

Chapter 6 Nano processing in Mg-based hydrogen storage materials: research progress and trends

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Abstract

Hydrogen economy is thought to be one of the ultimate carbon-free energy solutions. For a future vision, one may produce hydrogen from renewable power, e.g., wind or solar energy, and this hydrogen can be provided to fuel cell component to supply electricity and thermal. For this energy storage and utilization route, one enabling technology is hydrogen storage because hydrogen as energy carrier here is gas state at normal temperature and atmosphere conditions and the energy density of hydrogen gas is low. Therefore, a critical thing is to find one hydrogen storage method with low cost and high energy density. Mg-based materials are very promising candidates for hydrogen storage due to the great abundance of Mg in earth's crust, large hydrogen capacity and low cost. Mg-based materials have been investigated as possible onboard applications for decades. Onboard storage was the beginning and also the major aim of Mg-based hydrogen storage materials research. The challenges in Mg-based materials for onboard development are in both kinetics and thermodynamics. Numerous techniques have been adopted by different researchers in order to improve the kinetics and thermodynamics. Here the authors will review the methods used by themselves and some collaborators to synthesize Mg-based hydrogen storage materials with nanostructure as well as some novel techniques from other researchers, and focus on how nanostructure in the materials could affect hydrogen capacity, kinetics, thermodynamics and thermal conductivity in Mg-based materials for hydrogen storage. These methods include ball milling, thin film synthesis, hydrogen plasma metal reaction and catalyzed chemical solution synthesis etc. Some classic work from some pioneers, important milestones and latest achievements of development for these possible applications will be summarized and the future prospects in these fields will be addressed.

6.1 Introduction

In the process of social development, the energy development always changed with human activities. From early fossil energies (coal, oil and natural gas) to electricity, and even nowadays, modern energies such as solar energy, wind energy, tidal energy, nuclear energy etc. are all playing a significant role in the human's progress. However, because of limited

amount and fast consumption of fossil fuel, it was said that current fossil energy could only be able to maintain to no more than year 2050. On the other hand, pollution and the greenhouse effect caused by long term using fossil energy are seriously influencing our daily life. What we are called with increasing urgency is to find an alternative energy which is not only environmental friendly, but also no contribution to the greenhouse effect. Based on the situation, hydrogen energy become one of favorable candidates since its no emission, high energy density and high energy transform efficiency [1, 2]. And hydrogen energy society (Figure 1) have attracted great attention in recent years. When it comes to hydrogen energy society, hydrogen is collected from the renewable energies such as wind energy, solar energy and geothermal energy. And hydrogen is used for onboard and residential hydrogen energy system or directly stored in renewable hydrogen storage system for backup power.



Figure 1. A scenario of hydrogen energy society. Hydrogen can be produced from various energy sources, especially from renewable power. Through fuel cell energy conversion technologies, hydrogen can be utilized for onboard storage, residential applications, backup power, as well as large scale stationery energy storage.

The key problem need to be solved urgently is hydrogen storage. Currently, the relatively mature method is physical storage, such as compressed hydrogen storage and cryogenic storage. Nevertheless, there are more and more groups [3-14] focusing their research on solid-state hydrogen storage like metal hydride (Pd-H, Mg-H, Ca-H), alloys (MgCo, MgNi, TiFe), carbon based materials (carbon nanotube, graphene) and metal-organic framework materials, since their intrinsic characteristics in sorption kinetics, working temperature, cycle ability etc. Mg-based materials have become a very promising hydrogen storage material due to its large hydrogen capacity (7.7 wt.% for MgH₂), great abundance of Mg (2.3% in the

crust of earth), and relative lower price of Mg (2-3 USD/kg) [1, 15]. Compared to other hydrogen storage materials, from Table 1 [1], it is clearly seen that MgH_2 shows an apparent advantage of high H_2 density (110 kg/m^3), and its energy density can be as high as 13.3 MJ/L or 3700 Wh/L , which is much higher than that of traditional compressed hydrogen gas and most hydrogen storage materials. In the perspective system of onboard hydrogen storage for fuel cell vehicle, H_2 storage tank provides H_2 for fuel cell, which generates energy to supply motor's operation. Simultaneously, the heat generated from motor is exactly used for hydrogen desorption from material tank. Based on the targets for year 2020 onboard hydrogen storage from US Department of Energy, the gravimetric storage capacity should reach to 5.5 wt.%, no more than 3.3 minutes for filling 5 kg H_2 , and it requires a temperature in the range of $-40\text{-}85 \text{ }^\circ\text{C}$ (Figure 2).

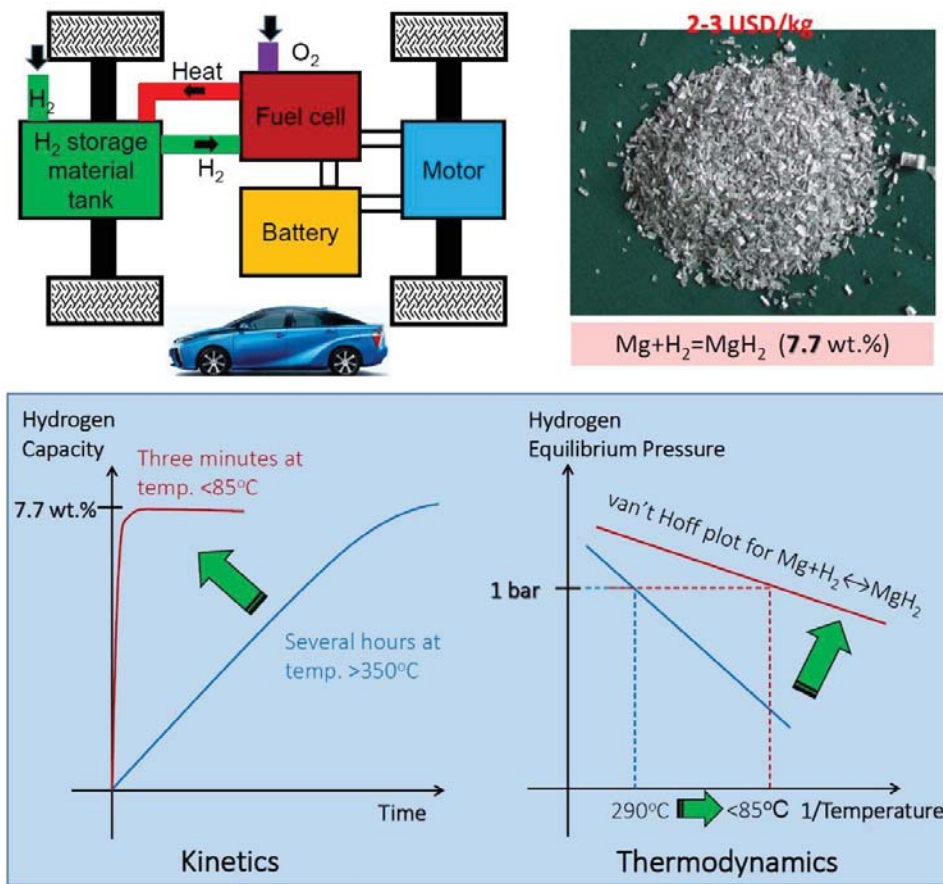


Figure 2. Mg-based materials for onboard hydrogen storage due to the great advantages of Mg, such as low cost and high energy density. The challenges for development of Mg-based materials for this application lie in the kinetics and thermodynamics properties. Reprinted with permission [16].

Unfortunately, although MgH_2 could absorb 7.7 wt.% hydrogen, it needs higher than 300 °C to absorb and desorb hydrogen for common micrometer Mg due to the thermodynamic stability of MgH_2 [1, 17]. In addition, because of the poor kinetics, when the temperature is below 300 °C, the hydrogen absorption and desorption rates are extremely low. As a result, we need to improve the hydrogen absorption reaction kinetics and optimize the hydrogen desorption reaction thermodynamics to faster reaction rate and lower the working temperature. So far, nanostructured materials are confirmed to have a good performance in hydrogen absorption and desorption kinetics when compared with common micrometer scale materials. Because the nanostructured materials have larger surface area, much more hydrogen reaction nucleation sites and faster hydrogen diffusion rate due to shorter distance in the metals and hydrides [1]. On the other hand, according to the calculation work of Wagemans et al. [18] Hydrogen desorption enthalpy decreases apparently when the crystal grain size comes to less than 1.3 nm. In that way, the stability of Mg-based materials and their hydrides will be reduced greatly.

Table 1. Hydrogen capacity and energy density of hydrogen storage materials and the comparison with other storage methods. Reprinted with permission [16].

		H ₂ Content (mass%)	H ₂ density (kg/m ³)	Specific energy (MJ/kg)	Specific energy (Wh/kg)	Energy density (MJ/L)	Energy density (Wh/L)
Li-ion battery	^a Panasonic NCR18650A	-	-	0.9	250	2.4	675
Gaseous and compressed hydrogen	H ₂	100	0.089	^b 120	33000	0.01	2.8
	700 bar H ₂	100	42	120	33000	5	1400
	Liquid H ₂	100	71	120	33000	8.5	2400
Hydrogen storage materials	LaNi ₅ H ₆	1.4	90	1.7	470	10.8	3000
	TiFeH ₂	1.9	105	2.3	640	12.6	3500
	Mg ₂ NiH ₄	3.6	93	4.5	1300	11.3	3100
	NaAlH ₄	^c 5.7	71	6.8	1900	8.5	2400
	MgH ₂	7.7	110	9.2	2600	13.3	3700

^aSource: industrial.panasonic.com

^bLower heating value (LHV)

^cDesorbed to NaH, Al

6.2 Nanoscale effect

For a better performance on kinetics and thermodynamics, thermal conductivity should be taken into consideration. Recent years, efforts are devoted to studying thermal conductivity properties of hydrogen storage materials [19], especially in Mg-based materials.

