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Abstract

NaAlH₄ has been widely regarded as a potential hydrogen storage material due to its favorable thermodynamics and high energy density. The high activation energy barrier and high dehydrogenation temperature, however, significantly hinder its practical application. In this paper, CeO₂ hollow nanotubes (HNTs) prepared by a simple electrospinning technique are adopted as functional scaffolds to support NaAlH₄ nanoparticles (NPs) towards advanced hydrogen storage performance. The nanoconfined NaAlH₄ inside CeO₂ HNTs, synthesized via the infiltration of molten NaAlH₄ into the CeO₂ HNTs under high hydrogen pressure, exhibited significantly improved dehydrogenation properties compared with both bulk and ball-milled CeO₂ HNTs-catalyzed NaAlH₄. The onset dehydrogenation temperature of the NaAlH₄@CeO₂ composite was reduced to below 100 °C, with only one main dehydrogenation peak appearing at 130 °C, which is 120 °C and 50 °C lower than for its bulk counterpart and for the ball-milled CeO₂ HNTs-catalyzed NaAlH₄, respectively. Moreover, ~5.09 wt% hydrogen could be released within 30 min at 180 °C, while only 1.6 wt% hydrogen was desorbed from the ball-milled NaAlH₄ under the same conditions. This significant improvement is mainly attributed to the synergistic effects contributed by the CeO₂ HNTs, which could act as not only a structural scaffold to fabricate and confine the NaAlH₄ NPs, but also as an effective catalyst to enhance the hydrogen storage performance of NaAlH₄.

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NaAlH₄ has been widely regarded as a potential hydrogen storage material due to its favorable thermodynamics and high energy density. The high activation energy barrier and high dehydrogenation temperature, however, significantly hinder its practical application. In this paper, CeO₂ hollow nanotubes (HNTs) prepared by a simple electrospinning technique are adopted as functional scaffolds to support NaAlH₄ nanoparticles (NPs) towards advanced hydrogen storage performance. The nanoconfined NaAlH₄ inside CeO₂ HNTs, synthesized via the infiltration of molten NaAlH₄ into the CeO₂ HNTs under high hydrogen pressure, exhibited significantly improved dehydrogenation properties compared with both bulk and ball-milled CeO₂ HNTs-catalyzed NaAlH₄. The onset dehydrogenation temperature of the NaAlH₄@CeO₂ composite was reduced to below 100 °C, with only one main dehydrogenation peak appearing at 130 °C, which is 120 °C and 50 °C lower than for its bulk counterpart and for the ball-milled CeO₂ HNTs-catalyzed NaAlH₄, respectively. Moreover, ~ 5.09 wt.% hydrogen could be released within 30 min at 180 °C, while only 1.6 wt.% hydrogen was desorbed from the ball-milled NaAlH₄ under the same conditions. This significant improvement is mainly attributed to the synergistic effects contributed by the CeO₂ HNTs, which could act as not only a structural scaffold to fabricate and confine the NaAlH₄ NPs, but also as an effective catalyst to enhance the hydrogen storage performance of NaAlH₄.

1 Introduction

Considering the increasing energy demands of human societies, it is an urgent necessity to find an alternative to the limited sources of fossil fuels. Hydrogen has been widely recognized as one of the most promising renewable environmentally friendly energy carriers, owing to its high energy content.^{1–5} In order to realize the widespread utilization of hydrogen, one of the main challenges has been how to store hydrogen safely and efficiently. In comparison with cryogenically liquefied hydrogen or highly compressed hydrogen technologies, hydrogen storage in solid-state materials is attracting an increasing amount of attention due to its high energy density and unique safety characteristics. Sodium alanate (NaAlH₄), which possesses high gravimetric ($\rho_m = 7.5$ wt.% H₂) and volumetric ($\rho_v = 94$ gH₂ L⁻¹) hydrogen densities with moderate thermodynamic properties, is regarded as one of the most promising solid-state hydrogen-storage materials. The equilibrium chemical reactions of NaAlH₄ for hydrogen storage are shown in the following equations:

Because the decomposition temperature of NaH exceeds 300 °C, only the first two reversible reaction steps are suitable for practical applications. Accordingly, the hydrogen storage capacity of NaAlH₄ for practical application approaches approximately 5.6 wt.%.^{6,7} The slow dehydrogenation/hydrogenation kinetics and poor reversibility, however, significantly impede the application of NaAlH₄ as a hydrogen storage material.

The pioneering work of Bogdanović and Schwickardi has demonstrated that Ti-doped NaAlH₄ is capable of reversible hydrogen storage under mild conditions.⁶ Subsequently, a series of catalysts was employed to further improve the hydrogen storage properties of NaAlH₄. Recently, it has been verified that Ce-based catalysts are superior to TiCl₃ in terms of enhancing the hydrogen storage performance of NaAlH₄.¹¹ For example, the introduction of CeO₂ nanoparticles (NPs) could lower the dehydrogenation temperature of NaAlH₄ down to around 100 °C and induce further enhancement of its hydriding and dehydriding kinetics.¹² Furthermore, Zhang et al. prepared a nanocrystalline CeO₂@C-containing NaAlH₄ composite, by hydrogenating a NaH-Al mixture doped with CeO₂@C.¹³ This composite could rapidly release approximately ~ 4.7 wt.% hydrogen at temperatures ranging from 95 to 190 °C under dynamic heating, and the onset dehydrogenation temperature could be reduced to only 77 °C.

