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Realizing 6.7 wt% reversible storage of hydrogen at ambient temperature with non-confined ultrafine magnesium hydrides

Non-confined MgH₂ nanoparticles predominantly of 4–5 nm in size have been successfully synthesized *via* a metathesis reaction assisted by ultrasound. The support-free ultrafine MgH₂ stores 6.7 wt% of hydrogen reversibly at 30 °C, satisfying the targets of capacity and operating temperature set by the US Department of Energy.







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Broader context

Nowadays, efficient and safe storage of hydrogen is a main obstacle for the implementation of this clean energy. Materials based solid-state hydrogen storage featuring high hydrogen capacity and better safety has attracted strong interest. However, it is still challenging to produce a material that contains a sufficient amount of hydrogen (~ 6.5 wt% and 50 g H₂ L⁻¹) and readily releases/absorbs hydrogen on demand under practical operating conditions (≤ 85 °C). Light metal hydrides have high gravimetric and volumetric energy densities. The problems with these hydrides lie in their stable thermodynamics and high kinetic barriers, which require unacceptably high temperatures (>250 °C) to release hydrogen. The present study demonstrates a first successful attempt at synthesizing non-confined MgH₂ nanoparticles with 4–5 nm diameter by a metathesis process between MgCl₂ and LiH with the assistance of ultrasound in THF. The non-confined ultrafine MgH₂ nanoparticles enable the reversible desorption and absorption of 6.7 wt% H₂ at 30 °C and moderate H₂ pressure, achieving a significant breakthrough in ambient-temperature hydrogen storage with MgH₂. Our findings bring MgH₂ one step forward towards a practical hydrogen reservoir for on-board applications, and the methodology for nanostructuring provides a feasible and scalable approach to the fabrication of sensitive nanoparticles.

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Realizing 6.7 wt% reversible storage of hydrogen at ambient temperature with non-confined ultrafine magnesium hydrides†

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Using light metal hydrides as hydrogen carriers is of particular interest for safe and compact storage of hydrogen. Magnesium hydride (MgH₂) has attracted significant attention due to its 7.6 wt% hydrogen content and the natural abundance of Mg. However, bulk MgH₂ is stable ($\Delta H_f \sim 76 \text{ kJ mol}^{-1}$) and releases hydrogen only at impractically high temperatures (>300 °C). Herein, we demonstrate a first attempt to achieve ambient-temperature reversibility of hydrogen storage for MgH₂ by fabricating non-confined ultrafine nanoparticles. Taking advantage of the big discrepancies in the solubility of metal hydrides and chlorides in THF, a novel metathesis process of liquid–solid phase driven by ultrasound was proposed. Ultrafine MgH₂ nanoparticles predominantly of around 4–5 nm in size were successfully obtained without scaffolds or supports. A reversible hydrogen storage capacity of 6.7 wt% at 30 °C was measured, which has never been achieved before, thanks to thermodynamic destabilization and decreased kinetic barriers. The bare nanoparticles exhibited a stable and rapid hydrogen cycling behaviour in 50 cycles at 150 °C, a remarkable improvement compared with bulk MgH₂. Our finding brings MgH₂ a step closer to practical applications and the methodology presented here opens new pathways for fabricating sensitive nanoparticles.

Introduction

Hydrogen is an attractive substitute for traditional fossil fuels to power a sustainable society.¹ However, hydrogen exists as a low density gas under standard atmospheric and temperature conditions, which poses a significant challenge for storage.^{2–4} Conventional storage techniques based on compression and liquefaction are not practical for many applications where safety is highly critical and space is limited.⁵ Materials based hydrogen storage featuring high hydrogen capacity and better safety has therefore attracted strong interest.^{6–11} However, a candidate is yet to be found with a sufficient content of hydrogen (~6.5 wt% and 50 g H₂ L⁻¹) that can be released/absorbed on demand under



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[†] Electronic supplementary information (ESI) available: MS signal, volumetric release, volumetric capacity, isothermal hydrogenation, particle distribution, SEM image, XRD, XPS, TEM image, PCI curves, JMA plots, energy barrier diagram, HRTEM, DFT calculations, and equilibrium pressure data. See DOI: 10.1039/ d0ee03160g

practical operating conditions (\leq 85 °C).¹² Among the various candidates reported to date (*i.e.*, metal hydrides, alloys, and metal–organic frameworks),²⁻¹¹ magnesium hydride (MgH₂) has been intensively studied over the past few decades due to its high hydrogen content of 7.6 wt% and the natural abundance of Mg.^{13–17} However, release of hydrogen from bulk MgH₂ demands temperatures > 300 °C due to its high thermodynamic stability ($\Delta H_{\rm f} \sim 76$ kJ mol⁻¹ H₂) and high kinetic barrier ($E_{\rm a} \sim 160$ kJ mol⁻¹).^{18,19}

Nanostructuring can exert profound influences on the properties of solid hydrogen storage materials by increasing specific surface area, enriching grain boundaries/defects and shortening the mass transport path.^{20–24} For example, a considerable number of theoretical calculations have shown that nanoscaled MgH₂ is thermodynamically more feasible in dehydrogenation than its bulk counterpart.^{25–27} As the particles become smaller (*i.e.*, down to a few nanometres), MgH₂ becomes thermodynamically destabilized, and the shortened diffusion distance for H₂ molecules results in fast kinetics. As a result, H₂ desorption even at ambient temperature has been predicted theoretically.²⁵ However, this has never been experimentally confirmed.