In order to realize the onboard application, hydrogen absorption and desorption kinetics are urgently to be optimized. When Mg-based materials absorb hydrogen, the chemical reaction in this system is an exothermic reaction. As a result, the problem of how to deal with the heat transfer is worth studying. And according to a group's work [19], hydrogen absorption kinetics in a Mg-MgH₂ tank system are usually dominated by the heat transfer ability while not intrinsic kinetics. It is a very practical work to design Mg-based hydrogen storage materials which are not only with fast absorption and desorption kinetics, but also with good thermal conductivity.

Kinetics

One of our work [20] was committed to study different structure or size of Mg-based hydrogen storage materials and tried to figure out the relationship among the size, hydrogen absorption kinetics and thermal conductivity. In the author's work, He measured hydrogen absorption kinetics and thermal diffusivity values with six different Mg-based materials (325 mesh Mg, single crystal Mg, Mg nanoparticles, nanocrystalline Mg₅₀Co₅₀ body-centered cubic (bcc) alloy and Mg thin film samples). Figure 3 are SEM images of the six different samples. From the SEM images, we can see that the grain sizes are in the range of 40-50 μm for 325 mesh Mg sample particles, and 100-700 nm for the Mg nanoparticles, respectively. The bcc Mg₅₀Co₅₀ alloy sample shows a particle size about 1 to 3 μm with a few nanometers in crystallite size [21].

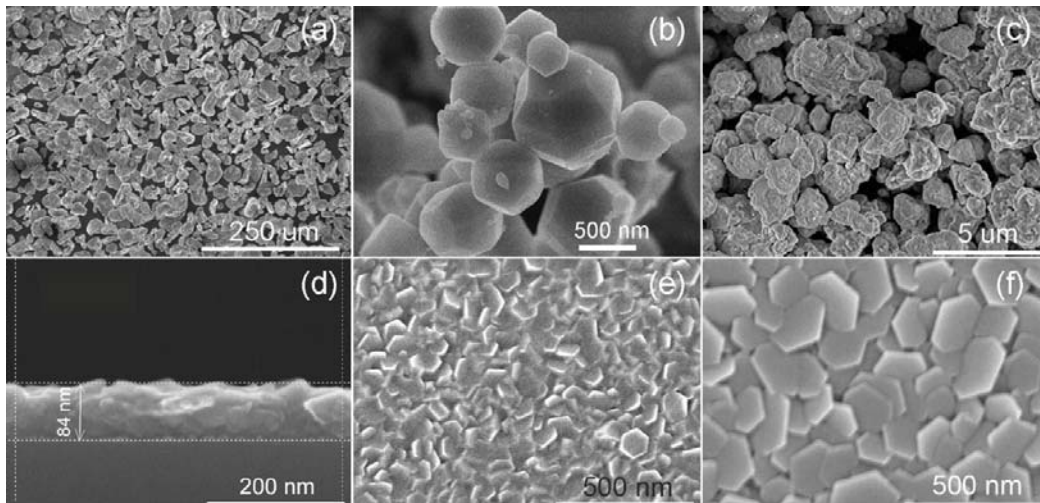


Figure 3. SEM images of (a) 325 mesh Mg, (b) Mg nanoparticle sample, (c) milled Mg₅₀Co₅₀ bcc alloy, (d) cross-section observation of Mg thin film without Pd layer, (e) top view of Mg thin film without Pd layer and (f) top view of Pd capped Mg thin film. Reprinted with permission [20].

For the 84 nm-thick Mg thin film capped by 10 nm Pd layer, the crystallite size is around 50-100 nm. Based on these materials, he got hydrogen absorption kinetics curves of several samples and delivered a conclusion that the absorption kinetics have a significant difference from nanoscale samples to micrometer scale samples. For example, Mg nanoparticles have better absorption kinetics than 325 mesh Mg due to their smaller crystallite size. As a result, hydrogen has more chance and contact area to react with Mg samples. In addition, the diffusion distance for hydrogen is much shorter in Mg nanoparticles. In the experiment, the several nanometer's bcc structure $Mg_{50}Co_{50}$ alloy was able to absorb hydrogen at near room temperature (303 K) under 3.3 MPa of hydrogen pressure, and even at 258 K, this sample could present a result of 2.65 wt% hydrogen capacity under 8 MPa hydrogen pressure (Figure 4), which is the lowest absorption temperature published for Mg-based materials so far. On the contrary, the single crystal Mg with a millimeter scale doesn't present any hydrogen absorption ability below 573 K. On the other hand, based on the experimental date, the author found that once the pressure is much higher than the equilibrium pressure at one certain temperature, the pressure could not change the absorption kinetics quite a little.

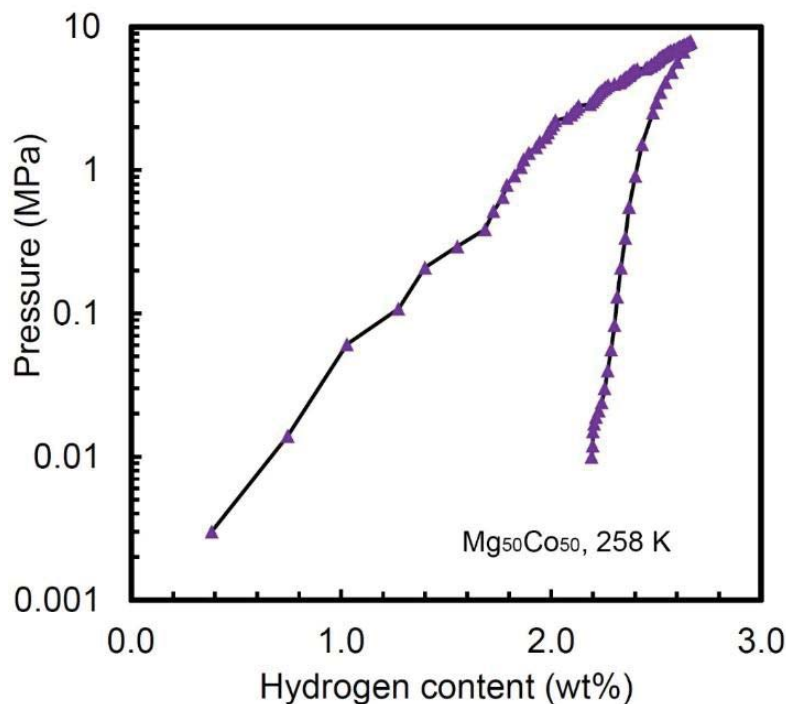


Figure 4. Pressure-composition isotherm at 258 K of the ball milled $Mg_{50}Co_{50}$ bcc structure alloy. Reprinted with permission [20].

Thermal conductivity

Figure 5 shows thermal diffusivity measurement results of the pressed pellet sample from 325 mesh Mg powder by laser flash technique (Figure 5(a)) and the Pd capped Mg thin film sample by thermoreflectance system (Figure 5(b)). And other samples' thermal diffusivity

data were from the obtained half time/diffusion time and the thickness data of the samples. And from Table 2, Mg single crystal gives the largest value of thermal conductivity about 168.0 W/m/K due to its crystal structure while the lowest hydrogen absorption kinetics because of its large particle size. The bcc structure Mg₅₀Co₅₀ alloys, the smallest size among the five samples, show the worst thermal conductivity about 0.432 W/m/K but a superior hydrogen absorption kinetics because of its few-nanometers nanostructure particles. And it is because of the small nanoscale particles that there are much more boundaries and interfaces greatly scattering the electron or phonon transfer than that in the micrometer scale materials [22]. Story is different when it comes to Pd capped Mg thin film, it not only has a relatively good thermal conductivity, but also a superior hydrogen absorption kinetics for its good crystallinity of Mg phase and it is helpful to electron transfer during the measurement. In summary, the nanoscale Mg-based materials present good hydrogen absorption kinetics but demonstrate poor thermal conductivity. And the thin film sample could be a breakthrough and gives us a new orientation to design an energy storage material with both good kinetics and superior thermal conductivity properties.

Table 2. Thermal physics and kinetics properties of Mg-based hydrogen storage materials. Reprinted with permission [20].

Sample	Thermal diffusivity (10 ⁻⁶ m ² /s)	Heat capacity (J/kg/K)	Bulk density (kg/m ³)	Thermal conductivity (W/m/K)	Hydrogen absorption kinetics
325 mesh Mg	7.290	1046	1367	10.42	poor
Mg single crystal (0001)	91.04	1082	1706	168.0	poor
Mg nanoparticles	3.992	954	1309	4.985	good
Mg ₅₀ Co ₅₀ bcc alloy	0.293	594	2483	0.432	superior
Pd capped Mg thin film	46.2	1020	1740	82.0	superior

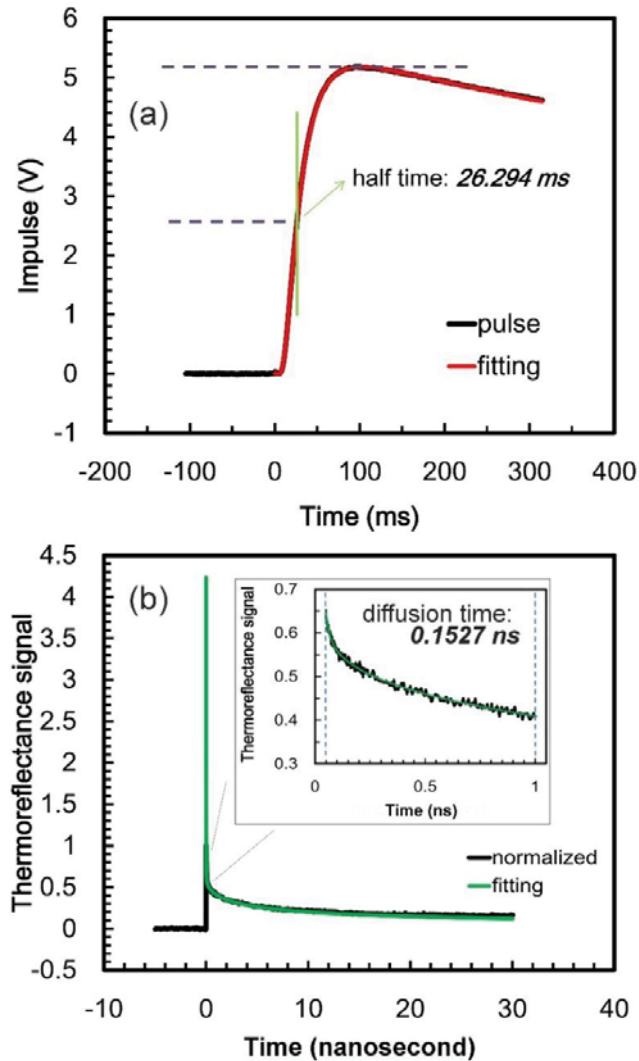


Figure 5. (a) Normalized temperature signal and fitting result vs. time curve of one laser flash measurement of 325 mesh Mg sample, (b) thermoreflectance signal and fitting result vs. time curve of Mg thin film measurement. Reprinted with permission [20].

