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**First-principles predictions of potential hydrogen storage materials: Nanosized Ti(core)/Mg(shell) hydrides**

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MgH$_2$ is one of the most promising hydrogen storage materials. However MgH$_2$ is thermodynamically too stable, leading to a too high desorption temperature of 300 $^\circ$C at atmospheric pressure, which is a major impediment for practical applications. In this study, aiming to tune the thermodynamic stability of the MgH$_2$, nanosized two-dimensional Mg/Ti/Mg sandwich and three-dimensional Ti(core)/Mg(shell) hydrides have been investigated by using density functional theory calculations. For both structures, four types of hydrogen atoms can be distinguished: on the surface of the Mg (H$_{surf}$), within the Mg (H$_{Mg}$), at the Mg/Ti interface (H$_{MgTi}$), and within the Ti (H$_{Ti}$). For the dehydrogenation reaction, the hydrogen desorption from the hydride is in the order H$_{surf}$, H$_{Mg}$, H$_{MgTi}$, H$_{Ti}$. The desorption energy of H$_{surf}$ is unexpectedly high. As expected, due to the well-preserved fluorite structure of the partially hydrogenated hydride, the desorption energy of H$_{Mg}$ is significantly lower than that of bulk rutile MgH$_2$. The further desorption of H$_{MgTi}$ and H$_{Ti}$ becomes more difficult due to the strong Ti-H bonding. We propose that partial hydrogenation without adsorption of H$_{surf}$ and partial dehydrogenation without desorption of H$_{Mg}$, H$_{MgTi}$, and H$_{Ti}$ would keep the fluorite symmetry with its favorable thermodynamics. The reversible hydrogen capacity (H$_{Mg}$) of the Mg/Ti/Mg sandwich structure is low, whereas the reversible hydrogen capacity of the Ti(core)/Mg(shell) is calculated to be reasonable high. Our results predicted Ti(core)/Mg(shell) structures are potential useful materials for hydrogen storage application.

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**I. INTRODUCTION**

MgH$_2$ is one of the most attractive hydrogen storage materials because it is inexpensive and light.$^{1−3}$ However, the kinetics of the hydrogen uptake and release in Mg is poor. It is generally accepted that the diffusion limitations, high oxidation sensitivity of the Mg surface, and high activation barrier of hydrogen molecule dissociation leads to poor hydrogen kinetics in Mg. Another disadvantage of MgH$_2$ is too stable, leading to too high desorption temperatures (T$_d$) at atmospheric pressure. For example, the desorption energy of MgH$_2$ is 75 kJ/mol H$_2$, i.e., 0.78 eV/H$_2$ ($T_d = 300$ $^\circ$C),$^4$ while a desorption energy of 20--50 kJ/mol H$_2$, i.e., 0.21--0.52 eV/H$_2$ ($T_d = 20$--100 $^\circ$C) is desirable. Tuning kinetics of MgH$_2$ has been achieved by means of alloying Mg with transition metals (TMs), adding catalyst and mechanical ball milling.$^5$–$^28$ Among the Mg-TM-H hydrides, Mg-Ti-H is one of the most widely investigated systems because of its tremendous potential for improving the (de)hydrogenation kinetics.$^{18}$–$^{21}$ The fcc symmetry of the Mg-Ti-H system has been claimed to be responsible for the improved kinetics.$^{19}$–$^{21}$ The structural transformation from rutile to fluorite in Mg-Ti-H has been theoretically confirmed for both bulk$^{29}$ and multilayered systems.$^{30}$

Besides the improved kinetics, tuning of the thermodynamics of Mg-Ti-H has been reported for various morphologies, i.e., nanostructured particles,$^{26}$ thin films,$^{27}$ and multilayers.$^{28}$ Nanostructured Mg-Ti-H by mixing MgH$_2$ and TiH$_2$ and ultrahigh energy high-pressure mechanical milling has been prepared by Lu et al.$^{26}$ Their results show that the dehydrogenation energy of MgH$_2$-0.1TiH$_2$ is lower than that of MgH$_2$. For the rehydrogenation of the dehydrogenated alloys, fast hydrogen absorption was also observed at room temperature. Baldi et al.$^{27}$–$^{28}$ managed to tune the thermodynamics of hydrogen absorption in the Mg-Ti-Pd system by means of elastic clamping. Their results show that the thermodynamics of hydrogen absorption in Pd-capped Mg films are strongly dependent on the Mg thickness.$^{27}$ Furthermore, Mg/Ti multilayers with various monolayer thicknesses between 0.5 and 20 nm were prepared. The layer thickness dependence of the hydrogenation properties was reported. Besides the elastic clamping effect of the Pd layer, the interface effect was also proposed to be responsible for the different thermodynamics.$^{28}$

