Supplementary Material (ESI) for Faraday Discussions

The role of Ni in increasing the reversibility of the hydrogen release from nanoconfined $LiBH_4$

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Supplementary information

Porosity of the carbon in the nanocomposites (Nitrogen physisorption)

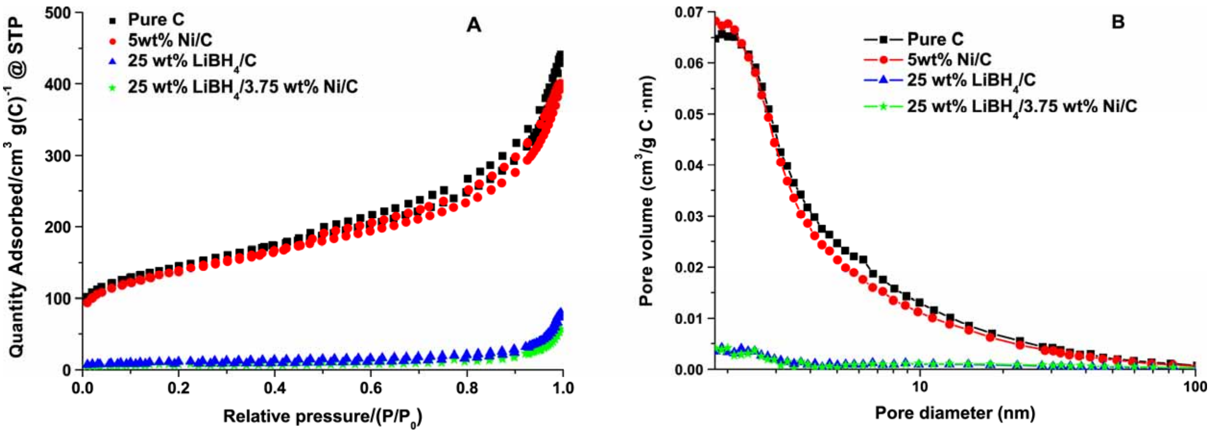
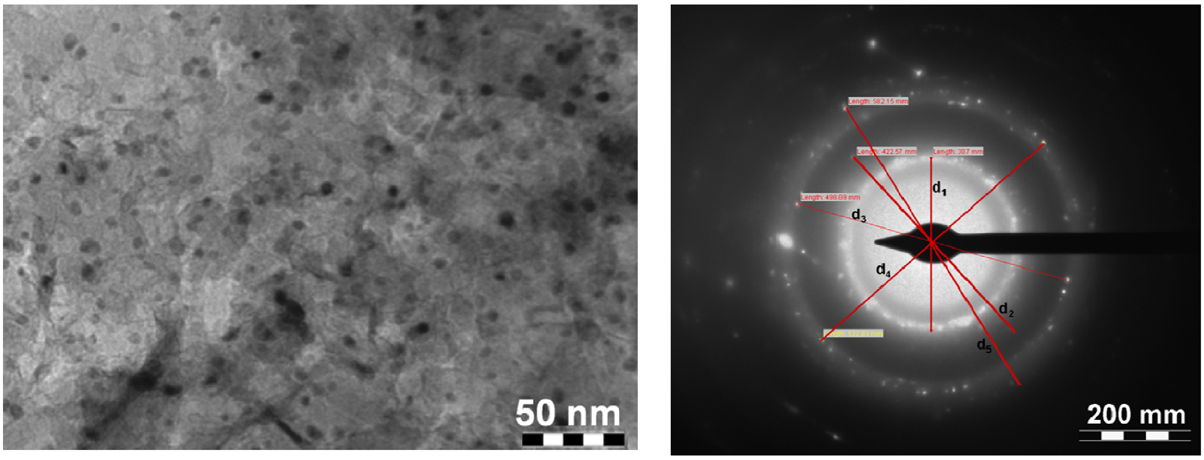


Figure S1. Nitrogen adsorption isotherms (A) and pore size distribution (B) of pure HSAG-500 carbon, 5wt% Ni/C, and nanocomposites $25LiBH_4/C$ and $25LiBH_4/3.75NiC$.

Fig. 1(A) shows that after melt infiltration with 25 wt% $LiBH_4$, the accessible pore volume has decreased drastically. Figure 1(B) illustrates that most of the micropores and also the mesopores were filled upon melt infiltration. The total pore volume decreased from 0.66 cm^3/g [C] to 0.11cm^3/g [C]. This corresponds to 84% pore filling, in line with the volume of $LiBH_4$ in the nanocomposites. No noticeable difference exists between the sample containing Ni and the sample without Ni.

