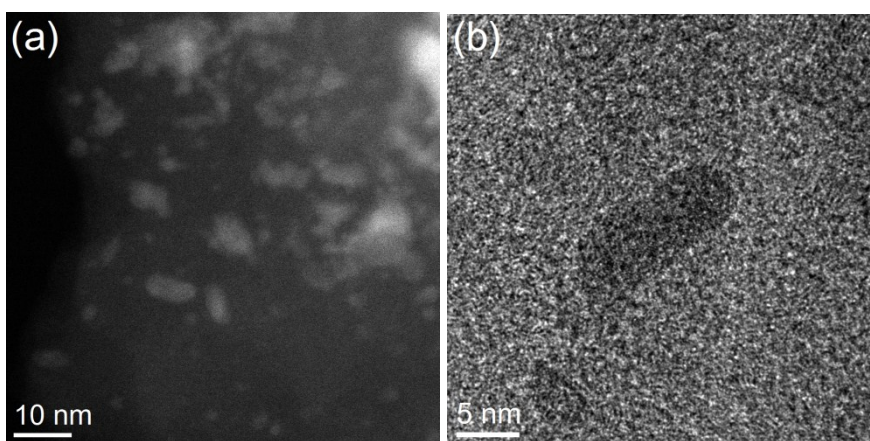
Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were conducted on a JEOL 2000FX microscope equipped with a field emission gun and operated at 200 kV. High-resolution imaging and selected area electron diffraction (SAED) were performed in the TEM mode. High angle annular dark field imaging (HAADF) with *Z* contrast was performed in the STEM mode (STEM-HAADF). Elemental analysis was achieved using energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) in the STEM mode (STEM-EDS and STEM-EELS). For sample preparation, a small amount of the sample was dispersed in the acetone by ultrasonic vibration and placed on a 200 mesh Cu grid coated with a carbon film for measurement.



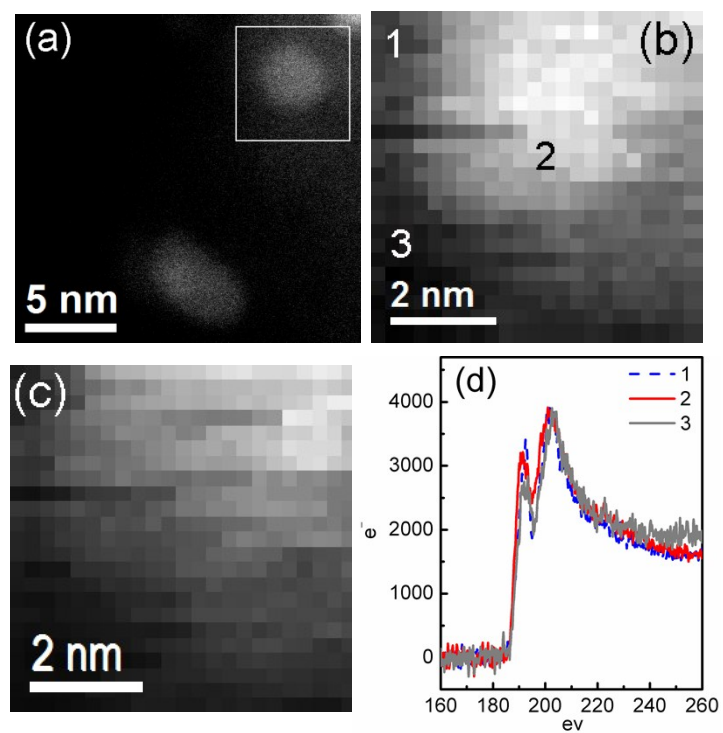
**Fig. S1** XRD diffraction pattern of  $\text{Mg}_2\text{NiH}_4$  sample synthesized by mechanochemistry of Mg and 2Ni powders under 7.5 MPa of hydrogen gas.



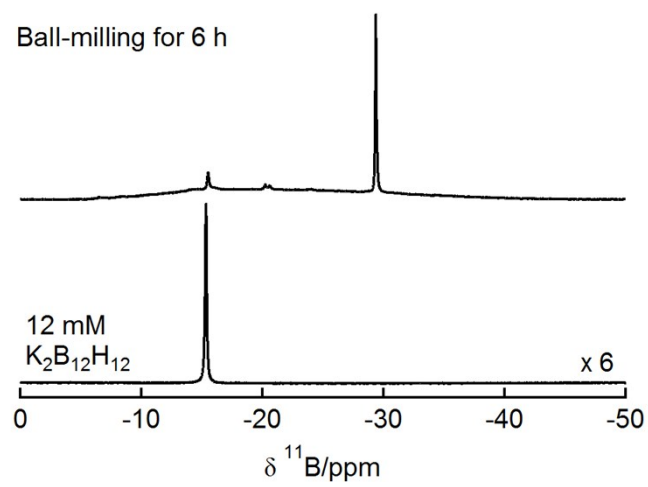
**Fig. S2** Nonet splitting of the <sup>1</sup>H-coupled <sup>11</sup>B NMR spectrum of the as synthesized [B<sub>3</sub>H<sub>8</sub>]<sup>-</sup> species. The coupling constant equals 33 Hz.<sup>5</sup>



**Fig. S3** (a) STEM-HAADF image, (b) High-resolution TEM image of  $\text{Mg}_2\text{NiH}_4/\text{C}$  ball milled under  $\text{B}_2\text{H}_6$  for 24 h.



**Fig. S4** (a) STEM-HAADF image of nanoparticles; (b) the magnification image and (c) B mapping signal of selected area in (a); (d) EELS (B) signal on the different areas of 1, 2 and 3 in (b).



**Fig. S5** Solution-state  $^{11}B$  NMR spectrum of  $Mg_2NiH_4/C$  ball milled under  $B_2H_6$  for 6 h, compared to the reference sample DMSO- $d_6$  solution of  $K_2B_{12}H_{12}$  (12 mM).



## References

1. J. Zhang, F. Cuevas, W. Zaïdi, J.-P. Bonnet, L. Aymard, J.-L. Bobet and M. Latroche, *J. Phys. Chem. C*, 2011, **115**, 4971-4979.
2. R. W. Pekala and F. M. Kong, *J. Phys. Paris*, 1989, **50**, C433-C440.
3. O. Friedrichs, A. Remhof, A. Borgschulte, F. Buchter, S. I. Orimo and A. Züttel, *Phys. Chem. Chem. Phys.*, 2010, **12**, 10919-10922.
4. R. Cerny, K. C. Kim, N. Penin, V. D'Anna, H. Hagemann and D. S. Sholl, *J. Phys. Chem. C*, 2010, **114**, 19127-19133.
5. A. Remhof, Y. Yan, D. Rentsch, A. Borgschulte, C. M. Jensen and A. Züttel, *J. Mater. Chem. A*, 2014, **2**, 7244-7249.