Electronic Supplementary Information

Nanoconfinement of Lithium Borohydride in Cu-MOFs Towards Low Temperature Dehydrogenation

Weiwei Sun, Shaofeng Li, Jianfeng Mao, Zaiping Guo*, Huakun Liu, Shixue Dou and Xuebin Yu*

Experimental section:

$LiBH_4$@Cu-MOFs:

0.05 g $LiBH_4$ (97%, Aldrich) was dissolved in 20 mL ether under ultrasonic treatment, and 0.5 g dehydrated copper metal-organic frameworks (Cu-MOFs, as-prepared) was purged into the solution to yield a dark blue suspension. The mixture was kept under ultrasonic treatment for another 10 minutes, and then the solvent was removed at room temperature under vacuum over three hours to yield the target compound.

$LiBH_4$@Cu-MOFs-H_2O:

$LiBH_4$@Cu-MOFs-H_2O was synthesized by a method similar to that described above, with the only difference being that hydrated Cu-MOFs with coordinated water molecules were used instead of dehydrated Cu-MOFs.

All samples were handled in an argon-filled glove box which kept both water and oxygen concentrations below 1 ppm during operation. Heat treatments were carried out in a closed test tube under an argon atmosphere, and hydrogen was released into a carrier stream of argon through a T-joint with a thin connection tube to maintain the argon atmosphere over the samples.

IR: Solid-state infrared (IR) spectra of the samples (as KBr pellets) were collected with a Nicolet Nexus 470 in the range of 500 cm^{-1} to 4000 cm^{-1}. During the IR measurement (KBr pellets), samples were loaded into a single closed tube with CaF_2 windows.

XRD: Powder X-ray diffraction (XRD) patterns were obtained with a Bruker X'PERT diffractometer (Cu Kα radiation, 16 kV). During the XRD measurement, samples were mounted in a glove box, and an amorphous polymer tape was used to cover the surface of the powder to avoid oxidation.

TPD: Hydrogen release property measurements were performed by Sieverts method temperature programmed desorption (TPD) from ambient temperature to 200 °C at the heating rate of 2 °C/min.

MS: Mass spectrometry (MS) was conducted under 1 bar argon between room temperature and 600 °C at a heating rate of 10 °C/min using a Netzsch STA 409C analyzer equipped with a quadrupole mass spectrometer for the analysis of the evolved gas.

BET: Nitrogen adsorption/desorption isotherms at the temperature of liquid nitrogen were obtained with an ASAP 2020 V3.03 H instrument after degassing the samples at 100 °C (for dehydrated Cu-MOFs) / room temperature (for $LiBH_4$@Cu-MOFs) for 10 hours prior to measurements. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation.

NMR: The solid-state ^{11}B nuclear magnetic resonance (^{11}B NMR) was recorded (Brucker 300) using a Doty CP-MAS probe with no probe background. All of those solid samples were spun at 12 kHz, using 4 mm ZrO_2 rotors filled up in purified argon atmosphere glove boxes. The NMR shifts (d) are reported in parts per million (ppm), externally referenced to H_3BO_3 at 0 ppm for ^{11}B nuclei. A 0.55 μs single-pulse excitation was employed, with repetition times of 1.5 s.

Density measurement and results

The pycnometric method, [1] which estimates according to Archimedes' principle, was used for density measurements. Simply, the sample was placed into a specific-gravity bottle full of *n*-hexane, and the volume of the sample was then obtained from that of the overflowing *n*-hexane. On the basis of the known density of *n*-hexane, the specific density of the sample can be calculated with the formula below (Scheme S1). By this method, the densities of dehydrated Cu-MOFs and $LiBH_4$@Cu-MOFs were calculated to be 2.05 and 1.47 g/cm^3, respectively (measured density of $LiBH_4$ is 0.67 g/cm^3). Combined with the pore volume of Cu-MOFs in the BET results, we calculated that the maximum density would be 1.73 g/cm^3 when $LiBH_4$ was totally loaded into the pores of Cu-MOFs, while the minimum density would be 1.26 g/cm^3 when $LiBH_4$ blocked the openings in the Cu-MOFs. Comparison of the measured density of $LiBH_4$@Cu-MOFs with the calculated densities revealed that the majority of the pores in the Cu-MOFs had been impregnated by $LiBH_4$, and as calculated by the formula given in Scheme S2, the filling rate (r_{filling}) of $LiBH_4$ is up to 84 %.

