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High-Performance Hydrogen Storage Nanoparticles Inside Hierarchical Porous Carbon Nanofibers with Stable Cycling

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Abstract
An effective route based on space-confined chemical reaction to synthesize uniform Li2Mg(NH)2 nanoparticles is reported. The hierarchical pores inside the one-dimensional carbon nanofibers (CNFs), induced by the creation of well-dispersed Li3N, serve as intelligent nanoreactors for the reaction of Li3N with Mg-containing precursors, resulting in the formation of uniformly discrete Li2Mg(NH)2 nanoparticles. The nanostructured Li2Mg(NH)2 particles inside the CNFs are capable of complete hydrogenation and dehydrogenation at a temperature as low as 105 °C with the suppression of ammonia release. Furthermore, by virtue of the nanosize effects and space-confinement by the porous carbon scaffold, no degradation was observed after 50 de/rehydrogenation cycles at a temperature as low as 130 °C for the as-prepared Li2Mg(NH)2 nanoparticles, indicating excellent reversibility. Moreover, the theoretical calculations demonstrate that the reduction in particle size could significantly enhance the H2 sorption of Li2Mg(NH)2 by decreasing the relative activation energy barrier, which agrees well with our experimental results. This method could represent an effective, general strategy for synthesizing nanoparticles of complex hydrides with stable reversibility and excellent hydrogen storage performance.

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High-Performance Hydrogen Storage Nanoparticles Inside Hierarchical Porous Carbon Nanofibers with Stable Cycling

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KEYWORDS: nanoparticles, hydrogen storage, amide, carbon nanofibers, cycle.
ABSTRACT: An effective route based on space-confined chemical reaction to synthesize uniform Li$_2$Mg(NH)$_2$ nanoparticles is reported. The hierarchical pores inside the one-dimensional carbon nanofibers (CNFs), induced by the creation of well-dispersed Li$_3$N, serve as intelligent nanoreactors for the reaction of Li$_3$N with Mg-containing precursors, resulting in the formation of uniformly discrete Li$_2$Mg(NH)$_2$ nanoparticles. The nanostructured Li$_2$Mg(NH)$_2$ particles inside the CNFs is capable of complete hydrogenation and dehydrogenation at a temperature as low as 105 °C with the suppression of ammonia release. Furthermore, by virtue of the nanosize effects and space-confinement by the porous carbon scaffold, no degradation was observed after 50 de-/re-hydrogenation cycles at a temperature as low as 130 °C for the as-prepared Li$_2$Mg(NH)$_2$ nanoparticles, indicating excellent reversibility. Moreover, the theoretical calculations demonstrate that the reduction in particle size could significantly enhance the H$_2$ sorption of Li$_2$Mg(NH)$_2$ by decreasing the relative activation energy barrier, which agrees well with our experimental results. This method could represent an effective, general strategy for synthesizing nanoparticles of complex hydrides with stable reversibility and excellent hydrogen storage performance.
INTRODUCTION

As a renewable fuel, hydrogen has been widely acknowledged as the ideal synthetic fuel for on-board application because of its abundance, high chemical energy, and environmental friendliness (with water as the sole product from combustion).\textsuperscript{1, 2} The storage of \( \text{H}_2 \) in a safe, efficient, and economical manner, however, remains a big challenge to the realization of the so-called hydrogen economy.\textsuperscript{3-5} Metal-N-H systems have been considered among the most promising materials, after Li\(_3\)N was shown to reversibly store \(~11.4\) wt.\% \( \text{H}_2 \) via the following two-step reaction (1). Related systems have received growing attention due to their relatively high reversible hydrogen capacity.\textsuperscript{6, 7}

\[
\text{Li}_3\text{N} + 2\text{H}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 \leftrightarrow \text{LiNH}_2 + 2\text{LiH} \quad (1)
\]