Despite all the experimental progress, the origin of the tuned thermodynamics of Mg-H bonding is still not well understood. Theoretical studies$^{32}$–$^{37}$ have reported that using nanoparticles instead of bulk or coarse particles of hydrides can alter the thermodynamics of hydrogen uptake and release. Because the energies of both metals and hydrides change going from bulk materials to nanosized particles, the reaction thermodynamics will be affected by the size of the grains. Moreover, our previous theoretical study has shown that the structural transformation of MgH$_2$ from rutile to fluorite induced by contacting with a TM plays an important role in tuning the thermodynamics in the MgH$_2$/TMH$_2$ multilayers.$^{31}$ In MgH$_2$/TMH$_2$ multilayers, notable destabilization of Mg-H bonding could be observed with a high Ti:Mg ratio and very thin Mg layers (a few nanometers). This, however, leads to a significant reduction of the reversible hydrogen storage capacity due to the fact that parts of the hydrogen atoms are trapped in the TM. Stabilized by the promising results reported above, we consider combining the destabilized Mg-H bondings in the fluorite structure by alloying with Ti, and the surface effect in the nanosized materials. We propose that by extending the two-dimensional (2D) structure to three...
dimensions (3D), the kinetics and thermodynamics can be improved and that a larger reversible hydrogen storage capacity can be expected. To verify this hypothesis, 2D Mg/Ti/Mg sandwich and 3D Ti(core)/Mg(shell) structures have been designed and studied by large-scale density functional theory (DFT) calculations. We intend to give a prediction of the thermodynamic properties in such nanostructured materials, thus helping to design unique hydrogen storage materials.

II. STRUCTURAL MODELS AND COMPUTATIONAL METHODS

Figure 1 shows the models for the Mg/Ti/Mg sandwich and Ti(core)/Mg(shell) structures. For simplicity, the 2D slab is cut from fluorite hydride with a (100) plane and the 3D particle is cut from fluorite hydride with a cubic symmetry. Four types of hydrogen atoms can be recognized in both structures: hydrogen cut from fluorite hydride with a (100) plane and the 3D particle is constructed by putting one, two, or three atomic layers of Mg on a fixed-sized Ti slab or Ti core.

All calculations were performed using DFT as implemented in the Vienna Ab Initio Simulation Package (VASP).\(^{38,39}\) The Kohn-Sham equations were solved using a basis of plane-wave functions with a plane-wave energy cutoff of 400 eV,\(^{40}\) and using pseudopotentials\(^{41}\) to describe the core electrons. The Perdew-Wang 1991 generalized gradient approximation was used for the electron-exchange correlation potential.\(^{42}\) For the 2D Mg/Ti/Mg sandwich structure (Fig. 2), \((2 \times 2)\) supercells were always used. A total of \(7 \times 7 \times 1\) \(k\) points were used to model the Brillouin zone. For the 3D Ti(core)/Mg(shell) structures, \(k\)-space integration is restricted to the \(\Gamma\) point only. Since periodic boundary conditions are involved, the size of the supercell containing the 2D nanoslab and 3D nanoparticle was chosen such that the distance between atoms of the periodic images exceeded 15 Å. This was sufficient to avoid interaction of the cluster with its images. Therefore, the calculations of \(\text{Ti}_{14}\text{Mg}_{48}\), \(\text{Ti}_{14}\text{Mg}_{158}\), and \(\text{Ti}_{14}\text{Mg}_{350}\) (shown in Fig. 3) have been performed using a cubic supercell with sizes of \(22 \times 22 \times 22\), \(30 \times 30 \times 30\), and \(38 \times 38 \times 38\) Å\(^3\) respectively. For all structures, the lattice parameters, the volume, and the atom positions were allowed to relax.

III. RESULTS AND DISCUSSIONS

This section is divided into two parts. In the first part, the Mg/Ti/Mg sandwich structure is studied. The absorption sites and concentration of \(H_{\text{surf}}\) and the absorption and desorption sequences of the four types of hydrogen atoms are investigated. After that, the size dependence of the dehydrogenation energies is studied. In the second part, extending the 2D structure to a 3D one, the Ti(core)/Mg(shell) structure is studied in a similar manner to the sandwich structure. We focus on the tuned thermodynamics, in particular, the relations between the thermodynamics and the structures and the Ti:Mg ratios. Furthermore, an oversaturation of the Ti(core)/Mg(shell) structure with extra \(H_{\text{surf}}\) is studied by electronic and geometric structure calculations. Finally, the reversible capacities are determined and compared to the 2D structure.