In addition to the adoption of catalytic agents, nanoconfinement has been proved to be an effective

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approach to improving both the kinetics and thermodynamics of the hydrogen storage reactions of NaAlH_4 .^{10,29,35} This strategy is mainly achieved via wet impregnation or melt infiltration of NaAlH_4 into various kind of scaffold materials which could significantly decrease the particle size of NaAlH_4 by taking advantage of the structural support of scaffolds. As early as 2006, Baldé et al. investigated the hydrogen absorption and desorption characteristics of NaAlH_4 supported by surface-oxide carbon nanofibers, which exhibited a hydrogen storage capacity of 3.7 wt.% of hydrogen below 160 °C.¹⁴ Subsequently, various carbon nanomaterials, such as carbon nanofibers,¹⁶ porous carbon,¹⁹ carbon aerogels,²⁴⁻²⁵ and C_{60} ,²⁰ as well as metal organic frameworks (MOF), such as MOF-74 (Mg)²⁷ and $\text{Cu}_3(\text{BTC})_2$ MOF,²⁸ and ordered mesoporous silica, were used to support and confine NaAlH_4 to enhance both the kinetics and the thermodynamics of dehydrogenation.¹⁵ The reduction of particle size down to the nanoscale, induced by nanoconfinement, could significantly decrease the hydrogen diffusion distance, leading to tremendously improved kinetics for hydrogenation and dehydrogenation. Remarkably, it has been demonstrated that the addition of catalysts, i.e., TiCl_3 into porous scaffolds could further improve the hydrogen storage performance of nanoconfined NaAlH_4 , decreasing the peak temperature for dehydrogenation to 125 °C, which is 34 °C lower than for nanoconfined NaAlH_4 without TiCl_3 .²⁹ This result indicates that the combination of catalysts and nanoconfinement could have a synergetic effect towards improving the hydrogenation and dehydrogenation performance of NaAlH_4 . Nonetheless, it should be pointed out that the inhomogeneous distribution of catalysts in these scaffolds leads to a limited catalytic effect on the nanoconfined NaAlH_4 . Therefore, it is highly desirable to develop catalytic structural supports to confine NaAlH_4 , which could result in intimate contact between NaAlH_4 nanoparticles on the inside and the catalyst, leading to advanced hydrogen storage performance.

In this work, porous CeO_2 hollow nanotubes (HNTs), as catalytic nanoscaffolds, were fabricated to improve the

hydrogen storage performance of NaAlH_4 . Taking advantage of the porous nanostructure and thermal stability of CeO_2 HNTs, the molten NaAlH_4 can be homogeneously filled into the CeO_2 HNTs by thermal melt impregnation under high-pressure H_2 , with the product denoted as $\text{NaAlH}_4@ \text{CeO}_2$. Induced by the reduction of the particle size of NaAlH_4 to nanometer range as well as the catalytic effects of CeO_2 , the $\text{NaAlH}_4@ \text{CeO}_2$ could release approximately 5.09 wt.% hydrogen within 30 min at 180 °C, with the dehydrogenation onset temperature decreased to about 75 °C, which is 55 °C and 95 °C lower than for bulk NaAlH_4 and ball-milled $\text{NaAlH}_4/\text{CeO}_2$, respectively.

Experimental section

Preparation of CeO_2 HNTs

In order to synthesize CeO_2 HNTs, a two-step process was adopted, which included a simple one-step electrospinning process and an annealing process. In the first step, 1 mmol of cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich Inc., USA) was dissolved in 10 mL of N,N-dimethylformamide (DMF) with magnetic stirring at room temperature for 30 min. Then, an appropriate amount of polyvinylpyrrolidone (PVP, Mw $\approx$ 1300000, Sigma-Aldrich Inc., USA) was added into the mixed solution. The weight ratio of PVP to inorganic salt was 3. Finally, a homogenous precursor solution was obtained after vigorous magnetic stirring for 3 h. The viscous composite solution was poured into a syringe equipped with an 18-gauge blunt-tip stainless steel needle. The flow rate of solution was approximately 500 μLh^{-1} , controlled by a syringe pump (Longer, TJP-3A, China). During the electrospinning process, the needle and a collector plate were connected to a high-voltage generator. In this case, a voltage of 16 kV was applied between the cathode (metal collector plate) and the anode (needle) with a collection distance of 15 cm. The precursor solution was ejected from the needle under the effect of the high voltage that was applied. With the evaporation of solvent, the solution jet solidified on the collector. The whole experiment was conducted in an extremely dry environment. After the collected samples were dried for 12 h at 80 °C under vacuum, the fibers were annealed in a tube furnace with a temperature ramp rate of 1 °C min^{-1} from room temperature to 600 °C and sintered for 3 h. The slow heating rate could ensure that the organic phase was removed, without destroying the structure of the nanofibers. After cooling down to room temperature, the nanotubes were formed.

Nanoconfinement of NaAlH_4 in CeO_2 HNTs

NaAlH_4 was confined in short CeO_2 HNTs by the following thermal melt-impregnation process. Typically, a mixture of NaAlH_4 (95 % purity, Sigma-Aldrich) and as-prepared CeO_2 HNTs, with a mass ratio of 1:1, was obtained by manual grinding. Then, the mixture was loaded into and sealed in a stainless-steel autoclave in an N_2 -filled glove box. The stainless-steel autoclave was subsequently evacuated and refilled with H_2 (99.999 % purity) to 3.5 MPa to prevent the

Fig. 1 Schematic illustration of the synthesis process for $\text{NaAlH}_4@ \text{CeO}_2$.

decomposition of NaAlH_4 during the heating process. After that, the autoclave was heated to 180°C (close to the melting temperature of NaAlH_4) from room temperature with a heating rate of 5°C min^{-1} and kept at this temperature for 30 min. This operation was repeated three times, which could impregnate the molten NaAlH_4 into the CeO_2 HNTs as a result of capillary action. After cooling to room temperature, the autoclave was transferred back into the glove box, where the infiltrated sample, denoted as $\text{NaAlH}_4@\text{CeO}_2$, could be collected.