The rather high dehydrogenation enthalpy for the leftmost reaction, \(~115\) kJ mol\(^{-1}\) \( \text{H}_2 \), places thermodynamic constraints on this system, such that the complete generation of Li\(_3\)N can be achieved only at temperatures above 320 °C, even under dynamic vacuum.\textsuperscript{8} Given the favorable enthalpy value (\(~45\) kJ mol\(^{-1}\)), only the second reaction step is considered to be practical for hydrogen storage, which significantly degrades the practical \( \text{H}_2 \) storage capacity to \(~6.5\) wt.\%, based on pure Li\(_2\)NH.\textsuperscript{9} Furthermore, numerous experimental and theoretical results have verified that simple chemical modification of the Li-N-H system by Mg creates the novel Li-Mg-N-H system (Equation 2), whose dehydrogenation enthalpy is significantly reduced to approximately 39 kJ mol\(^{-1}\) \( \text{H}_2 \), which corresponds to an operating temperature of 90 °C at 1 bar of equilibrium hydrogen pressure.\textsuperscript{10-13} These parameters satisfy the practical requirements for operation in proton exchange membrane fuel cells (PEMFCs).\textsuperscript{14, 15}

\[
\text{Mg(NH}_2\text{)}_2 + 2\text{LiH} \leftrightarrow \text{Li}_2\text{Mg(NH)}_2 + 2\text{H}_2 \quad (2)
\]
Nonetheless, it must be pointed out that both the dehydrogenation and the hydrogenation of any metal-N-H composites involve the interaction of multiple solid-state intermediate phases, including amides, imides, and hydrides.\textsuperscript{16, 17} The sluggish interface reactions, resulting from the relocation of atoms (such as Li\textsuperscript{+}, Mg\textsuperscript{2+}, and H\textsuperscript{+} ions) across amide-imide and imide-hydride phase boundaries and the mass transport along the thus-formed imide layer during the H\textsubscript{2} ab-/de-desorption for the metal-N-H system, normally exhibit rather high activation energy barriers. These constraints tremendously raise the operating temperatures required for hydrogen storage and therefore preclude its practical applications.\textsuperscript{14, 18, 19} In particular, the activation energy for the dehydrogenation of Mg(NH\textsubscript{2})\textsubscript{2}/2LiH composite is up to \textasciitilde102 – 120 kJ mol\textsuperscript{-1}, which renders it a reasonable kinetics only at temperatures above 200 °C.\textsuperscript{20-22} It should be noted that, in order to realize the practical applications of hydrogen storage materials, the thermodynamics and kinetics of storage reaction, which are the key parameters to determine the reversible storage performance of materials, should be dual-tuned.\textsuperscript{23-25} One effective strategy for dual-tuning the thermodynamics and kinetics of the metal-N-H system is to reduce the particle sizes down to the nanometer range, which would effectively improve the hydrogen storage performance due to the shortened diffusion distances between amides/imides and hydrides, and the increased surface area.\textsuperscript{6, 26-29} A strong dependence of the de-/re-hydrogenation kinetics (and thermodynamics) on particle size has been demonstrated both experimentally and theoretically.\textsuperscript{30-41} For instance, the Li\textsubscript{3}N obtained from the decomposition of precursors that are space-confined in mesoporous carbonaceous hosts shows much faster absorption and desorption kinetics than its bulk counterpart, so that the hydrogen storage process of the nanoconfined Li\textsubscript{3}N was found to be fully reversible at 200 °C.\textsuperscript{42, 43} Unfortunately, due to its multiphase constitution with high chemical activity, low solubility, and/or high melting point, the nanoengineering of Li-Mg-N-H composite
has, to date, been limited to the technique of ball milling.\textsuperscript{13} Although, compared to the hand-milled composite, a dramatic 61\% reduction of activation energy and the onset temperature of \textasciitilde 80 °C for hydrogenation can be realized for the nanosized Li\textsubscript{2}Mg(NH)\textsubscript{2} by long ball milling. Unfortunately, the particles with small sizes are apt to grow and aggregate to minimize their surface energy during long-term cyclic heat treatment for H\textsubscript{2} release and uptake.\textsuperscript{28, 34} This inevitable particle growth and phase separation result in heavy degradation of the sorption kinetics and cycling capacity. Additionally, it is well-known that it is difficult to control the particle size and particle agglomeration with mechanical milling, while cold welding during the milling process limits the decrease in particle size to a minimum of 1 \( \mu \)m.\textsuperscript{29, 44} Therefore, it is still a significant challenge and of key importance to develop effective strategies for the synthesis of high-temperature-stable nanoparticles of Li\textsubscript{2}Mg(NH)\textsubscript{2} with high hydrogen cycling stability.

