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Hydrogen Release and Uptake of MgH₂ Modified by Ti₃CN MXene

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Abstract: MgH₂ has a high hydrogen content of 7.6 wt%, and possesses good reversibility under
normal conditions. However, pristine MgH₂ requires a high temperature above 300 °C to release
hydrogen, with very slow kinetics. In this work, we utilized Ti₃CN MXene to reduce the operating
temperature and enhance the kinetics of MgH₂. The initial temperature of MgH₂ decomposition can
be lowered from 322 °C for pristine MgH₂ to 214 °C through the employment of Ti₃CN. The desorbed
MgH₂ + 7.5 wt% Ti₃CN can start absorption at room temperature, while the desorbed pristine MgH₂
can only start absorption at 120 °C. The employment of Ti₃CN can significantly improve the hydrogen
release kinetics of MgH₂, with the desorption activation energy decreasing from 121 to 80 kJ mol⁻¹.
Regarding thermodynamics, the desorption enthalpy changes of MgH₂ and MgH₂ + 7.5 wt% Ti₃CN
were 79.3 and 78.8 kJ mol⁻¹, respectively. This indicates that the employment of Ti₃CN does not
alter the thermal stability of MgH₂. Phase evolution studies through the use of X-ray diffraction
and electron diffraction both confirm that Ti₃CN remains stable during the hydrogen release and
uptake process of the composite. This work will help understand the impact of a transition metal
carbonitride on the hydrogen storage of MgH₂.

Keywords: hydrogen storage materials; magnesium hydride; transition metal carbonitride; 2D materials;
layered materials

1. Introduction

Hydrogen energy is acknowledged as an ideal strategy to solve energy shortages and
environmental pollution issues. However, hydrogen under ambient conditions is a gas of
low density (0.089 kg m⁻³) [1]. In addition, it is flammable and combustible with a wide
explosion limit of 4—75 vol%. Therefore, the safe and compact storage of hydrogen is an
important issue when utilizing hydrogen energy on a large scale [2—4].

Solid-state hydrogen storage, with the hydrogen bonded in a hydrogen storage ma-
terial, is a good method to store hydrogen since it has a very large capacity (>50 kg m⁻³). In
addition, the method is safe since it can be operated under low hydrogen pressure
(generally <5 MPa). Construction of high-performance materials for hydrogen storage is
the key issue in developing a solid-state hydrogen storage system [5—11].

MgH₂ has attracted extensive attention as a material for hydrogen storage due to
its large capacity of 7.6 wt% and the ability to reversibly store hydrogen [12—14]. In
addition, there is an abundant resource of Mg on Earth, which makes large-scale application possible. However, MgH₂ with high thermal stability requires a high temperature to desorb hydrogen. Moreover, the hydrogen sorption process is very slow for MgH₂ when the temperature is not high enough. These two drawbacks have severely limited the practical application of MgH₂. Constructing nanoscale Mg-based materials [12,15–20], alloying Mg with other metals [8,21–24], or introducing additives [25–38] are the commonly utilized strategies to modify the hydrogen sorption properties of MgH₂.

In the past decade, MXenes (transition metal carbides/nitrides with layered structures) have received much attention in catalysis, energy storage, and conversion. MXene has also been demonstrated to show the positive impact on MgH₂ [35,39–47]. In 2016, Liu et al. [47] first reported the enhancing impact of Ti₃C₂ MXene on MgH₂. It was shown that the employment of 7 wt% Ti₃C₂ can reduce the starting hydrogen desorption temperature of MgH₂ to 180 °C. Li et al. [44] used Ti₂C MXene to reduce the temperature of MgH₂ by 37 °C. It was suggested that the Ti elements with multivalences will enhance the electron transfer during hydrogen sorption. Lu et al. [31] showed that VₓC MXene can tailor both the kinetics and thermodynamics of MgH₂. Liu et al. [40] demonstrated that the hybrid of Ti₃C₂ and VₓC MXenes exhibits a synergistic impact on MgH₂. The starting temperature of the hydrogen release of MgH₂–Ti₃C₂/VₓC can be reduced by 140 °C. Bimetallic MXene which contains two transition metals also has a good enhancing impact on MgH₂. For example, Shen et al. [46] reported that MgH₂ + 10 wt% (Ti₀5.5V₀5.5)C₂ can start desorption at 196 °C. Wang et al. [42] displayed that NbTiC MXene reduces the starting hydrogen desorption temperature of MgH₂ to 195 °C. It has been supposed by many researchers that the unique layered structures and the active transition metals contained within both contribute to the enhanced hydrogen storage properties of MgH₂ [40,42–44,46,47].