A. Mg/Ti/Mg sandwich structure

1. \(H_{\text{surf}}\)

Figure 4 displays the top view of the optimized Mg/Ti/Mg sandwich structure with five different distributions of \(H_{\text{surf}}\). After optimization, the hydrogen molecules in structure (a) and (b) have been “pushed” out from the Mg surfaces. The optimized Mg-H\(_2\) distances are 3.79 and 3.76 Å for (a) and (b), respectively. The desorption energies of these hydrogen molecules are nearly zero. This indicates that molecular hydrogen does not form chemical bonds with the Mg surface. For atomic hydrogen with a concentration of \(H/M = 2\) shown in (c), half of the hydrogen atoms have associated to molecular hydrogen after optimization. These hydrogen molecules are far away from the Mg surface with a distance of \(\sim 3.50\) Å. The remaining half of the hydrogen atoms are located closely to the Mg surface at short bridge sites. The optimized structures of (d) and (e) both demonstrate that short bridge sites with a concentration of \(H/M = 1\) is the most stable structure. Altogether, considering two Mg surfaces per 2D slab, a hydrogen concentration of \(H/M = 2\) for the whole system can be obtained. Therefore, the possibility of the oversaturated hydride can be excluded.

2. Hydrogen absorption and desorption sequences

To study the different thermodynamic properties for the four types of hydrogen atoms, hydrogen absorption and desorption energies in the Mg/Ti/Mg sandwich structure [\(\text{Ti}_{12}\text{Mg}_{32}\text{H}_x\) in Fig. 2(b)] have been calculated according to the following equations,

\[
\Delta E_{H_{\text{absorption}}} = E_{\text{Mg}, \text{Ti}_{1-\text{H}}x} - E_{\text{Mg}, \text{Ti}_{1-x}H} - \frac{z}{2} E_{\text{H}_2}, \tag{1}
\]

\[
\Delta E_{H_{\text{desorption}}} = E_{\text{Mg}, \text{Ti}_{1-x}H} + \frac{z}{2} E_{\text{H}_2} - E_{\text{Mg}, \text{Ti}_{1-x}H_{x+z}}, \tag{2}
\]

where \(E_{\text{Mg}, \text{Ti}_{1-x}H}\) and \(E_{\text{Mg}, \text{Ti}_{1-x}H_{x+z}}\) are the total energy of \(\text{Mg}_x\text{Ti}_{1-x}H_x\) and \(\text{Mg}_x\text{Ti}_{1-x}H_{x+z}\) normalized to the number of metal atoms.

The hydrogen absorption and desorption sequences are determined by comparing the hydrogen absorption and desorption energies at different hydrogen locations. The calculated energies are summarized in Table I. For instance,
FIRST-PRINCIPLES PREDICTIONS OF POTENTIAL...

\[ \text{FIG. 2. (Color online) Optimized 2D Mg/Ti/Mg sandwich alloys and their fully and partially hydrogenated hydrides involved in the (de)hydrogenation processes. For each Ti/Mg composition, the structures from the left-hand side to the right-hand side indicate the dehydrogenation process.} \]

\[ \text{Ti}_{24}\text{Mg}_{32}\text{H}_{112-16} \] denotes that 16 hydrogen atoms are removed from each type of hydrogen location in the Ti\(_{24}\text{Mg}_{32}\text{H}_{112}. \] Four types of hydrogen are considered and the desorption energy of H\(_{\text{surf}}\) is the lowest, therefore H\(_{\text{surf}}\) will desorb first. After the desorption of H\(_{\text{surf}}\), Ti\(_{24}\text{Mg}_{32}\text{H}_{96-32}\) denotes desorption of 32 hydrogen atoms of H\(_{\text{Mg}}\), H\(_{\text{MgTi}}\), or H\(_{\text{Ti}}\) from Ti\(_{24}\text{Mg}_{32}\text{H}_{96}. \) The desorption energy of H\(_{\text{Mg}}\) is the lowest, therefore it will desorb secondly. When there are only H\(_{\text{MgTi}}\) and H\(_{\text{Ti}}\) left, H\(_{\text{MgTi}}\) will desorb before H\(_{\text{Ti}}\). Therefore, for the dehydrogenation reaction, the desorption of hydrogen follows the order of H\(_{\text{surf}}\), H\(_{\text{Mg}}\), H\(_{\text{MgTi}}\), and H\(_{\text{Ti}}\). For the stepwise dehydrogenation energies are 1.15 eV/H\(_2\) for H\(_{\text{surf}}\), 0.38 eV/H\(_2\) for H\(_{\text{Mg}}\), 1.30 eV/H\(_2\) for H\(_{\text{MgTi}}\), and 1.10 eV/H\(_2\) for H\(_{\text{Ti}}\). The desorption energy of H\(_{\text{surf}}\) is surprisingly high. They are many higher than the hydrogen desorption energy in bulk MgH\(_2\) (0.65 eV/H\(_2\)).\(^{31}\)