Recently, we successfully synthesized carbon-coated Li\textsubscript{3}N nanoparticles inside carbon nanofibers (CNFs) via a simple electrospinning technique with low-cost.\textsuperscript{43} Remarkably enhanced kinetics and thermodynamics were achieved due to the significant reduction in particle size and the even distribution of as-prepared Li\textsubscript{3}N nanoparticles. The cycling temperature, however, was still higher than 200 °C, resulting from thermodynamic limitations. Fortunately, the special yolk-shell-type Li\textsubscript{3}N@C nanostructure inside the hierarchical porous CNFs renders it a potential intelligent nanoreactor to fabricate a new system \textit{via} further chemical modification. Herein, a novel approach to the synthesis of uniformly discrete Li\textsubscript{2}Mg(NH)\textsubscript{2} nanoparticles with high purity through confined nanospace synthesis (CNS) is reported, as schematically illustrated in Figure 1. The chemical transformation of Li\textsubscript{3}N into Li\textsubscript{2}Mg(NH)\textsubscript{2} within the nanoscale range is realized \textit{via} the introduction of magnesium precursors by solution infiltration into the void spaces of every discrete carbon-encapsulated Li\textsubscript{3}N nanostructure, which is then annealed under ammonia and
vacuum within the confined nanospace. The carbon framework physically separates the individual Li$_2$Mg(NH)$_2$ nanoparticles, allowing them to keep their original shape, size, and surface state, and thus tremendously improves their stability at the high temperatures required for hydrogenation and dehydrogenation. Remarkably, the physical space-confinement effects and nanostructural features that are provided by the Li$_2$Mg(NH)$_2$@C nanostructure induce low-temperature reversible hydrogenation and dehydrogenation; fast sorption kinetics; and long-term cycling stability.

RESULTS AND DISCUSSION

Panoramic field-emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) images show that the spinning process produces a highly uniform nonwoven mat of polyvinyl alcohol (PVA) nanofibers (NFs) containing LiN$_3$ (Figure S1 in the Supporting Information), and the fibrous architecture was well maintained after calcination of the as-electrospun NFs (Figure 2a). Additionally, during heat treatment, the explosive decomposition of LiN$_3$ inside the PVA NFs could effectively push the surrounding flexible PVA aside, leaving behind visible void space around the as-formed Li$_3$N nanoparticles. After carbonization of the PVA into sturdy carbon, the thus-formed Li$_3$N@C NFs consist of a carbon framework that surrounds uniform spherical voids with embedded Li$_3$N nanoparticles. This results in mesopores and macropores with various diameters on the surfaces along the length of the NFs (Figure 2b) and inside the fibers as shown in the cross-sectional images (Figure 2c), in which carbon-encapsulated Li$_3$N nanoparticles are enclosed inside the CNFs. TEM studies provide further insight into the porous interior and detailed structure of the as-synthesized CNFs. In agreement with the FESEM observations, the even dispersion of mesopores and micropores is clearly confirmed (Figure 3a, b). Based on the Brunauer-Emmett-Teller (BET) analysis, N$_2$ adsorption-
desorption isotherms (Figure S2) of the obtained CNFs with Li$_3$N nanoparticles exhibit representative type IV curves with a sharp increase in the nitrogen absorption at a high relative pressure, which is indicative of a pore-size distribution in the mesoporous and macroporous ranges, with a pore volume of 0.681 cm$^3$ g$^{-1}$. It is worth noting that the good dispersion of holes inside the CNFs indirectly confirms the homogeneous distribution of Li$_3$N, which was further verified by the homogeneous distribution of both carbon and nitrogen atoms (Figure S3) in the elemental mapping. The holes provide sufficient room for accommodating the infiltration of subsequent precursors, i.e., Mg-containing species, inside the porous carbon-encapsulated Li$_3$N nanostructure. The interfiber pores, a signature feature of fibrous membranes derived from electrospinning, provide abundant macroporous channels for the convenient transportation of liquid-phase-containing precursors to uniformly diffuse into each individual CNF. The extensive presence of micropores and/or mesopores across the whole CNF is attributed to the free volume and microporosity derived from the disordered packing of turbostratic carbon sheets and clusters during carbonization of the polymeric framework. A BET surface area of 72 cm$^2$ g$^{-1}$ was determined for the micropores by the t-plot method. This offers a sufficient driving force for the diffusion of the liquid precursors via capillary effects into the pores containing Li$_3$N. Therefore, the one-dimensional hierarchical porous morphology of the as-obtained CNFs provides special spatial advantages for the fine-tuning of a homogeneous distribution of the precursors.