Thermodynamics

From the author's and other group's work [1, 23-25], we could easily deliver a conclusion that kinetics can be significantly improved by nanostructure processing. However, whether nanostructure could optimize the desorption thermodynamics is still controversy [1, 24-26]. The author tried to figure out the relationship between them and synthesize different Mg-based materials using different methods to study the desorption enthalpy with different materials. And based on our work in recent years, we find that desorption thermodynamics do not change with nano processing when the particle size is above 5 nm. From Shao's work [27-29], using hydrogen plasma metal reaction, several Mg-based materials (Mg, Mg₂Ni, Mg₂Co and Mg₂Cu) were synthesized with an average particle size in the range of 50 to 200 nm. And after measurement of pressure composition isotherms under desorption hydrogen

reaction, van't Hoff equations were written for each sample. From those van't Hoff equations, we could derive the enthalpy and entropy information. From Table 3, we could clearly see that the enthalpy and entropy values do not change obviously in different hydrogen desorption reaction system. Besides, experimental work in various MgH₂ system were conducted to better study the hydrogen desorption reaction thermodynamics [30, 31]. In Table 4, there are four types of MgH₂ samples prepared: MgH₂ by hydrogen plasma metal reaction, MgH₂ by catalyzed solution synthesis, MgH₂ by reactive ball milling and the commercial MgH₂. Similarly, we got hydrogen desorption van't Hoff equations and derived the enthalpy and entropy values. Compared with other groups' work [32-36], all the enthalpy and entropy values do not have a great fluctuation, which means those results agreed well with each other. From above work, we could come to the conclusion that there is no apparent change in hydrogen desorption reaction thermodynamics in the size range of above 5 nm, which is consistent with what Wagemans reported in their computational study[18].

Table 3. Van't Hoff equation, enthalpy and entropy for desorption reaction of different Mg-based nanostructure systems [37-40]. Reprinted with permission [1].

System	Van't Hoff equation	Enthalpy (ΔH) kJ/mol H ₂	Entropy(ΔS) J/(K·mol H ₂)
MgH ₂	$\ln (p/0.1 \text{ Mpa}) = -9604/T + 16.93$	-79.8	-140.8
Mg ₂ NiH ₄	$\ln (p/0.1 \text{ Mpa}) = -7977/T + 15.07$	-66.32	-125.3
Mg ₂ CoH ₅	$\ln (p/0.1 \text{ Mpa}) = -9895/T + 16.70$	-82.27	-138.8
Mg ₃ CoH ₅	$\ln (p/0.1 \text{ Mpa}) = -8800/T + 14.80$	-73.16	-123.0
MgH ₂ + MgCu ₂	$\ln (p/0.1 \text{ Mpa}) = -9275/T + 17.61$	-77.11	-146.4

Table 4. Van't Hoff equation, enthalpy and entropy change values of desorption for various MgH₂ systems. Reprinted with permission [1].

System No.	ΔH (kJ·mol ⁻¹ H ₂)	ΔS (J H ₂ K ⁻¹ ·mol ⁻¹)	Desorption temperature range (°C)	Reference
1	77.7	138.3	258-299	Catalyzed solution synthesis [31]

2	77.4	137.5	269-301	Reactive ball milling [30]
3	79.8	140.8	350-400	Hydrogen plasma metal reaction [38]
4	78.5	140.0	330-370	Commercial MgH ₂ from Alfa Aesar [41]
5	74.4	135	314-576	[32]
6	77.4	138	276-350	[33]
7	79	-	302-336	[36]
8	78.2	-	300-343	[35]
9	81.25	144.29	240-360	[34]

In summary, to design a nanostructured material, it could significantly improve the kinetics. But for thermal conductivity and thermodynamics properties, nanoscale does not exhibit a positive effect on them. For the onboard hydrogen storage, we need a desorption enthalpy of around 15 to 30 kJ/mol and the corresponding hydrogen desorption temperature of below 150 °C. In other words, there is still a long way to develop Mg-based materials for the application of onboard hydrogen storage.

6.3 Nano processing technologies

To reduce the size of hydrogen storage materials can lead to a dramatic change in their physical and chemical properties [42]. It has been well proved that to prepare nano structures is a most efficient way to enhance the hydrogen storage properties of Mg-based materials mainly due to the shortened hydrogen diffusion and dissociation pathways, enlarged surface free energy, and even altered thermodynamics when the size decreases to below a few nanometers. Mg-based materials with grain and/or particle sizes in nanoscale are usually prepared with enhanced hydrogen storage kinetics and thermodynamics properties. Up to date, Mg-based hydrogen storage nanomaterials could be synthesized by many technical routes. Morphologies of the synthesized materials in different dimensions, including zero-dimensional (0D; e.g., nanoparticles, quantum dots, and hollow spheres), one-dimensional (1D; e.g., nanowires, nanofibers, nanorods, nanobelts, and hierarchical nanostructures), two-dimensional (2D; e.g., thin films, nanosheets, and branched structures), and three-dimensional (3D; e.g., frameworks, nanoflowers, and dendritic structures) have been successfully fabricated via well-designed techniques and processes [43].

There are numerous techniques which have been explored for preparation of Mg-based hydrogen storage materials, typically including ball milling, thin film formation, melt spinning, nanoconfinement, hydrogen plasma metal reaction, hydriding chemical vapor deposition, severe plastic deformation etc. The practical technique methods are usually

realized via one or several different strategies like nanostructuring, alloying, catalyzing, modifying surface property, forming composites, confinement and so on. Herein, some of the classical and novel synthesis techniques for Mg-based hydrogen storage materials will be discussed together with their impact on the hydrogen storage properties.

Ball milling

Ball milling is the most commonly used method to synthesize Mg-based material in the hydrogen storage area. The lab used ball milling machine is in small size and the operation procedure is quite simple. Moreover, morphologies and chemical states of the materials could be controlled by controlling the milling parameters (such as ball-to-powder ratio, size of balls, milling speed, time and atmospheres), leading to controlled particle size and grain size, and alloying products etc. During the ball milling process, it could introduce a great many defects, dislocations and fresh surface of the sample. And ball milling is well known as an effective method to reduce the crystallite size and prepare the sub equilibrium state. Generally, based on the different function, ball milling roughly has three branches-mechanical grinding, mechanical alloying and reactive ball milling [1]. Mechanical grinding is more like a simple mix technology of different samples, and is used to reduce the particle size and crystal grain size to nanoscale but not change the composition of samples. And we could get the sample with size range from nanometer to micrometer scale by mechanical grinding. Mechanical alloying is a very significant technology to synthesize metal alloying such as Mg-Ni, Mg-Cu, Mg-Co etc. [11, 13, 17, 21, 27, 28] for hydrogen storage. Since Mg-based alloys are plastic materials, the milling speed should not be too high (usually < 400 rpm), otherwise the materials are easy to stick to the inner wall of milling jars and balls. In order to reduce the grain size of Mg-based materials to below 10 nm, milling time as long as tens of hours is necessary [44]. During the mechanical alloying, because of the diffusion in atomic scale between the starting materials, the composition will change and form a nanoscale alloy with a sub equilibrium state. Shao et al. [21] fabricated bcc structure $Mg_{50}Co_{50}$ alloys from Mg and Co metal powders milling from 0.5 to 400 h. He got the bcc structure alloy after milling for 100 h with particle size about 1-3 μm and crystallite size is around a few nanometers from the TEM observation. Table 5 illustrates the phase information of the $Mg_{50}Co_{50}$ alloys with different milling time from 0.5 to 400 h. Figure 6 presents PCT curves of $Mg_{50}Co_{50}$ alloys with different milling time at 258 K and 323 K and shows the hydrogen capacity of 2.67 wt% and 2.86 wt% when milled for 100 h and 300 h, respectively at 258K. which is the lowest temperature reported to the best knowledge of us. Usually in mechanical grinding and mechanical alloying, the milling process is conducted under inert gas (Nitrogen or Argon). For some cases, in order to synthesize metal or alloy hydrides, milling under certain hydrogen pressure is chosen, which is called reactive ball milling. Shao et al. [25] synthesized a nanoscale $MgH_2/0.1TiH_2$ composite from Mg and Ti metal powders under an initial hydrogen pressure of 30 MPa by reactive ball milling and got

a MgH_2 sample with size around 5 nm. He used this sample to explore different types of thermodynamic properties we mentioned above.

Table 5. $\text{Mg}_{50}\text{Co}_{50}$ alloys after ball milling for different periods. Reprinted with permission [13]. (hcp: hexagonal close packed, fcc: face-centered cubic, bcc: body-centered cubic).

