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Oxygen Vacancy-Rich 2D TiO₂ Nanosheets: A Bridge Toward High Stability and Rapid Hydrogen Storage Kinetics of Nano-Confined MgH₂

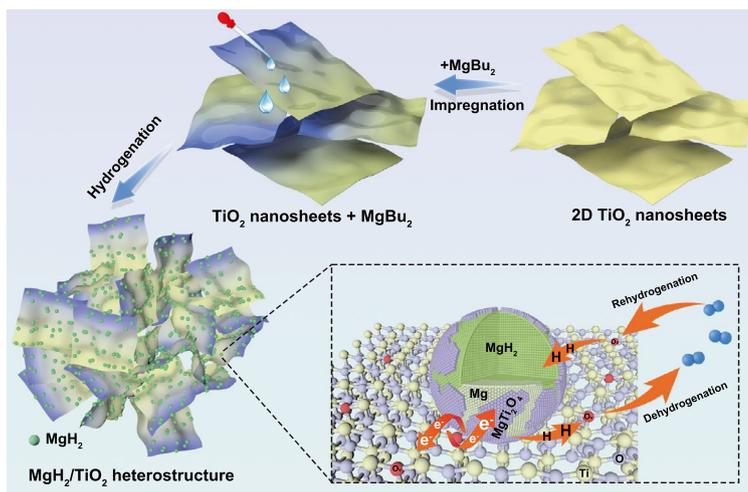
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HIGHLIGHTS

- A MgH₂/TiO₂ heterostructure with nano MgH₂ assembled on oxygen vacancy-rich 2D TiO₂ nanosheets was successfully fabricated via a simple solvothermal strategy.
- The MgH₂/TiO₂ heterostructure shows rapid desorption kinetics, low dehydrogenation temperature, and excellent cycling stability.
- In situ HRTEM observations and ex situ XPS analyses reveal that multi-valence of Ti species, presence of abundant oxygen vacancies, formation of catalytic Mg-Ti oxides, and confinement of TiO₂ nanosheets, contribute to the high stability and kinetically accelerated hydrogen sorption performances of Mg.

ABSTRACT MgH₂ has attracted intensive interests as one of the most promising hydrogen storage materials. Nevertheless, the high desorption temperature, sluggish kinetics, and rapid capacity decay hamper its commercial application. Herein, 2D TiO₂ nanosheets with abundant oxygen vacancies are used to fabricate a flower-like MgH₂/TiO₂ heterostructure with enhanced hydrogen storage performances. Particularly, the onset hydrogen desorption temperature of the MgH₂/TiO₂ heterostructure is lowered down to 180 °C (295 °C for blank MgH₂). The initial desorption rate of MgH₂/TiO₂ reaches 2.116 wt% min⁻¹ at 300 °C, 35 times of the blank MgH₂ under the same conditions. Moreover, the capacity retention is as high as 98.5% after 100 cycles at 300 °C, remarkably

higher than those of the previously reported MgH₂-TiO₂ composites. Both in situ HRTEM observations and ex situ XPS analyses confirm that the synergistic effects from multi-valence of Ti species, accelerated electron transportation caused by oxygen vacancies, formation of catalytic Mg-Ti oxides, and stabilized MgH₂ NPs confined by TiO₂ nanosheets contribute to the high stability and kinetically accelerated



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hydrogen storage performances of the composite. The strategy of using 2D substrates with abundant defects to support nano-sized energy storage materials to build heterostructure is therefore promising for the design of high-performance energy materials.

KEYWORDS Hydrogen storage; MgH₂; TiO₂ nanosheets; Oxygen vacancies; Nanoconfinement

1 Introduction

With the ever-increasing global energy demands and environmental concerns, clean and renewable energy is urgently demanded worldwide. Hydrogen has been considered as one of the most promising candidates to alternate fossil fuels, due to its intrinsic clean nature, environmental-friendliness, and high gravimetric energy density (142 MJ kg⁻¹) [1–4]. However, an effective strategy to store hydrogen is essential to realizing the "hydrogen economy" [5, 6]. Compared with hydrogen storage in pressurized tanks or cryogenic containers, solid-state hydrogen storage methods potentially have the advantages of high safety, low cost, and exceptional hydrogen storage capacity [7]. Among various solid-state hydrogen storage materials, magnesium hydride (MgH₂) has attracted tremendous attention, due to its high gravimetric (~7.6 wt% H₂) and volumetric (~110 kg m⁻³ H₂) hydrogen storage density, excellent reversibility, low cost, and nontoxicity [8, 9]. Unfortunately, the industrial application of MgH₂ has been seriously hampered by its high operating temperature and slow de/re-hydrogenation kinetics. Particularly, a high temperature of at least 280 °C is required at 1 bar for desorption of coarse-grained MgH₂, which far exceeds the working temperature of the proton exchange membrane fuel cell (PEMFC). Consequently, it is essential to improve the hydrogen storage performances of MgH₂ for possible applications in the hydrogen energy field.

In the last few decades, extensive researches have been executed toward fabricating novel Mg-based hydrogen storage materials with enhanced performances, such as adding catalysts [10–13], alloying [14–16], and reducing the particle size of MgH₂ [17–19]. From the extrinsic perspective, the use of additives to weaken the Mg-H bonding and promote the diffusion rate of hydrogen atoms, thus reducing the dehydrogenation temperature and accelerating the desorption rates, is regarded as an efficient strategy for enhancing the hydrogen desorption properties of MgH₂. These additives include transition metals (TM) [20, 21], transition metal oxides [22, 23], nitrides [24, 25], halides [26, 27], and hydrides [28, 29]. Among them, transition metals (Ti, V, Nb, Ni, Co) and their compounds (TiO₂, Nb₂O₅, V₂O₃)

strike more attentions and have been proven to be the most effective additives to ameliorate the hydrogen sorption performances of MgH₂, since transition metals with multiple valences favor the electron transfer during the de/re-hydrogenation processes [26]. The Fermi level of transition metals is located around s-type orbitals, which is a necessary condition to promote hydrogen dissociation and recombination [30]. Cui et al. [21] systematically investigated the catalytic mechanism of TM on the MgH₂ by the synthesis of core (Mg)-shell (TM) structure. The results show that Mg-Ti composites, which can release hydrogen even under 200 °C, exhibit optimal desorption performances, owing to the lower electronegativity of Ti. Notably, it has been proved that TiO₂ possesses a superior catalytic effect than metallic Ti [31]. Furthermore, TiO₂ has many advantages, such as high natural abundance, low cost, and nontoxicity. Though the addition of catalysts through simple ball milling method can indeed ameliorate the kinetics of MgH₂ to some extent, the improvement is restricted by the inevitable self-aggregation and growth of the additives during cycling, as well as the low density of exposed active sites.