After the desorption of H\(_{\text{surf}}\), the desorption of H\(_{\text{Mg}}\) becomes much easier with very low desorption energy. As expected, after the desorption of H\(_{\text{surf}}\) and H\(_{\text{Mg}}\), the desorption of H\(_{\text{MgTi}}\) and H\(_{\text{Ti}}\) becomes more difficult due to the introduction of strong Ti-H bonding. The absorption sequence was determined in a similar manner: The location with the lowest absorption energy (H\(_{\text{Ti}}\)) absorbs hydrogen first; after the absorption of the H\(_{\text{Ti}}\), the absorption of the H\(_{\text{MgTi}}\) is the most favorable in the remaining three. The absorption sequence is calculated to be the opposite to the desorption sequence: H\(_{\text{Ti}}\), H\(_{\text{MgTi}}\), H\(_{\text{Mg}}\), H\(_{\text{surf}}\).

3. The size dependence of the dehydrogenation energies

The different thermodynamic properties of the four types of hydrogen species predicted above indicates the potential to tune the thermodynamics of dehydrogenation reaction of the 2D Mg/Ti/Mg sandwich structure. In particular, the populations of different types of hydrogen depend highly on the size and composition of the structure. Average and stepwise dehydrogenation energies of the Ti\(_{24}\text{Mg}_{16}\text{H}_{80}\) [Fig. 2(a)] and Ti\(_{24}\text{Mg}_{48}\text{H}_{144}\) [Fig. 2(c)] have been calculated and compared to those of the Ti\(_{24}\text{Mg}_{32}\text{H}_{112}\) [Fig. 2(b)] studied in Sec. III A 2. The calculated hydrogen desorption sequence of H\(_{\text{surf}}\), H\(_{\text{Mg}}\), H\(_{\text{MgTi}}\), and H\(_{\text{Ti}}\) in Sec. III A 2 were applied.

As one can see in Table II, the dehydrogenation energies of all the three structures with the desorption of H\(_{\text{surf}}\) are surprisingly high. The reason will be explained further with the structural analyses in Sec. III B 2. Similar to that of Ti\(_{24}\text{Mg}_{32}\text{H}_{112}\), the desorption of H\(_{\text{Mg}}\) for Ti\(_{24}\text{Mg}_{32}\text{H}_{112}\) is 1.15 eV/H\(_2\)

<table>
<thead>
<tr>
<th>Desorption</th>
<th>H(_{\text{surf}})</th>
<th>H(_{\text{Mg}})</th>
<th>H(_{\text{MgTi}})</th>
<th>H(_{\text{Ti}})</th>
<th>Absorption</th>
<th>H(_{\text{surf}})</th>
<th>H(_{\text{Mg}})</th>
<th>H(_{\text{MgTi}})</th>
<th>H(_{\text{Ti}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(<em>{24}\text{Mg}</em>{32}\text{H}_{112-16})</td>
<td>1.15</td>
<td>1.56</td>
<td>1.45</td>
<td>1.60</td>
<td>Ti(<em>{24}\text{Mg}</em>{32}\text{H}_{96-16})</td>
<td>0.09</td>
<td>0.48</td>
<td>-1.10</td>
<td>-1.21</td>
</tr>
<tr>
<td>Ti(<em>{24}\text{Mg}</em>{32}\text{H}_{96-32})</td>
<td>-</td>
<td>0.38</td>
<td>1.40</td>
<td>1.49</td>
<td>Ti(<em>{24}\text{Mg}</em>{32}\text{H}_{96-16})</td>
<td>-0.43</td>
<td>-0.19</td>
<td>-1.39</td>
<td>-</td>
</tr>
<tr>
<td>Ti(<em>{24}\text{Mg}</em>{32}\text{H}_{48-32})</td>
<td>-</td>
<td>-</td>
<td>1.30</td>
<td>1.38</td>
<td>Ti(<em>{24}\text{Mg}</em>{32}\text{H}_{96-16})</td>
<td>-0.31</td>
<td>-0.36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti(<em>{24}\text{Mg}</em>{32}\text{H}_{32-32})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.10</td>
<td>Ti(<em>{24}\text{Mg}</em>{32}\text{H}_{96-16})</td>
<td>-1.11</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
FIG. 3. (Color online) Optimized 3D Ti(core)/Mg(shell) alloys and their fully and partially hydrogenated hydrides involved in the (de)hydrogenation processes. For each Ti/Mg composite, the structures from the left-hand side to the right-hand side indicate the dehydrogenation process.