Based on the above introduction, MXene materials have shown excellent enhancing influence on MgH₂. However, the studies mainly focus on carbides. The impact of transition metal nitrides or carbonitrides on MgH₂ is not clear currently. In this work, we first synthesized a layered transition metal carbonitride (Ti₃CN MXene) and then used it to modify the hydrogen sorption properties of MgH₂. The hydrogen release and uptake kinetics and thermodynamics of MgH₂ modified by Ti₃CN MXene will be investigated. Microstructures will be studied to reveal the role of Ti₃CN MXene in modifying MgH₂.

2. Results

Ti₃CN MXene was synthesized by the exfoliation of Ti₃AlCN MAX (hexagonal layered transition metal carbides and nitrides). A hydrofluoric acid solution was used to remove the Al layers from Ti₃AlCN to synthesize the layered Ti₃CN MXene. Figure 1a shows the XRD spectrum of Ti₃AlCN MAX and Ti₃CN MXene. The diffraction peak of the (002) crystalline plane shifting to a lower angle indicates the exfoliation of Ti₃AlCN MAX to form the layered Ti₃CN MXene. The SEM picture in Figure 1b indicates that Ti₃CN MXene has a layered structure. In Figure 1c, the elemental mappings show that the Ti, C, and N elements are all distributed uniformly in the material. Some traces of the Al element were also observed in the material. The above characteristics indicate the successful synthesis of the layered Ti₃CN MXene.

The Ti₃CN MXene was mixed with MgH₂ by ball milling to obtain MgH₂ + m wt% Ti₃CN (m = 0, 5, 7.5, 10) composites. Figure 2a shows the hydrogen release curves of the MgH₂ + m wt% Ti₃CN (m = 0, 5, 7.5, 10) composites when the temperature was increased from room temperature (RT) to about 400 °C at 2 °C min⁻¹. The as-milled MgH₂ without additive starts desorbing hydrogen at 322 °C and could offer a capacity of 7.0 wt% when the temperature reached 400 °C. Excitingly, the addition of Ti₃CN can significantly lower the starting temperature of MgH₂ desorption to 214 °C. This means a reduction of 108 °C in the starting temperature. The 7.5 wt% Ti₃CN-doped MgH₂ has a slightly lower hydrogen desorption temperature than the 5 wt% Ti₃CN-doped MgH₂. However, further increasing the Ti₃CN content to 10 wt% does not further reduce the temperature of MgH₂ but will slightly reduce the capacity of the composite. Considering achieving both low temperature
and high capacity, the MgH$_2$ with the addition of 7.5 wt% of Ti$_3$CN was selected for further absorption studies. Figure 2b shows the hydrogen absorption curves of the desorbed MgH$_2$ + 7.5 wt% Ti$_3$CN composite and the pristine MgH$_2$ at 4 MPa H$_2$. During absorption, the temperature was increased from RT to 400 °C at 2 °C min$^{-1}$. The desorbed MgH$_2$ starts to absorb hydrogen at about 120 °C and could absorb 7.4 wt% H$_2$ after the temperature was ramped to 400 °C. It is exciting that the desorbed MgH$_2$ + 7.5 wt% Ti$_3$CN sample can start to absorb hydrogen at RT and absorb 7.0 wt% H$_2$ at 400 °C. Therefore, Ti$_3$CN MXene can significantly improve the non-isothermal hydrogen desorption and absorption performance of MgH$_2$.

![Figure 1](image1.jpg)

Figure 1. (a) XRD spectrum of Ti$_3$AlCN and Ti$_3$CN. (b) SEM image of Ti$_3$CN. (c) EDS elemental distributions of Ti$_3$CN.