On the other hand, from an intrinsic point of view, nano-sized MgH₂, which owes the shortened diffusion path for hydrogen atoms and increased active sites for re/de-hydrogenation, has been successfully synthesized through various nanotechnologies, giving rise to improved hydrogen storage performances. For instance, the nano-confinement method has been proved to be a facile strategy to simultaneously improve the thermodynamics and kinetics of MgH₂ while reducing the capacity loss as little as possible. Nano-sized MgH₂ confined into porous carbon has demonstrated a noticeable decrease in its initial desorption temperature (~90 °C) compared with its bulk counterpart [32]. Yu et al. [33] synthesized Ni nanocrystal-decorated MgH₂ nanoparticles anchored on graphene sheets that exhibit excellent hydrogen sorption properties. The composites absorb 5.4 wt% H₂ within 10 min at 200 °C, and identical capacity can be released at the same temperature within 150 min. It is noted, however, that neither graphene nor porous carbon possesses good catalytic activities, and additional catalysts are needed to further improve hydrogen storage performances

of MgH_2 . Although huge achievements have been achieved, it is still far from enough to enhance the hydrogen storage performances of MgH_2 by solely depending on any methods mentioned above. In this respect, it is essential to fabricate MgH_2 with extraordinary hydrogen storage performances by taking full advantage of both the intrinsic (nano-size) and the extrinsic (catalyst addition) strategy.

Recently, graphene-like two-dimensional (2D) transition metal oxides have been extensively studied due to their potential in energy-related applications with high surface area and unique electronic/thermal properties [34–37]. However, preparing hydrogen storage composites composed of graphene-like 2D TiO_2 nanosheets (TiO_2 NS) and MgH_2 by a simple ball milling method would cause irreversible agglomeration of TiO_2 NS, leading to seriously reduced catalytic active sites and deterioration of various spectacular intrinsic properties of 2D materials [38]. Thus, the idea of fabricating MgH_2 (0D)/ TiO_2 (2D) heterostructure using graphene-like 2D TiO_2 NS is triggered as it can not only facilitate the formation of nano-sized MgH_2 through the confinement effect of TiO_2 NS but also possess catalytic effect for MgH_2 . More importantly, the construction of $\text{MgH}_2/\text{TiO}_2$ heterostructure can effectively inhibit the self-stacking of TiO_2 layers, leading to increased surface catalytic sites for MgH_2 . Additionally, defect engineering has also aroused more attention to adjusting the band structure and providing more catalytic active sites [39]. Among them, oxygen vacancy-rich TiO_2 has been proved to remarkably promote electron transportation, enhance electrical conductivity, and provide more active sites for the capture and diffusion of hydrogen [40, 41].

In light of the above consideration, herein, taking full advantage of the intrinsic (nano-size) and extrinsic (catalyst addition) effects, we report a first attempt to design a novel self-assembled $\text{MgH}_2/\text{TiO}_2$ heterostructure with remarkably enhanced hydrogen sorption properties through facile solvothermal approach, where 2D TiO_2 NS exhibit both nano-confinement and catalytic effects. Surprisingly, we found that the oxygen vacancies were introduced into TiO_2 NS in the process of solvothermal treatment. Owing to the presence of oxygen vacancies and unique heterostructure, the obtained $\text{MgH}_2/\text{TiO}_2$ heterostructure exhibits impressive hydrogen storage performances with high stability and accelerated kinetics. Specifically, the $60\text{MgH}_2/\text{TiO}_2$ heterostructure presents low onset desorption temperature (180 °C) and

superior long-term cycling stability with a capacity retention of 98.5% after 100 cycles at 300 °C, remarkably higher than that of the state-of-the-art TiO_2 catalyzed MgH_2 systems.

2 Experimental Section

2.1 Synthesis of $\text{MgH}_2/\text{TiO}_2$ Heterostructure

2.1.1 Synthesis of Graphene-like 2D TiO_2 Nanosheets

TiO_2 nanosheets were synthesized by a surfactant self-assembly method [34]. Firstly, 1.48 mL titanium isopropoxide (TTIP, 99.9%, Macklin) was added to 2.1 mL concentrated HCl under vigorous stirring (solution A). Meanwhile, 0.4 g poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer (P123, $M_n = 5,800$) was dissolved in 8 mL ethanol (solution B) by ultrasonication. Afterward, solution B was added dropwise into solution A and kept stirring for 30 min at room temperature. Then, 5 mL of the above resultants with 40 mL ethylene glycol was then transferred into a 100 mL stainless steel autoclave and heated at 150 °C for 20 h. Finally, the products were centrifuged and washed with ethanol, followed by freeze-drying to obtain 2D TiO_2 NS. Moreover, to improve the crystallinity and remove the impurities in TiO_2 NS, the pristine TiO_2 NS were annealed at different temperatures (300, 400, and 500 °C) for 2 h in the air (denoted as TiO_2 -T, T represents the annealing temperature).

2.1.2 Synthesis of the $\text{MgH}_2/\text{TiO}_2$ Heterostructure

$\text{MgH}_2/\text{TiO}_2$ heterostructure was prepared by a bottom-up solvothermal strategy of in situ growth of MgH_2 nanoparticles on TiO_2 substrates. *Di-n*-butyl-magnesium (MgBu_2 , 1 M solution in hexane, Sigma-Aldrich) and cyclohexane (C_6H_{12} , 99.5%, extra Dry, Sigma-Aldrich) were used as received states without further treatment. As provided in Table S1, different loading capacities of MgH_2 on TiO_2 NS of 40, 50, 60, 70, and 80 wt% were synthesized by changing the ratio between MgBu_2 and TiO_2 NS, which were denoted as $40\text{MgH}_2/\text{TiO}_2$, $50\text{MgH}_2/\text{TiO}_2$, $60\text{MgH}_2/\text{TiO}_2$, $70\text{MgH}_2/\text{TiO}_2$, and $80\text{MgH}_2/\text{TiO}_2$, respectively. In a typical synthesis of $60\text{MgH}_2/\text{TiO}_2$, 30 mg as-prepared TiO_2 -300 NS and 1.8 mL MgBu_2 were firstly dispersed in 40 mL cyclohexane

under sonication. The mixture was then transferred into a 100 mL custom-designed autoclave, filled with 4.5 MPa H₂ pressure, and heated at 200 °C for 12 h under vigorous magnetic stirring [19, 42]. Finally, the resultants (named 60MgH₂/TiO₂ heterostructure) were collected by centrifugation, washed with cyclohexane several times, and dried at 80 °C overnight under dynamic vacuum. Moreover, blank MgH₂ without TiO₂ NS were also prepared under the same conditions for comparison.