Scheme S1 Formula for density measurement (*n*-hexane as solvent; sa = sample, so = solvent, bo = bottle).

$$\rho_{sa}=\frac{\rho_{so}(m_{sa+bo}-m_{bo})}{(m_{so+bo}-m_{bo})-(m_{sa+so+bo}-m_{sa+bo})}$$

Scheme S2 Formulas to calculate the filling rate of $LiBH_4$. (V_{occupied}, V_{vacancy}, and V_{total} represent the volume that has been filled by $LiBH_4$, the volume that has not been filled, and the total pore volume of Cu-MOFs from the BET results, respectively.)

$$\rho_{LiBH_4@Cu-MOFs}=\frac{m_{Cu-MOFs}+m_{LiBH_4}}{V_{Cu-MOFs}+V_{LiBH_4}+V_{vacancy}}$$

$$1.47=\frac{10+1}{10/2.05+1/0.67+V_{vacancy}}$$

$$V_{vacancy}=1.13$$

$$r_{filling(LiBH_4)} = \frac{\rho_{LiBH_4} \times V_{occupied}}{m_{LiBH_4}} \times 100\%$$

$$r_{filling(LiBH_4)} = \frac{0.67 \times (2.38 - 1.13)}{1} \times 100\% = 83.8\%$$

Table S1 Surface areas of Cu-MOFs and $LiBH_4$@Cu-MOFs samples.

	Cu-MOFs (m^2/g)	$LiBH_4$@Cu-MOFs (m^2/g)
Single Point Surface Area at P/Po = 0.156977410	763.668	67.646
BET Surface Area	738.374	67.999
Langmuir Surface Area	923.525	87.210

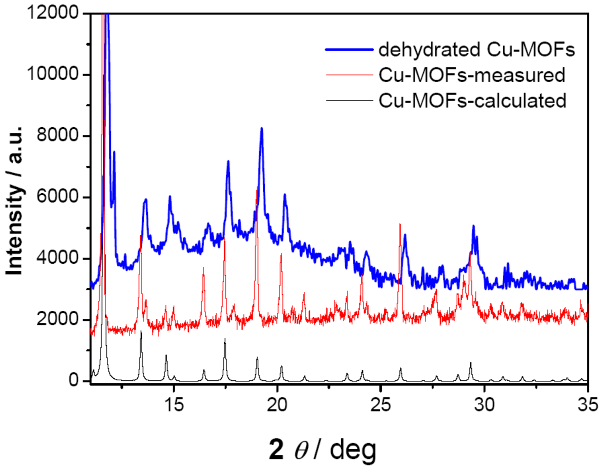

Figure S1. XRD spectra of as-prepared and dehydrated Cu-MOFs compared with calculated result.

As shown in Figure S1, the XRD spectra of the Cu-MOFs samples were compared with a pattern calculated from crystallographic data. The overall agreement is good, however, some deviation is observed in the relative intensities, which may be due to variations in the degree of hydration. Meanwhile, for the Cu-MOFs sample that was dehydrated at 100 °C for six hours, the peaks of the original spectrum are still retained with only a slight shift, indicating that this sample maintains structural integrity after dehydration.

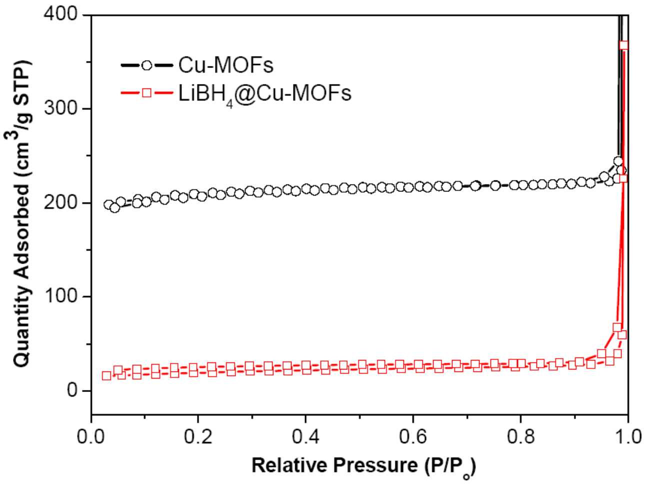

Figure S2 Adsorption and desorption isotherm linear plots of Cu-MOFs and $LiBH_4$@Cu-MOFs samples.

