

## Supporting Information

### **Catalyst-Free Synthesis of Lithium Hydride at Room Temperature**

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## Experimental section

### 1. Materials and preparations

Li particle (99%, ~ 1 cm) was purchased from Sigma-Aldrich. Acetone (99%, AR), THF (99%, AR), and pyridine (99%, AR) were purchased from Sinopharm chemical. Pyrrole (99%, AR), acetonitrile (99%, AR) and cyclohexane (99%, AR), and methylbenzene (99%, AR) were purchased from Aladdin. Organic solvents were dried and preserved with 4 Å molecular sieves before use.

All samples were handled and prepared in a glovebox with an argon circulative purification system ( $O_2 < 0.1$  ppm,  $H_2O < 0.1$  ppm) to avoid the influence of oxygen and moisture. Firstly, Li particle was ball-milled with different organic solvents in a mass ratio of 4:1 for 15 h under  $H_2$  atmosphere (3 MPa) with each batch weight of 1 g; Li + x acetone was prepared by ball milling Li particle with acetone (where mass quantity “x” equals 0, 10, 25, 50 wt.%) for 15 h under 3 MPa  $H_2$  with each batch weight of 1 g; the impact of milling time on Li +10 wt.% acetone products were investigated by changing the milling time (8, 12, 15, and 20 h) under the same conditions. All samples obtained were dried for 12 h at room temperature in vacuum. All the milling processes were performed using a Retsch 400 machine at room temperature with a rotation speed of 200 RPM. The mixtures were sealed in 150 ml stainless steel vials in the glovebox with a ball-to-powder weight ratio (BPR) of about 100:1. The milling process was interrupted for 0.5 min after every 3 min of rotation to dissipate accumulated heat.

### 2. Characterization methods

**2.1 Power X-Ray diffraction (XRD) characterization.** XRD measurements were conducted using an X'Pert3 Materials Research Diffractometer (Malvern Panalytical) with Cu  $K\alpha$  radiation ( $\lambda = 0.154$  nm) at 40 kV and 40 mA. Samples were loaded into steel sample holders and covered with Kapton film to avoid contamination during the measurements. Each measurement was done at a scan speed of 10 °/min over diffraction angles of 5 to 90 °.

**2.2 Fourier transform infrared measurements (FT-IR).** FT-IR were conducted on a Tensor II FTIR spectrometer in a diffuse reflection mode with a resolution of 4  $cm^{-1}$  and an accumulation of 32 scans each time.

**2.3 Morphological characterization.** The microstructure and morphology of the samples were investigated using JSM-7800F electron microscopy (SEM) and JEM-2100 transmission

electron microscopy (TEM). For TEM analysis, the samples were dispersed onto a thin holey carbon film in the glovebox to avoid the influence of oxygen and moisture. Image processing was performed using Digital Micrograph (Gatan) software.

**2.3 Thermal analysis.** The thermal decomposition properties of the samples were investigated by a homemade temperature-programmed desorption system equipped with a mass spectrometer (HPR20, Hiden) (TPD-MS). About 20 mg of the samples were loaded into an air-tight sample holder in the glovebox. The analysis was carried out between room temperature and 650 °C at a heating rate of 4 °C/min under 30 mL/min argon flow.

**2.4 Calculation of hydrogen capacity.** Hydrogen contents of the products were evaluated using a home-made drainage gas collection device, and calculated by ideal gas equation of state (Clapeyron equation).