Preparation of the ball-milled sample

The CeO_2 HNTs and NaAlH_4 with a mass ratio of 1:1 were introduced into a stainless steel vessel together with stainless steel balls in an N_2 -filled glove box. The milling was carried out at 350 rpm, and the ball-to-powder weight ratio was 50:1. After 12 h of milling, the sample was obtained and denoted as $\text{NaAlH}_4/\text{CeO}_2$.

Characterizations

The composition of powdered samples was investigated on an X-ray diffractometer (XRD; D8 Advance, Bruker AXS) with $\text{Cu K}\alpha$ radiation at 50 kV and 30 mA. The preparation of samples for XRD measurements was entirely conducted in an N_2 -filled glove box, and the surfaces of samples were covered with Scotch tape to protect the samples from moisture and air. Fourier transform infrared (FTIR) spectra were collected at room temperature by using a FTIR-650 spectrometer (Tianjin Gangdong) at a resolution of 4 cm^{-1} . The morphology, microstructure, and elemental distribution were analysed on a JEOL JEM-2100F transmission electron microscope (TEM) and a Shimadzu JEOL 7500FA scanning electron microscope (SEM). For the TEM measurements, the samples were

Fig. 2 XRD patterns for the samples: (a) as-prepared CeO_2 , (b) ball-milled $\text{NaAlH}_4/\text{CeO}_2$, and (c) as-prepared $\text{NaAlH}_4@\text{CeO}_2$.

Fig. 3 SEM images of the precursor PVA- $\text{Ce}(\text{NO}_3)_3$ nanofibers (a), as-prepared CeO_2 (b, c), as-prepared $\text{NaAlH}_4@\text{CeO}_2$ (d, e), and as-milled $\text{NaAlH}_4/\text{CeO}_2$ (f). The characteristics of the cross-sections of CeO_2 fibers are marked with red boxes.

dispersed in dried acetone solvent by ultrasonic treatment, and then spread on a copper grid. For SEM measurements, the samples were dispersed on electrically conducting adhesive tape. All the samples in the glove box were rapidly transferred into the equipment, which was filled with N_2 , and then they were diverted into the chambers for TEM and SEM measurements as soon as possible. The distribution of elemental O, Ce, Na, and Al in the samples was detected with an energy-dispersive X-ray spectrometer (EDS) attached to the TEM. Mass spectrometer analysis (MS; Hiden HPR 20), in conjunction with thermogravimetric analysis (TG; Netzsch STA449 F3), was protected by N_2 gas, flowing at the rate of 80 mL min^{-1} , with a heating rate of 5°C min^{-1} . The kinetic properties were measured by a volumetric method based on Sieverts' law using an automatic device from SUZUKI HOKAN.CO., LTD. in Japan. The H_2 desorption kinetics properties were measured at various temperatures with an H_2 pressure around 0.01 atm. For comparison, the weight of CeO_2 was excluded in the calculation of dehydrogenation capacity from the $\text{NaAlH}_4@\text{CeO}_2$ and $\text{NaAlH}_4/\text{CeO}_2$.

Results and discussion

Synthesis and characterization of $\text{NaAlH}_4@\text{CeO}_2$

As shown in Fig. 1, CeO_2 HNTs were synthesized by annealing the precursor, i.e., PVA- $\text{Ce}(\text{NO}_3)_3$ nanofibers, via tuning the heating rate and annealing temperature. Firstly, PVA- $\text{Ce}(\text{NO}_3)_3$ nanofibers were heated to 600°C at a rate of 1°C min^{-1} to remove the PVP. During this process, the rate of decomposition of PVP was higher than the gas diffusion through the fiber surface, owing to the slow heating rate, and therefore, the pressure inside the nanofibers increased faster than that outside of the composite fibers, leading to the constriction of outside nanoparticles.³²⁻³⁴ Subsequently, the

Fig. 4 TEM images of CeO₂ (a) and NaAlH₄@CeO₂ (c, d), HRTEM image of CeO₂ (b), EDS spectrum (e), and the corresponding EDS maps of (f) O, (g) Ce, (h) Al, and (i) Na elements for image (d).

Fig. 5 FTIR spectra of the bulk NaAlH₄ and as-prepared NaAlH₄@CeO₂.

precursor was calcined at 600 °C for 3 h to synthesize nanocrystalline CeO₂. Due to the rapid increase in the reaction rate at 600 °C, the particles inside expanded owing to the large strain and Ostwald ripening, leading to the formation of nanotubes.³³⁻³⁴ The X-ray diffraction (XRD) pattern of the as-prepared CeO₂ HNTs, as shown in Fig. 2a, exhibits the characteristic diffraction peaks of CeO₂ (PDF 34-0394), which confirms the formation of CeO₂ crystallites. The SEM (Fig. 3a-c) images reveal that both the as-synthesized PVA-Ce(NO₃)₃ nanofibers and the CeO₂ HNTs exhibit uniform fibrous structures, with a diameters of ~ 300 nm and 70 nm respectively. The hollow structure of the as-synthesized CeO₂ nanofibers could be verified from the cross-sections of some broken fibers (Fig. 3b-c). The TEM image further demonstrates the formation of CeO₂ HNTs (Fig. 4a), which confirms that the thickness of the walls of the as-synthesized CeO₂ HNTs composed of CeO₂ NPs with a diameter of ~ 13 nm, is approximately 17 nm. By analyzing the high-resolution TEM (HRTEM) images (Fig. 4b), the interplanar spacings of the nanoparticles were measured to be 0.326 nm, 0.270 nm, and 0.161 nm, corresponding to the (112), (200), and (403) plane of CeO₂, respectively, which provides further evidence for the formation of CeO₂ nanocrystals. According to the above observations, it is concluded that the CeO₂ HNTs were synthesized successfully.