After infiltration of a solution of dibutylmagnesium (MgBu$_2$) by the capillary effect into the porous carbon-encapsulated Li$_3$N structure, removal of the solvent, and hydrogenation, the Li$_3$N particles can be transformed into a mixture of LiNH$_2$ and LiH that are in-situ coated by the resulting MgH$_2$. The particles are completely hydried via Equations (3) and (4), and then
annealed under ammonia to form a nanostructured composite of Mg(NH$_2$)$_2$-2LiNH$_2$ (Equations (5) and (6)).

\[
\text{Li}_3\text{N} + 2\text{H}_2 \rightarrow \text{LiNH}_2 + 2\text{LiH} \quad (3)
\]

\[
\text{Mg(C}_4\text{H}_9)_2 + \text{H}_2 \rightarrow \text{MgH}_2 + 2\text{C}_4\text{H}_{10} \quad (4)
\]

\[
\text{LiH} + \text{NH}_3 \rightarrow \text{LiNH}_2 + \text{H}_2 \quad (5)
\]

\[
\text{MgH}_2 + 2\text{NH}_3 \rightarrow \text{Mg(NH}_2)_2 + 2\text{H}_2 \quad (6)
\]

\[
\text{Mg(NH}_2)_2 + 2\text{LiNH}_2 \rightarrow \text{Li}_2\text{Mg(NH}}_2_2 + 2\text{NH}_3 \quad (7)
\]

Due to the physical confinement by the surrounding carbon framework, further calcination under vacuum leads to the formation of Li$_2$Mg(NH)$_2$ on the nanometer scale, accompanied by the release of ammonia according to Equation (7).\textsuperscript{13} The structural morphology of the CNFs is well maintained without apparent deformation after the thermolysis reaction, which results in the formation of Li$_2$Mg(NH)$_2$. The porous structure is mostly preserved (Figure 3c), indicating the formation of the porous carbon-encapsulated Li$_2$Mg(NH)$_2$ nanostructures inside the CNFs as well. This network provides a favorable channel for hydrogen loading and unloading of the confined Li$_2$Mg(NH)$_2$ nanoparticles.

The chemical transformation from Li$_3$N via the diffusion of Mg-containing precursors to Li$_2$Mg(NH)$_2$ inside the CNFs is clearly confirmed by the combination of powder X-ray diffraction (PXRD) (Figure S4) and Fourier transform infrared (FTIR) spectra (Figure S5). The phase composition after calcination of the as-electrospun NFs can be unambiguously assigned to Li$_3$N. After hydrogenation, the appearance of peaks belonging to MgH$_2$ is accompanied by the
The disappearance of Li$_3$N. The appearance of the characteristic peaks of LiNH$_2$ in the FTIR spectra suggests the successful generation of LiNH$_2$ and LiH. Nonetheless, no Bragg peaks of LiH and LiNH$_2$ are visible in the PXRD patterns, indicating the formation of an amorphous and/or nanocrystalline structure due to the physical confinement by the CNFs. After ammoniation, absorbances readily assigned to both LiNH$_2$ and Mg(NH$_2$)$_2$ are observed, and further heating under vacuum leads to the formation of pure cubic $\beta$- Li$_2$Mg(NH)$_2$ phase, as evidenced by the PXRD (Figure S4) and FTIR (Figure S5) spectra. These results indicate the complete conversion of the precursors to crystalline high purity products. Using the Scherrer formula, the average crystallite sizes of the Li$_2$Mg(NH)$_2$ particles were calculated to be approximately 4.2 nm. The nanosize nature of the particles can be attributed to the good dispersion and the effective steric hindrance effects of the carbon shells during the synthetic process. In addition, the C map in the electron energy loss spectrum (EELS) (Figure 3d) agrees well with the fibrous structure of the CNFs, and the Li, Mg, and N elemental maps correspond well with the C map from EELS, directly confirming the good dispersion of Li$_2$Mg(NH)$_2$ nanoparticles inside the CNFs.