2.2 Characterization and Measurements

The phase composition was characterized by using X-ray diffraction (XRD, Mini Flex 600) with Cu K_α radiation operated at 40 kV and 15 mA. The samples were prepared in an argon-filled glovebox and sealed in a custom-designed holder covered by the Scotch tape to avoid the possible oxidation during the XRD tests. The microstructure and morphological analyses were performed by scanning electron microscope (SEM, MIRA3 LHM) and transmission electron microscope (TEM, FEI Talos F200X G2). For TEM observations, the preparation of samples was carried out in the glovebox. The samples were dispersed in cyclohexane, sonicated, dropped on a copper grid, and rapidly transferred to the equipment. The preparation conditions of samples for SEM tests were similar to those for the TEM observation, except that the samples were dispersed in cyclohexane and dropped onto the silicon wafer. The in situ high-resolution transmission electron microscope (HRTEM) observation was applied to explore the microstructural evolution during the decomposition of the MgH₂/TiO₂ heterostructure under an irradiation beam current of 3 nA [43]. The valence state and chemical bonding nature of constituent elements of MgH₂/TiO₂ composites were analyzed by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD). For XPS analyses, a special air-proof transfer vessel was used to transfer the samples from glovebox to the equipment. Electron paramagnetic resonance (EPR) measurement was performed at room temperature using a Bruker spectrometer (EMXplus-9.5/12). Solid-state ¹H magic-angle spinning nuclear magnetic resonance (MAS NMR) was carried out on a Bruker AVANCE NEO 600 spectrometer. Brunner–Emmet–Teller (BET) surface areas of all samples were measured by the N₂ isothermal ad/desorption tests at 77 K on Autosorb-IQ3 apparatus. Differential scanning

calorimetry (DSC, NETZSCH STA 449 F3) measurements were performed at different heating rates (3, 5, and 10 °C min⁻¹) under a flowing Ar atmosphere to analyze the desorption kinetic properties. The DSC data were further processed by the Kissinger method to figure out the desorption apparent activation energy (E_a) according to the following equation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + C \quad (1)$$

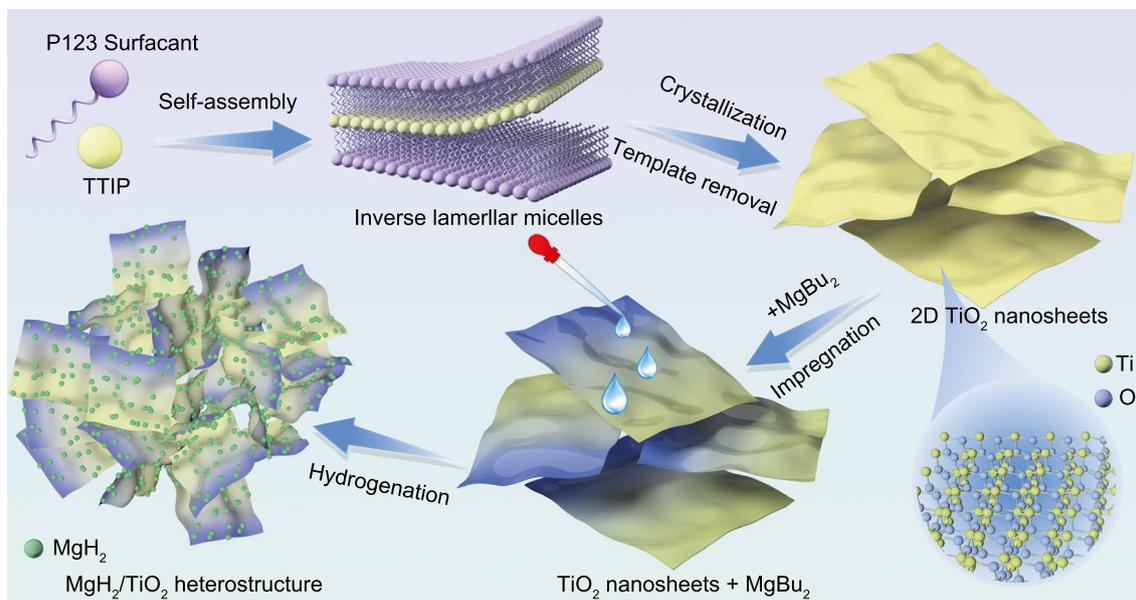
where β represents the heating rate, T_p refers to the peak temperature, R is the universal gas constant ($R=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and C is a constant.

The isothermal ab/desorption tests and temperature program desorption (TPD) measurements of samples were carried out by a Sievert-type pressure-composition-temperature apparatus (PCT, Shanghai Institute of Microsystem and Information Technology). For the isothermal ab/desorption tests, samples were loaded into the vessel in the glove box and were heated to the preset temperature at a heating rate of 10 °C min⁻¹. The initial hydrogen pressures for isothermal ab/desorption were 3 and 0.001 MPa, respectively. Besides, the hydrogenated samples were heated from room temperature to 350 °C with a heating rate of 2 °C min⁻¹ to perform TPD measurements. The hydrogen pressure/duration/temperature parameters for cycling tests are set as 3 MPa/15 min/300 °C for re-hydrogenation and 0.001 MPa/15 min/300 °C for dehydrogenation. The hydrogen storage capacity was calculated in the weight percent of the entire composites including the TiO₂ scaffold.

3 Results and Discussion

3.1 Synthesis and Characterizations of the MgH₂/TiO₂ Heterostructure

The preparation procedure of the MgH₂/TiO₂ heterostructures is schematically illustrated in Scheme 1, including the synthesis of 2D TiO₂ NS and subsequent impregnation of MgBu₂ as well as the bottom-up self-assembly of MgH₂ nanoparticles anchored on TiO₂ NS. In a typical surfactant self-assembly synthesis process of TiO₂ NS, P123 and ethylene glycol (EG) acted as co-surfactants which played the role of structure-directing agents to form inverse lamellar micelles. The precursor oligomers (TTIP) were then self-assembled



Scheme 1 Synthesis process illustration of the $\text{MgH}_2/\text{TiO}_2$ heterostructure

into lamellar structures with surfactant molecules, inducing the formation of layered inorganic oligomer agglomerates. Afterward, solvothermal treatment was carried out to promote the organization and crystallization of 2D TiO_2 NS. Subsequently, the TiO_2 NS were ultrasonically dispersed into the C_6H_{12} solution followed by the dropwise addition of MgBu_2 . Finally, the $\text{MgH}_2/\text{TiO}_2$ heterostructure was obtained in the above dispersed suspension by hydrogenation of MgBu_2 on TiO_2 NS through a facile solvothermal method.

The typical morphology and structural features of the ultrathin 2D TiO_2 NS were observed using SEM and TEM. As shown in Fig. 1a–c, the pristine TiO_2 NS exhibit a morphology of 2D corrugated ultrathin nanosheets with their edges roll up owing to the surface tension, which is also observed in graphene as a general phenomenon. The sizes of the TiO_2 NS vary from 150 to 200 nm as seen from the TEM images. The thickness of the prepared TiO_2 NS was further characterized using AFM and TEM (Fig. S1). The obtained TiO_2 NS have a thickness of around 3.7 nm, corresponding to 5–6 monolayers, which confirms the formation of ultrathin nanosheets. In addition, the sheet-like structure of TiO_2 can be clearly distinguished in the HAADF and BF images (Fig. 1d), which may play a morphology-directing role in the solution-phase synthesis of nanostructured MgH_2 .