The XRD pattern in Figure 2b shows that the as-prepared NaAlH₄/CeO₂ composite presents the typical peaks belonging to CeO₂ and NaAlH₄. Because the particle size of NaAlH₄ remains large, the diffraction peaks are obvious and sharp, which is similar to the pure NaAlH₄. In comparison, although the characteristic peaks of CeO₂ are still observed, only weak and broad peaks indexed to NaAlH₄ are present in the NaAlH₄@CeO₂ (Fig. 2c). This indicates the loss of the

crystalline structure of NaAlH₄ due to the melt infiltration process and the significant reduction in the particle size down to nanometer range that was induced by nanoconfinement by the CeO₂ HNTs.²²⁻²³

Therefore, Fourier transform infrared spectroscopy (FTIR) was further adopted to characterize the presence of NaAlH₄ inside the CeO₂ HNTs in NaAlH₄@CeO₂. Fig. 5 displays the FTIR spectra of the bulk NaAlH₄ and the as-prepared NaAlH₄@CeO₂ in the wavenumber range of 600–2000 cm⁻¹. The peaks of the bulk NaAlH₄ at 1676 cm⁻¹ and 738 cm⁻¹ correspond to the stretching mode ν₃ of the Al–H vibration and the bending mode ν₄ of the AlH₄ group, respectively. After melt infiltration of NaAlH₄ into the CeO₂ HNTs, these two peaks could be clearly observed, but slightly shifted to higher wavenumbers, which indicates the presence of NaAlH₄ phase in the CeO₂ HNTs after the infiltration process without decomposition. Furthermore, as shown in Fig. S3, after infiltration of NaAlH₄, BET specific surface area and BJH total pore volume decreased from 24 to 2.5 m² g⁻¹ and 0.063 cm³ g⁻¹ to 0.0079 cm³ g⁻¹, respectively, which indicates the confinement of NaAlH₄ into the CeO₂ tubes.

The morphology and structure of the nanoconfined NaAlH₄ NPs inside the CeO₂ HNTs were further investigated by SEM (Fig. 3d-e) and TEM (Fig. 4). It could be clearly observed from the cross-section of the as-prepared NaAlH₄@CeO₂ (Fig. 3d-e) that NaAlH₄ NPs had successfully filled the hollow cavities and the wall defects of the CeO₂ HNTs without any aggregation, with a fraction of the NaAlH₄ NPs deposited on the external surfaces of these nanotubes. EDS analysis (Fig. 4e) demonstrates the presence of the elements Ce, O, Al, and Na inside the CeO₂ HNTs, suggesting the encapsulation of NaAlH₄ in the CeO₂ HNTs in NaAlH₄@CeO₂. The scanning TEM (STEM) image (Fig. 4d), combined with the corresponding EDS mapping results for the O, Ce, Na, and Al elements of the NaAlH₄@CeO₂ sample, as shown in Fig. 4f-i, confirms that all four element maps apparently match very well with the shape of the as-prepared NaAlH₄@CeO₂, indicating the homogeneous distribution of NaAlH₄ inside the CeO₂ HNTs. Specifically, both the Na-map and the Al-map, originating

Fig. 6 MS curves (a) and TG curves (b) for bulk NaAlH₄, NaAlH₄/CeO₂, and NaAlH₄@CeO₂, with a heating rate of 5 °C min⁻¹.

from the NaAlH₄ NPs, are slightly different from the O-map and Ce-map originating from the CeO₂ HNTs, in which the element densities at the edges of the nanotubes are larger than in the middle of the tubes. This difference indicates that a large percentage of the NaAlH₄ NPs were embedded and well dispersed inside the interior cavities of the nanotubes, with only a small part of the Na and Al distributed on the outside of the CeO₂ HNTs, which coincides well with the SEM results.

In order to investigate the hydrogen storage properties of the as-prepared NaAlH₄@CeO₂, both mass spectroscopy (MS) and thermogravimetric analysis (TGA) (Fig. 6) were conducted with the bulk NaAlH₄ and the milled NaAlH₄/CeO₂ composite included for comparison. As expected, the decomposition of bulk NaAlH₄ started at around 170 °C, and two dehydrogenation peaks at about 250 °C and 280 °C (Fig. 6a), corresponding to the stepwise reactions shown in Eqs. (1–2), respectively, were observed, which agrees well with the reported values.²² Compared with the bulk NaAlH₄, the ball-milled NaAlH₄/CeO₂ composite showed significantly improved dehydrogenation behaviour, with the onset dehydrogenation temperature reduced to 130 °C, which was 40 °C lower than for its bulk counterpart. Moreover, the peak temperatures for the initial two dehydrogenation reactions were decreased to 180 °C and 213 °C, which are 70 °C and 67 °C lower than for the bulk NaAlH₄, respectively. This result obviously verifies the

catalytic effect of CeO₂ on the dehydrogenation of NaAlH₄, in good agreement with the previous reports.^{12, 13, 40} In strong contrast, the MS result indicates that the process of hydrogen desorption of NaAlH₄@CeO₂ took place at a much lower temperature of approximately 75 °C, and only one distinct main peak was observed at about 130 °C, which were both significantly lower than for the milled NaAlH₄/CeO₂ composite. Additionally, it is remarkable that the first two decomposition steps of NaAlH₄ tended merged into one single hydrogen release step for the as-prepared NaAlH₄@CeO₂, comparing with NaAlH₄@CeO₂ and bulk NaAlH₄.^{19, 26, 31} It has been calculated that when particle size was reduced to less than 50 nm, NaAlH₄ could decompose in a single step to directly form NaH and Al at a temperature below its melting point (~ 180 °C) in reported papers.³⁴ Due to Jahn-Teller distortion in small clusters, the decomposition of NaAlH₄ may occur in a single step, without any Na₃AlH₆ intermediate.³⁰ Therefore, these results directly demonstrate the synergetic effects of the catalysis and nanoconfinement provided by CeO₂ HNTs towards significantly enhancing the dehydrogenation properties of NaAlH₄.