In principle, nanostructuring can be carried out either on MgH₂ or on metallic Mg because of their reversible conversion upon dehydriding/rehydriding. Physical gas-phase condensation or plasma deposition,^{28,29} chemical or electrochemical reduction,^{30,31} and thermal decomposition of organometallic Mg precursors³²⁻³⁴ have been employed to obtain nanosized Mg. However, capping ligands, supports, or stabilizers had to be introduced to prevent Mg from reaction or coalescence, due to the high reactivity of Mg nanoparticles.³⁰⁻³⁴ These host materials can sometimes account for up to 80 wt% of the mixture, resulting in a severe loss of H₂ capacity. Mechanical milling has been employed to fabricate MgH₂ nanoparticles.³⁵ However, this technique is unsuitable for preparing particles smaller than 100 nm in diameter because of the extensive agglomeration and cold welding effects caused by local overheating in the milling process. Although MgH₂ of \sim 7 nm in size was obtained through ball-milling MgCl₂ and LiH powders, excess LiCl was used as a buffer material to separate the resultant MgH₂ nanoparticles and restrict particle growth, which gave rise to a composite and substantially lowered the gravimetric hydrogen storage capacity.³⁶ In addition, the hydrogen desorption temperature of these nanosized particles was still above 270 °C at 1 bar equilibrium pressure, and the kinetics was quite slow, likely due to the encapsulation by LiCl. More recently, MgH_2 nanoparticles <5 nm were also prepared by confinement or impregnation of MgH₂ into microporous carbon scaffolds.37-40 However, the peak temperature of desorption was higher than 200 °C along with a heavy penalty in hydrogen capacity. A possible explanation for high desorption temperature is the local confinement environment. We therefore believe that the breakthrough point for achieving reversible ambient-temperature hydrogen storage predicated theoretically lies in the controllable fabrication of non-confined MgH₂ nanoparticles in the size range of a few nanometers. However, no successful attempt has been reported because of the huge technical challenges in separating and stabilizing ultrafine nanoparticles without scaffolds and supports.

In this work, we realized a significant breakthrough in ambienttemperature reversible hydrogen storage with non-confined ultrafine MgH₂. Instead of ball milling, we developed a novel strategy to synthesize nanoscale MgH₂ in an organic solvent with the assistance of ultrasound taking advantage of the thermodynamically favored reaction between MgCl₂ and LiH. MgCl₂ and LiCl are highly soluble in tetrahydrofuran (THF),⁴¹ whereas the hydrides LiH and MgH₂ are insoluble. The metathesis between MgCl₂ and LiH became a liquid–solid process in THF as a reaction medium, which provided immediate protection for the newly formed MgH₂. Separation of LiCl from MgH₂ was saved. In contrast to previous studies, no scaffold or support was needed during and after the synthesis. Ultrafine MgH₂ nanoparticles predominantly of around 4-5 nm in size were successfully obtained, which enables reversible storage of hydrogen up to 6.7 wt% under ambient conditions.

Results and discussion

Hydrogen storage properties of the non-confined ultrafine $\rm MgH_2$

Hydrogen storage properties of the prepared MgH₂ are shown in Fig. 1. Temperature-programmed desorption measurements with a mass spectrometer (TPD-MS) reveal that only hydrogen was evolved upon heating the non-confined ultrafine MgH₂ (Fig. 1a), and no THF signal was detected (Fig. S1, ESI⁺). Unexpectedly, hydrogen release was detected at ambient temperature (\sim 30 °C). To the best of our knowledge, such low dehydrogenation temperature has never been experimentally observed before for any light metal hydride systems for reversible hydrogen storage (Fig. 1b).^{11,32,33,40,42-59} More importantly, the most intense peak corresponds to H₂ release at 84 °C, which is dramatically reduced by ca. 238 °C in comparison with the milled bulk MgH₂ (\sim 322 °C), representing the lowest peak temperature of hydrogen desorption from MgH₂ known to date. Additionally, there is also a small peak at ~ 265 °C, close to the peak temperature of hydrogen release from the milled bulk sample. This was related to the small number of larger particles formed as discussed later.