Figure 4a shows the mass spectroscopy (MS) results for the as-prepared Li$_2$Mg(NH)$_2$@C NFs in comparison with the Li$_3$N@C NFs and the ball-milled Li$_2$Mg(NH)$_2$ composite after full hydrogenation. It is demonstrated that the nanoscale Li$_3$N entrapped in the CNFs starts to release hydrogen at ~120 °C, with a peak temperature as high as ~250 °C. Upon the introduction of Mg into the Li-N-H system, the resulting Mg(NH$_2$)$_2$-2LiH composite exhibits a peak temperature of ~198 °C after only a slight ball milling. This confirms the importance of Mg substitution for the improvement of the hydrogen storage properties of Li-N-H composite. It should be noted, however, that a simultaneous release of ammonia was detected for the ball-milled Mg(NH$_2$)$_2$-2LiH composite, which can be attributed to the incomplete reaction of the components.\textsuperscript{27} By
contrast, chemical modification of the Li$_3$N@C NFs by reaction with Mg through the CNS route in the porous CNFs gives rise to the synthesis of Li$_2$Mg(NH)$_2$ nanoparticles, which, after hydrogenation, exhibit an onset temperature of ~80 °C with a peak temperature of ~118 °C. This is 80 °C and 132 °C lower than for the ball-milled counterpart and the as-prepared Li$_3$N@C NFs, respectively. More importantly, the release of detectable ammonia during the thermal dehydrogenation process is tremendously hindered, possibly due to the intimate contact between Mg(NH$_2$)$_2$ and LiH induced by the nanosize effects. The desorption of high purity hydrogen was confirmed by the thermogravimetric (TG) method (Figure S6), which gives a weight loss of ~5.5 wt.% (2.1 wt.% in overall composite mass), corresponding well with its theoretical value (5.6 wt.%) based on Equation (2). Moreover, volumetric temperature-programmed desorption (TPD) results (Figure S7) verify a storage capacity of ~0.0105 mol g$^{-1}$ released from Li$_2$Mg(NH)$_2$@C NFs after complete hydrogenation, corresponding to a weight loss of 2.1 wt.% from overall composite mass, which therefore further confirms the high-purity of the released hydrogen. The transformation between Li$_2$Mg(NH)$_2$ and Mg(NH$_2$)$_2$/LiH composite accounting for the hydrogen storage reaction of Li$_2$Mg(NH)$_2$@C NFs could be further demonstrated by PXRD results (Figure S8), which provides direct evidence for the formation of Mg(NH$_2$)$_2$/LiH composite after hydrogenation and the synthesis of Li$_2$Mg(NH)$_2$ after dehydrogenation.

Thermodynamic stabilities and the reversibility at various temperatures were determined from pressure-composition-isotherm (PCI) measurements that were carried out on the nanosized and ball-milled Li$_2$Mg(NH)$_2$ (Figures 4b and S9). It can be observed that, the plateau pressures for the nanoscale Li$_2$Mg(NH)$_2$ show a well-defined plateau region at each temperature and, at a temperature as low as 105 °C, a complete cycle of H$_2$ absorption and desorption with a capacity of ~5.5 wt.% (~ 2.1 wt.% per mass of the overall composite) could be achieved, approaching its
theoretical value from Equation (2). The capacities for both hydrogenation and dehydrogenation for the ball-milled \( \text{Li}_2\text{Mg(NH)}_2 \) are much less than 1 wt.%, even at the high temperature of 130 \(^\circ\)C. Apparently, the plateau pressure increases with increasing temperature. The values for the enthalpy (\( \Delta H_{\text{des}} \)) and entropy (\( \Delta S_{\text{des}} \)) in dehydrogenation for the nanosized \( \text{Li}_2\text{Mg(NH)}_2 \) derived from the van’t Hoff equation (Figure S10) were 35.7 \( \pm \) 0.5 kJ mol\(^{-1}\) H\(_2\) and 100.2 \( \pm \) 1.3 J K\(^{-1}\) mol\(^{-1}\) H\(_2\), respectively, which are slightly lower than those of the bulk counterpart (44.1 kJ mol\(^{-1}\) H\(_2\) and 112 J K\(^{-1}\) mol\(^{-1}\) H\(_2\))\(^{14}\), indicating that thermodynamic destabilization occurs due to either reduction of the particle size down to the nanometer scale or the interaction of the confined \( \text{Li}_2\text{Mg(NH)}_2 \) with the carbon framework.