The TGA curves (Fig. 6b) demonstrate that the first two stages of hydrogen release were completed at around 310 °C

Fig. 7 (a) XRD patterns of the dehydrogenated products of bulk NaAlH₄, the ball-milled NaAlH₄/CeO₂ composite, and NaAlH₄@CeO₂ at 200 °C; (b) FTIR spectra of the dehydrogenated products of the ball-milled NaAlH₄/CeO₂ and NaAlH₄@CeO₂ at 200 °C.

for the bulk NaAlH_4 , and a total amount of approximately 5.5 wt.% H_2 is evolved, which coincides well with its theoretical capacity. It should be noted that all the hydrogen capacity is calculated based on the NaAlH_4 in the composite. By comparison, 5.5 wt.% hydrogen could be released from $\text{NaAlH}_4/\text{CeO}_2$ composite at temperatures below 250 °C. In addition, the onset temperature declined from 175 °C for the bulk NaAlH_4 to 130 °C for the $\text{NaAlH}_4/\text{CeO}_2$ composite, suggesting that the presence of CeO_2 provided effective catalytic effects towards the decomposition of the NaAlH_4 and Na_3AlH_6 . In terms of $\text{NaAlH}_4@\text{CeO}_2$, the desorption kinetics were significantly enhanced, which is supported by the decrease of the onset dehydrogenation temperature to below 80 °C and the completion of the dehydrogenation process at a temperature as low as 180 °C. The hydrogen capacity released based on the NaAlH_4 in $\text{NaAlH}_4@\text{CeO}_2$ approaches ~ 5.45 wt.%, indicating complete dehydrogenation. These features correspond well with the MS results, demonstrating the tremendously improved dehydrogenation performance of NaAlH_4 owing to the homogeneous nanoconfinement of NaAlH_4 in CeO_2 HNTs.

In order to elucidate the mechanism by which the nanoconfinement of NaAlH_4 in CeO_2 HNTs enhances the dehydrogenation properties, the XRD patterns of bulk NaAlH_4 , the ball-milled $\text{NaAlH}_4/\text{CeO}_2$ composite, and the as-prepared $\text{NaAlH}_4@\text{CeO}_2$, collected at 200 °C, are shown in Fig. 7a. Only NaAlH_4 is present for bulk NaAlH_4 upon heating to 200 °C, indicating that no dehydrogenation occurred at this temperature. The complete dehydrogenation of bulk NaAlH_4 could be achieved upon heating to 350 °C (Fig. S1 in the Supporting Information) as verified by the formation of NaH (JCPDS 02-0809) and Al (JCPDS 65-2869) without the presence of NaAlH_4 , which agrees well with the TG and MS results. For the ball-milled $\text{NaAlH}_4/\text{CeO}_2$ composite, characteristic reflections of Na_3AlH_6 and NaAlH_4 are observed, suggesting the partial decomposition of NaAlH_4 under the catalytic effects of CeO_2 . In the case of the as-prepared $\text{NaAlH}_4@\text{CeO}_2$, only peaks of CeO_2 and $\text{CeH}_{2.51}$ (JCPDS 32-0190) phases appeared, with the absence of any peaks for NaAlH_4 and/or Na_3AlH_6 after heating to 200 °C. It could be clearly observed that after dehydrogenation at 100 °C (Fig. S4), which is approaching the onset dehydrogenation temperatures, weak $\text{CeH}_{2.51}$ peaks for the sample after dehydrogenation at 100 °C were observed, attributed to the reaction between NaH and CeO_2 .^{12-13,40} It indirectly indicates the generation of NaH at only 100 °C. Comparing with previous report,¹¹ in which the Na_3AlH_6 and NaH are formed at 136 °C and 150 °C, respectively, the NaH is formed at a much lower temperature in the as-prepared $\text{NaAlH}_4@\text{CeO}_2$, and Na_3AlH_6 phase can be hardly detected, which is in accordance with the theoretical calculation prediction.³⁸ The destabilization of Na_3AlH_6 and NaH leads to a fast decomposition of NaAlH_4 . Based on the FTIR results (Fig. 7b), all the peaks belonging to Al–H bonds of $\text{NaAlH}_4@\text{CeO}_2$ disappeared after dehydrogenation at 200 °C, which suggests the complete decomposition of the NaAlH_4 . By comparison, the peaks of the Al–H bonds of $\text{NaAlH}_4/\text{CeO}_2$ at 1682 cm^{-1} and 733 cm^{-1} are still present upon heating to 200

