Supporting Information

Advanced H₂-Storage System Fabricated via Chemical Layer Deposition in a Well-Designed Porous Material Template

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**Figure S1** SEM image of colloidal crystals consisting of uniform silica spheres of 250 nm. The inset shows the photograph of a piece of colloidal silica crystals.
Figure S2  N\textsubscript{2} sorption isotherms and pore size distributions of the hierarchically macro-mesoporous carbon with macropore of 250 nm and mesopore of 12.7 nm.
Figure S3. Schematic representation of the procedure for the deposition of ammine aluminum borohydrides (AAB) in ce-confined into carbon scaffolds via the CLD methodology.
Figure S4 TGA-MS spectra of the pure $\text{Al(BH}_4\text{)}_3\text{NH}_3_6$ (in black line) and the physical mixture of $\text{Al(BH}_4\text{)}_3\text{NH}_3_6$ with HOPC (in red line).
Figure S5. The increment of uploading capacity with the proceeding of reaction cycles for various carbon templates under different conditions; a: C-20; b: C-30; c: C-40 d: C-50 with the time of 2 h for ammonia physisorption and then the time of 0.5 h for vacuuming to remove residual ammonia during the first cycle; e: C-20; with the absorption time of ammonia for 2 h and then the time of 0.8 h for vacuuming to remove residual ammonia during the first cycle.

It clearly indicates that, with the proceeding of reaction cycles, the kinetics of the increment of loading capacity decreases, which can be attributed to the fact that upon the uploading of ammine aluminum borohydrides, the entrance become fewer and smaller, which hinders the transmission of precursors into the pore. Moreover, via adjusting the capacity of NH$_3$ adsorbed inside the templates during the first cycle, i.e., increasing the time of removing NH$_3$ from 0.5 h to 0.8 h, the weight gain for every cycle decreased for the same carbon scaffolds with a diameter of 250 nm. Therefore, the morphology and capacity of the uploaded Al(BH$_4$)$_3$(NH$_3$)$_6$ can be readily tuned by adjusting the capacity of NH$_3$ adsorbed during the 1$^{st}$ cycle.
Figure S6 SEM image of C-30
Figure S7. XRD patterns of a physical mixture of 30 wt.% Al(BH$_4$)$_3$(NH$_3$)$_6$ with carbon (PM), and Al(BH$_4$)$_3$(NH$_3$)$_6$ confined into carbon scaffold with various weight capacity, including bulk Al(BH$_4$)$_3$(NH$_3$)$_6$ for reference.
Figure S8. FT-IR spectra of Al(BH$_4$)$_3$(NH$_3$)$_6$ confined into carbon scaffold with various weight capacity via CLD, including bulk Al(BH$_4$)$_3$(NH$_3$)$_6$ and carbon templates for reference.

The presence of similar absorption peaks for N-H and B-H bonds of nanoconfined Al(BH$_4$)$_3$(NH$_3$)$_6$ with bulk Al(BH$_4$)$_3$(NH$_3$)$_6$ provides the further evidences for the formation of BH$_4$ and NH$_3$ moieties of Al(BH$_4$)$_3$(NH$_3$)$_6$ inside the pores of carbon templates. Moreover, the B-N bonds at around 780 cm$^{-1}$ indicates the interaction of BH$_4$ with NH$_3$ groups within Al(BH$_4$)$_3$(NH$_3$)$_6$, in which the combination of B-H and N-H bonds mainly affords its H$_2$ release.
Figure S9 Deposition of HAAB with various thickness on QC substrate.
The spectra of bulk and nanoconfined Al(BH$_4$)$_3$(NH$_3$)$_6$ show the characteristic peaks of B-H and N-H bonds. Upon heating, the combination of H$^-$ of BH$_4$ with H$^{+}$ of NH$_3$ mainly accounts for the H$_2$ desorption from ammine metallic borohydrides. Therefore, after heating to 160 °C, B-H and N-H bonds disappeared for the nanoconfined Al(BH$_4$)$_3$(NH$_3$)$_6$, indicating the participation of BH$_4$ groups and NH$_3$ groups in the process towards H$_2$ release, which amounts to over 95% of its total releasable H$_2$ capacity as evinced from TG and TPD results. In contrast, for the bulk Al(BH$_4$)$_3$(NH$_3$)$_6$ heated to 160 °C, there are clear peaks attributed to the B-H and N-H bonds, suggesting only partial decomposition for a small amount of H$_2$ and NH$_3$ release, which accords well to the TG and TPD results. Upon further elevating the heating temperature to 210 °C, all the absorption bands of bulk Al(BH$_4$)$_3$(NH$_3$)$_6$ assigned to the NH$_3$ group and the BH$_4$$^{-1}$ ion disappeared, due to the combination of N-H bonds and B-H bonds for H$_2$ desorption. These results indicate the significantly improved H$_2$ release kinetics at relatively lower temperature of Al(BH$_4$)$_3$(NH$_3$)$_6$ space-confined into carbon scaffolds via the CLD methodology.