(0.36 eV/H₂) is very low and after the desorption of Hsurf and HMg. Because of the strong Ti-H bonding, the desorption energies of HMgTi and HTi are always larger than the rutile MgH₂ (0.65 eV/H₂). To save computational time, we combined the desorption of HMgTi with HTi and only the average desorption of the two was calculated.

Comparing the three hydrides, one can notice the particle size dependence of the hydrogen thermodynamics. On the one hand, the average dehydrogenation energies of all the hydrogen atoms are decreasing with increasing size of the Mg layer, i.e., from 1.22, 0.97, and 0.91 eV/H₂ for Ti24Mg16H80, Ti24Mg32H112, and Ti24Mg48H144, respectively. This can be explained as follows: The larger the population of the Mg-related sites, and the smaller the average hydrogen desorption energy. On the other hand, the desorption energy of Hsurf increases with increasing Mg layer thickness, from 0.95 eV/H₂ for Ti24Mg16H80, to 1.15 eV/H₂ for Ti24Mg32H112, to 1.42 eV/H₂ for Ti24Mg48H144. The reason for the unexpectedly high desorption energies of Hsurf and the size dependence will be explained together with the 3D Ti(core)/Mg(shell) structure in Sec. III B 2.

It is worth noting that, for Ti24Mg32H112 and Ti24Mg48H144, the desorption energies of HMg (0.38 and 0.36 eV/H₂) are much lower than that of bulk rutile MgH₂ (0.65 eV/H₂). The desorption energy of HMg is low because the HMg always occupy the tetrahedral sites in the partially dehydrogenated fluorite type hydrides [see Figs. 2(b)(ii) and 2(c)(ii)]. This is favorable for hydrogen storage application. However, the population of these destabilized hydrogen atoms (HMg) is low: 1.7 wt % for Ti24Mg32H112 and 2.7 wt % for Ti24Mg48H144. To obtain a larger population of HMg, we extend the 2D Mg/Ti/Mg sandwich structure to a 3D Ti(core)/Mg(shell) structure in the next section.

### TABLE II. Stepwise and average dehydrogenation energies (in eV/H₂) of three Mg/Ti/Mg sandwich hydrides with different particle sizes and compositions.

<table>
<thead>
<tr>
<th>Fig. 2 Mg/Ti/Mg sandwich</th>
<th>Hsurf</th>
<th>HMg</th>
<th>HMgTi+HTi</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Ti24Mg16H80</td>
<td>0.95</td>
<td>—</td>
<td>1.29</td>
<td>1.22</td>
</tr>
<tr>
<td>(b) Ti24Mg32H112</td>
<td>1.15</td>
<td>0.38</td>
<td>1.31</td>
<td>0.97</td>
</tr>
<tr>
<td>(c) Ti24Mg48H144</td>
<td>1.42</td>
<td>0.36</td>
<td>1.33</td>
<td>0.91</td>
</tr>
</tbody>
</table>

**B. Ti(core)/Mg(shell) structure**

Because the same hydrogen locations can be found in the 2D and 3D structures, we assume that the adsorption sites of Hsurf, and absorption and desorption sequences found in the 2D structure, also apply for the 3D Ti(core)/Mg(shell) structure. However, it should be emphasized at this point that in the 2D structure, the Mg surfaces are infinitely extended two dimensionally. When hydrogen adsorbs on the Mg surface with a ratio of H/M = 1, an overall ratio of H/M = 2 can always