The EDS elemental mapping images demonstrate the homogeneous distribution of Ti and O elements (Fig. 1d).

Furthermore, the influence of the annealing temperature on the morphology of TiO_2 NS was also taken into account (Fig. S2). It is worth emphasizing that TiO_2 -300 and TiO_2 -400 exhibit a similar sheet-like structure as the pristine TiO_2 NS, except for the slight granulation after annealing at 400 °C. However, the crystallite size and crystallinity of TiO_2 -500 increase obviously and the 2D nanostructures can hardly be observed. This phenomenon coincides well with the previous report [44]. Moreover, we also explored the stability of TiO_2 NS in the hydrogen atmosphere and it can be seen that the sheet-like structure of TiO_2 is still preserved after treatment in H_2 at 300 °C for 2 h (Fig. S2). Figure 1e shows the XRD patterns of pristine TiO_2 , TiO_2 -300, TiO_2 -400, and TiO_2 -500. According to the XRD patterns, pristine TiO_2 NS are mainly composed of the anatase phase (JCPDS No. 21–1272), as well as a small amount of rutile phase (JCPDS No. 21–1276). After calcination treatment, the intensities of the diffraction peaks are much sharper and stronger, manifesting an increase in crystallinity, coinciding well with the SEM and TEM results (Fig. S2). Additionally, the diffraction peaks of rutile phase disappear and crystalline diffraction peaks assigned to anatase TiO_2 crystal can be identified when the annealing temperature increases up to 400 and 500 °C. The specific surface area

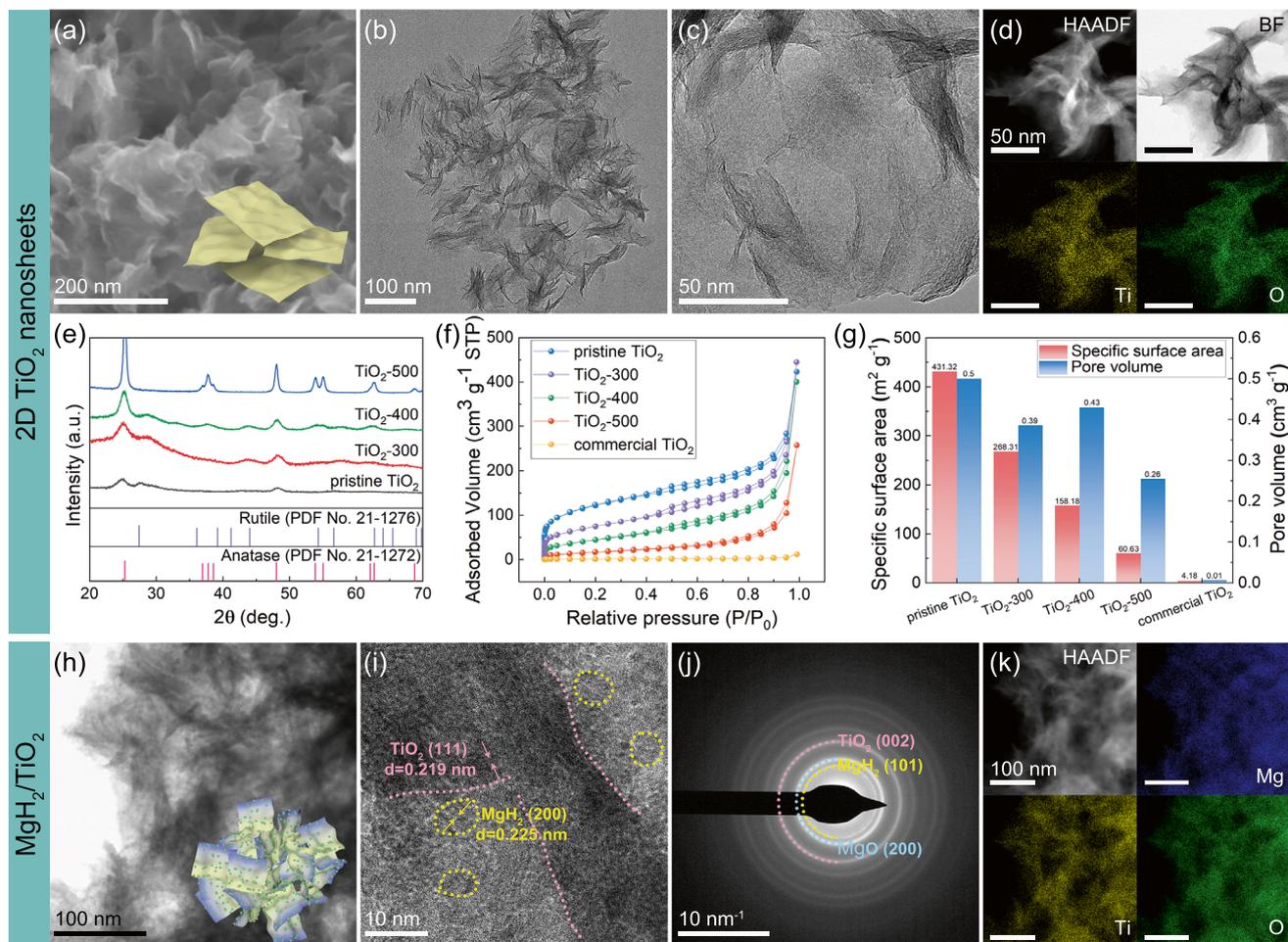


Fig. 1 **a** Typical SEM image of TiO₂ NS. **b, c** Typical TEM images at different scales. **d** Representative HAADF and BF images of TiO₂ NS as well as corresponding EDS elemental mapping results. **e** XRD patterns of TiO₂ NS. **f, g** N₂ ad/de-sorption isotherms and corresponding specific surface areas and pore-size distribution of pristine TiO₂ NS, commercial TiO₂, and TiO₂ NS treated at different annealing temperatures. **h–j** BF, HRTEM, and SAED images of as-synthesized 60MgH₂/TiO₂ heterostructure. **k** HAADF images of as-synthesized 60MgH₂/TiO₂ heterostructure and corresponding EDS elemental mapping results

and pore size distribution of TiO₂ NS were further investigated (Fig. 1f–g). Compared with commercial TiO₂, the specific surface area of TiO₂ NS is increased by 14–100 times, attributed to the special 2D sheet-like structures. The TiO₂ NS possess a specific surface area of 431.32 m² g⁻¹, which is almost 100 times higher than that of the commercial TiO₂ (~4 m² g⁻¹). Besides, it still possesses a high specific surface area of 268.31 m² g⁻¹ even after calcination treatment (300 °C). Thus, we selected TiO₂-300 as the substrates to fabricate the MgH₂/TiO₂ heterostructure, and the TiO₂ mentioned below all refers to TiO₂-300 unless otherwise specified. The TiO₂ NS with ultrahigh specific surface area will provide more nucleation sites for nanoparticles, which could

be ingeniously employed as the excellent scaffold for the self-assembly of MgH₂ NPs.