As in Figure S2, the N_2 adsorption and desorption of Cu-MOFs at 77 K show the characteristics of a microporous material and indicate the permanent microporosity and architectural stability of the evacuated framework, while the $LiBH_4$@Cu-MOFs shows non-porous characteristics.

From the BET results, the volume of pores at P/Po = 0.991585464 for $LiBH_4$@Cu-MOFs is 0.56 cm^3/g, while for Cu-MOFs, it is 2.38 cm^3/g. The BET and Langmuir surface areas of $LiBH_4$@Cu-MOFs and Cu-MOFs are compared in Table S1.

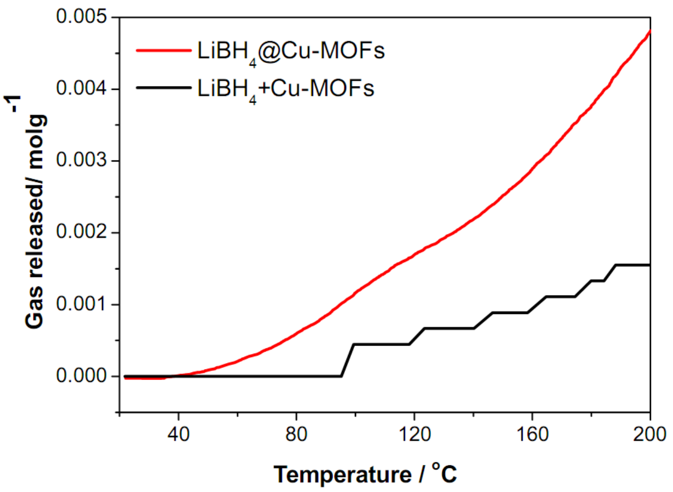

Figure S3 Temperature-programmed hydrogen release properties of $LiBH_4$@Cu-MOFs (red line) and direct mixture of $LiBH_4$ and Cu-MOFs (black line). The heating rate for all the samples is 2 °C /min.

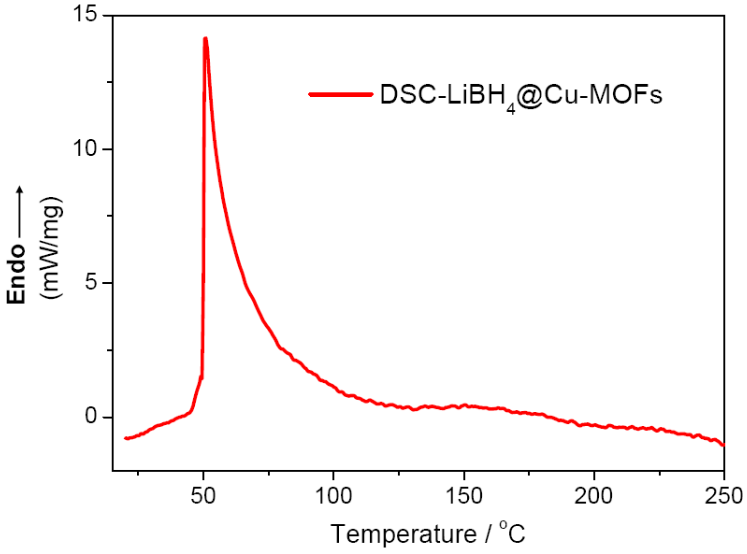

Figure S4 DSC result of LiBH$_4$@Cu-MOFs samples.

The differential scanning calorimetry (DSC) curve of LiBH$_4$@Cu-MOFs shows an endothermal peak around 60 °C, which is consistent with the results of MS and TPD measurements.

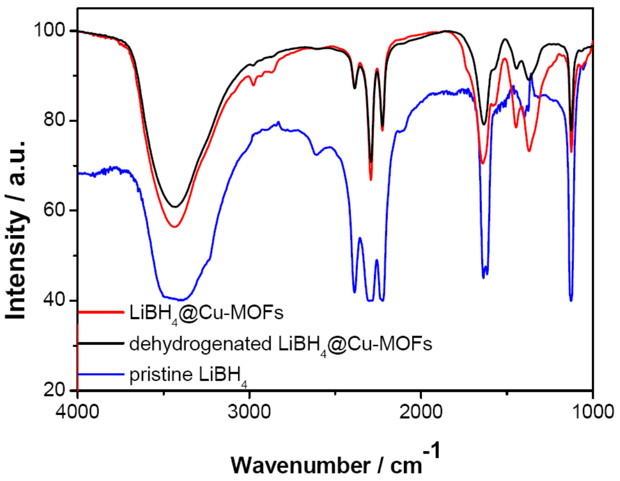

Figure S5 FT-IR spectra of pristine $LiBH_4$, $LiBH_4$@Cu-MOFs, and dehydrogenated $LiBH_4$@Cu-MOFs samples.