°C in the FTIR spectra, which corresponds well to the XRD results. Notably, no well crystallized Al phase was observed in the dehydrogenated products of $\text{NaAlH}_4@\text{CeO}_2$, which indirectly confirms that the Al grains did not agglomerate into large particles due to the nanoconfinement by CeO_2 HNTs, providing structural support for the uniform distribution of NaAlH_4 . Furthermore, as shown in Fig. S2, the hollow nanotube structure of CeO_2 was still well preserved after the dehydrogenation process. This indicates the high thermal stability induced by the physical contact between the NaAlH_4 and the CeO_2 HNTs. Besides, the homogeneous distribution of O, Ce, Al and Na in the original and dehydrogenated $\text{NaAlH}_4@\text{CeO}_2$ indicates that CeO_2 HNTs prevent the phase segregation of NaAlH_4 . CeO_2 HNTs could serve as “nano-reactor”²³, where NaAlH_4 particles are limited to a nanoscale level which facilitates the interaction between NaAlH_4 and CeO_2 and shortens the H_2 diffusion distance, to achieve the sample with excellent kinetics. What’s more, it should be noted that the presence of $\text{CeH}_{2.51}$ phase on the external surfaces to some extent could act as active species in the following hydrogen storage process.^{13,36,37}

Fig. 8 Hydrogen desorption (under 0.01 atm hydrogen pressure) curves of the bulk NaAlH_4 , ball-milled $\text{NaAlH}_4/\text{CeO}_2$, and $\text{NaAlH}_4@\text{CeO}_2$ at 180 °C (a). Hydrogen desorption kinetic curves of the $\text{NaAlH}_4@\text{CeO}_2$ at different temperatures (b). The inset shows the Arrhenius plot according to the isothermal H_2 desorption of $\text{NaAlH}_4@\text{CeO}_2$.

1 Isothermal dehydrogenation kinetics of NaAlH₄@CeO₂ 57

2 The isothermal dehydrogenation properties (Fig. 8a) of the 58
3 NaAlH₄@CeO₂, in comparison to the bulk NaAlH₄ and the 59
4 milled NaAlH₄/CeO₂, were further investigated using a Sieverts 60
5 pressure-composition-temperature (PCT) apparatus at various 61
6 temperatures. Specifically, the ball-milled NaAlH₄/CeO₂ 62
7 composite released about 1.22 wt.% H₂ in less than 10 min 63
8 while there was no distinct signs of hydrogen release for the 64
9 bulk NaAlH₄ within the initial 10 min at 180 °C. This further 65
10 demonstrates the catalytic effects of CeO₂ towards the
11 dehydrogenation of NaAlH₄. The hydrogen desorption rate of 66
12 NaAlH₄/CeO₂ fell drastically after 10 min, and only a small 67
13 amount of hydrogen was slowly released in the following 100
14 min, according to Eq. (2), whereas the dehydrogenation of 68
15 NaAlH₄@CeO₂ carried on at a higher rate throughout the 69
16 whole process and was completed within 50 min. The amount 70
17 of hydrogen released from the milled NaAlH₄/CeO₂ was 1.8 71
18 wt.% in 30 min, while the hydrogen capacity of the 72
19 NaAlH₄@CeO₂ reached 5.09 wt.% through the same operation 73
20 time at 180 °C, which was nearly three times as much as in the 74
21 former case. In addition, only one hydrogen desorption step 75
22 was observed in the dehydrogenation curve of NaAlH₄@CeO₂, 76
23 which is in agreement with the MS results. These results 77
24 directly demonstrate that the nanoconfinement effect of the 78
25 CeO₂ HNTs is significantly effective towards enhancing the 79
26 hydrogen storage performance of NaAlH₄. 80

27 The dehydrogenation outlines of the NaAlH₄@CeO₂ at 81
28 150, 160, 170, and 180 °C are presented in Fig. 8b. ~ 0.7 wt.% 82
29 hydrogen was released from NaAlH₄@CeO₂ at 150 °C in 30
30 min, while the outcome went up to ~ 2.9 wt.% and ~ 4.6 wt.% 84
31 at 160 and 170 °C, respectively, which is much better than for 85
32 the reported dehydrogenation properties of NaAlH₄ using 86
33 other scaffold materials for the mesoporous matrix.²³ Finally, 87
34 2.16 wt.%, 5.21 wt.%, and 5.22 wt.% of hydrogen could be 88
35 desorbed at 150, 160, and 170 °C, respectively. When the 89
36 temperature was increased to 180 °C, 5.09 wt.% hydrogen 90
37 could be rapidly released within 30 min, and the whole 91
38 hydrogen capacity of 5.51 wt.% could be achieved,
39 approaching the theoretical value of 5.6 wt.%, in good
40 agreement with the MS and TG results (Fig. 6). The apparent 92
41 activation energy (E_a) for the hydrogen release reaction is 93
42 calculated by configuring the isothermal dehydriding curves at 94
43 different temperatures for the quantitative evaluation of the 95
44 considerably improved dehydriding kinetics of the as- 96
45 prepared NaAlH₄@CeO₂, using the Johanson–Mehl–Avrami- 97
46 Kolmogorov (JMAK) Equation (4): 98

$$47 \quad \alpha(t) = 1 - \exp[-(kt)^n] \quad (4) \quad 99$$

48 Eq. (4) can be reformulated as:

$$49 \quad \ln[-\ln(1-\alpha(t))] = n \ln t + n \ln k \quad (5)$$

50 where α is the reacted fraction with respect to time t , k is 100
51 the rate constant, and n is the Avrami exponent, which is 101
52 commonly used to discern the dehydrogenation mechanism. 102
53 On plotting $\ln[-\ln(1-\alpha(t))]$ against $\ln t$, good linearity was 103
54 achieved over the range of $0.03 \leq \alpha \leq 0.8$, with a correlation 104
55 coefficient of $R^2 > 0.99$. Subsequently, the apparent activation 105
56 energy was calculated to be approximately 76.32 kJ·mol⁻¹ for 106
107

the NaAlH₄@CeO₂, based on the slopes ($-E_a/R$), where R is the
gas constant, of the straight lines according to Arrhenius
equation (inset of Fig. 8b), which is much lower than the
values reported for CeO₂@C doped-NaAlH₄ ($E_{a1} = 90.3$ kJ·mol⁻¹
and $E_{a2} = 81.7$ kJ·mol⁻¹) obtained by ball milling¹¹ and bulk
NaAlH₄.²⁰ The significant decrease in the apparent E_a directly
verifies the improvement of the dehydrogenation kinetics due
to the synergistic effects of nanoconfinement and the
catalytic effects of CeO₂ HNTs.