TEM measurements

(A)



(B)

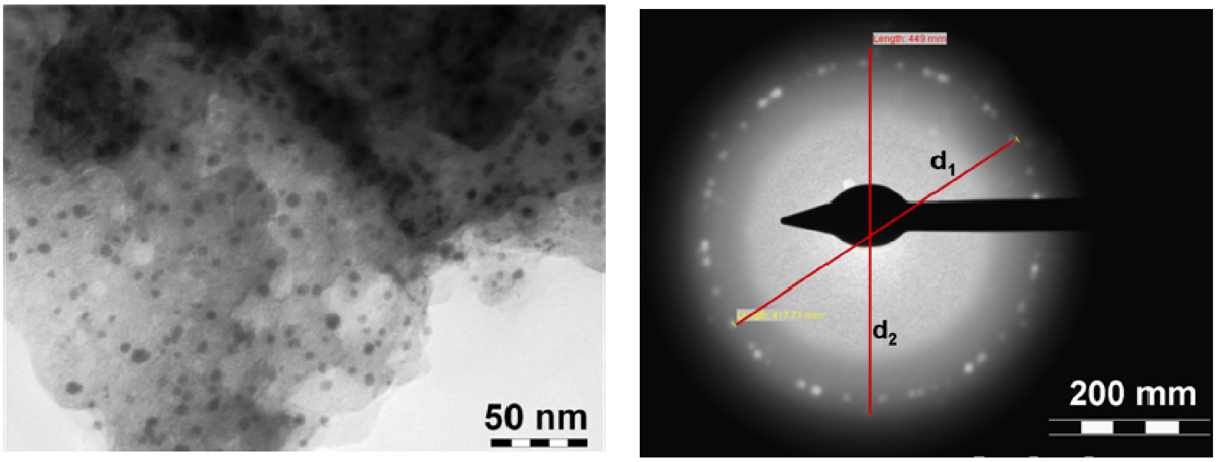


Figure. S2 TEM image of (A) 5wt% Ni/C and (B) $25LiBH_4/3.75Ni/C$ nanocomposites after synthesis The electron diffraction pattern shown on the right was taken on the area of the sample shown on the left.

The diffraction rings are analysed using

$$\lambda L = Rd \quad (1)$$

Where λL is the camera constant of the TEM = 720, R is the ring diameter and d is the d-spacing of the substance measured.Since λL is a constant, this implies that

$$R_1d_1 = R_2d_2 = R_3d_3 = R_nd_n \quad (2)$$

For graphite d_1 = 3.34Å, d_2 = 1.68 Å and d_3 =1.54 Å

For Ni, d_1 = 2.03 Å, d_2 = 1.76 Å and d_3 =1.25 Å.

From Figure 2(A), there are scattered diffraction rings however the ring diameters that can be identified are

R_1 = 307 mm, R_2 = 422.57 mm, R_3 = 498.89 mm, R_4 = 532.83 mm and R_5 = 582.15 mm

For Ni, it can be shown that

$R_1d_1 = (307 * 2.03) \approx R_3d_3 = (1.25 * 498.89) = 623$, which corresponds to the Ni d spacing of 2.03 and 1.25 Å

Also for the graphite, it can be shown that

$R_4d_2 = (532.83 *1.68) \approx R_5d_3 = (1.54 * 582.15) = 895$

Therefore, for the 5wt% Ni/C, two diffraction rings due to Ni (d values of 2.03 and 1.25 Å) can be seen and two diffractions from the graphite (d values of 1.68 and 1.54 Å) can be resolved.

From Figure 2(B), the diffraction rings have diameter R_1 = 417.71 mm and R_2 = 449 mm

Substituting these values into equation 2

$417.71 * 1.68 \approx 449 * 1.54$

Therefore the diffraction ring is due to the graphite d spacing of 1.68 and 1.54 Å showing that the Ni is amorphous after synthesis.