To fabricate MgH₂/TiO₂ heterostructure, MgBu₂ was used as the precursor and added into TiO₂ suspension followed by the solvothermal method under 4.5 MPa of hydrogen pressure. Impressively, the color of TiO₂ suspension fortuitously changed from white to dark blue with the addition of MgBu₂. The obvious blue color indicates the presence of oxygen vacancies caused by MgBu₂ [39], which will be discussed in detail in the following section. Figure 1h shows the typical TEM images of as-synthesized 60MgH₂/TiO₂ heterostructure. It can be seen that TiO₂ nanosheets still maintain a graphene-like structure after the self-assembly of MgH₂

nanoparticles on them. Besides, 2D TiO₂ nanosheets are automatically arranged into flower-like structures to support and encapsulate MgH₂ nanoparticles, tremendously restricting the agglomeration of MgH₂ NPs and simultaneously hampering the re-stacking of TiO₂ NS in turn. According to the measurement of lattice spacing in HRTEM images (Fig. 1i), the interplanar spacings of 0.225 and 0.219 nm could be attributed to the (200) plane of MgH₂ (JCPDS No. 12–0697) and (111) plane of TiO₂ (JCPDS No. 21–1276), respectively. In addition, the diffraction rings in SAED pattern of 60MgH₂/TiO₂ (Fig. 1j) reveal the formation of polycrystalline structure. Furthermore, the 2D wrinkled sheet-like structure of TiO₂ could be well distinguished from the HAADF images. EDS elemental mapping images confirm the homogeneous distribution of Mg, Ti, and O elements in the MgH₂/TiO₂ heterostructure (Fig. 1k).

3.2 Improved Hydrogen Storage Properties of the MgH₂/TiO₂ Heterostructure

The hydrogen storage performances of the MgH₂/TiO₂ heterostructure were further examined. Figure 2a shows the TPD profiles of blank MgH₂ and the MgH₂/TiO₂ with different loading of MgH₂ and Fig. 2b shows the comparison of the onset desorption temperature and hydrogen capacity of different samples. As the control sample, the blank MgH₂ starts to desorb hydrogen at about 295 °C, which is higher than those of MgH₂/TiO₂ composites, indicating that the TiO₂ NS indeed have a positive effect on the dehydrogenation of MgH₂. Concerning the MgH₂/TiO₂ with different loading capacities of MgH₂, the onset desorption temperatures decrease in the sequence of 50MgH₂/TiO₂ (260 °C), 70MgH₂/TiO₂ (233 °C), and 60MgH₂/TiO₂ (200 °C). Thus, we further explored the hydrogen storage performances of 60MgH₂/TiO₂, and the MgH₂/TiO₂ heterostructure mentioned below refers to the 60MgH₂/TiO₂ unless otherwise specified. In the first non-isothermal desorption process, the 60MgH₂/TiO₂ exhibits the initial desorption temperature of 200 °C with a total hydrogen release of 4 wt%. Notably, the 60MgH₂/TiO₂ composite possesses a lower onset desorption temperature of 180 °C along with a hydrogen capacity of 3.4 wt% in the second non-isothermal dehydrogenation process. The lower desorption temperature in the second cycle reveals that the catalytic activity of TiO₂ NS varies upon de/ab-sorption behavior. The capacity loss after the

first desorption may be attributed to the irreversible reaction between MgH₂ and TiO₂. It is therefore reasonable to speculate that the chemical environment of MgH₂ and TiO₂ in the first dehydrogenated sample should be considerably different from the as-synthesized sample, indicating the formation of catalytic species during initial hydrogen cycling, which is similar to what shown in previous reports [45–48], and will be discussed in later sections. In addition, DSC profiles (Figs. 2c and S3) show that the peak desorption temperature of commercial MgH₂ is 408.6 °C under the heating rate of 3 °C min⁻¹, while it tremendously reduces to 220.2 °C for the 60MgH₂/TiO₂ heterostructure. According to the fitting results of DSC by Kissinger's equation, the apparent activation energy of 60MgH₂/TiO₂ is determined to be 106.7 kJ mol⁻¹ H₂, much lower than that of the commercial MgH₂ (142.27 kJ mol⁻¹ H₂).

In order to further explore the influence of TiO₂ NS on MgH₂, the isotherm de/ab-sorption measurements were carried out for the 60MgH₂/TiO₂ heterostructure as well as control samples (blank MgH₂ and commercial MgH₂). Figure 2d shows the isotherm desorption curves of the 60MgH₂/TiO₂. As can be seen, the 60MgH₂/TiO₂ releases hydrogen of 0.51, 1.56, 2.14, 2.83, and 2.43 wt% at the temperature of 180, 200, 250, 275, and 300 °C within 10 min, respectively. Moreover, even at a lower temperature of 180 °C, the composite can still desorb 1.24 wt% of hydrogen within 60 min, corresponding to 41% of the maximum hydrogen storage capacity. At 250 °C, 2.14 wt% of hydrogen can be desorbed within 10 min, while no hydrogen desorption is detected for the blank MgH₂ and commercial MgH₂ under identical conditions (Fig. S4). In addition, blank MgH₂ needs 68 min to release 80% of its theoretical hydrogen capacity at 300 °C. In contrast, it takes only 1.8 min for the 60MgH₂/TiO₂ composite to reach the identical reaction extent (Fig. 2e). Impressively, the initial desorption rate is increased by 35 times for the 60MgH₂/TiO₂ (Fig. 2f) when compared to that of blank MgH₂. This demonstrates the remarkably improved hydrogen storage performances of MgH₂ through the introduction of TiO₂ NS.

The isothermal re-hydrogenation curves of samples are presented in Fig. 2g-i. The 60MgH₂/TiO₂ could absorb hydrogen even at a temperature as low as 80 °C with a hydrogen capacity of 1.86 wt% within 60 min. Such a low hydrogenation temperature meets the target of working temperature set by DOE for light-duty vehicle applications [7]. A