Sample No.	Milling time (h)	Phase
1	0.5	Mg, Co-hcp
2	2	Mg, Co-hcp
3	5	Mg, Co-hcp
4	10	Mg, Co-hcp
5	25	Mg, Co-hcp, Co-fcc
6	30	Mg, Co-hcp, Co-fcc
7	35	Mg, Co-hcp, Co-fcc
8	40	Mg, Co-hcp, Co-fcc
9	45	bcc, Co-fcc
10	50	bcc, Co-fcc
11	75	bcc, Co-fcc
12	100	bcc
13	200	bcc
14	300	bcc
15	400	bcc

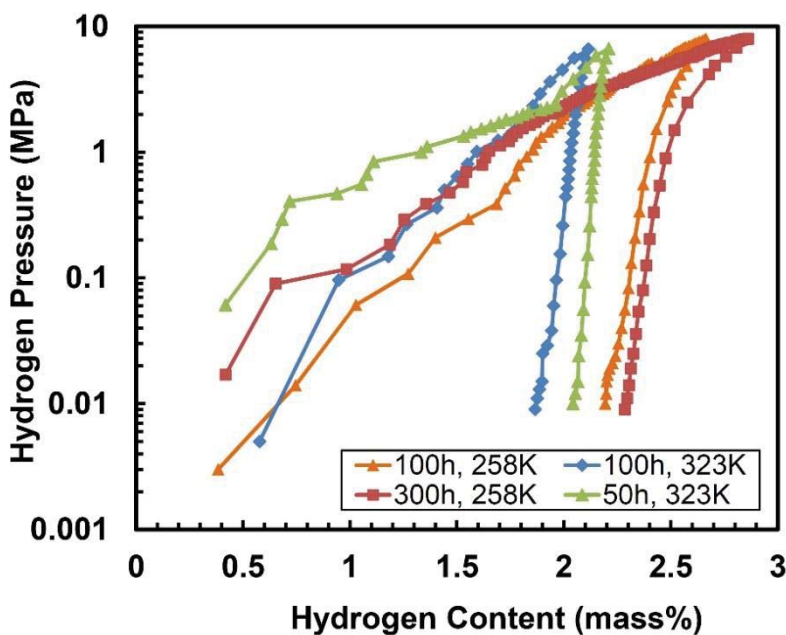
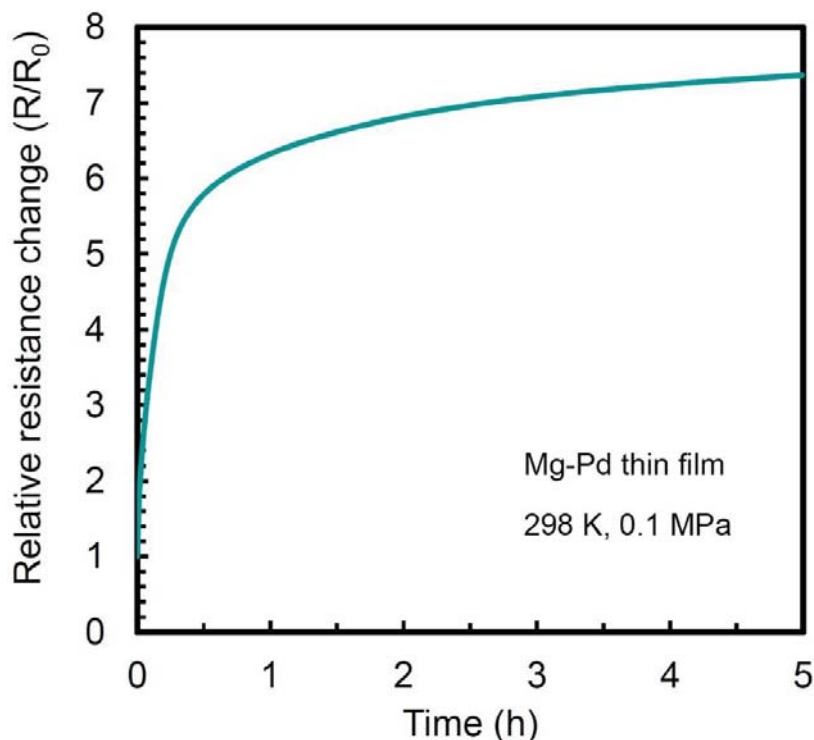


Figure 6. PCT curves at 258 K and 323 K of the $\text{Mg}_{50}\text{Co}_{50}$ alloys milled for different durations (50 h, 100 h and 300 h). Reprinted with permission [13].

Doping catalysts/additives by ball milling is commonly used to enhance the hydrogen storage kinetics of Mg-based materials [45]. Many chemicals have been doped into Mg-based materials. The catalysts/additives as milling agents help reduce the particle size and grain size of the Mg-based materials. More importantly, the introduced catalytic effects lead to excellent catalysis to accelerate the hydrogen storage kinetics of Mg-based materials. Up to date, a huge number chemicals and compounds have been proved to show catalytic effect on hydrogen storage of Mg-based materials, such as transition metals (TMs) [46], metal hydrides[30], oxides[47], halides[48], and so on. MgH₂ catalyzed by 0.02 mol% of Nb₂O₅, firstly reported by Barkhordarian et al. [49] is one of the best catalyzed Mg-based materials system. It shows that the catalytic effect of Nb₂O₅ is superior in absorption as well as desorption. At 300 °C, 7 wt.-%-H could be absorbed within 60 s and desorption is facilitated within 130 s. Cui et al. [50] coated Mg by different TMs, including Ti, Nb, V, Co, Mo, and Ni, with a grain size in the nanoscale to form a core (Mg)-shell (TM) like structure by reaction of Mg powder in THF solution with TMCl_x, leading to remarkably reduced hydrogen absorption and desorption temperatures. The improvements should be attributed to the catalytic effect of TMs on hydrogen storage of Mg/MgH₂ and the nanosized effect from nanocoating. Lin et al. [48] reported the hydrogen desorption property of the ball-milled MgH₂ + 0.02 mol CeF_x (x = 3 and 4). After ball milling for 4 hours, CeF₃ doped MgH₂ shows the same hydrogen desorption temperature and activation energy as those of the as-milled MgH₂, however, the addition of CeF₄ significantly reduced the hydrogen desorption temperature and activation energy of MgH₂ because of the easy electron transfer induced from the high valence Ce-cation and the formation of the F-containing Ce-F-Mg species on the CeF₄/MgH₂ interface. Although numerous efforts have been devoted to developing efficient catalysts for Mg-based hydrogen storage, and some appear to be good. The catalyzed Mg-based materials still could not satisfy the demand of practical hydrogen storage because of the too stable thermodynamics of MgH₂ which catalysis could hardly destabilize. It is thus suggested that combining catalyzing with other strategies such as nanostructuring and alloying could be one of the future directions to realize Mg-based hydrogen storage materials for practical onboard applications.

To form new Mg-based hydrides composites is another efficient pathway to alter the thermodynamics properties because of altered hydrogenation/dehydrogenation reaction paths. Ball milling is commonly used to realize the preparation of composites materials, such as MgH₂ + LiBH₄[51], Mg₂NiH₄ + LiAlH₄ [52] and many others. Formation of composites remarkably changes the hydrogen storage reactions therefore it may lead to different hydrogen storage kinetics, thermodynamics, capacity, working temperature etc. for the materials. To form reactive composites, reactions between Mg-based hydrides and other hydrides should occur during ball milling, or in the subsequent hydrogenation/dehydrogenation processes.

Thin film synthesis



Thin film formation is a suitable technique to prepare Mg-based nanomaterials in 2D for hydrogen storage, hydrogen sensor, optical switchable windows [53-55] and so on. Generally, thermal evaporation, electron-beam evaporation and magnetron sputtering and other methods could be adopted to fabricate Mg-based thin films. Thin films in nanometer scale show some interesting physical and chemical phenomena which could hardly be observed in bulk cases. Figure 7. Relative resistance change of the Pd capped Mg thin film sample with hydrogen absorption process under 0.1 MPa hydrogen at 298 K. Reprinted with permission [20].

Thin films possess large surface area, fast hydrogen diffusion rate and could do some coating to protect from poisoning or catalyze the reaction [14]. Compared with bulk materials, it is more convenient to tailor the structure. On the other hand, thin film materials could absorb and desorb hydrogen in more mild conditions. Shao et al. [20] fabricated 85 nm Mg thin film capped by 10 nm Pd layer by direct current magnetron sputtering technique. From Figure 7, relative resistance change was applied to demonstrate its absorption kinetics due to the very small amount hydrogen absorption of thin film. And this sample presents not bad thermal conductivity and superior hydrogen absorption kinetics. Xin et al. [53, 54] also reported promising gaseous and electrochemical hydrogen storage characteristics in Mg-Pd-based nano films at room temperature, making them promising candidates for hydrogen sensors and smart windows. Victoria et al. [55] added glassy Ni-Zr alloy to amorphous Mg-Ni-H thin film system for optical hydrogen sensing. It is found that the sensitivity of transparent hydrides is strongly increased by changing the intrinsic mechanism of

hydrogenation. Using the robust behavior of the glassy Ni-Zr alloy upon hydrogenation, amorphous Mg–Ni–Zr alloys films have been fabricated showing unprecedented advantages because they combine with the interplay of transparent Mg_2NiH_4 and glassy Ni–Zr alloys. Baldi et al. [56] reported that strain constraint could cause the change of hydrogen absorption of Mg in the aspect of thermodynamics, they demonstrated that the obvious elevation of hydrogenation equilibrium pressure in Mg/Pd/Ti multilayer film and ascribed to the elastic clamping by the Pd or Ti layers. Fast hydrogenation kinetics and low hydrogenation temperature are obtainable in the nano films, however, hydrogen storage capacity of the 2D systems is too low to practical use. Nano films therefore have attracted much attentions in the field of hydrogen sensors, optical switchable windows and fundamental research on hydrogen in nanomaterials, instead of the hydrogen storage use.