The significantly reduced dehydrogenation temperatures were confirmed by both thermogravimetric (TGA) (Fig. 1c) and volumetric methods (Fig. S2a, ESI[†]), respectively. Indeed, the TGA results indicate that the on-set dehydrogenation temperature was about 30 °C for the non-confined ultrafine MgH₂, as shown in Fig. 1c. Meanwhile, the middle-point temperature corresponding to the release of half of the hydrogen amount was ca. 92 °C, reduced largely by 218 °C. Upon heating to 275 °C, a total usable hydrogen capacity of 7.2 wt% was determined, close to the theoretical H content of 7.6 wt% in MgH₂. Further volumetric release measurements deliver an identical capacity value (Fig. S2a, ESI[†]), much higher than those previously reported for nanoconfined MgH₂ with porous carbon scaffolds, as summarized in Fig. 1b. However, it is noteworthy that for the same degree of dehydrogenation, TGA recorded a slightly lower temperature than that determined by the volumetric H₂ release

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Fig. 1 TPD-MS (a), comparison of dehydrogenation performance (b), TGA (c), isothermal TGA dehydrogenation (d), isothermal TGA dehydrogenation under different conditions (e), hydrogenation with temperature (f), and isothermal hydrogenation (g) curves of bulk and non-confined ultrafine MgH₂.

(Fig. S2b, ESI[†]). This discrepancy can be attributed to the different working principles of the two methods. MgH₂ has a low equilibrium pressure, particularly at low temperatures (Table S1, ESI[†]). Equilibrium can be readily reached in a closed system, as in the case of volumetric tests, and further H₂ release must overcome the equilibrium H₂ pressure, which requires a higher temperature. In the context of TGA, the system is open and the measurements took place inside an argon-filled glove box; therefore, a hydrogen capacity close to the theoretical value of MgH₂ was obtained at lower temperatures. Accordingly, the follow-up isothermal desorption measurements were conducted using TGA to eliminate the restricting effect of equilibrium pressure.

Isothermal measurements using TGA demonstrate greatly improved dehydrogenation kinetics of the prepared MgH_2 sample (Fig. 1d and e). At 85 °C, which is the upper limit of the

target operating temperature set by the Department of Energy (DOE),¹² the prepared MgH₂ released up to 6.0 wt% hydrogen within 40 min and 6.7 wt% hydrogen after 200 min (Fig. 1d), which outperformed the MgH₂-based hydrogen storage materials in the literature in terms of capacity and kinetics even at temperatures above 200 °C.^{33,34} Here, the 0.5 wt% difference between the value at 85 °C (6.7 wt%) and that obtained with temperature ramping (7.2 wt%) can be attributed to the small high-temperature peak observed in the TPD-MS curve (Fig. 1a). Notably, hydrogen release took place even at temperatures lower than 85 °C though in a wider time range. About 4.5 wt% H₂ was released at 30 °C within 2500 min in TGA mode (Fig. 1e). More encouragingly, hydrogen release amounted to 6.7 wt% using a dynamic vacuum for TGA dehydrogenation measurement at 30 °C. This is the best overall dehydrogenation performance reported to date for MgH₂

in terms of capacity and operating temperature as well as for any reversible complex metal hydrides at all (Fig. 1b).

Moreover, a high volumetric hydrogen capacity was obtained by cold pressing 150 mg of ultrafine MgH₂ nanoparticles into a pellet under 200 MPa (Fig. S3a and b, ESI†). Here, forming the pellets did not change the dehydrogenation behavior of ultrafine MgH₂ and bulk MgH₂ with temperatures analyzed by volumetric measurements (Fig. S3c and d, ESI†). The volumetric hydrogen capacity was calculated to be 65.6 g H₂ L⁻¹ for ultrafine MgH₂ nanoparticles, close to that of bulk MgH₂ (67.5 g H₂ L⁻¹) but higher than the criterion proposed by the US DOE for mobile applications (50 g H₂ L⁻¹).

Rehydrogenation of the dehydrogenated samples as a function of temperature was carried out under a moderate H₂ pressure of 30 bar (Fig. 1f). Hydrogen uptake took place at 25 °C for the prepared sample and was saturated at 100 °C, largely superior to the bulk sample. Also, 6.7 wt% H₂ was reabsorbed over 360 min at 30 °C and 30 bar H₂ pressure (Fig. 1g), which is the highest hydrogenation yield reported so far at such a low temperature. At 85 °C, the absorption of 6.3 wt% H (94% of the usable capacity) was achieved within 25 min (Fig. S4, ESI†), and full hydrogenation (6.7 wt%) was completed within 60 min. In comparison, the Mg nanocrystals with particle size (5 nm), similar to our work but encapsulated in poly(methyl methacrylate) required 200 °C and 70 min to achieve a ~4 wt% H₂ capacity for the composite at 35 bar.³² The difference may be caused by the use of a polymer encapsulating layer, which stabilizes the MgH₂ and also slows down mass transfer during hydrogen cycling. Our experimental results attest the importance of preparing nanoscale MgH_2 without the introduction of additional components for protection in order to enhance H_2 sorption kinetics.