Conclusions

In summary, this work investigates the adoption of CeO₂ HNTs
as effective catalytic nanoscaffolds to improve the hydrogen
storage performance of NaAlH₄. The hollow nanotube
structure of the CeO₂ HNTs could act not only as a structural
support to synthesize and stabilize the NaAlH₄ nanoparticles,
but also as an effective catalyst to further enhance the
hydrogen storage properties of nanosized NaAlH₄. Owing to
the synergistic effects contributed by the CeO₂ HNTs towards
improving the dehydrogenation properties of NaAlH₄, the
hydrogen storage performance of NaAlH₄ is significantly
improved. For instance, the onset temperature of
dehydrogenation for the NaAlH₄@CeO₂ was reduced to 75 °C,
which is ~ 95 °C and ~ 55 °C lower than for bulk and CeO₂-
catalyzed NaAlH₄, respectively, and 5.5 wt.% hydrogen was
released rapidly within 100 min at a temperature as low as
180 °C. Additionally, an apparent activation energy of 76.32
kJ·mol⁻¹ was observed for the nanoconfined NaAlH₄ inside the
CeO₂ HNTs, which is significantly lower than for the bulk and
catalyst-doped NaAlH₄. This provides direct evidence for the
significantly enhanced dehydrogenation kinetics due to the
nanoconfinement of NaAlH₄ inside CeO₂ HNTs. Moreover, the
novel strategy of using a scalable electrospinning technique to
synthesize catalytic scaffolds that was explored in this work
provides new avenues for enhancing the hydrogen storage
performance of NaAlH₄.

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Notes and references

- 1 L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353.
- 2 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U.S.A.*,
2006, **103**, 15729.
- 3 P. E. de Jongh and P. Adelhelm, *ChemSusChem*, 2010, **3**,
1332.
- 4 G. L. Xia, D. Li, X. Chen, Y. Tan, Z. Tang, Z. Guo, H. Liu, Z. Liu,
and X. Yu, *Adv. Mater.*, 2013, **25**, 6238.