Melt spinning

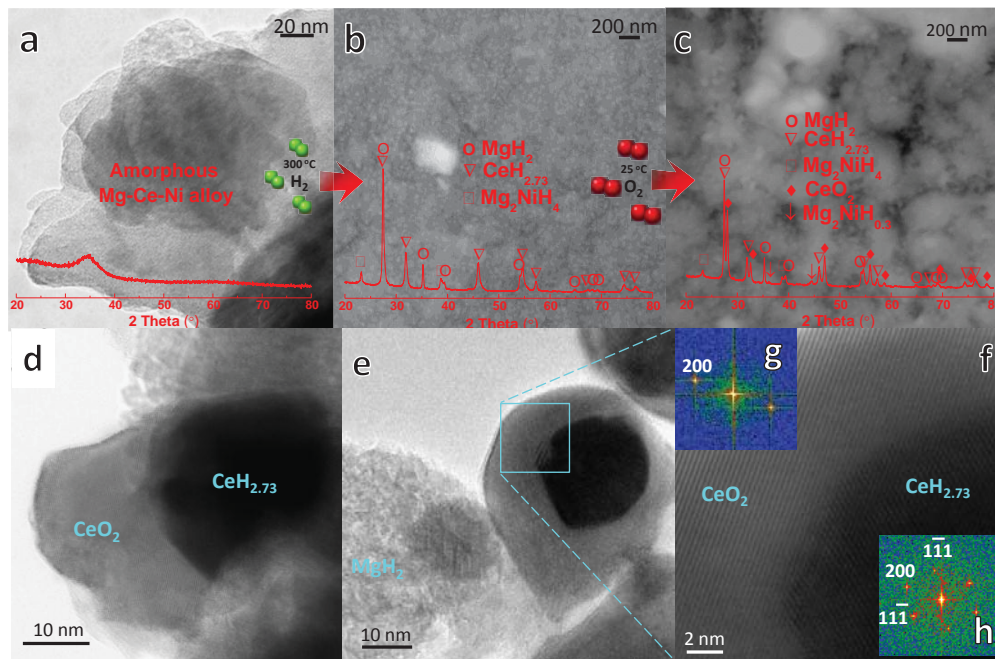


Figure 8. (a-c) XRD patterns and TEM(SEM) images of amorphous $\text{Mg}_{80}\text{Ce}_{10}\text{Ni}_{10}$ alloy, $\text{MgH}_2\text{-Mg}_2\text{NiH}_4\text{-CeH}_{2.73}$ and $\text{MgH}_2\text{-Mg}_2\text{NiH}_4\text{-CeH}_{2.73}/\text{CeO}_2$ nanocomposites, respectively. (d-f) TEM and HRTEM images showing the symbiotic $\text{CeH}_{2.73}/\text{CeO}_2$ nanoparticle, (g-h) are the corresponding FFT patterns of $\text{CeH}_{2.73}$ and CeO_2 . Reprinted with permission [57].

Melt spinning is a rapid solidification technique which is particularly suitable for preparing Mg-based nanocrystalline and/or amorphous alloys for hydrogen storage. [58, 59] The Mg-rich Mg-RE-Ni (RE=Rear Earth) system has an excellent glass-forming ability and thus easily becomes nanocrystalline and/or amorphous by melt spinning. The melt-spun Mg-RE-Ni alloys decompose into composites containing MgH_2 , Mg_2NiH_4 and REH_{2-3} hydrides upon a hydrogenation activation treatment at the temperature range of 300-350 °C, and show

much improved hydrogenation/dehydrogenation kinetics compared with those of induction-melt [59] and ball-milled alloys [60]. The kinetics improvements are due to the refined and homogenized alloys by melt spinning which lead to smaller size of MgH_2 , thus benefits the hydrogen diffusion and dissociation. Furthermore, the *in situ* hydrogenation induced Mg_2NiH_4 and REH_{2-3} hydrides in nanoscale size show remarkable catalytic effect on enhancing the hydrogen storage properties of Mg [59, 61].

Taking the amorphous Mg-based alloys as precursors, Lin et al. [57] recently reported a novel method to *in situ* generate a symbiotic $\text{CeH}_{2.73}/\text{CeO}_2$ nano-catalyst in Mg-based hydrides via hydrogenation and oxidation (Figure 8(a)). The CeO_2 is epitaxially formed from $\text{CeH}_{2.73}$ in a cubic-to-cubic orientation relationship. Interestingly, a spontaneous hydrogen release effect at the interface of symbiotic $\text{CeH}_{2.73}/\text{CeO}_2$ nanoparticle has been revealed, which leads to dramatic increase of catalysis than either sole $\text{CeH}_{2.73}$ or CeO_2 . The dynamic boundary evolution during hydrogen desorption was observed in the symbiotic $\text{CeH}_{2.73}/\text{CeO}_2$ at atomic resolution using *in situ* HRTEM experiments. Combining the *ab-initio* calculations, it was demonstrated that the outstanding catalytic activity should be attributed to the spontaneous hydrogen release effect at the $\text{CeH}_{2.73}/\text{CeO}_2$ interface.

Amorphization is a novel strategy to prepare Mg-based materials with a new hydrogen storage pathway compared with that of crystalline counterparts[62]. Therefore, altered thermodynamics and kinetics in the amorphous alloys could be expected. Compared with crystalline alloys which generally only provide specific octahedral and/or tetrahedral sites for hydrogen occupation, amorphous alloys might offer extra potential vacancies for hydrogenation. Furthermore, some amorphous alloys systems have excellent glass-forming ability, therefore the chemical compositions can be easily tuned by adding elements to alter their chemical interaction with hydrogen while maintaining amorphous structures, hence leading to tunable hydrogen storage capacity, kinetics and thermodynamics. Mg-RE-Ni amorphous alloys are a group of materials attracting the most interest because of the hydrogen density as high as 7.7 wt.% in the case of MgH_2 , however, they usually suffer from disproportion reactions and decompose into hydride composites containing MgH_2 , Mg_2NiH_4 and REH_{2-3} upon activation. Lin et al. [63] recently reported a glass-to-glass' transition in amorphous $\text{Mg}_{80}\text{Ce}_{10}\text{Ni}_{10}$ alloy induced via gaseous hydrogenation with a storage capacity as high as 5 wt.%-H. The hydrogen storage capacity of the amorphous Mg-Ce-Ni alloys is obviously higher than that of their crystalline counterparts due to the free volume and disordered atomic structure associated with glasses. The glass-to-glass' transition is demonstrated by direct experimental observation using aberration-corrected scanning transmission electron microscopy combined with *ab initio* molecular dynamics simulations. Remarkably, the dehydrogenation temperature of the amorphous Mg-Ce-Ni hydrides can be efficiently tuned as it shows a close relationship with the enthalpy of mixing between the alloying element and hydrogen, and can be decreased from ~ 350 °C to ~ 150 °C when alloying with 5 at.%-Cu. It has also been demonstrated that to prepare nanoporous

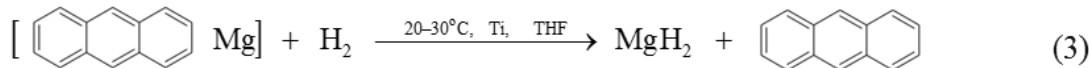
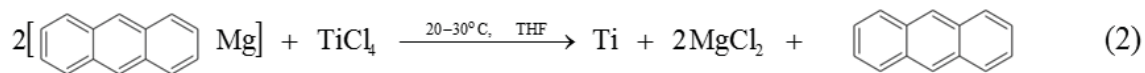
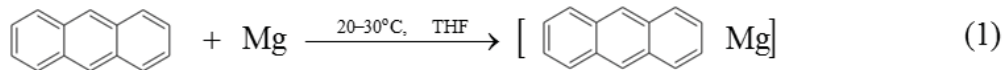
amorphous alloys could further benefit the hydrogen absorption properties due to the enlarged specific surface areas. [64]

Hydrogen plasma metal reaction

Hydrogen plasma metal reaction is used to generate nanoparticles from bulk metal. Bulk metal is put into the reaction chamber, vaporized by the arc voltage and current under the mixed gas of Ar and H₂, then the vaporized metal flows to the collecting room and is filtered by the filter where we could collect the metal nanoparticles after evacuation. Shao et al. did numerous works [12, 17, 28, 29] based on the hydrogen plasma metal reaction method. They synthesized Mg₂Ni, Mg₂Co and Mg₂Cu with an average size about 50 to 200 nm by using this method and sample nanoparticles are smaller than starting Mg particles, which means the size of starting metal particles decreases during the hydrogen plasma metal reaction, indicating some inspiration on decreasing the size of materials. Shao et al. used those alloys to study the hydrogen desorption reaction thermodynamic properties with different particle sizes and found hydrogen desorption enthalpy does not change quite a lot with different dimensional Mg-based materials.

Catalyzed solution synthesis

Nanocrystalline Ti-catalyzed MgH₂ could be fabricated by homogeneously catalyzed synthesis method. Equations 1-3 are a typical procedure to synthesize Ti-catalyzed MgH₂. In Shao's work [31], the Ti-catalyzed MgH₂ nanocrystalline samples were made up by two kinds of MgH₂ phases, 11% orthorhombic high-pressure modification γ -MgH₂ and 89% tetrahedral β -MgH₂ phase. The crystallite size is in the range of 5-100 nm and the N₂ adsorption measurement presents a high BET surface area of 108 m² g⁻¹. When applied to hydrogen storage, the sample shows a hydrogen absorption temperature of 130 °C lower and a hydrogen absorption rate at 300 °C of 40 times higher than that of commercial MgH₂ (Figure 9). In addition, this nanocrystalline sample was also used to explore thermodynamic properties with different nanostructures and showed an unchanged hydrogen desorption enthalpy.