Morphology and structure of the non-confined ultrafine MgH₂

To understand the outstanding hydrogen storage properties shown above, the morphology and structure of the prepared MgH₂ were systematically characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and high-resolution TEM (HRTEM). As shown in Fig. 2a and b, SEM and TEM images reveal welldefined nanoparticles with average diameters of 4-5 nm. This is further evidenced with the results of particle size distribution (Fig. S5, ESI⁺), where the majority of particles are 4-5 nm in diameter with a very small number of larger particles being > 20 nm in size. Such particle sizes are much smaller than those of the milled bulk MgH_2 (>200 nm, Fig. S6, ESI[†]). The SAED pattern (Fig. 2c) shows diffraction spot-rings indexed to crystalline MgH₂. The HRTEM images (Fig. 2d and e) clearly indicate that the nanocrystals have an interplanar spacing of 0.225 nm, which corresponds to the (200) plane of MgH₂. Further X-ray diffraction (XRD) characterization shown in Fig. S7a (ESI^{\dagger}) identifies the presence of β -MgH₂ (JCPDS reference card no. 12-0597). The quite low intensities of the reflections are associated with the small particle/crystallite sizes. Using the Scherrer equation, the crystallite size was calculated to be approximately 3.9 nm, agreeing well with the HRTEM observations.



Fig. 2 SEM image (a), TEM image (b), SAED pattern (c) and HRTEM images (d and e) of non-confined ultrafine MgH₂.

X-ray photoelectron spectroscopy (XPS) (Fig. S7b, ESI⁺) reveals that MgH₂ (1304.3 eV) was the main component of the nanoparticles, with minor amounts of MgO (1304.9 eV) and metallic Mg (1303.4 eV).^{60,61} Furthermore, the element Cl from the precursor MgCl₂ and the by-product LiCl was not detected in the samples (Fig. S7c, ESI⁺). The traced MgO likely originates from oxidation during analysis and/or preparation, whereas the metallic Mg may form upon the decomposition of MgH₂ during XPS measurements under ultrahigh vacuum because the obtained ultrafine MgH₂ can release H₂ at unexpectedly low temperatures, as mentioned above. Thus, we believe that non-confined ultrafine nanoparticles of MgH₂ with diameters of 4-5 nm have been successfully synthesized by a novel liquid-solid phase metathesis reaction between MgCl₂ and LiH in THF, driven by ultrasound. After dehydrogenation, XRD examination identified the formation of metallic Mg (Fig. S8, ESI⁺), which was also confirmed by the HRTEM image because the hexagonal Mg was clearly observed (the inset of Fig. S8, ESI⁺).

To shed light on the formation mechanism of non-confined ultrafine MgH₂ nanoparticles, the THF suspension was sampled at a 0.5 h interval during sonication for TEM and SAED analyses to monitor the chemical reaction progress. Only LiH was observed after 0.5 h of sonication (Fig. 3a and b). MgH₂ crystals became discernible on the LiH surface after 1 h (Fig. 3c and d), while a greater number of MgH₂ nanoparticles were observed after 1.5-2 h (Fig. 3e-h). This indicates that ultrasound stimulation initiated the metathesis reaction between MgCl₂ present as THF complexes in the liquid phase and the solid LiH phase to form MgH₂, as described by reaction 1. The reaction is thermodynamically favorable and ΔG_{298K} was calculated to be approx. -72.8 kJ mol⁻¹. The MgH₂ crystal nucleation and growth took place on the LiH surface with time. In a control experiment without sonication, however, the LiH surface remained smooth even after mechanical stirring for 2 h (Fig. S9, ESI⁺), implying that no chemical reaction occurred. With further sonication for 2.5 h, the edges of the LiH blocks became ragged (Fig. 3i and j), as the newlyformed MgH2 particles fell off into the solution due to the ultrasound shock, resulting in the formation of freestanding nanoparticles. The corresponding reaction process is schematically illustrated in Fig. 3k. Here, the aprotic THF was used as the reaction medium because it will not react with the newly formed MgH₂ but provide immediate surroundings to avoid agglomeration. In particular, MgH₂ has a higher density (1.45 g cm⁻³) than THF (0.89 g cm⁻³), it therefore precipitates readily from the solution, while the LiCl by-product dissolves in the solvent, creating fresh surface on the solid LiH for continuous reaction. On the other hand, the turbulence and microstreaming arising from exposure to ultrasonic waves assist collisions of the reactants and simultaneously deter the excess crystal growth so that ultrafine particles are obtained.^{62,63}

$$MgCl_2(l) + 2LiH(s) \xrightarrow{IHF} MgH_2(s) + 2LiCl(l)$$
 (1)