EDX

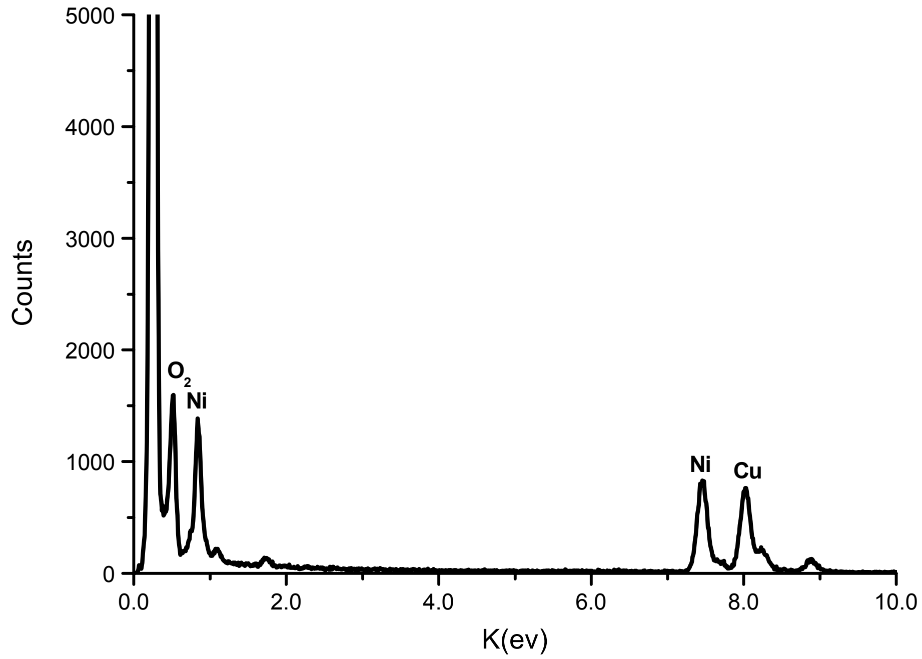


Figure S3 EDX signal from the LiBH4/Ni/C nanocomposites (sample 2B) showing the presence of Ni.

EXAFS fitting

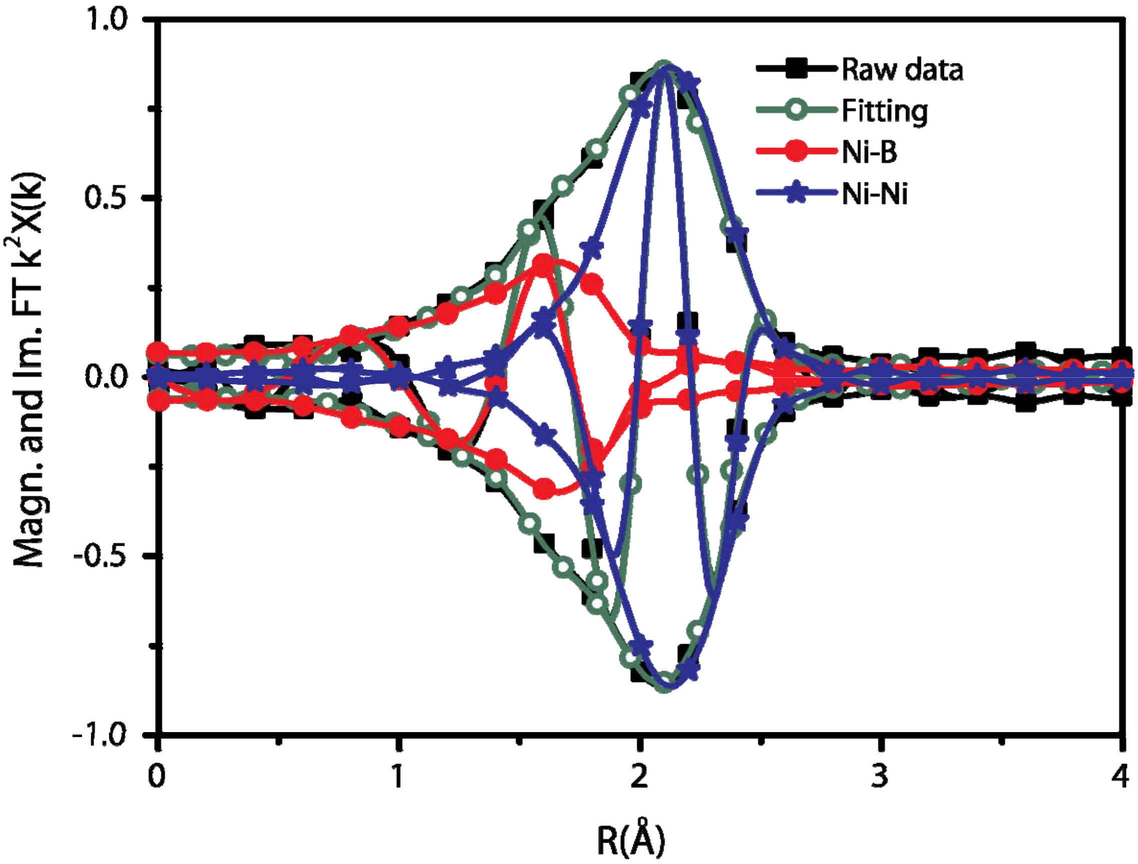


Figure S4. Magnitude and Imaginary part of the phase-uncorrected Fourier transformed $\chi(k)$ for the as-synthesized $LiBH_4$/Ni/C nanocomposites. The fit is optimized with Δk=3-13 $Å^{-1}$ and ΔR=1.2-3.0 with the k-weighting parameter of 2. The individual contributions of Ni-B and Ni-Ni are also included.