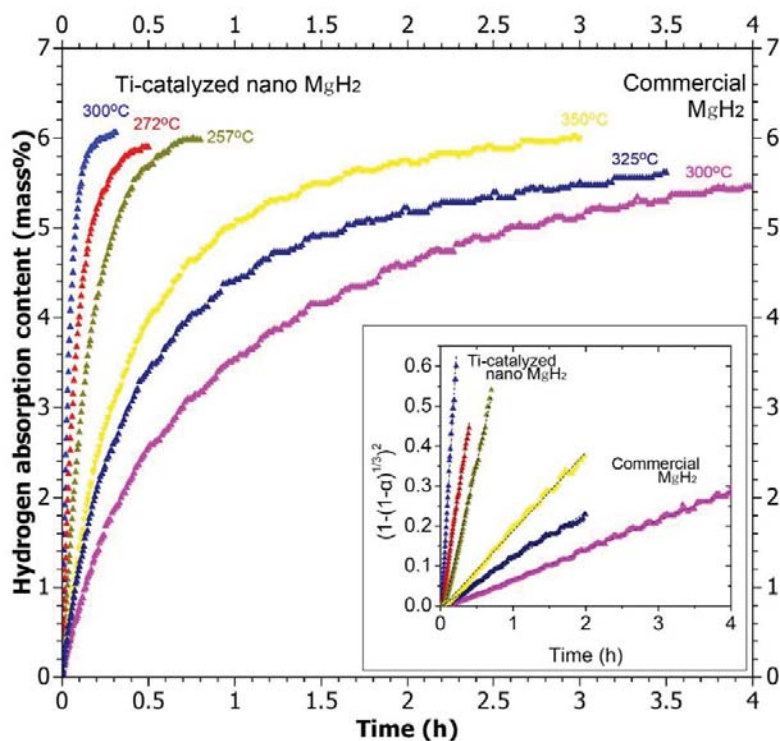


Figure 9. Hydrogen re-absorption curves of Ti-catalyzed MgH₂ nanocrystalline sample and commercial MgH₂ sample (Alfa Aesar) at different temperatures in 1 MPa hydrogen after complete desorption (inset: absorption curves simulated by Jander diffusion equation). Reprinted with permission [1].

Nano-confinement

Although nanostructuring remarkably improves the hydrogen storage performance of Mg-based materials, the prepared nanoparticles more or less aggregate during the hydrogenation/dehydrogenation cycling depends on temperature, pressure and cycling times, and thus the hydrogen storage property gradually deteriorates. In order to block the grain growth and preserve the nanostructure, a new technique strategy named “nano-confinement” has been developed[65-68]. In the past decades, various porous materials [69, 70] such as zeolite, silica gel, and template carbon were used to confine the nanoparticles in order to optimize the hydrogen absorption kinetics and improve the thermodynamic properties in the hydrogen storage area. Carbon materials are always used to confine nanoparticles due to its high specific surface area, good thermal conductivity and fast hydrogen diffusion rate [23, 71]. MgH₂ or Mg-based hydrides with size in a wide range from a few nanometers to 100 nm could be confined in scaffolds. Jia et al. [72] analyzed the nanoconfinement MgH₂ particles in the nanoporous carbon by studying high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM). From this work, the ultrafine 1-2 nm sized MgH₂ particles were found being confined in the nanoporous carbon scaffolds with diameter of 4 nm. The enthalpy value of hydrogen absorption for this nanoconfined MgH₂ is 55.4 kJ/mol. Zhao et al. [65] reported the thermodynamics destabilization in confined MgH₂

with size smaller than 3 nm in carbon scaffold, whose enthalpy and entropy are $63.8 \text{ kJ} \cdot \text{mol}^{-1} \text{ H}_2$ and $117.2 \text{ J} \cdot \text{mol}^{-1} \text{ H}_2$, respectively, which are reduced from $75.7 \text{ kJ} \cdot \text{mol}^{-1} \text{ H}_2$ and $136.3 \text{ J} \cdot \text{mol}^{-1} \text{ H}_2$ for the bulk case. Liu et al. [71] demonstrates that the Mg nanoparticles with the size range of 5-20 nm has been fabricated in the carbon aerogels through wet impregnation technique. And the hydrogen desorption enthalpy value of the confined Mg nanoparticles is $68.8 \pm 1.03 \text{ kJ/mol}$. They claimed that compared with MgH_2 nanoparticles synthesized by ball milling, the nanoconfinement sample has a smaller enthalpy value due to its smaller particle size.

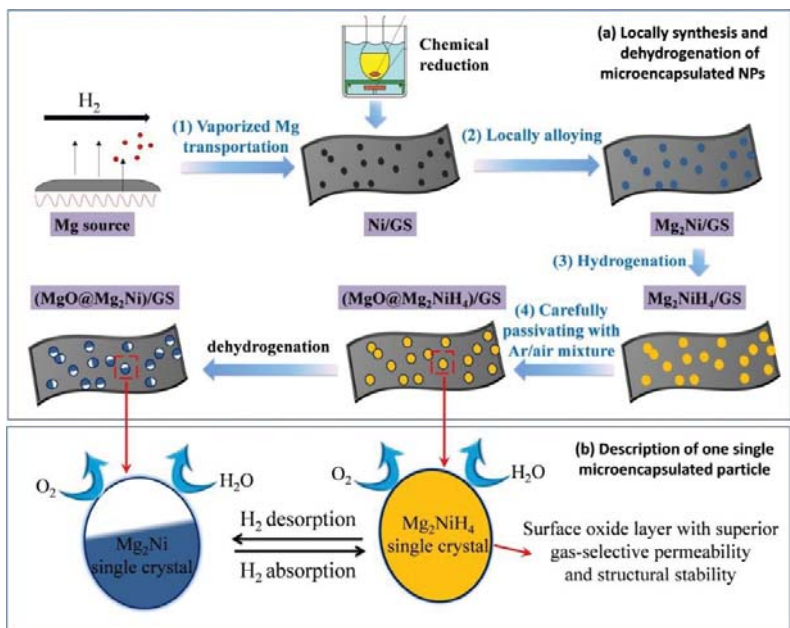


Figure 10. Schematic of (a) the local synthesis of monodispersed Mg_2NiH_4 nanoparticles locally derived from Ni/GS by HCVD and the structural evaluation after hydrogen desorption. Four steps are involved in the HCVD synthesis: (1) under H_2 atmosphere, gasified Mg transports to the Ni/GS substrate; (2) the Ni dopants act as positive cores to attract gaseous Mg atoms, and the alloying reaction between them locally generates monodispersed Mg_2Ni NPs on the GS surface; (3) Mg_2Ni absorbs H_2 and transforms to Mg_2NiH_4 ; (4) careful *in situ* passivation of the NPs to form an MgO coating with a thickness of $\sim 3 \text{ nm}$ occurs during the cooling process. (b) Detailed description of a single microencapsulated particle. A “semi-hollow” structure is formed upon hydrogen desorption. Reprinted with permission [68].

Zhang et al. [68] recently reported a new strategy named microencapsulated nanoconfinement to realize local synthesis of nano- Mg_2NiH_4 , which possess ultrahigh structural stability and superior desorption kinetics. Monodispersed Mg_2NiH_4 single crystal nanoparticles are *in situ* encapsulated on the surface of graphene sheets (GS) through hydriding chemical vaporation deposition (HCVD) (Figure 10(a)). The MgO coating layer

with a thickness of about 3 nm efficiently separates the nanoparticles from each other to prevent aggregation during hydrogen absorption/desorption cycles, leading to excellent thermal and mechanical stability. More interestingly, the MgO layer shows superior gas-selective permeability to prevent further oxidation of Mg₂NiH₄ meanwhile accessible for hydrogen absorption/desorption (Figure 10 (b)). As a result, an extremely low activation energy of 31.2 kJ mol⁻¹ for the dehydrogenation reaction is achieved. The study provides alternative insights into designing nanosized metal hydrides with both excellent hydrogen storage activity and thermal/mechanical stability exempting surface modification by agents.

Others

Besides the above-mentioned techniques, severe plastic deformation (such as equal channel angular pressing and high-pressure torsion) [73-75], spark discharge generation [76, 77], chemical solution synthesis [1, 78], hydrogen combustion synthesis [79, 80], high pressure gas synthesis [81] and other techniques have been developed to prepare Mg-based materials with advanced hydrogen storage property. It could be summarized that all these techniques have advantages, meanwhile possessing disadvantages. It might be beneficial to combine two or several of the techniques to realize fabrication of advanced Mg-based hydrogen storage materials suitable for massive use.

6.4 Future prospect

Hydrogen is regarded as an ideal energy for vehicle application due to its good intrinsic properties. Many groups are dedicated to exploring new materials for hydrogen storage. And Mg-based materials become potential candidate due to high gravimetric and volumetric capacity, large abundance, and lower price. However, the hydrogen adsorption kinetics and hydrogen desorption thermodynamics are two barriers need to be handled. Urgent priority is to lower the hydrogen desorption temperature and faster hydrogen absorption time for onboard practical usage. Many technologies and methods are developed to design the nanoscale materials and provide many strategies to break the limitations of Mg-based materials. The biggest challenge is to fabricate a few nanometers Mg-based materials to optimize hydrogen desorption reaction enthalpy and fix the hydrogen desorption temperature below 100 °C in a few bars of pressure. Nanoconfinement technology gives us a new orientation to study Mg-based materials for onboard development. On the other hand, because of the large enthalpy during hydrogen absorption and desorption, Mg-MgH₂ was proposed to store heat [82]. In the daytime, the excess solar power or industry exhaust energy is used to hydrogen desorption from MgH₂ and store energy; while at night, Mg reacts with H₂ and releases the stored heat. Or one may use Mg-MgH₂ system to store the excess renewable energy and to provide hydrogen to solid oxide fuel cell, which supplies exhaust heat for the desorption reaction in the Mg-based storage system [16].