Thermodynamics and kinetics of hydrogen storage in the non-confined ultrafine MgH₂

To understand the much improved hydrogen storage performance of the non-confined ultrafine MgH₂ compared with its bulk counterpart, the thermodynamic and kinetic parameters in the hydrogen storage process were further investigated. For this purpose, pressure-composition isotherms (PCIs) was used to determine the equilibrium hydrogen pressures at different temperatures.⁶⁴ It is well known that measurements for the bulk MgH₂ were usually conducted at temperatures higher than 250 °C owing to its stable thermodynamics and sluggish kinetics.65 Excitingly, we could perform PCI on non-confined ultrafine MgH₂ at significantly lower temperatures (*i.e.*, 80 °C), as shown in Fig. 4. Here, for recording extremely low H₂ pressures at low temperatures, a homemade Sieverts' type instrument was employed which is equipped with a 0.1 bar pressure transducer with an accuracy of 0.1%. The reaction equilibrium was judged when the inside pressure of the reactor remained unchanged for 12 h. The hydrogenation and dehydrogenation data were acquired at the tested temperatures and determined a reversible hydrogen capacity of 6.5-6.7 wt% (Fig. 4a-e), which is consistent with the TGA and volumetric release results (Fig. 1c and Fig. S2, ESI⁺). The dehydrogenation equilibrium pressure values obtained by PCI are listed in Table S1 (ESI⁺). They were 0.0038, 0.0108, 0.0304, 0.151 and 1.014 bar at 80, 100, 120, 160 and 215 °C, respectively. With these values, the dehydrogenation enthalpy change was calculated to be 59.5 kJ mol⁻¹ H₂ by means of a van't Hoff plot as shown in Fig. 4f. This represents an $\sim 22\%$ decrease in enthalpy compared with bulk MgH₂ (76 kJ mol⁻¹ H₂) (Fig. S10, ESI[†]). Here, it is worth highlighting that the equilibrium pressure for hydrogen release from non-confined ultrafine MgH₂ reaches above 1 bar at 215 °C, which is one order of magnitude higher than the value for bulk MgH_2 (0.095 bar) at the same temperature (Table S1, ESI[†]). These results ascertained that thermodynamic destabilization of MgH₂ has been experimentally achieved through fabrication of non-confined ultrafine nanoparticles. For practical applications, however, the equilibrium pressures below 100 °C are too low. A possible solution for this issue is to use a diaphragm pump to drive dehydrogenation from MgH₂ and to build up the hydrogen pressure, as demonstrated by Cheung et al.66

The activation energies for hydrogen absorption ($E_{a(abs)}$) and desorption ($E_{a(des)}$) were further determined for the non-confined ultrafine MgH₂ by analyzing the isothermal hydrogenation/ dehydrogenation curves with a Johnson–Mehl–Avrami (JMA) model (Fig. S11, ESI†).^{67,68} By fitting the data points, the values of approximately 28 kJ mol⁻¹ for $E_{a(abs)}$ and 80 kJ mol⁻¹ for $E_{a(des)}$ were obtained (Fig. 4g), which are significantly lower than the respective values reported for bulk MgH₂ ($E_{a(abs)} = 90$ kJ mol⁻¹, $E_{a(des)} = 160$ kJ mol⁻¹) (Fig. S12, ESI†).¹⁸ Thus, $E_{a(abs)}$ and $E_{a(des)}$ were reduced by 69% and 50%, respectively. The significantly lowered kinetic energy barriers coupled with destabilized thermodynamics enable non-confined ultrafine MgH₂ to desorb and absorb hydrogen at ambient temperature.

The cycling stability of the non-confined ultrafine MgH_2 was also evaluated using the Sieverts' type instrument in isothermal mode. To reduce the measurement period, the cycling test was carried out at an increased temperature of 150 °C to ensure rapid hydrogen absorption and desorption. Dehydrogenation



Fig. 3 HRTEM images (a, c, e, g and i) and SAED patterns (b, d, f, h and j) of the samples after different sonication durations (0.5 h (a and b), 1 h (c and d), 1.5 h (e and f), 2 h (g and h) and 2.5 h (i and j)) and schematic illustration of the liquid–solid metathesis reaction (k).