As shown in Figure S3, the broad band at ~3400 cm^{-1} in all the spectra could be assigned to water molecules that are present in the atmosphere of the sample capsule during the IR measurement. In the spectra of $LiBH_4$@Cu-MOFs before and after dehydrogenation, the three peaks in the range of 2200-2400 cm^{-1} and another two peaks at around 1120 and 1640 cm^{-1} are the characteristic peaks of $LiBH_4$, while the peak at 1370 cm^{-1} could be assigned to the vibration of C-H bonds from the Cu-MOFs.

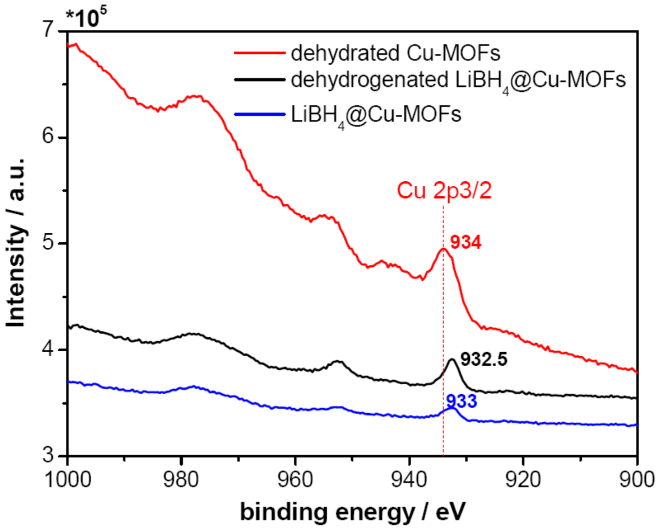

Figure S6 XPS results on dehydrated Cu-MOFs compared with $LiBH_4$@Cu-MOFs before and after dehydrogenation.

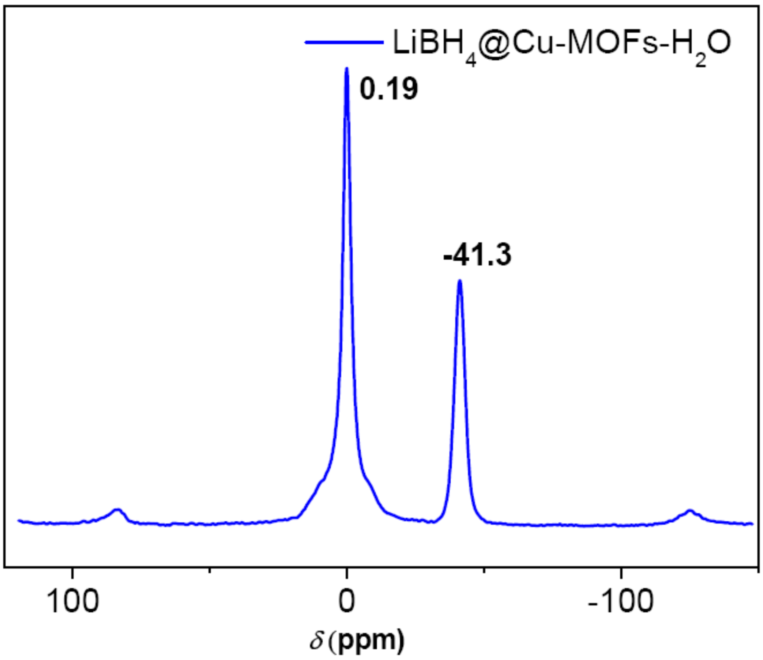

Figure S7 ^{11}B NMR results for as-prepared LiBH$_4$@Cu-MOFs-H$_2$O.

Reference:

[1] M. W. G. Burt, C. A. Fewtrell, R. A. Wharton. *Powder Technology*, 1973, **8**, 223.