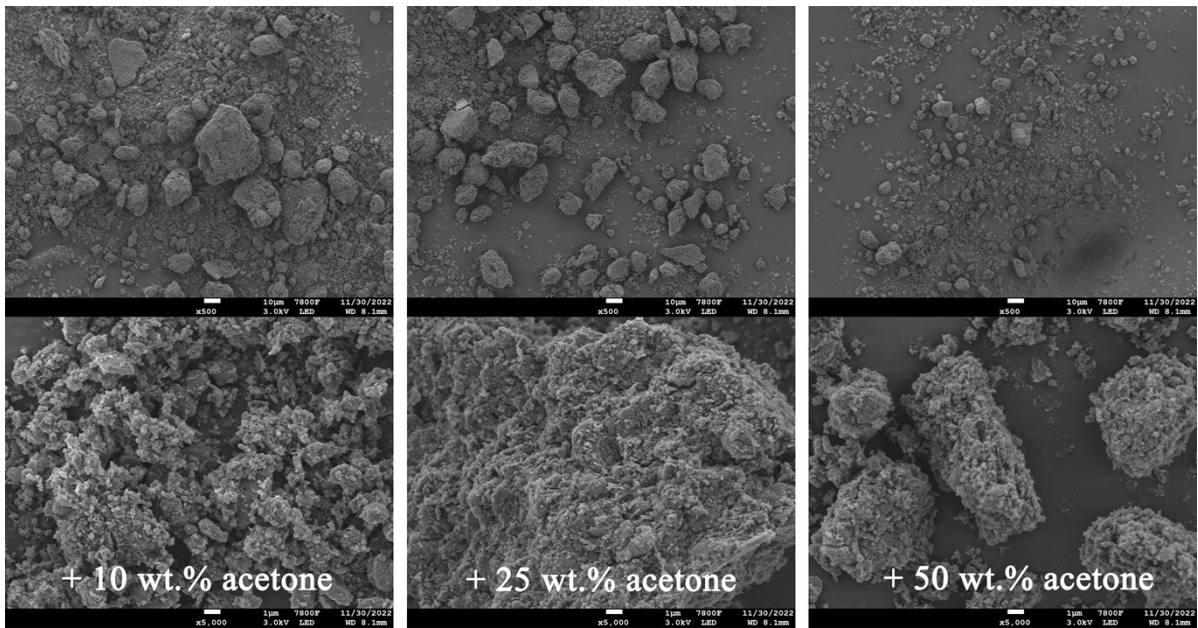
$$PV = nRT \tag{1}$$

P is the absolute pressure of the gas, V is the volume of the gas, n is the amount of substance of gas (also known as number of moles), R is the ideal gas constant, equal to the product of the Boltzmann constant and the Avogadro constant, T is the absolute temperature of the gas.

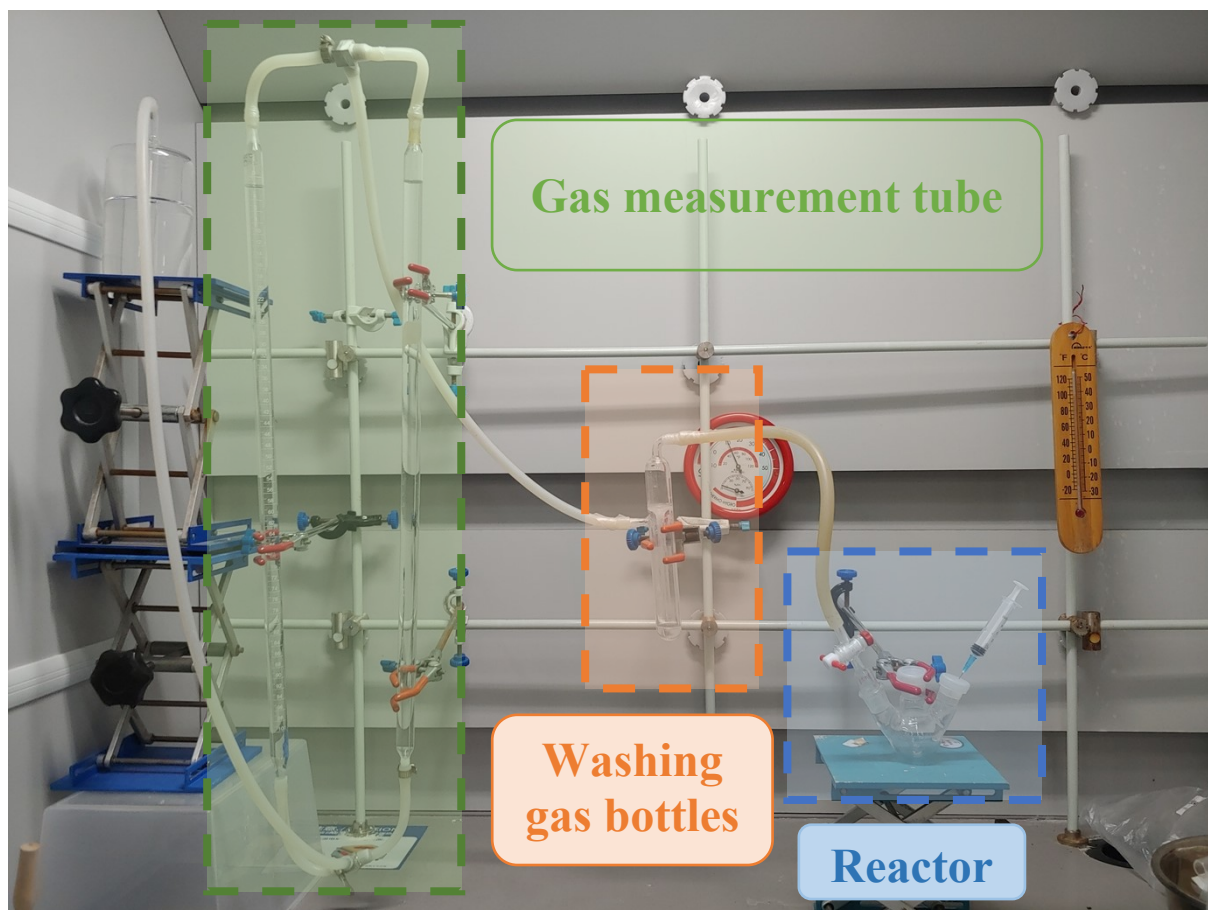
Samples were pressed prior to testing, the sample mass was 10 mg, and the pressure is one ton. To avoiding the effect of lithium hydroxide on the hydrolysis of LiH, 1.5 mol/L dilute hydrochloric acid was used as a reaction solution (5 mL). Three sets of parallel experiments were performed to reduce errors.