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References

1. Shao, H., et al., *Nanotechnology in Mg-based materials for hydrogen storage*. Nano Energy, 2012. **1**(4): p. 590-601.
2. Grochala, W. and P.P. Edwards, *Thermal Decomposition of the Non-Interstitial Hydrides for the Storage and Production of Hydrogen*. Chemical Reviews, 2004. **104**(3): p. 1283-1316.
3. Sakintuna, B., F. Lamari-Darkrim, and M. Hirscher, *Metal hydride materials for solid hydrogen storage: A review*. International Journal of Hydrogen Energy, 2007. **32**(9): p. 1121-1140.
4. Abdellaoui, M., et al., *Structural, solid-gas and electrochemical characterization of Mg₂Ni-rich and Mg_xNi_{100-x} amorphous-rich nanomaterials obtained by mechanical alloying*. International Journal of Hydrogen Energy, 2006. **31**(2): p. 247-250.
5. Rosi, N.L., et al., *Hydrogen storage in microporous metal-organic frameworks*. Science, 2003. **300**(5622): p. 1127-9.
6. Dillon, A.C., et al., *Storage of hydrogen in single-walled carbon nanotubes*. Nature, 1997. **386**(6623): p. 377-379.
7. Yildirim, T. and S. Ciraci, *Titanium-decorated carbon nanotubes as a potential high-capacity hydrogen storage medium*. Phys Rev Lett, 2005. **94**(17): p. 175501.
8. Alapati, S.V., J.K. Johnson, and D.S. Sholl, *Large-Scale Screening of Metal Hydride Mixtures for High-Capacity Hydrogen Storage from First-Principles Calculations*. The Journal of Physical Chemistry C, 2008. **112**(14): p. 5258-5262.
9. Liu, C., et al., *Hydrogen storage in single-walled carbon nanotubes at room temperature*. Science, 1999. **286**(5442): p. 1127-9.
10. Varin, R.A., et al., *Synthesis of nanocomposite hydrides for solid-state hydrogen storage by controlled mechanical milling techniques*. Journal of Alloys and Compounds, 2009. **483**(1): p. 252-255.
11. Shao, H., et al., *Preparation and hydrogen storage properties of nanostructured Mg-Ni BCC alloys*. Journal of Alloys and Compounds, 2009. **477**(1-2): p. 301-306.
12. Liu, T., H. Shao, and X. Li, *Synthesis and characteristics of Ti-Fe nanoparticles by hydrogen plasma-metal reaction*. Intermetallics, 2004. **12**(1): p. 97-102.
13. Shao, H., et al., *Phase and morphology evolution study of ball milled Mg-Co hydrogen storage alloys*. International Journal of Hydrogen Energy, 2013. **38**(17): p. 7070-7076.
14. Jain, I.P., et al., *Hydrogen in FeTi thin films by ERDA with Ag¹⁰⁷ ions*. International Journal of Hydrogen Energy, 2000. **25**(6): p. 517-521.

15. Yang, J., et al., *High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery*. Chemical Society Reviews, 2010. **39**(2): p. 656-675.
16. Shao, H., et al., *Progress and Trends in Mg-based Materials for Energy Storage Research: A Review*. Energy Technology: p. n/a-n/a.
17. Shao, H., et al., *Thermodynamic Property Study of Nanostructured Mg-H, Mg-Ni-H, and Mg-Cu-H Systems by High Pressure DSC Method*. Journal of Nanomaterials, 2013. **2013**: p. 1-7.
18. Wagemans, R.W.P., et al., *Hydrogen Storage in Magnesium Clusters: Quantum Chemical Study*. Journal of the American Chemical Society, 2005. **127**(47): p. 16675-16680.
19. Chaise, A., et al., *Enhancement of hydrogen sorption in magnesium hydride using expanded natural graphite*. International Journal of Hydrogen Energy, 2009. **34**(20): p. 8589-8596.
20. Shao, H., et al., *Hydrogen storage and thermal conductivity properties of Mg-based materials with different structures*. International Journal of Hydrogen Energy, 2014. **39**(18): p. 9893-9898.
21. Shao, H., et al., *Fabrication, hydrogen storage properties and mechanistic study of nanostructured Mg₅₀Co₅₀ body-centered cubic alloy*. Scripta Materialia, 2009. **60**(9): p. 818-821.
22. Toberer, E.S., L.L. Baranowski, and C. Dames, *Advances in Thermal Conductivity*. Annual Review of Materials Research, 2012. **42**(1): p. 179-209.
23. Sadhasivam, T., et al., *Dimensional effects of nanostructured Mg/MgH₂ for hydrogen storage applications: A review*. Renewable and Sustainable Energy Reviews, 2017. **72**: p. 523-534.
24. Li, W., et al., *Magnesium Nanowires: Enhanced Kinetics for Hydrogen Absorption and Desorption*. Journal of the American Chemical Society, 2007. **129**(21): p. 6710-6711.
25. Lu, J., et al., *Hydrogen Storage Properties of Nanosized MgH₂-0.1TiH₂ Prepared by Ultrahigh-Energy-High-Pressure Milling*. Journal of the American Chemical Society, 2009. **131**(43): p. 15843-15852.
26. Adam, F.G., et al., *Fabrication and hydrogen sorption behaviour of nanoparticulate MgH₂ incorporated in a porous carbon host*. Nanotechnology, 2009. **20**(20): p. 204005.
27. Shao, H., et al., *Preparation and hydrogen storage properties of nanostructured Mg₂Cu alloy*. Journal of Solid State Chemistry, 2005. **178**(7): p. 2211-2217.
28. Huaiyu, S., et al., *Preparation and hydrogen storage properties of Mg₂Ni intermetallic nanoparticles*. Nanotechnology, 2004. **15**(3): p. 269.
29. Shao, H., et al., *Preparation of Mg-based hydrogen storage materials from metal nanoparticles*. Journal of Alloys and Compounds, 2008. **465**(1-2): p. 527-533.
30. Shao, H., M. Felderhoff, and F. Schüth, *Hydrogen storage properties of nanostructured MgH₂/TiH₂ composite prepared by ball milling under high hydrogen pressure*. International Journal of Hydrogen Energy, 2011. **36**(17): p. 10828-10833.

31. Shao, H., et al., *Nanostructured Ti-catalyzed MgH₂ for hydrogen storage*. Nanotechnology, 2011. **22**(23): p. 235401.
32. Stampfer, J.F., C.E. Holley, and J.F. Suttle, *The Magnesium-Hydrogen System 1-3*. Journal of the American Chemical Society, 1960. **82**(14): p. 3504-3508.
33. Reilly, J.J. and R.H. Wiswall, *Reaction of hydrogen with alloys of magnesium and nickel and the formation of Mg₂NiH₄*. Inorganic Chemistry, 1968. **7**(11): p. 2254-2256.
34. Gross, K.J., et al., *Mechanically milled Mg composites for hydrogen storage the transition to a steady state composition*. Journal of Alloys and Compounds, 1996. **240**(1): p. 206-213.
35. Akiba, E., et al., *Pressure-Composition Isotherms of Mg-Ni-H₂ Alloys*. Journal of the Less-Common Metals, 1982. **83**(2): p. L43-L46.
36. Buchner, H., O. Bernauer, and W. Straub. in *Proceedings of the Second World Hydrogen Energy Conference*. 1978. Zürich: Pergamon press, Oxford.
37. Shao, H.Y., T. Liu, and X.X. Li, *Preparation of the Mg₂Ni compound from ultrafine particles and its hydrogen storage properties*. Nanotechnology, 2003. **14**(3): p. L1-L3.
38. Shao, H.Y., et al., *Hydrogen storage properties of magnesium ultrafine particles prepared by hydrogen plasma-metal reaction*. Materials Science and Engineering B-Solid State Materials for Advanced Technology, 2004. **110**(2): p. 221-226.
39. Shao, H.Y., et al., *Synthesis and hydrogen storage behavior of Mg-Co-H system at nanometer scale*. Journal of Solid State Chemistry, 2004. **177**(10): p. 3626-3632.
40. Shao, H.Y., et al., *Preparation and hydrogen storage properties of nanostructured Mg₂Cu alloy*. Journal of Solid State Chemistry, 2005. **178**(7): p. 2211-2217.
41. Shao, H., M. Felderhoff, and F. Schuth, *Hydrogen storage properties of nanostructured MgH(2)/TiH(2) composite prepared by ball milling under high hydrogen pressure*. International Journal of Hydrogen Energy, 2011. **36**(17): p. 10828-10833.
42. Berube, V., et al., *Size effects on the hydrogen storage properties of nanostructured metal hydrides: A review*. Int J Energy Res, 2007. **31**(6-7): p. 637-663.
43. Yu, X., et al., *Recent advances and remaining challenges of nanostructured materials for hydrogen storage applications*. Prog Mater Sci, 2017. **88**: p. 1-48.
44. Varin, R.A., T. Czujko, and Z. Wronski, *Particle size, grain size and γ -MgH₂ effects on the desorption properties of nanocrystalline commercial magnesium hydride processed by controlled mechanical milling*. Nanotech., 2006. **17**(15): p. 3856.
45. Huot, J., et al., *Mechanochemical synthesis of hydrogen storage materials*. Prog Mater Sci, 2013. **58**(1): p. 30-75.
46. Pozzo, M. and D. Alfè, *Hydrogen dissociation and diffusion on transition metal (= Ti, Zr, V, Fe, Ru, Co, Rh, Ni, Pd, Cu, Ag)-doped Mg(0001) surfaces*. Int J Hydrogen Energy, 2009. **34**(4): p. 1922-1930.
47. Jia, Y., et al., *Catalytic De/Hydrogenation in Mg by Co-Doped Ni and VO_x on Active Carbon: Extremely Fast Kinetics at Low Temperatures and High Hydrogen Capacity*. Adv Energy Mater, 2011. **1**(3): p. 387-393.