![Figure 2](image2.jpg)

Figure 2. (a) Hydrogen release curves of MgH$_2$ + m wt% Ti$_3$CN (m = 0, 5, 7.5, 10) with the temperature rising from RT to 400 °C at 2 °C min$^{-1}$. (b) Hydrogen uptake curves of MgH$_2$ and MgH$_2$ + 7.5 wt% Ti$_3$CN at 6 MPa H$_2$ with the same temperature program as (a).
The hydrogen release kinetics of MgH$_2$ and MgH$_2$ + 7.5 wt% Ti$_3$CN were studied by testing the isothermal hydrogen desorption curves, as shown in Figure 3a,d, respectively. The MgH$_2$ without an additive can achieve fast kinetics only at a temperature higher than 350 °C. However, the MgH$_2$ + 7.5 wt% Ti$_3$CN composite has fast hydrogen desorption kinetics even at a lower temperature below 300 °C. At a constant temperature of 300 °C, MgH$_2$ + 7.5 wt% Ti$_3$CN can desorb 6.6 wt% H$_2$ within 10 min and 6.9 wt% within 60 min. Therefore, the hydrogen release kinetics were greatly improved by Ti$_3$CN addition. The curves in Figure 3a,d were further studied by the Johnson–Mehl–Avrami (JMA) equation and the Arrhenius equation. The JMA equation is:

$$\ln[-\ln(1 - \alpha)] = nl\ln k + nlnt, \tag{1}$$

where $\alpha$ refers to the extent of the reaction; $n$ represents the Avrami index; $t$ is the time; $k$ stands for the reaction rate constant. The isothermal hydrogen desorption curves were converted to JMA plots ($\ln[-\ln(1 - \alpha)]$ vs. ln$t$) as shown in Figure 3b,e. Then, linear fitting was performed to obtain the $n$ and $nl\ln k$ from the slopes and the intercepts. The ln$k$ values were then plotted vs. 1000/$T$ based on the Arrhenius equation, which is:

$$\ln k = -\frac{E_a}{RT} + \ln A, \tag{2}$$

where $E_a$ refers to the activation energy; $R$ represents the universal gas constant; and $A$ stands for a constant. The Arrhenius plots (ln$k$ vs. 1000/$T$) are shown in Figure 3c,f. Then, linear fitting was performed to obtain the values of $E_a$ from the slope. The desorption activation energy for MgH$_2$ + 7.5 wt% Ti$_3$CN was estimated to be 80 kJ mol$^{-1}$, which is much lower compared to MgH$_2$ without an additive (121 kJ mol$^{-1}$). This indicates that Ti$_3$CN improved the hydrogen release kinetics of MgH$_2$.

![Figure 3](image-url). Hydrogen release curves at various temperatures (a,d), JMA plots (b,e), and Arrhenius plots (c,f) of MgH$_2$ without addition (upper) and MgH$_2$ + 7.5 wt% Ti$_3$CN (down).
The thermodynamics of MgH$_2$ were further studied by testing the pressure–concentration isotherms (PCT) and using the van’t Hoff equation written as:

$$\ln(p/p_0) = -\Delta H/RT + \Delta S/R,$$

where $p$ refers to the plateau hydrogen pressure; $p_0$ stands for the standard atmosphere pressure; $\Delta H$ represents the enthalpy change of the reaction; and $\Delta S$ represents the entropy changes of the reaction. Figure 4a,c shows the hydrogen desorption PCT curves of the two samples at various temperatures. From the PCT curves, the plateau hydrogen pressures ($p$) can be obtained. Then, the van’t Hoff plots ($\ln(p/p_0)$ vs. $1000/RT$) can be made (Figure 4b,d). The slopes of the linear fitting lines give the values of $\Delta H$. The enthalpy change for the hydrogen release reaction of MgH$_2$ + 7.5 wt% Ti$_3$CN was estimated to be 78.8 kJ mol$^{-1}$, which is very equal to that of MgH$_2$ without an additive (79.3 kJ mol$^{-1}$). Therefore, Ti$_3$CN addition does not alter the thermodynamics of MgH$_2$.

![Figure 4](image_url)

**Figure 4.** Hydrogen desorption PCT curves (a,c) and van’t Hoff plots (b,d) of MgH$_2$ without addition (upper) and MgH$_2$ + 7.5 wt% Ti$_3$CN (down).