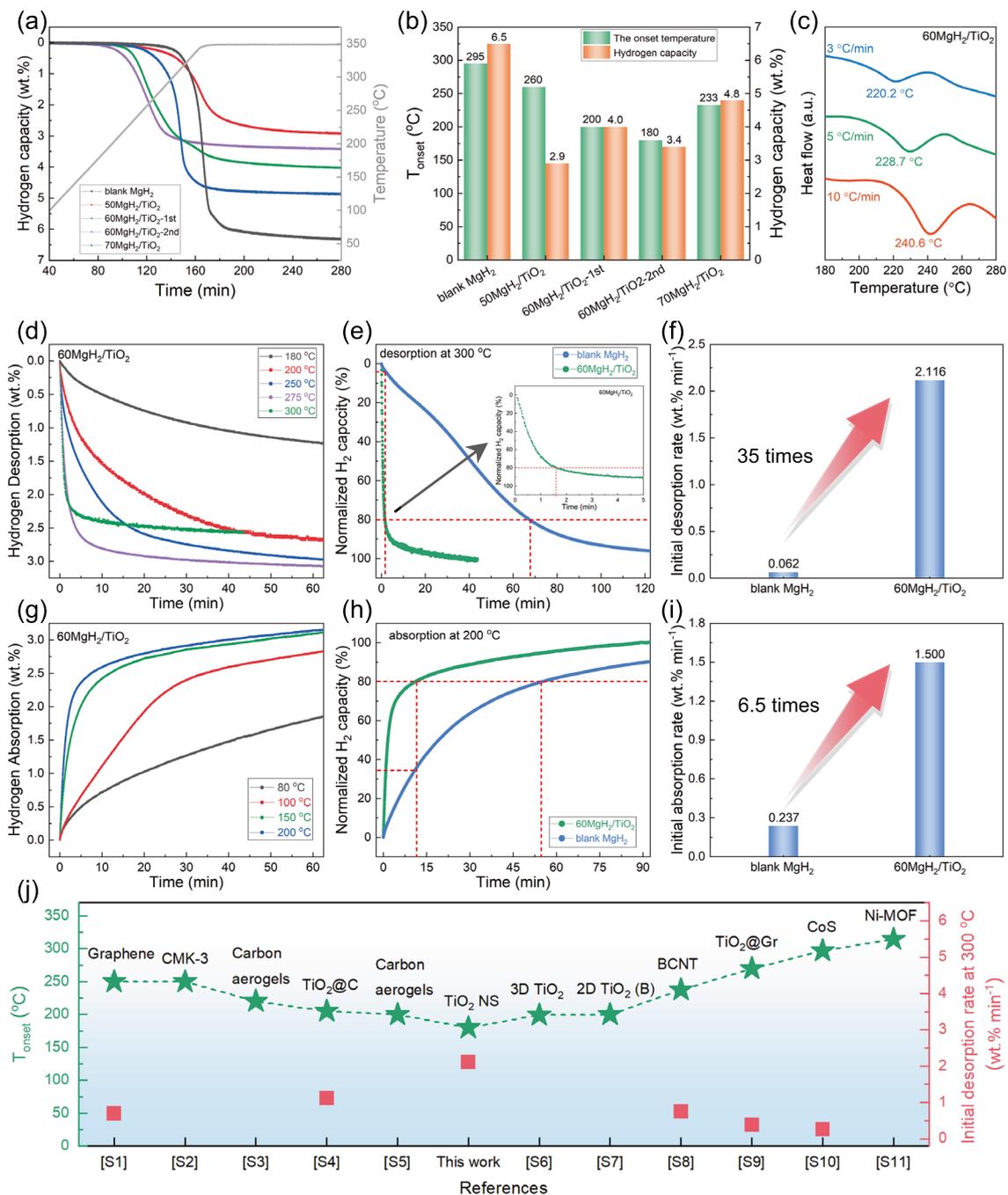


Fig. 2 **a, b** TPD curves and corresponding onset desorption temperature and hydrogen capacity of blank MgH₂, 50MgH₂/TiO₂, 60MgH₂/TiO₂-1st, 60MgH₂/TiO₂-2nd, and 70MgH₂/TiO₂. **c** DSC curves of 60MgH₂/TiO₂. **d** Isothermal dehydrogenation profiles of 60MgH₂/TiO₂. **e** Isothermal dehydrogenation curves and **f** initial desorption rate of 60MgH₂/TiO₂ and blank MgH₂ at 300 °C. **g** Isothermal re-hydrogenation profiles of 60MgH₂/TiO₂. **h** Isothermal re-hydrogenation curves and **i** initial absorption rate of 60MgH₂/TiO₂ and blank MgH₂ at 200 °C. **j** Comparison of the onset desorption temperature and initial desorption rates at 300 °C of MgH₂/TiO₂ heterostructure with those of other nano-confined MgH₂ systems and TiO₂ catalyzed MgH₂ systems in the literature (Table S2)

hydrogen capacity of 2.65 wt%, corresponding to 80% of the maximum hydrogen capacity, is achieved at 200 °C within 11.9 min for the 60MgH₂/TiO₂ heterostructure. However, it

takes a long time of 54.8 min for the blank MgH₂ to achieve the same reaction extent (Fig. 2h). Additionally, it is noteworthy that the initial absorption rate of 60MgH₂/TiO₂ at

200 °C is 6.5 times that of the blank MgH_2 (Fig. 2i). The superior hydrogen desorption performances, such as high initial desorption rate and low desorption temperature of the $60\text{MgH}_2/\text{TiO}_2$, remarkably exceed those of the state-of-the-art MgH_2 systems reported in literature (Fig. 2j and Table S2).

Cycling stability is also a key factor for the practical application of hydrogen storage materials. To further evaluate the stability of the $60\text{MgH}_2/\text{TiO}_2$, long-term (100 cycles) isothermal de/re-hydrogenation was tested at a relatively high temperature of 300 °C (Fig. 3a). It can be seen that $\text{MgH}_2/\text{TiO}_2$ shows negligible degradation of the capacity even after 100 cycles (from 2.71 to 2.67 wt%) and a capacity retention as high as 98.5% is achieved (Fig. 3b), which is highly comparable with and even surpasses those of the previously reported Mg-based hydrogen storage materials catalyzed by TiO_2 and other transition metal oxides. Additionally, compared to the first cycle, the $\text{MgH}_2/\text{TiO}_2$ heterostructure

exhibits a faster initial desorption rate during the second cycle (Fig. S5), which is associated with the formation of the catalytic oxide mentioned above. Moreover, the $\text{MgH}_2/\text{TiO}_2$ heterostructure still maintains flower-like structures and shows no obvious agglomeration of MgH_2 and restacking of TiO_2 NS even after 100 cycles (Fig. 3c). However, with the absence of TiO_2 NS, blank MgH_2 exhibits severe growth and agglomeration after several de/re-hydrogenation cycles (Fig. S6). The high stability of the $\text{MgH}_2/\text{TiO}_2$ heterostructure is presumably ascribed to the confinement effect of 2D TiO_2 NS on MgH_2 and robust interfacial contact between host and support materials.

Therefore, the $\text{MgH}_2/\text{TiO}_2$ heterostructure exhibits rapid hydrogen ab/de-sorption kinetics and excellent long-term cycling stability than those of blank MgH_2 , highlighting the crucial role of the 2D TiO_2 nanosheets, which simultaneously possess catalytic effect to MgH_2 and inhibit the agglomeration of MgH_2 .