**Figure S10.** FTIR spectra for bulk (in red line) and nanoconfined (in black line) Al(BH$_4$)$_3$(NH$_3$)$_6$ at room temperature (RT) and its products after heating to 160 °C and 210 °C, respectively. The heating rate is 5 °C/min.
Figure S11. TGA and TPD profiles of Al(BH$_4$)$_3$(NH$_3$)$_6$ confined into scaffolds upon heating to 250 °C using a heating rate of 5 °C/min, including bulk Al(BH$_4$)$_3$(NH$_3$)$_6$ (HAAB) for comparison.
Figure S12 Histogram of capacity and purity of hydrogen evolution from HAAB, physical mixture of HAAB and carbon scaffold (PM), and HAAB@HOPC (C-20, C-30, C-40, C-50) by 250 °C.
The as-prepared Al(BH$_4$)$_3$(NH$_3$)$_6$ exhibits a single exothermic peak at 172 °C with a shoulder, corresponding to an enthalpy of approximately -6.75 KJ/mol H$_2$. Comparable traces upon hydrogen liberation were observed for Al(BH$_4$)$_3$(NH$_3$)$_6$ nanoconfined into scaffolds at relatively lower temperature, with one exothermic signal significantly broadened in comparison with bulk reagent in good accordance with the MS results. However, the integration of the endothermic peaks (Table S1) indicates that the total enthalpy of the reaction increases slowly with the decreasing capacity of Al(BH$_4$)$_3$(NH$_3$)$_6$ inside the carbon matrix, which is consist with the diminution of ammonia released upon dehydrogenation due to the fact that ammonia release is significantly endothermic from borohydrides. The similar phenomenon was also found for the hydrogen release process of ammonia borane (AB) infiltrated into the mesopores of SBA-15. It suggests that different solid products formed for Al(BH$_4$)$_3$(NH$_3$)$_6$ inside the carbon scaffolds derived from more ammonia participates in hydrogen release compared with the pure one resulting in the more exothermicity for dehydrogenation. Moreover, compared to decomposition of the other typical hydrogen storage materials based on HB-NH combination, e.g., neat AB (-21 KJ/mol H$_2$), the significantly less exothermic characterization of nanoconfined Al(BH$_4$)$_3$(NH$_3$)$_6$ provides a great potential for its reversible hydrogen storage with proper chemical modification. Therefore, the tremendous enhancement of hydrogen desorption performance at low temperature not only relates to the improved dehydrogenation kinetics but also the more favorable thermodynamics to some extent, compared to bulk counterparts, due to the reduction of particle sizes induced by the nanoconfinement procedure.
Figure S14. TPD results of C-30 and Al(BH$_4$)$_3$(NH$_3$)$_5$@HOPC (●) upon heating to 250 °C using a heating rate of 5 °C/min.
Table S1. The peak temperature and Enthalpy data for hydrogen release from Al(BH$_4$)$_3$(NH$_3$)$_6$ loaded in carbon scaffolds, the data of bulk Al(BH$_4$)$_3$(NH$_3$)$_6$ were also listed for comparison.

<table>
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<tr>
<th>Sample</th>
<th>Peak Temperature (°C)</th>
<th>Enthalpy (KJ/mol H$_2$)</th>
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<tr>
<td>C-20</td>
<td>112.5</td>
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<tr>
<td>C-30</td>
<td>122.9</td>
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<td>C-40</td>
<td>135.8</td>
<td>-6.79</td>
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<tr>
<td>C-50</td>
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<td>-6.78</td>
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<tr>
<td>Al(BH$_4$)$_3$(NH$_3$)$_6$</td>
<td>172.1</td>
<td>-6.75</td>
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