To gain further insight into the hydrogen storage properties of \( \text{Li}_2\text{Mg(NH)}_2 \) nanoparticles inside the CNFs, the H\(_2\) sorption in the isotherm models was investigated at different temperatures and in the H\(_2\)-pressure range of 2.9-3.0 MPa for absorption and 0.001-0.01 MPa for desorption (Figures 5 and S11). At the temperature of 135 \(^\circ\)C, a sharp weight increase upon exposure to hydrogen for the carbon-coated \( \text{Li}_2\text{Mg(NH)}_2 \) composite was observed during the first 20 min, which plateaus off to constant mass in less than 40 min with a capacity of \( \sim \)5.5 wt.% (2.1 wt.% in overall composite mass), and the following dehydrogenation confirmed that the charged H\(_2\) could be completely discharged when the dehydrogenation time was extended to 80 min. The capacity of H\(_2\) uptake and release for the ball-milled \( \text{Li}_2\text{Mg(NH)}_2 \), however, is only \( \sim \)0.8 wt.% and \( \sim \)0.7 wt.%, respectively, at the same temperature. The significant improvement of both the dehydrogenation and the hydrogenation kinetics for the \( \text{Li}_2\text{Mg(NH)}_2@\text{C NFs} \) was quantitatively determined by the apparent activation energies (\( E_a \)) during H\(_2\) release and uptake, as determined by the Arrhenius equation via fitting the experimental results at various temperatures. The apparent activation energies for hydrogenation and dehydrogenation of the porous
Li$_2$Mg(NH)$_2$@C NFs, from the slopes of the linear plots of ln ($k$) ($k$, rate constant) versus 1/$T$ ($T$, absolute temperature), were calculated to be $\sim$ 34.1 and 37.2 kJ mol$^{-1}$ H$_2$ (Figure S12), respectively, dramatically lower than for the bulk composite and other catalyst-added Li$_2$Mg(NH)$_2$ (Table S1). Therefore, these results provide direct evidence of the enhancement of the hydriding/dehydriding kinetics in the nanosized Li$_2$Mg(NH)$_2$ confined in the porous CNFs, owing to the decrease in the diffusion distances induced by the reduction of particle size.