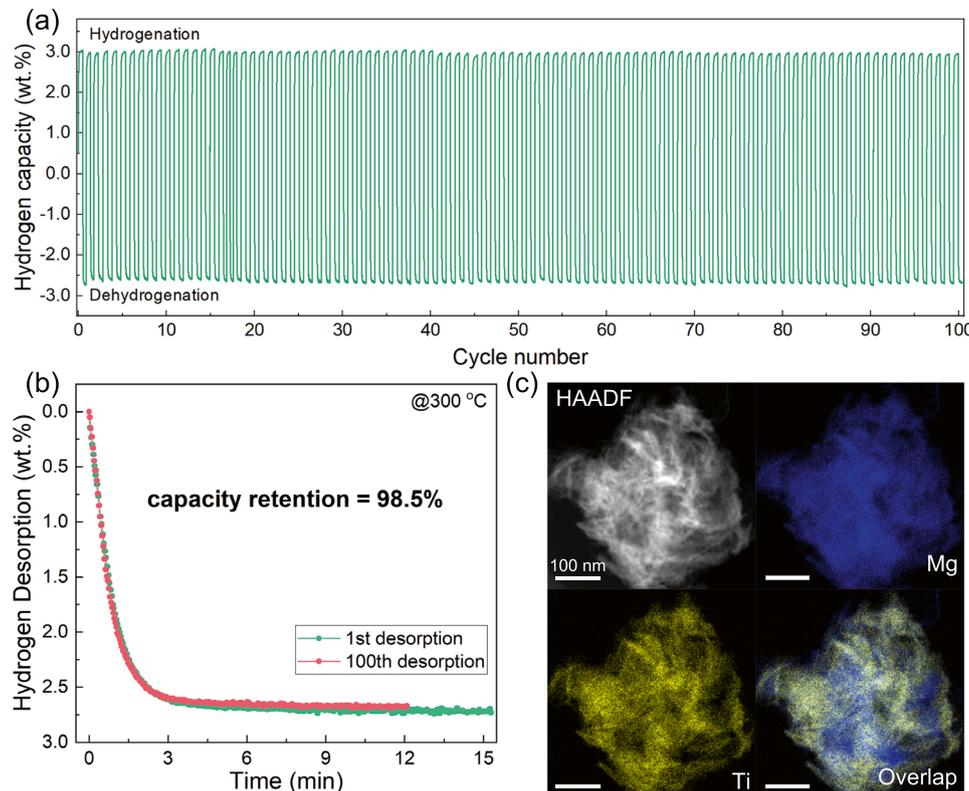


Fig. 3 **a** Reversible hydrogen absorption and desorption cycling profiles of $60\text{MgH}_2/\text{TiO}_2$ at 300 °C. **b** Hydrogen desorption curves of $60\text{MgH}_2/\text{TiO}_2$ at different cycles (1st and 100th). **c** HAADF images of $60\text{MgH}_2/\text{TiO}_2$ after 100 cycles and corresponding EDS elemental mapping results

3.3 Catalytic Mechanism of the MgH₂/TiO₂ Heterostructure

In order to further understand the mechanism of improved sorption performances of the MgH₂/TiO₂ heterostructure, we further characterized the phase components and microstructure of samples at different states. Figure 4 displays the optical photographs and microstructure of pristine TiO₂ NS and MgBu₂-treated TiO₂ NS. As shown in Fig. 4a, the MgBu₂-treated TiO₂ NS exhibit in different colors ranging from blue to black, in marked contrast with the white pristine TiO₂ powders. The color change of TiO₂ is ascribed to the presence of oxygen vacancies, which coincides well with the previous work [39–41, 49]. Herein, we introduce oxygen vacancies into TiO₂ NS by a facile strategy, that is, the impregnation of MgBu₂ into TiO₂ NS. We discover that the MgBu₂ could not only act as the reducing agent to fabricate oxygen vacancy-rich blue TiO₂ NS but also serve as the precursor of MgH₂ to promote the self-assembly of MgH₂ nanoparticles onto TiO₂ NS through subsequent solvothermal

approaches. Such a "one-stone-two-birds" effect enables the MgH₂/TiO₂ heterostructure as a promising hydrogen storage material with superior performances. Figure 4b displays the identical crystalline structure with the anatase phase in the majority and that of rutile in minority for different TiO₂ samples, indicating that the impregnation of MgBu₂ does not destroy the intrinsic crystal structure of the TiO₂ nanosheets. Besides, XPS spectra of elemental Ti (Fig. 4c) and O (Fig. S7) are provided. The high-resolution XPS spectra of Ti 2*p* of the pristine TiO₂ NS and TiO₂-300 at 464.4 and 458.6 eV can be attributed to Ti⁴⁺ 2*p*_{1/2} and Ti⁴⁺ 2*p*_{3/2}, respectively, while the peaks of TiO₂ NS treated with MgBu₂ slightly shift toward lower binding energy, indicating that Ti³⁺ is generated with the formation of oxygen vacancies. The O 1*s* peaks located at 531.8, 530.8, and 529.5 eV belong to adsorbed oxygen (O_A), oxygen vacancy (O_V), and lattice oxygen (O_L) in the MgBu₂-treated TiO₂ NS, respectively (Fig. S7). Based on the peak area of O_V to the overall peak area of O 1*s*, the percentage of O_V on the surface of the MgBu₂-treated TiO₂ is determined to be 32.53%. Additionally, the concentration