- 1 5 J. Huang, L. Ouyang, Q. Gu, X. Yu, and M. Zhu, *Chem. Eur. J.* **21**, 14931. 68
- 2 2015, **21**, 14931. 69
- 3 6 J. Yang, S. Hirano, *Adv. Mater.*, 2009, **21**, 3023. 70
- 4 7 U. Eberle, M. Felderhoff, F. Schüth, *Angew. Chem. Int. Ed.* **48**, 6608. 71
- 5 2009, **48**, 6608. 72
- 6 8 B. Bogdanović and M. Schwickardi, *J. Alloys Compd.*, 1997, **173**, 253. 73
- 7 253. 74
- 8 9 B. Bogdanović, M. Felderhoff, A. Pommerin, F. Schüth and N. Spielkamp, *Adv. Mater.*, 2006, **18**, 1198. 75
- 9 Spielkamp, *Adv. Mater.*, 2006, **18**, 1198. 76
- 10 10 G. L. Xia, Y. Tan, X. Chen, D. Sun, Z. Guo, H. K. Liu, L. Ouyang, M. Zhu, and X. Yu, *Adv. Mater.*, 2015, **27**, 5981. 77
- 11 M. Zhu, and X. Yu, *Adv. Mater.*, 2015, **27**, 5981. 78
- 12 11 X. Fan, X. Xiao, L. Chen, S. Li, H. Ge and Q. Wang, *J. Phys. Chem. C*, 2011, **115**, 2537.
- 13 *Chem. C*, 2011, **115**, 2537.
- 14 12 X. Fan, X. Xiao, L. Chen, L. Zhang and J. Shao, *J. Mater. Chem. A*, 2013, **1**, 9752.
- 15 A, 2013, **1**, 9752.
- 16 13 X. Zhang, Y. Liu, K. Wang, Y. Li, M. Gao and H. Pan, *ChemSusChem*, 2015, **8**, 4180.
- 17 *ChemSusChem*, 2015, **8**, 4180.
- 18 14 C. P. Baldé, B. P. C. Hereijgers, J. H. Bitter and K. P. de Jong, *Angew. Chem. Int. Ed.*, 2006, **45**, 3501.
- 19 *Angew. Chem. Int. Ed.*, 2006, **45**, 3501.
- 20 15 S. Zheng, F. Fang, G. Zhou, M. Zhu and D. Sun, *Chem. Mater.*, 2008, **20**, 3954.
- 21 2008, **20**, 3954.
- 22 16 P. A. Berseth, A. G. Harter, R. Zidan, A. Blomqvist and C. M. Araújo, *Nano Letters*, 2009, **9**, 1502.
- 23 Araújo, *Nano Letters*, 2009, **9**, 1502.
- 24 17 C. P. Baldé, O. Leynaud, P. Barnes, E. Peláez-Jiménez, K. P. de Jonga and J. H. Bitter, *Chem. Commun.*, 2011, **47**, 2143.
- 25 de Jonga and J. H. Bitter, *Chem. Commun.*, 2011, **47**, 2143.
- 26 18 P. Adelhelm, J. Gao, M. H. W. Verkuijen, C. Rongeat, M. Herrich and P. Jan M. van Bentum, *Chem. Mater.*, 2010, **22**, 2233.
- 27 *Chem. Mater.*, 2010, **22**, 2233.
- 28 2233.
- 29 19 J. Gao, P. Adelhelm, M. H. W. Verkuijen, C. Rongeat, M. Herrich and P. Jan M. van Bentum, *J. Phys. Chem. C*, 2010, **114**, 4675.
- 30 *J. Phys. Chem. C*, 2010, **114**, 4675.
- 31 114, 4675.
- 32 20 Y. Li, F. Fang, H. Fu, J. Qiu, Y. Song, Y. Li, D. Sun and M. Zhu, *J. Mater. Chem. A*, 2013, **1**, 5238.
- 33 *J. Mater. Chem. A*, 2013, **1**, 5238.
- 34 21 S. Chumphongphan, U. Filsø, M. Paskevicius, D. A. Sheppard, T. R. Jensen and C. E. Buckley, *Int. J. Hydrogen Energy*, 2014, **39**, 11103.
- 35 *Int. J. Hydrogen Energy*, 2014, **39**, 11103.
- 36 39, 11103.
- 37 22 R. Xiong, G. Sang, X. Yan, G. Zhang and X. Ye, *J. Mater. Chem.*, 2012, **22**, 17183.
- 38 *J. Mater. Chem.*, 2012, **22**, 17183.
- 39 23 Y. Li, G. Zhou, F. Fang, X. Yua, Q. Zhang, L. Ouyang, M. Zhu and D. Sun, *Acta Materialia*, 2011, **59**, 1829.
- 40 *Acta Materialia*, 2011, **59**, 1829.
- 41 24 T. K. Nielsen, P. Javadian, M. Polanski, F. Besenbacher and T. R. Jensen, *Nanoscale*, 2013, **10**, 1039.
- 42 *Nanoscale*, 2013, **10**, 1039.
- 43 25 M. Paskevicius, U. Filsø, F. Karimi, J. Puszkiel, P. K. Pranzas, C. Pistidda and A. Hoell, *Int. J. Hydrogen Energy*, 2016, **41**, 4159.
- 44 *Int. J. Hydrogen Energy*, 2016, **41**, 4159.
- 45 41, 4159.
- 46 26 X. Fan, X. Xiao, J. Shao, L. Zhang, S. Li, H. Ge, Q. Wang and L. Chen, *Nano Energy*, 2013, **2**, 995.
- 47 *Nano Energy*, 2013, **2**, 995.
- 48 27 V. Stavila, R. K. Bhakta, T. M. Alam, E. H. Majzoub and M. D. Allendorf, *ACS Nano*, 2012, **6**, 9807.
- 49 *ACS Nano*, 2012, **6**, 9807.
- 50 28 R. K. Bhakta, J. L. Herberg, B. Jacobs, A. Highley, R. Behrens and M. D. Allendorf, *J. Am. Chem. Soc.*, 2009, **131**, 13198.
- 51 *J. Am. Chem. Soc.*, 2009, **131**, 13198.
- 52 29 T. K. Nielsen, M. Polanski, D. Zasada, P. Javadian, F. Besenbacher and J. Bystrzycki, *ACS Nano*, 2011, **5**, 4056.
- 53 *ACS Nano*, 2011, **5**, 4056.
- 54 30 E.H. Majzoub, F. Zhou and V. Ozoliņš, *J. Phys. Chem. C*, 2011, **115**, 2636.
- 55 *J. Phys. Chem. C*, 2011, **115**, 2636.
- 56 31 W. Lohstroh, A. Roth, H. Hahn and M. Fichtner, *ChemPhysChem*, 2010, **11**, 789.
- 57 *ChemPhysChem*, 2010, **11**, 789.
- 58 32 Y. Cheng, B. Zou, C. Wang, Y. Liu, X. Fan, L. Zhu, Y. Wang, H. Ma and X. Cao, *CrystEngComm*, 2011, **13**, 2863.
- 59 *CrystEngComm*, 2011, **13**, 2863.
- 60 33 L. Xu, H. Song, B. Dong, Y. Wang, J. Chen, and X. Bai, *Inorg. Chem.*, 2010, **49**, 10590.
- 61 *Inorg. Chem.*, 2010, **49**, 10590.
- 62 34 S. M. Hwang, S. Y. Kim, J-G. Kim, K. J. Kim, J-W. Lee, M-S. Park, Y-J. Kim, M. Shahabuddin, Y. Yamauchif and J. H. Kim, *Nanoscale*, 2015, **7**, 8351.
- 63 *Nanoscale*, 2015, **7**, 8351.
- 64 35 T. K. Nielsen, P. Javadian, M. Polanski, F. Besenbacher, J. Bystrzycki and T. R. Jensen, *J. Phys. Chem. C*, 2012, **116**, 21046.
- 65 *J. Phys. Chem. C*, 2012, **116**, 21046.
- 66 21046.
- 67 21046.
- 36 J. Hu, S. Ren, R. Witter and M. Fichtner, *Adv. Energy Mater.*, 2012, **2**, 560.
- 37 A. Leon, J. Rothe, K. Chlopek, O. Zabara and M. Fichtner, *Phys. Chem. Chem. Phys.*, 2009, **11**, 8829.
- 38 T. Mueller, G. Ceder, *ACS Nano* 2010, **4**, 5647.
- 39 D. Pukazhselvan, M. S. L. Hudson, A. S. K. Sinha, O. N. Srivastava, *Energy*, 2010, **35**, 5037.
- 40 X. Fan, X. Xiao, L. Chen, S. Li and Q. Wang, *J. Alloys Compd.*, 2011, **509**, S750.