The major obstacles to the practical application of the Li-Mg-N-H system in the bulk form are: sintering effects, phase separation, and the simultaneous release of ammonia upon heat treatment, which result in substantial degradation of hydrogen capacity during cycling. This is in contrast to the as-prepared Li$_2$Mg(NH)$_2$@C NFs, which exhibit much lower de-/re-hydrogenation temperatures and the depression of ammonia due to the reduction of particle size down to the nanometer scale. Moreover, the uniform porous carbon coating surrounding the Li$_2$Mg(NH)$_2$ nanoparticles as a continuous and flexible shell inside the CNFs serves as a nanoreactor and physically prevents particle growth and phase separation of the nanoparticles during the thermal reaction, while simultaneously accommodating the volume change that occurs during H$_2$ uptake and release. This scaffold provides superior structural features for preserving the morphology of Li$_2$Mg(NH)$_2$ and enhancing its hydrogen storage performance. Therefore, the cycling stability of the as-prepared Li$_2$Mg(NH)$_2$@C NFs, in comparison with their bulk counterpart, was further evaluated by isothermal hydrogenation and dehydrogenation at 130 °C using the volumetric method (Figure 6a). Notably, even with a dwell time of 400 min for one cycle at 130 °C, the capacity retention of the bulk counterpart is already lower than 50% after 5 cycles of sorption. Nonetheless, there was only a minor loss in hydrogen capacity ($\sim$ 0.1 wt.% per mass of the overall composite) for the Li$_2$Mg(NH)$_2$@C NFs, even after a total of 50 cycles.
More importantly, the kinetics and reversible hydrogen capacities of both dehydrogenation and hydrogenation remained intact from the first to the last cycle (Figure 6c). Also, ammonia is still undetectable during the 50th desorption cycle (Figure S13), indicating the significantly improved robustness and cycling stability of Li$_2$Mg(NH)$_2$ on the nanometer scale, resulting from the space-confined synthesis inside the porous CNFs. It is well-known that the transformation of Li$_2$Mg(NH)$_2$ into LiH and Mg(NH$_2$)$_2$ according to Equation (2) necessitates the formation of N-H bonds and the removal of Li atoms, thus indicating that not only lithium-related, but also hydrogen-related defects are required. The formation energies of the charged hydrogen interstitial (I$_H^+$) and the lithium vacancy (V$_{Li^-}$) for Li$_2$Mg(NH)$_2$ as a function of the Fermi energy ($\varepsilon_F$) are plotted in Figure 7a. The lower limit for the Fermi level, $\varepsilon_F = 0$ eV, corresponds to the top of the valence band (VBM), while the upper limit, $\varepsilon_F = 2.3$ eV, represents the bottom of the conduction band (CBM). The vertical dotted line in Figure 7a denotes the position of the relevant value of the Fermi energy, which is found by determining the system with the lowest formation energy that is charge-neutral overall. Among the charged defects considered in this paper, the lowest formation energy is associated with V$_{Li^-}$ and I$_H^+$, with formation energy of -0.06 eV. Thus, in the absence of extrinsic impurities, charge neutrality must be achieved by equal concentrations of V$_{Li^-}$ and I$_H^+$ in the bulk, which pins the Fermi level at $\sim$2.01 eV. Compared to the bulk composite, however, samples composed of relatively small particles have a relatively larger surface-to-volume ratio, and therefore, the formation and diffusion of defects on their surfaces may prevail. Subsequently, we further calculated the formation of V$_{Li^-}$ and I$_H^+$ pairs on the surface of Li$_2$Mg(NH)$_2$. The Li$_2$Mg(NH)$_2$ (100) surface has a substantially lower energy than the (010) and (001) surfaces, and therefore, we used this surface for the following calculations. Interestingly, our calculation results show that the
formation energy of $V_{Li}^-$ and $I_{H}^+$ pairs on the Li$_2$Mg(NH)$_2$ (100) surface is as low as -1.61 eV. Hence, it can be expected that an increase in the surface-to-volume ratio would lead to a significant increase in the concentration of $V_{Li}^-$ and $I_{H}^+$ pairs on the surface.

Further investigation was focused on the migration process of the H and Li related defects, which involves mass transport and is related to the hydrogenation of Li$_2$Mg(NH)$_2$. The energy barriers for diffusion were estimated by using the climbing image – nudged elastic band (CI-NEB) method. Although numerous diffusion pathways in Li$_2$Mg(NH)$_2$ were examined, only the lowest energy paths observed are described herein. As shown in Figure 7b and Figure S14, the diffusion barriers of $V_{Li}^-$ and $I_{H}^+$ are 1.46 and 0.78 eV, respectively. The relatively low diffusion barrier for $I_{H}^+$ indicates that $I_{H}^+$ could migrate at moderate temperature. The migration of $V_{Li}^-$ with relatively higher energy barriers would limit the transport of Li in bulk Li$_2$Mg(NH)$_2$. By contrast, our calculations also indicate that the diffusion barrier for $V_{Li}^-$ on the surface is decreased to only 1.13 eV, ~0.32 eV lower than in the bulk matrix. These results suggest that increasing the surface-to-volume ratio by reducing particle size could significantly promote both the formation and the diffusion of $V_{Li}^-$ and $I_{H}^+$, thereby significantly improving the hydrogenation of Li$_2$Mg(NH)$_2$ to form LiH and Mg(NH$_2$)$_2$. The trend in our experimental activation energies agrees well with the computational results in terms of a bulk- versus surface-dominated mechanism for the hydrogenation of Li$_2$Mg(NH)$_2$. In the case of the ball-milled Li-Mg-N-H composite, the sizes of most of the particles are larger than 1 μm (Figure S15), and therefore, the surface-to-volume ratio is small, which endows it with high activation energy. By contrast, it is notable that the fabrication of the porous carbon-encapsulated Li$_2$Mg(NH)$_2$ nanostructure via CNS can, on the one hand, realize the direct synthesis of nanosized
Li$_2$Mg(NH)$_2$ (~4.2 nm) and its homogenous distribution, significantly improving its hydrogen storage performance (Figures 4 and 5), while, on the other hand, the additional geometric confinement effect of the porous carbon shells surrounding each Li$_2$Mg(NH)$_2$ nanoparticle can well preserve the nanostructural features down to the nanometer scale during consecutive cycles of heating, which therefore gives the Li$_2$Mg(NH)$_2$ stable reversibility without apparent degradation, even up to 50 cycles of de-/re-hydrogenation (Figure 6). Moreover, the 3D porous structure formed *in situ* also provides a favorable channel for the transportation of H$_2$.