started from a primary vacuum, while rehydrogenation occurred under a moderate H₂ pressure of 30 bar. After 50 cycles, only 0.07 wt% of capacity was lost, which corresponds to 99% of capacity retention, representing a remarkable stability in cycling operation (Fig. 4h). Re-examining the cycled sample by TEM found no obvious change in the particle size and morphology after 50 cycles of hydrogen release and uptake (Fig. S13, ESI†). This excellent stability is likely related to several factors. First, during the synthesis, the MgH₂ crystals are separated by the THF molecules immediately after formation and become matured under the protection of THF. Second, the frictions among the crystalline particles induced by the ultrasound waves prevent coalescence of nanoparticles, leading to the formation of single crystallite based particles (TEM image in Fig. 2d) with stable surfaces. This is different from MgH₂ nanoparticles prepared by ball-milling where one nanoparticle is composed of many crystallites, and recrystallization as well as crystal growth occur readily, resulting in the degradation of the nanostructural properties.⁶⁹ In addition, the low operating temperature below 150 °C for reversible hydrogen storage limits the growth of nanoparticles upon cycling. As a result, no obvious change in the particle size and morphology was observed after 50 cycles of hydrogen cycling



Fig. 4 PCI curves measured at 80-215 °C (a-e), van't Hoff plot (f), Arrhenius plots (g) and cycling stability (h) of non-confined ultrafine MgH₂.

(Fig. S13, ESI†). Further investigations on the stability of the non-confined ultrafine MgH_2 are in progress in our laboratory.

Dependence of dehydrogenation on particle size

The particle size-dependent dehydrogenation behaviors were further studied by tuning the sonication treatment time. As shown in Fig. 5, the particle size of non-confined MgH₂ was found to increase with sonication time. More specifically, the size distribution peak gradually shifts from 4-5 nm (Fig. 2a) to 15–16 nm (Fig. 5c, f and i) as the sonication time increases from 2 h to 12 h, and accordingly, the peak temperature of dehydrogenation shifts from 84 °C (Fig. 1a) to 215 °C (Fig. 5l), which confirms the size dependence of the hydrogen desorption properties. However, there were a small number of particles with diameters of 20-50 nm (Fig. 5g-i) requiring high dehydrogenation temperatures of almost 300 °C (Fig. 5j-l). These larger particles might have formed due to uneven local sonication conditions. The reaction conditions, such as the power and frequency of the ultrasound irradiation, duty cycle of the pulsed ultrasound, temperature, concentration, and solvent, can be adjusted to minimize the formation of large particles in the next step.

Theoretical understanding of the size effect

To understand the strong size effect on the thermodynamics and kinetics, density functional theory (DFT) calculations were performed by focusing on the initial state of absorption and desorption of one single hydrogen molecule over nanoclusters and bulk structures. Bulk and nanosized Mg structures were modelled by a Mg(001) slab and a 1 nm cluster for absorption, respectively, while a MgH₂(110) slab and a fully hydrogenated cluster were created as the initial state of desorption (Fig. 6a). Here, it should be mentioned that we firstly tested nano clusters of 1 nm and 3 nm, respectively, which led to similar reaction energy (Fig. S14, ESI†). Therefore, it is reasonable to select a 1 nm cluster as a typical one to compare its performance with bulk-derived slabs for the illustration of the size effect. The transition states were verified by the frequency eigenvalue with only one imaginary value (Fig. S15, ESI†).

Calculations revealed that the reaction energy for H₂ disassociation on the Mg(001) slab was as high as -1.72 eV (Fig. 6b), with H atoms fixed by four Mg-H bonds. In contrast, the reaction energy was only -0.40 eV for the Mg cluster, which agrees with the H-termination configuration, as each H atom was bonded by only one or two Mg atoms. For the kinetics, H₂ dissociation on the



Fig. 5 SEM images (a-c), HRTEM images (d-f), particle size distribution (g-i), and TPD curves (j-l) of MgH₂ nanoparticles prepared after different sonication reaction times (4–12 h).

Mg(001) slab needs to get over a barrier of 0.32 eV, which is larger than that on the Mg cluster (0.13 eV). Similarly, H-diffusion from the cluster surface to the inner layers shows a barrier ($E_a = 0.26 \text{ eV}$), being remarkably lower than that on the Mg(001) slab ($E_a = 1.04 \text{ eV}$; Fig. 6c). Overall, H₂ dissociation and diffusion over the nano cluster is thermodynamically and kinetically favourable with respect to bulk materials.

In terms of H_2 desorption, a barrier of 2.95 eV must be overcome for the desorption of two two-coordinate H atoms from the MgH₂(110) slab (Fig. 6d), resulting in a reaction energy of 1.51 eV. However, this process becomes easier on MgH₂ clusters, as the barrier and desorption energy are effectively reduced to 1.87 and 0.71 eV, respectively. Here, the different reaction barriers for the transition states of absorption and desorption are directly related to their initial states. Only one hydrogen molecule was considered for absorption onto the Mg cluster or slab and desorption from the MgH₂ cluster or slab, respectively, so their initial states and transition states are different in our calculations. As reflected from the transition states in Fig. 6d, the H–H geometries are similar on the MgH₂ cluster and slab, but weakly coordinated Mg has been shifted slightly towards neighbouring Mg for the cluster, leading to stronger Mg–Mg bonding and better stabilization. This stabilization effect stems from the flexibility of surface atoms on the clusters, such as at corners and edges. Accordingly, nanosized clusters can deliver better H₂ desorption performance, which agrees well with our experimental observation.