To reveal the role of Ti$_3$CN MXene in tailoring the hydrogen storage of MgH$_2$, the structures of MgH$_2$ + 7.5 wt% Ti$_3$CN in different states were studied by X-ray diffraction (XRD). Figure 5b–d shows the XRD profiles of MgH$_2$ + 7.5 wt% Ti$_3$CN at different stages, with the as-synthesized Ti$_3$CN MXene for reference (Figure 5a). After ball milling (Figure 5b), MgH$_2$ and Ti$_3$CN were observed in the sample, suggesting that it is a physical mixture of the starting materials. After hydrogen desorption (Figure 5c), MgH$_2$ decomposes and Mg forms. Ti$_3$CN is still observed in the desorbed sample, which indicates that Ti$_3$CN does not react with other components and stays stable in the sample. It should be noted that MgO is observed in the sample, which may be due to the partial oxidation of MgH$_2$/Mg during sample transfer or testing. After hydrogen absorption (Figure 5d), MgH$_2$ is fully recovered.
and Ti$_3$CN is still observed in the sample. From the above structure evolution studies, it can be seen that Ti$_3$CN stays stable during the hydrogen release and uptake process. Therefore, Ti$_3$CN mainly plays the role of an efficient catalyst for the hydrogen release and uptake of MgH$_2$. This is consistent with the results in Figure 4 in that the thermodynamics of MgH$_2$ is not altered by the addition of Ti$_3$CN.

Figure 5. XRD profiles of Ti$_3$CN MXene (a) and MgH$_2$ + 7.5 wt% Ti$_3$CN after ball milling (b), after hydrogen desorption (c), and after hydrogen absorption (d).

The microstructures of the MgH$_2$ + 7.5 wt% Ti$_3$CN composite after rehydrogenation were further studied by SEM, TEM, EDS, and SAED methods. Figure 6a shows the SEM image of the composite, which displays that the particles of the composite are of several microns. Figure 6b shows the EDS elemental mappings of the composite. The Mg, Ti, C, and N elements are all distributed very uniformly in the composite. Figure 6c shows the TEM image of the composite with its SAED pattern shown in Figure 6d. In the SAED pattern, MgH$_2$, Mg, and Ti$_3$CN are observed. These three components are also observed in the HRTEM images in Figure 6e−i. The presence of Ti$_3$CN is consistent with the XRD results in Figure 5d, which again suggests that Ti$_3$CN mainly plays the role of an efficient catalyst for MgH$_2$. It is interesting that Mg is detected in the rehydrogenated composite, which is different from Figure 5d. In Figure 5d, Mg is not observed in the XRD pattern. This indicates that the high-energy electron beam may have stimulated the partial decomposition of the Ti$_3$CN-modified MgH$_2$. It should be also noted that only those MgH$_2$ particles that are contacting with Ti$_3$CN can be stimulated to decompose by the high-energy electron beam, as shown in regions 1 and 3 of Figure 6e. In region 4 of Figure 6e, MgH$_2$ without contacting with Ti$_3$CN is not decomposed. Therefore, Ti$_3$CN indeed is an excellent catalyst for MgH$_2$. 
3. Discussion

From the above results, it can be said that Ti₃CN MXene can greatly enhance the hydrogen sorption kinetics of MgH₂. The addition of Ti₃CN can lower the initial hydrogen release temperature of MgH₂ from 322 °C to 214 °C, with a reduction of 108 °C. Moreover, the desorbed MgH₂ starts to absorb hydrogen at about 120 °C, while the desorbed MgH₂ + 7.5 wt% Ti₃CN sample can start to absorb hydrogen at RT. The MgH₂ + 7.5 wt% Ti₃CN has a desorption activation energy of 80 kJ mol⁻¹, which is significantly lower than that of pristine MgH₂ (121 kJ mol⁻¹).

However, it seems that Ti₃CN does not alter the thermodynamics of MgH₂. Many published papers have demonstrated that MXene materials such as Ti₃C₂ [41,45,47], Ti₂C [44], NbTiC [42], (Ti₀.₅V₀.₅)₃C₂ [46], etc., can enhance the hydrogen sorption kinetics of MgH₂. However, there is barely any work that has reported that MXene materials can reduce the thermal stability of MgH₂ except for V₂C MXene [31]. Therefore, it can be deduced that
most MXene materials do not change the thermodynamics of MgH₂ but mainly alter the kinetics of MgH₂.