**CONCLUSION**

In summary, we report a facile, confined nanospace synthesis procedure for the preparation of high-performance, porous carbon-encapsulated Li$_2$Mg(NH)$_2$ nanostructures as hydrogen storage materials. The hierarchical porous CNFs that were synthesized through simple, low-cost electrospinning contain pores that arise during the formation of Li$_3$N that serve as intelligent nanoreactors. The carbon framework endows the as-prepared Li$_2$Mg(NH)$_2$ nanoparticles with a uniform distribution and effective space-confinement. The unique architecture of the Li$_2$Mg(NH)$_2$ nanoparticles allows complete cycles of hydrogenation and dehydrogenation at 105 °C with long-term cycling stability. Moreover, this strategy represents a highly novel approach to synthesizing nanostructured hydrogen storage materials that exhibit superior storage properties, including outstanding hydrogen cycling performances.

**ASSOCIATED CONTENT**

**Supporting Information.**

The following files are available free of charge.
Additional text with experimental details; XRD, SEM images, FTIR, and TG results of the nanosized Li2Mg(NH)2 (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Figure 1. Schematic illustration of the preparation of Li$_2$Mg(NH)$_2$ nanoparticles inside the hierarchical porous CNFs from the as-electrospun PVA-coated LiN$_3$ NFs. PVA is polyvinyl alcohol.
Figure 2. SEM images of the as-prepared (a, b, c) Li$_3$N@C NFs and (d) Li$_2$Mg(NH)$_2$@C NFs.
Figure 3. TEM images of (a, b) Li$_3$N@C NFs and (c) Li$_2$Mg(NH)$_2$@C NFs. TEM image (d) and the corresponding elemental mapping of Li$_2$Mg(NH)$_2$@C NFs.
Figure 4. (a) Mass spectrum of the as-prepared Li$_2$Mg(NH)$_2$@C NFs (green) after hydrogenation, in comparison with the Li$_3$N@C NFs (blue) and the ball-milled Li$_2$Mg(NH)$_2$ composite (black). (b) Pressure-composition isotherms (PCI) of the Li$_2$Mg(NH)$_2$@C NFs at various temperatures, compared with the ball-milled Li$_2$Mg(NH)$_2$ composite at the temperature of 130 °C. The H$_2$ contents are expressed per mass of Li$_2$Mg(NH)$_2$. 
Figure 5. Hydrogenation and dehydrogenation of Li$_2$Mg(NH)$_2$@C NFs at different temperatures, including the ball-milled Li$_2$Mg(NH)$_2$ at 130 °C for comparison. The H$_2$ contents are expressed per mass of Li$_2$Mg(NH)$_2$. 
Figure 6. (a) Long-term cycling tests of hydrogenation (black lines) and dehydrogenation (pink lines) for Li$_2$Mg(NH)$_2$@C NFs at 130 °C; (b) normalized H$_2$ capacity as a function of cycle number, where the hydrogen capacities are normalized to unity for the first value; and (c) comparison of the kinetics for hydrogenation/dehydrogenation of Li$_2$Mg(NH)$_2$@C NFs between the 1$^{st}$ and 50$^{th}$ cycles at 130 °C, including the 1$^{st}$ and 5$^{th}$ cycles of bulk Li$_2$Mg(NH)$_2$ for comparison. The H$_2$ contents are expressed here per mass of the whole composite (i.e., including the weight of CNFs).
Figure 7. (a) Calculated formation energies for the charged hydrogen interstitial (H$_i$) and lithium vacancy (V$_{Li}$). V$_{Li}$ corresponds to removing a Li ion from pristine Li$_2$Mg(NH)$_2$, and H$_i$ corresponds to adding a H ion to form NH$_2$ units. (b) Energetic profiles for the low-energy diffusion pathway of V$_{Li}^-$ in Li$_2$Mg(NH)$_2$. 