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be obtained. However, for the Ti(core)/Mg(shell) structure slightly different situations were observed. During optimization, the hydrogen atoms adsorbed on the crystallographic facets were indeed stabilized at short bridge (sb) sites, whereas hydrogen atoms on the edges migrated from the sb to the long bridge (lb) sites. The number of sb and lb sites depend highly on the configuration of the core-shell alloy. For instance, 36 (24sb + 12lb), 144 (108sb + 36lb), and 228 (192sb + 36lb) sites are available for hydrogen atoms on the surfaces of Ti$_{14}$Mg$_{48}$, Ti$_{14}$Mg$_{158}$, and Ti$_{14}$Mg$_{350}$ (see Fig. 3), respectively. Together with H$_{Mg}$, H$_{MgTi}$, and H$_{Ti}$, the fully hydrogenated hydrides are Ti$_{14}$Mg$_{48}$H$_{124}$, Ti$_{14}$Mg$_{158}$H$_{360}$, and Ti$_{14}$Mg$_{350}$H$_{740}$, i.e., H/M = 2 or slightly larger than 2. Four single-point calculations with a concentration of Ti$_{14}$Mg$_{158}$H$_{352}$ (where eight hydrogen atoms of each type were taken out from Ti$_{14}$Mg$_{158}$H$_{360}$) were calculated. The results show the same desorption sequence with what was predicted for the 2D sandwich structure. Therefore, we are confident that the 3D (de)hydrogenation process is similar to that of the 2D structure.

1. The stepwise dehydrogenation energies

The average and stepwise dehydrogenation energies were calculated in the same manner as for the 2D structure. As one can see in Table III, the trends found for the energies in the 2D structure are reproduced: The desorption energies of H$_{surf}$ are very high (except that of Ti$_{14}$Mg$_{48}$H$_{124}$); after the desorption of H$_{surf}$, the desorption energies of H$_{Mg}$ become lower than that of bulk MgH$_2$; the desorption of H$_{MgTi}$ + H$_{Ti}$ become more difficult due to the strong Ti-H bondings. It is worth noting that for Ti$_{14}$Mg$_{158}$H$_{360}$ and Ti$_{14}$Mg$_{350}$H$_{740}$, the desorption energies of H$_{Mg}$ (0.39 and 0.27 eV/H$_2$) are much lower than that of the rutile MgH$_2$ (0.65 eV/H$_2$). They are within the desired thermodynamics range and even lower than the lowest H$_{Mg}$ desorption energy of 0.44 eV/H$_2$ predicted for the MgH$_2$/TiH$_2$ multilayers. The desorption energy of H$_{Mg}$ is low because the H$_{Mg}$ atoms always occupy the tetrahedral sites in the partially dehydrogenated hydrides [shown in Figs. 3(b)(ii), and 3(c)(ii)]. This is favorable for hydrogen storage applications.

Comparing the three hydrides, one can again notice the same size dependence of the energies to that of the 2D structure. On the one hand, the average dehydrogenation energies of all hydrogen atoms are decreasing with increasing size of the Mg shell, i.e., 0.80, 0.68, and 0.65 eV/H$_2$ for Ti$_{14}$Mg$_{48}$H$_{124}$, Ti$_{14}$Mg$_{158}$H$_{360}$, and Ti$_{14}$Mg$_{350}$H$_{740}$, respectively. On the other hand, the desorption energy of H$_{surf}$ increases with increasing size of the Mg shell, from 0.59 eV/H$_2$ for Ti$_{14}$Mg$_{48}$H$_{124}$, to 1.11 eV/H$_2$ for Ti$_{14}$Mg$_{158}$H$_{360}$, to 1.42 eV/H$_2$ for Ti$_{14}$Mg$_{350}$H$_{740}$. The reason for the unexpectedly high values and the size dependence of the desorption energies of H$_{surf}$ will be explained by comparing the structures of the fully and partially hydrogenated hydrides in Sec. III B 2.

2. Structures

To explain the trend found in the dehydrogenation energies of H$_{surf}$ in both 2D and 3D structures, Figs. 2 and 3 should be referred. As one can see, for the fully hydrogenated hydrides, the H$_{surf}$ atoms do not occupy the perfect short bridge site. The hydrogen atoms at the subsurface are also dislocated from perfect tetrahedral sites. These distortions are similar with the deformations which were found in the Mg/Ti multilayers, where with the increasing Mg thickness the fluorite structure tends to change into rutile. For instance, approximately half of the H$_{Mg}$ atoms are closely bonded to H$_{surf}$. These atoms are ∼0.2–0.4 Å closer to the surface Mg than the other half, which are less affected by H$_{surf}$. This effect extends from one layer to another through the H-H bonding, i.e., from the subsurface of the Mg layer to the Mg/Ti interface. It becomes minor for H$_{MgTi}$ and H$_{Ti}$ atoms as they are stabilized by the strong Ti-H bondings.