Fig. 6 Computational models for bulk and nanosized Mg and MgH₂ (a). Mg, green; H, white. Hydrogen uptake by Mg(001) slab and Mg cluster (b). Diffusion energy barrier of H atoms in the Mg(001) slab and Mg cluster (c). Hydrogen release from the MgH₂(110) slab and MgH₂ cluster (d). IS: initial state, TS: transition state, FS: final state.

Conclusions

In conclusion, the novel liquid-solid metathesis process developed in this work enabled a breakthrough in obtaining ultrafine MgH₂ of 4-5 nm without involving any scaffold or protection agent. A reversible storage of hydrogen at unprecedentedly ambient-temperature was realized with the non-confined ultrafine nanoparticles of this metal hydride, which can be attributed to the significantly destabilized thermodynamics and reduced kinetic barriers, compared to its bulk counterpart. To the best of our knowledge, it was for the first time that the reversible storage of hydrogen up to 6.7 wt% at 30 $^\circ\mathrm{C}$ was observed for this intensively studied hydride. Moreover, the nonconfined ultrafine MgH2 exhibited a stable property in hydrogenation/ dehydrogenation cycling. The dramatic improvement in the hydrogen sorption performance brings us one step closer to practical utilization of MgH₂ as a hydrogen carrier. Moreover, this ultrasound-driven liquid-solid phase metathesis strategy can be adopted to synthesize a wide range of nanomaterials, including complex metal hydrides with higher intrinsic hydrogen contents. Future research includes elimination of large particles and incorporation of high-efficiency catalysts during the synthetic process to further enhance the absorption/ desorption kinetics for practical applications.

Experimental section

Material preparation

All reagents and solvents are commercially available and used as received. Non-confined ultrafine MgH₂ nanoparticles were

synthesized using anhydrous magnesium chloride (MgCl₂, 95%, Alfa Aesar) and lithium hydride (LiH, 99.4%, Alfa Aesar) as the raw materials, which were first ball milled separately at 300 rpm for 3 h in a planetary ball mill (QM-3SP4, Nanjing, China). Dry THF was selected as the reaction medium not only to ensure an anaerobic and anhydrous environment, but also to provide immediate surrounding to avoid agglomeration. More importantly, both MgCl₂ and LiCl are highly soluble in THF, whereas LiH and MgH2 are insoluble, which greatly facilitates the separation of newly formed MgH₂ and the creation of fresh surface on the solid LiH for continuous reaction. In a typical procedure, MgCl₂ (2.6 mmol) was initially dissolved in anhydrous THF (100 mL, 99.9% Aladdin) with mechanical stirring, after which LiH (5.2 mmol) was added to the THF solution and mixed using a magnetic stirrer for 1 h. The resulting suspension was exposed to ultrasonic waves generated by an ultrasonic horn with an output power of 200 W (40 kHz, W-600D, Shanghai Ultrasonic Instrument, Shanghai, China) in a Rosset cell. The ultrasonic waves were applied in the pulsed mode with cycles consisting of a 5 s pulse and 5 s relaxation. A 10 min pause was set every 90 cycles to prevent the temperature increase. Here, ultrasound stimulation resulted in the oscillation and collapse of cavitation bubbles in liquids with sufficient energy that initiated chemical reactions. Moreover, the turbulence and microstreaming arising from exposure to ultrasonic waves led to surface erosion and interparticle collisions in liquids, which was beneficial for the formation of smaller

particles. The light grey powders of non-confined ultrafine MgH₂ were separated from the THF solution by centrifugation, washed several times with THF, and dried under vacuum.

For comparison, bulk MgH_2 was synthesized *via* a solid-state hydrogenation reaction. Typically, commercialized Mg powder (1 g, 99%, Macklin) was loaded into a stainless steel tube reactor and heated under a hydrogen atmosphere at 20 bar. The hydrogenation reaction was carried out in two steps: 580 °C for 2 h followed by 340 °C for 8 h. The resultant MgH₂ was milled for 24 h.