4. Materials and Methods

Ti₃AlCN MAX (500 mesh, 98% purity) was purchased from Laizhou Kaixi Ceramic Co., Ltd., Laizhou, China. MgH₂ (98% purity) was purchased from Langfang Beide Commerce and Trade Co., Ltd., Langfang, China. HF (analytical purity, 40%) was purchased from Aladdin, Shanghai, China. These reagents were used as received without any further treatment.

HF-etching was used to synthesize the layered Ti₃CN MXene. In the experiment, 3 g of Ti₃AlCN MAX was added into a 40 mL HF solution with a concentration of 40%. The solution was then stirred at 30 °C for 18 h followed by centrifugation three times. The rotation speed used for centrifugation was 3500 rpm. After that, the sediment was washed until the pH value of the deionized water used was higher than 6. Then, the sediment was dried in a freeze-dryer for 24 h. After that, Ti₃CN MXene can finally be obtained.

Ti₃CN was then mixed with MgH₂ by ball milling under an argon atmosphere to prepare MgH₂ + m wt% Ti₃CN (m = 0, 5, 7.5, 10) samples at a planetary ball mill (Pulverisette 7, Fritsch, Germany). The as-received MgH₂ and the as-synthesized Ti₃CN were first weighted based on the compositions in a glove box filled with high-purity argon and then placed in a milling jar. Some milling balls were also placed in the milling jar with a ball-to-powder ratio of 40:1. After sealing, the milling jar was transferred to the planetary ball mill. All samples were milled at 400 rpm for 10 h.

An X-ray diffraction (XRD) instrument (Miniflex 600, Rigaku, Japan) was utilized to determine the phase structures. The incident ray was Cu Kα radiation and the scanning speed was 2 °C min⁻¹. A working current of 200 mA and a working voltage of 40 kV were used during the tests. The samples for the XRD test were sealed with transparent tape to prevent the samples from oxidizing during the sample transfer and test. Scanning electron microscopy (SEM, JSM-6510A, JEOL, Japan) was employed to analyze the morphologies. The samples were adhered to conductive tape. The transfer of the samples was carried out carefully to protect the samples from contacting the air. An attached X-ray energy dispersive detector (EDS) was employed to collect the elemental distributions. A transition electronic microscope (TEM, Tecnai G2 F20, FEI, The Netherlands) with a voltage of 200 kV was used to study the microstructures of the samples. Anhydrous acetone was used to disperse the sample on Cu grids.

A Sievert-type apparatus built by the Institute of Metallic Materials, Zhejiang University, Hangzhou, China, was utilized to study the hydrogen release and uptake behavior of the samples. During the non-isothermal hydrogen release tests, the samples were heated gradually from RT to 400 °C at 2 °C min⁻¹ from an initial pressure of 10⁻⁴ MPa. During the non-isothermal hydrogen uptake tests, the temperature program was the same as the isothermal hydrogen release test. At the starting point of the heating program, hydrogen of 6 MPa was charged into the sample holder. During the isothermal hydrogen release tests, the samples were first heated to the target temperature with a hydrogen back pressure of 6 MPa. When the temperature was stabilized, hydrogen gas was rapidly vented to start hydrogen desorption. An automatic Sievert-type apparatus (IMI-Flow, Hiden, UK) was used to collect the PCT curves of the samples.

5. Conclusions

Layered Ti₃CN MXene was successfully synthesized by exfoliation of Ti₃AlCN MAX with HF as the etching solution. The layered Ti₃CN can significantly improve the kinetics of MgH₂. In particular, MgH₂ + 7.5 wt% Ti₃CN shows good hydrogen desorption performance, with an initial hydrogen release temperature of 214 °C and a low hydrogen release reaction activation energy of 80 kJ mol⁻¹. Moreover, the desorbed MgH₂ + 7.5 wt% Ti₃CN can absorb hydrogen at RT, while the desorbed pristine MgH₂ can only start absorption at 120 °C. The layered Ti₃CN barely changes the thermodynamics of MgH₂ since the enthalpy changes of the hydrogen release reactions of MgH₂ and MgH₂ + 7.5 wt% Ti₃CN are very
close (79.3 and 78.8 kJ mol⁻¹, respectively). Ti₃CN stays stable during the hydrogen release and uptake process of the MgH₂–Ti₃CN composite, which means that Ti₃CN mainly plays the role of an efficient catalyst for MgH₂. This work confirms that transition metal carbonylides also have a good catalytic impact on the hydrogen release and uptake properties of MgH₂.

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