<table>
<thead>
<tr>
<th>Ti(core)/Mg(shell) Structure</th>
<th>H$_{surf}$</th>
<th>H$_{Mg}$</th>
<th>H$<em>{MgTi}$ + H$</em>{Ti}$</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>{14}$Mg$</em>{48}$H$_{124}$</td>
<td>0.59</td>
<td>—</td>
<td>0.95</td>
<td>0.80</td>
</tr>
<tr>
<td>Ti$<em>{14}$Mg$</em>{158}$H$_{360}$</td>
<td>1.11</td>
<td>0.39</td>
<td>0.90</td>
<td>0.68</td>
</tr>
<tr>
<td>Ti$<em>{14}$Mg$</em>{350}$H$_{740}$</td>
<td>1.42</td>
<td>0.27</td>
<td>0.80</td>
<td>0.65</td>
</tr>
</tbody>
</table>
bonding. Therefore, the structural deformations depend on the size of the Mg layer. The thicker the layer, the more H$_{Mg}$ atoms dislocated by H$_{surf}$. The structural deformation is direct evidence that H$_{Mg}$ atoms are stabilized upon forming the H-H bonding by the absorption of H$_{surf}$. This also explains why H$_{Mg}$ becomes unstable upon the desorption of H$_{surf}$ in Sec. III A 2.

However, after the desorption of H$_{surf}$ from the Mg surface, H$_{Mg}$ atoms will relocate at the tetrahedral sites (see Figs. 2 and 3). A well-defined fcc structure is formed again. The fcc symmetry can be preserved in the continuing dehydrogenation process. The desorption energies of H$_{surf}$ were calculated by comparing the energies of the fully hydrogenated and partially hydrogenated hydrides. In this case, they consist of the energy cost of the breaking of the Mg-H$_{surf}$ bond and the energy difference of the Mg-H$_{Mg}$ bonding between the fully and partially hydrogenated hydrides. The latter closely relates to the population of H$_{Mg}$. Thus the thicker the Mg layer, the more H$_{Mg}$ is stabilized in the fully hydrogenated hydrides, and the larger the H$_{surf}$ desorption energy.

3. Oversaturation of the Ti(core)/Mg(shell) structure

The hydrogen storage capacities in nanosized materials can vary from their corresponding bulk materials. For instance, Kobayashi et al. reported that the capacity of the Pd-Pt nanoparticles with a Pt content of 8–21 at. % was higher than that of pure Pd nanoparticles. The amount of hydrogen absorption is controllable by altering the alloy compositions of Pd and Pt. Wagemans et al. predicted that small MgH$_2$ particles (smaller than Mg$_{13}$H$_{30}$) have the potential to take up 10%–15% extra hydrogen. They proposed these extra hydrogen atoms are less strongly adsorbed onto the surface of the cluster than the hydrogen absorbed within the cluster. The above results suggest oversaturation of the surface metal.

To verify the potential extra hydrogen in the present nanosized Ti(core)/Mg(shell) alloys, an oversaturation of the Ti$_{14}$Mg$_{158}$H$_{512}$ alloy has been studied. Figure 5(a) shows the initial structure of Ti$_{14}$Mg$_{158}$H$_{512}$ (H/M = 2.98), i.e., the fluorite structure with hydrogen terminations. As shown in Fig. 5(b), during the geometric optimization the hydrogen atoms on the Mg surface (H$_{surf}$) did not dramatically distort the structure of the alloy, but formed different types of hydrogen species. They can be classified as the hydrogen dimer (H-H), hydrogen trimer (H-H-H), hydrogen atoms on facets (H$_{face}$), and hydrogen atoms at vertices (H$_{ver}$ and H$_{ver2}$). Except for the hydrogen atoms on the Mg shell surface, the other ones occupy different tetrahedral sites within the Mg shell (H$_{Mg}$), at the Ti/Mg interface (H$_{MgTi}$), and within the Ti core (H$_{Ti}$).

To study the hydrogen bonding properties, the partial density of states (PDOS) of all types of hydrogen atoms in Ti$_{14}$Mg$_{158}$H$_{512}$ have been calculated [see Fig. 5(c)]. In the PDOS plot, a sharp peak ∼−7.5 eV can be found for the hydrogen dimer. The extremely localized density clearly indicates that no chemical bonds are formed between hydrogen molecules and the alloy. In fact, the hydrogen molecules are “pushed” out of the Mg surface with distances of 2.42 Å (facets) and 2.36 Å (edges), respectively. At vertices, each Mg atom is surrounded by one H$_{ver}$ and three H$_{verb}$. The H$_{ver}$ is very close to the Mg with a distance of 1.71 Å, whereas the other three H$_{verb}$ are further with a distance of 1.90 Å.