**Figure S1.** Lithium particles directly milled in hydrogen atmosphere.



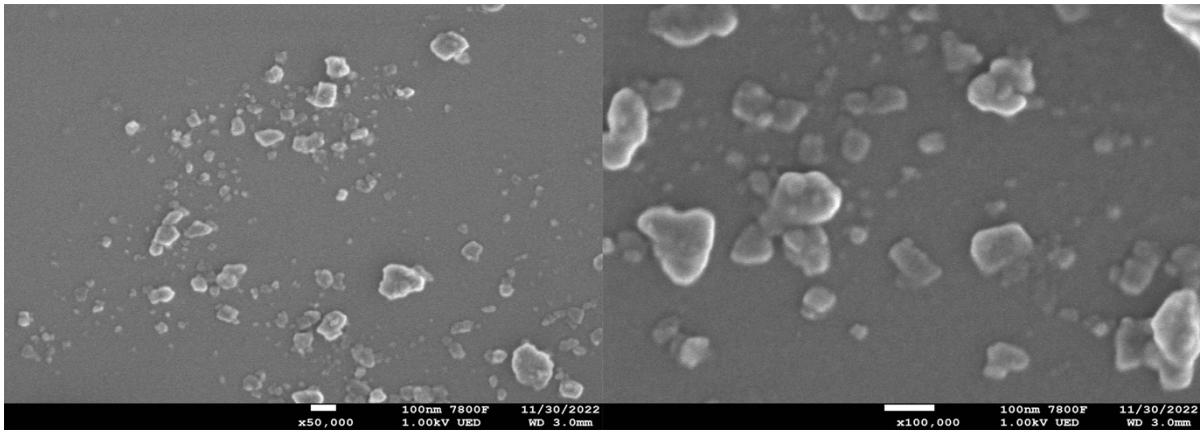
**Figure S2.** SEM images of as-milled samples with different acetone additions.



**Figure S3.** Home-made drainage gas collection device.

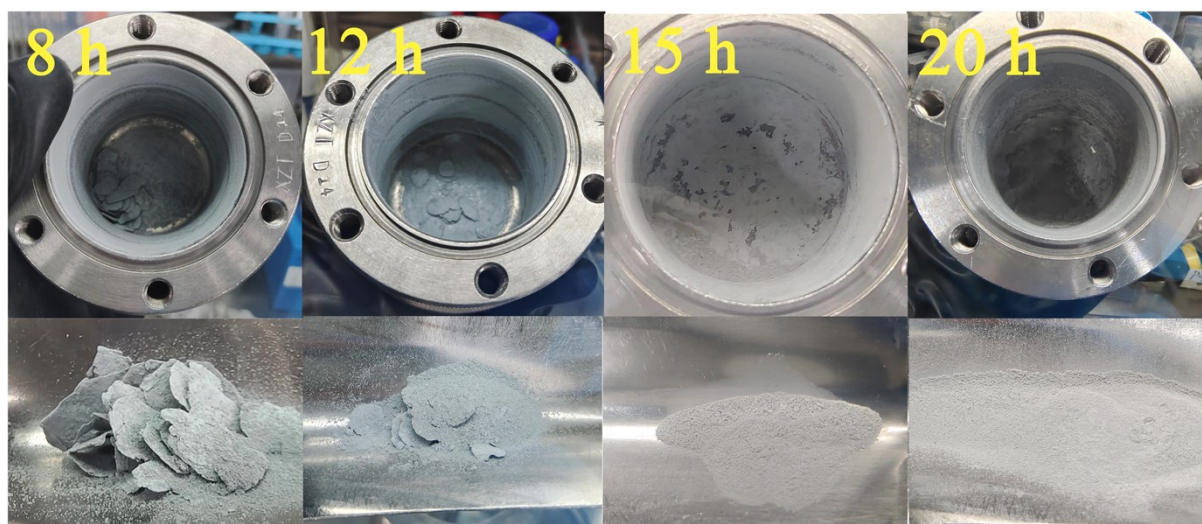
Sample name	Atmospheric pressure (KPa)	Temperature (K)	Amount of hydrogen released (mL)	Weight of samples (g)	hydrogen content (wt.%)	purity (%)
+ 10 wt.% actone	101.325	295.5	31.6	0.0104	12.52	99.53
			38.4	0.0128	12.38	98.42
			30.8	0.0103	12.39	98.50
+ 25 wt.% actone			30.2	0.0115	10.83	86.10
			36.6	0.0132	11.42	90.79
			31.2	0.0115	11.18	88.88
+ 50 wt.% actone			28.6	0.0116	10.17	80.85
			25.2	0.0100	10.38	82.52
			29.2	0.0118	10.21	81.17

**Figure S4.** Summary of parallel experiment data of different samples.



**Figure S5.** SEM images of + 10 wt.% acetone sample.





**Figure S6.** Appearances of + 10 wt.% acetone sample with different ball milling times.