48. Lin, H.-J., et al., *Enhanced hydrogen desorption property of MgH₂ with the addition of cerium fluorides*. J Alloys Compd, 2015. **645**(S1): p. S392-396.
49. Barkhordarian, G., T. Klassen, and R. Bormann, *Fast hydrogen sorption kinetics of nanocrystalline Mg using Nb₂O₅ as catalyst*. Scr Mater, 2003. **49**(3): p. 213-217.
50. Cui, J., et al., *Remarkable enhancement in dehydrogenation of MgH₂ by a nano-coating of multi-valence Ti-based catalysts*. J Mater Chem A, 2013. **1**(18): p. 5603-5611.
51. Vajo, J.J., S.L. Skeith, and F. Mertens, *Reversible Storage of Hydrogen in Destabilized LiBH₄*. J Phys Chem B, 2005. **109**(9): p. 3719-3722.
52. Li, S., et al., *Synergistic hydrogen desorption properties of the 4LiAlH₄ + Mg₂NiH₄ composite*. J Alloys Compd, 2017. **697**: p. 80-85.
53. Xin, G., et al., *Promising gaseous and electrochemical hydrogen storage properties of porous Mg-Pd films under mild conditions*. Physical Chemistry Chemical Physics, 2015. **17**(20): p. 13606-13612.
54. Xin, G., et al., *Promising hydrogen storage properties and potential applications of Mg-Al-Pd trilayer films under mild conditions*. Dalton T., 2012. **41**(38): p. 11555-11558.
55. Victoria, M., et al., *Amorphous Metal-Hydrides for Optical Hydrogen Sensing: The Effect of Adding Glassy Ni-Zr to Mg-Ni-H*. ACS Sensors, 2016. **1**(3): p. 222-226.
56. Baldi, A., et al., *Destabilization of the Mg-H System through Elastic Constraints*. Phy Rev Lett, 2009. **102**(22): p. 226102.
57. Lin, H.-J., et al., *Symbiotic CeH_{2.73}/CeO₂ catalyst: A novel hydrogen pump*. Nano Energy, 2014. **9**(0): p. 80-87.
58. Lin, H.J., et al., *Phase transition and hydrogen storage properties of melt-spun Mg₃LaNi_{0.1} alloy*. Int J Hydrogen Energy, 2012. **37**(1): p. 1145-1150.
59. Lin, H.J., et al., *Hydrogen storage properties of Mg-Ce-Ni nanocomposite induced from amorphous precursor with the highest Mg content*. Int J Hydrogen Energy, 2012. **37**(19): p. 14329-14335.
60. Wu, Y., et al., *Microstructure and hydrogenation behavior of ball-milled and melt-spun Mg-10Ni-2Mm alloys*. J Alloys Compd, 2008. **466**(1-2): p. 176-181.
61. Lin, H.-J., et al., *Controlling nanocrystallization and hydrogen storage property of Mg-based amorphous alloy via a gas-solid reaction*. J Alloys Compd, 2016. **685**: p. 272-277.
62. Bowman, R.C. and B. Fultz, *Metallic Hydrides I: Hydrogen Storage and Other Gas-Phase Applications*. MRS Bulletin, 2002. **27**(09): p. 688-693.
63. Lin, H.-J., et al., *Towards easily tunable hydrogen storage via a hydrogen-induced glass-to-glass transition in Mg-based metallic glasses*. Acta Mater., 2016. **120**: p. 68-74.
64. Jiao, W., et al., *Tunable Nanoporous Metallic Glasses Fabricated by Selective Phase Dissolution and Passivation for Ultrafast Hydrogen Uptake*. Chemistry of Materials, 2017. **29**(10): p. 4478-4483.
65. Zhao-Karger, Z., et al., *Altered thermodynamic and kinetic properties of MgH₂ infiltrated in microporous scaffold*. Chem Commun, 2010. **46**(44): p. 8353-8355.

66. Fichtner, M., *Nanoconfinement effects in energy storage materials*. *Phy Chem Chem Phy*, 2011. **13**(48): p. 21186-21195.
67. Zlotea, C., et al., *Tunable synthesis of (Mg–Ni)-based hydrides nanoconfined in templated carbon studied by in situ synchrotron diffraction*. *Nano Energy*, 2013. **2**(1): p. 12-20.
68. Zhang, J., et al., *Metal Hydride Nanoparticles with Ultrahigh Structural Stability and Hydrogen Storage Activity Derived from Microencapsulated Nanoconfinement*. *Adv. Mater.*, 2017. **29**(24): p. 1700760.
69. Peru, F., et al., *Ammonia-free infiltration of NaBH₄ into highly-ordered mesoporous silica and carbon matrices for hydrogen storage*. *Journal of Alloys and Compounds*, 2013. **580**(Supplement 1): p. S309-S312.
70. Pukazhselvan, D., et al., *Hydrogen storage characteristics of magnesium impregnated on the porous channels of activated charcoal scaffold*. *International Journal of Hydrogen Energy*, 2014. **39**(35): p. 20045-20053.
71. Liu, Y., et al., *Study on hydrogen storage properties of Mg nanoparticles confined in carbon aerogels*. *International Journal of Hydrogen Energy*, 2013. **38**(13): p. 5302-5308.
72. Jia, Y., et al., *Destabilization of Mg–H bonding through nano-interfacial confinement by unsaturated carbon for hydrogen desorption from MgH₂*. *Physical Chemistry Chemical Physics*, 2013. **15**(16): p. 5814-5820.
73. Edalati, K., et al., *New nanostructured phases with reversible hydrogen storage capability in immiscible magnesium–zirconium system produced by high-pressure torsion*. *Acta Mater.*, 2016. **108**: p. 293-303.
74. Edalati, K., et al., *Formation of metastable phases in magnesium–titanium system by high-pressure torsion and their hydrogen storage performance*. *Acta Materialia*, 2015. **99**: p. 150-156.
75. Kusadome, Y., et al., *Hydrogen storage capability of MgNi₂ processed by high pressure torsion*. *Scr Mater*, 2007. **57**(8): p. 751-753.
76. Anastasopol, A., et al., *Reduced Enthalpy of Metal Hydride Formation for Mg–Ti Nanocomposites Produced by Spark Discharge Generation*. *J Am Chem Soc*, 2013. **135**(21): p. 7891-7900.
77. Vons, V.A., et al., *Low-temperature hydrogen desorption and the structural properties of spark discharge generated Mg nanoparticles*. *Acta Mater*, 2011. **59**(8): p. 3070-3080.
78. Bogdanović, B., *Magnesium hydride: A homogeneous-catalysed synthesis and its use in hydrogen storage*. *Int J Hydrogen Energy*, 1984. **9**(11): p. 937-941.
79. Zhu, Y., et al., *Enhanced hydriding kinetics of Mg-10 at% Al composite by forming Al₁₂Mg₁₇ during hydriding combustion synthesis*. *J Alloys Compd*, 2017. **712**: p. 44-49.
80. Gu, H., Y. Zhu, and L. Li, *Hydrogen storage properties of Mg–Ni–Cu prepared by hydriding combustion synthesis and mechanical milling (HCS+MM)*. *Int J Hydrogen Energy*, 2009. **34**(6): p. 2654-2660.

81. Moser, D., et al., *Structure and stability of high pressure synthesized Mg-TM hydrides (TM = Ti, Zr, Hf, V, Nb and Ta) as possible new hydrogen rich hydrides for hydrogen storage*. J Mater Chem, 2009. **19**(43): p. 8150-8161.
82. Felderhoff, M. and B. Bogdanović, *High Temperature Metal Hydrides as Heat Storage Materials for Solar and Related Applications*. International Journal of Molecular Sciences, 2009. **10**(1): p. 325-344.

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He got his PhD in inorganic chemistry in Peking University, China. He worked as a postdoc in National Institute of Advanced Industrial Science and Technology, Japan from July of 2005 to March of 2009 and in Max-Planck-Institut für Kohlenforschung, Germany from April of 2009 to April of 2011. He has published 49 scientific papers at journals such as *Nano Energy*, *Journal of Materials Chemistry A*, *Nanotechnology*, *Journal of Physical Chemistry C*, with a total of over 850 citations (Scopus, *h*-index of 18). He has given more than 45 oral presentations in international conferences and academic visits and about 25 of them are invited talks or plenary ones. He contributes to organizing sessions for international conferences such as *American Chemical Society (ACS) National Meeting 2013 Fall (Indianapolis, USA)*, *U.S. National Congress on Theoretical and Applied Mechanics (USNCTAM2014, East Lansing, USA)*, *the 1st International Young Scientists Fusion Forum (2013, Chengdu, China)*, *2016 International Conference on Small Science (Prague, Czech)*, *2016 Macau Summit on Carbon and Energy Materials (Macau, China)*, *2017 International Conference on Environmental and Energy Engineering (Suzhou, China)*, *2018 International Conference on Nanoscience & Technology (New York, USA)*. He serves as reviewer for 30 scientific journals including *Nature Communications*, *Nano Energy*, *Journal of Materials Chemistry A*, *ACS Applied Materials & Interfaces*, etc. He also serves as editorial board member for 4 Journals including *Journal of Nanomaterials*, *Current Nanomaterials*, etc. Since 2011, he is an international grant-proposal reviewer for *Romanian National Research Council*.



Dr. Huaijun Lin serves as associate professor in Jinan University, Guangzhou, China. During his PhD study, he obtained a CSC scholar and studied as a visiting student in Kyushu University, Japan from 2013 to 2014. After completing his Ph.D. degree in Materials Science and Engineering from South China University of Technology, China in 2014, he worked in Kyushu University as a Postdoctoral fellow from 2015 to 2016. Since 2017, he moved to Jinan University as associate professor. His research interests include hydrogen storage materials, functional

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