Material characterization

A MiniFlex600 X-ray diffractometer (Rigaku, Japan) with Cu Ka radiation (λ = 0.15406 nm, 40 kV, 15 mA) was used to identify the phase structure of the samples. The XRD data were collected in the 2θ range of 10–90° with a 0.05° step increment at ambient temperature. To prevent air and moisture exposure, the samples were sealed in a custom-designed container with a window covered by Scotch tape for X-ray transmission. The morphology and nanostructure of the samples were observed using SEM (Hitachi S-4800) and TEM (FEI Titan G2 60-300, 80 kV). The sample was dispersed into THF and then dropped onto carbon film coated Cu grids. For SEM observations, the sample was transferred to the SEM facility under an argon atmosphere. For TEM examination, the sample was protected with a double-tilt vacuum transfer holder (Gatan 648, USA). XPS was carried out using a Kratos Axis Ultra DLD spectrometer. The powder sample was first pressed into a pellet and then mounted on a sample holder inside an argon-filled glove box. The sample holder was then transferred from the glove box to the XPS facility in a special transfer vessel to avoid air exposure. The XPS data were recorded using a monochromatic Al Ka X-ray source with a base pressure of 6.8×10^{-9} torr at 15 °C. The binding energy spectra were fitted using XPSPEAK41 software. The particle size distribution of nonconfined ultrafine MgH₂ synthesized sonochemically was estimated by a nanoparticle size analyzer (Zetasizer Nano-ZS, Malvern, Britain). Typically, the specimen was ultrasonically dispersed in THF, and then an aliquot of the mixture (1 mL) was transferred into a quartz cell and sealed with a Teflon plug inside an argonfilled glove box. The quartz cell was then transferred from the glove box to the nanoparticle size analyzer.

Performance evaluation

The dehydrogenation behaviour was evaluated using a homemade TPD system coupled to an online mass spectrometer. Pure argon with a flow rate of 20 mL min⁻¹ was used as the carrier gas. For each test, ~20 mg of the sample was heated from ambient temperature to a certain temperature at a rate of 2 °C min⁻¹. A homemade Sieverts-type apparatus was used to quantitatively measure dehydrogenation/hydrogenation under isothermal or non-isothermal conditions. The amount of sample for each measurement was ~70 mg. Non-isothermal volumetric hydrogen release was conducted under a primary vacuum (~10⁻³ torr) with temperature ramping of 2 °C min⁻¹, whereas hydrogenation was carried out at a heating rate of 1 °C min⁻¹ at 30 bar H₂. The isothermal measurements were conducted by rapidly heating

(10 °C min⁻¹) the sample to a preset temperature and then maintaining this temperature during the entire test. TGA was carried out on a Netzsch TG 209 F3 instrument under an argon atmosphere, with the same heating rates for the volumetric experiments for both non-isothermal and isothermal dehydrogenation. The sample loading was 8 mg. Dehydrogenation at 30 °C is slow; therefore, a dynamic vacuum was generated with an oilfree diaphragm pump (N950.50, KNF, Germany) during the isothermal TGA at 30 °C to accelerate the reaction.

Theoretical calculations

The DFT calculations were carried out using the DMol3 package.^{70,71} The spin-unrestricted DFT in the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE)⁷² functional was used for the exchange-correlation functional. Semicore pseudopotentials were adopted with an effective core potential for inner shell electrons. A double numerical polarized basis set was selected, including a d-polarization function for non-hydrogen atoms and p-polarization function for hydrogen atoms. A global orbital cut-off of 4.3 Å was set for all calculations. Geometries were fully relaxed until the total energy change was less than 10^{-5} Ha and the maximum force was less than 0.004 Ha A^{-1} . For geometric optimization and the search for the transition state (TS), the Brillouin zone integration was performed with gamma point sampling. A TS search was based on a combined linear synchronous transit and quadratic synchronous transit scheme.⁷³ Vibrational frequencies were further determined from the Hessian Matrix.⁷⁴ van der Waals interactions were included based on the Tkatchenko-Scheffler scheme.⁷⁵ In our calculations, the hydrogenation was modelled by introducing only one H₂ molecule onto Mg nanoparticles (1 nm in size) or Mg(001) slabs, whereas the dehydrogenation was simulated by taking only one H2 molecule away from MgH_2 clusters or $MgH_2(110)$ slabs accordingly. Here, Mg(001) and $MgH_2(110)$ were selected since they are energetically favourable surfaces for bulk Mg and MgH₂, respectively. The above models were used based on two principles: (i) the thicknesses of the clusters and slabs are similar (1 nm); (ii) for MgH2, the Mg/H atom ratio is kept at 1:2. For the slab models, a vacuum space of 15 Å was applied to minimize the interaction between neighbouring images. For the diffusion of H from the surface to the inner layers, the path was determined using dissociated H_2 as the starting geometry (initial state, IS), followed by one H atom moving to the interstitial site in the sublayers, generating the final state (FS).

Author contributions

X. Z. and Y. F. L. conceived the idea and designed the experiments. X. Z. and Y. F. L. conducted materials synthesis, characterisation, and measurements. Z. H. R. and Y. H. L. performed DFT studies. X. Z., Y. F. L., J. J. H., Z. G. H. and H. G. P. analysed the data. Z. H. R., X. L. Z., and M. X. G. contributed to the discussion of the results. X. Z., Y. F. L., J. J. H., Z. G. H. and H. G. P. prepared the manuscript. All the authors commented on and revised the manuscript.

Conflicts of interest

There are no conflicts to declare.

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