The overlap of PDOS of H$_{ver}$ and H$_{ver2}$ ∼−6 eV suggests relatively strong bonding between H$_{ver}$ (light blue) and H$_{ver2}$ (dark blue). Moreover, the sharp main peaks of these two indicate barely any bonds formed with the alloys. A similar overlap of the PDOS can be found for the hydrogen trimer but with relatively broader main peaks than the dimer. This indicates that the chemical bonding is mainly localized within the trimer and hardly between the alloy and the trimer. From the structural and electronic analyses above, we conclude that the nonbonding or weak bonding of the hydrogen (trimer, dimer, and the ones on the vertexes) with the Mg surface is a direct consequence of the artificial oversaturation of the alloy. The Ti$_{14}$Mg$_{158}$H$_{512}$ (H/M = 2.98) is not a stable hydride. This agrees with the conclusion drawn for the Mg/Ti/Mg sandwich structure in Sec. III A 1.

4. Reversible capacity

According to the calculated energies in Secs. III A 3 and III B 1, the very stable H$_{surf}$, H$_{MgTi}$, and H$_{Ti}$ prohibits the Mg/Ti/Mg sandwich and Ti(core)/Mg(shell) structures from being used for hydrogen storage materials. However, if one refers to the hydrogenation and dehydrogenation processes in Figs. 2 and 3, one can notice the adsorption of H$_{surf}$ and the desorption of H$_{MgTi}$ + H$_{Ti}$ are the last steps in the hydrogenation and dehydrogenation reactions, respectively. Therefore, partial hydrogenation without absorption of H$_{surf}$ and partial dehydrogenation without the desorption of H$_{MgTi}$ + H$_{Ti}$ would preserve the fluorite symmetry of the core-shell structure and only H$_{Mg}$ with desirable thermodynamic. Partial operation
means that only HMg will be reversible in the hydrogen cycles. Such reversible hydrogen capacities are estimated to be reasonable high: 3.3 and 4.8 wt % for Ti14Mg158H360 and Ti14Mg350H740, respectively. They are much higher than the reversible capacity of 1.4 wt % in the Mg/Ti multilayers with a HMgH2 desorption energy of 0.44 eV/H2,31 and also higher than the ones predicted in the Mg/Ti/Mg sandwich structures in Sec. III A 3 (1.7 and 2.7 wt %).

IV. CONCLUSIONS

Hydrogen storage properties of nanosized 2D Mg/Ti/Mg sandwich and 3D Ti(core)/Mg(shell) hydrides have been studied using large-scale DFT calculations. For both structures, four types of hydrogen atoms can be distinguished in the Ti(core)/Mg(shell) hydrides: Hsurf, HMg, HMgTi, and HTi. For the hydrogenation reaction, the hydrogen absorption in the alloys is in the order of Hsurf, HMg, HMgTi, and HTi. For the dehydrogenation reaction, the hydrogen desorption is in the reverse order. The desorption energies of Hsurf are calculated to be high. The reason is the structural transformation from fluorite to a deformed fluorite structure upon the adsorption of Hsurf. In other words, the absorption of Hsurf induces dislocation of HMg and stabilizes the hydrides. This stabilization effect increases with increasing thickness of the Mg layer. Due to the well-preserved fluorite structure of the partially hydrogenated hydrides, the desorption energies of HMg are significantly lower than that of bulk MgH2. This is favorable for hydrogen storage applications. But the further desorption of HMgTi and HTi is more difficult than that of bulk MgH2 due to the strong Ti-H bonding. Furthermore, oversaturation of the 3D Ti(core)/Mg(shell) structures is studied. Both the geometric and electronic structure analyses show that the oversaturation of the structure is not stable.

Based on the observed thermodynamic properties, partial hydrogenation without the adsorption of Hsurf and partial dehydrogenation without the desorption of HMgTi and HMgTi is proposed to preserve the fluorite structure of the hydride with desired thermodynamics. However, this leads to a reduction of the reversible hydrogen capacity. The reversible hydrogen capacity (HMg) of the Mg/Ti/Mg sandwich structures are low: 1.7 wt % for Ti24Mg32H112 and 2.7 wt % for Ti24Mg48H144. Those of the Ti(core)/Mg(shell) structures are estimated to be reasonable high: 3.3 and 4.8 wt % for Ti14Mg158H360 and Ti14Mg350H740, respectively. Our results indicate that the nanosized Ti(core)/Mg(shell) hydrides are very promising hydrogen storage materials with favorable thermodynamics and reasonable hydrogen capacity.