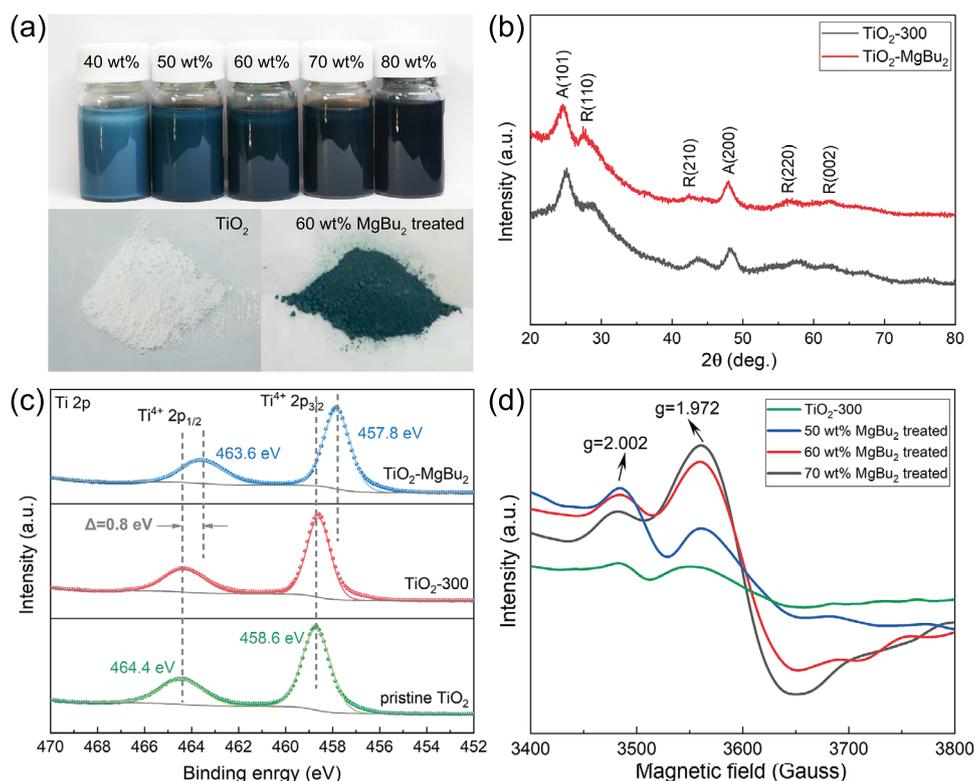


Fig. 4 **a** Optical photographs of TiO₂ NS suspension treated with different amounts of MgBu₂. **b** XRD patterns of TiO₂-300 and MgBu₂-treated TiO₂ NS. **c** High-resolution XPS spectra of Ti 2*p*. **d** EPR spectra of TiO₂-300 and TiO₂ NS treated with different amounts of MgBu₂ ("40wt%/50wt%/60wt%/70wt%/80wt%" refers to the weight percentage of MgH₂ in the MgH₂/TiO₂ heterostructure)

of oxygen vacancies on the surface of the as-synthesized $\text{MgH}_2/\text{TiO}_2$ heterostructure (33.4%) shows no significant change when compared to that on the TiO_2 NS treated with MgBu_2 (Fig. S7).

Moreover, EPR measurement was carried out to further explore the existence of oxygen vacancies in TiO_2 NS treated with MgBu_2 . As shown in Fig. 4d, the TiO_2 NS treated with MgBu_2 exhibit typical EPR signals at about $g = 1.972$ and $g = 2.002$, which could be attributed to Ti^{3+} and oxygen vacancies in the lattice, respectively [40, 50]. All these results strongly prove that the oxygen vacancies have been successfully introduced into TiO_2 nanosheets by the "one-stone-two-birds" strategy. Due to the higher electrical conductivity, numerous active sites, and enlarged lattice space derived from oxygen vacancies, the formation of oxygen vacancy-rich blue TiO_2 could not only accelerate the migration of electrons and diffusion of hydrogen atoms but also provide more active sites for the capture of hydrogen and nucleation of MgH_2/Mg . Thus, the $\text{MgH}_2/\text{TiO}_2$ heterostructure displays superior hydrogen ab/de-sorption kinetic properties.

In order to elucidate the catalytic mechanism, the structural stability of the $\text{MgH}_2/\text{TiO}_2$ composites during the hydrogen de/ab-sorption process was further investigated. Figure 5 shows the TEM images of dehydrogenated and re-hydrogenated $60\text{MgH}_2/\text{TiO}_2$ heterostructure. Surprisingly, there are no significant differences in morphology among the as-synthesized (Fig. 1h–k), dehydrogenated (Fig. 5a–d), and re-hydrogenated (Fig. 5e–h) samples, further confirming the thermal stability of the $\text{MgH}_2/\text{TiO}_2$ composites. Notably, by measuring the interplanar spacing of the well-resolved lattice fringes (Fig. 5b, f), we observe a new Mg-Ti ternary oxide, which is discussed in detail below. Thus, the establishment of the flower-like heterostructure has rendered the ability to well maintain the primary structure of the TiO_2 scaffold and MgH_2 nanoparticles, thereby improving the long-term cycling stability of MgH_2 and facilitating rapid transport of electrons and hydrogen.

We further explored the phase transformation and chemical valence state change of $\text{MgH}_2/\text{TiO}_2$ at different states. The XRD patterns of as-synthesized samples exhibit broad diffraction peaks indicating the presence of nano-sized MgH_2 (Fig. 6a). No peaks from MgO (which generally appear at the peak position of $\sim 42.9^\circ$ and 62.3° [11]) can be detected in the XRD pattern of as-synthesized $\text{MgH}_2/\text{TiO}_2$, indicating the absence of MgO . After dehydrogenation, in

addition to the main phase of Mg , two new broad peaks located at 42.7° and 62.0° appear in the XRD patterns, which are close to the peak positions of MgO . In the subsequent hydrogen absorption process, Mg phase transforms to MgH_2 and those two characteristic peaks assigned to Mg_2TiO_4 (JCPDS No. 16–0215) show no obvious change. Additionally, as shown in Fig. S8, the phase composition of the $\text{MgH}_2/\text{TiO}_2$ heterostructure remains unchanged after 100 de/re-hydrogenation cycles by showing very similar XRD patterns. Such a Mg-Ti oxide phase may possess a catalytic effect for the de/re-hydrogenation of MgH_2 [45, 47]. As is well known, the existence of MgO will deteriorate the performance of MgH_2 ; hence, higher temperature is required for the release of hydrogen [51]. However, the $\text{MgH}_2/\text{TiO}_2$ composites perform excellent hydrogen desorption properties. To further prove that these two peaks belong to the highly catalytic Mg-Ti oxide instead of less-catalytic MgO , ^1H NMR test was conducted (Figs. 6b and S9). A shorter spin–lattice relaxation time of $\text{MgH}_2/\text{TiO}_2$ (~ 1.54 s) compared with that of blank MgH_2 (~ 4.50 s) indicates a faster H motion in $\text{MgH}_2/\text{TiO}_2$. In particular, the $\text{MgH}_2/\text{TiO}_2$ heterostructure exhibits a much shorter spin–lattice relaxation time of 1.49 s after the 1st re-hydrogenation than that of the as-synthesized $\text{MgH}_2/\text{TiO}_2$, indicating that new species with catalytic activity have formed during the first dehydrogenation process. Thus, it is demonstrated that two characteristic peaks centered at 42.7° and 62.0° are assigned to the ternary Mg-Ti oxide phase (MgTi_2O_4), having much higher catalytic activity than MgO . It can be deduced that the Mg-Ti oxide is formed by the chemical reaction at the interface between MgH_2 and TiO_2 NS during the first hydrogen desorption process. The similar phenomenon, for which Ti/Nb oxide could react with MgH_2 and result in the formation of a new ternary oxide, has also been reported in the previous work [48]. Compared to Mg/MgH_2 , the broader diffraction peaks of the ternary Mg-Ti oxide phase manifest its smaller crystallite size than that of Mg/MgH_2 .

To further clarify the role of the ternary Mg-Ti oxide in the dehydrogenation process, in situ HRTEM observations were carried out by real-time recording of the structure and composition evolution of hydrogenated $\text{MgH}_2/\text{TiO}_2$ during the hydrogen desorption process (Fig. 6c). Additional images with more details are shown in Fig. S10. Before electron beam irradiation (at 0 min), MgH_2 (101) and TiO_2 nanosheets could be identified according to the lattice fringe spacings. After irradiation under a beam current of 3 nA

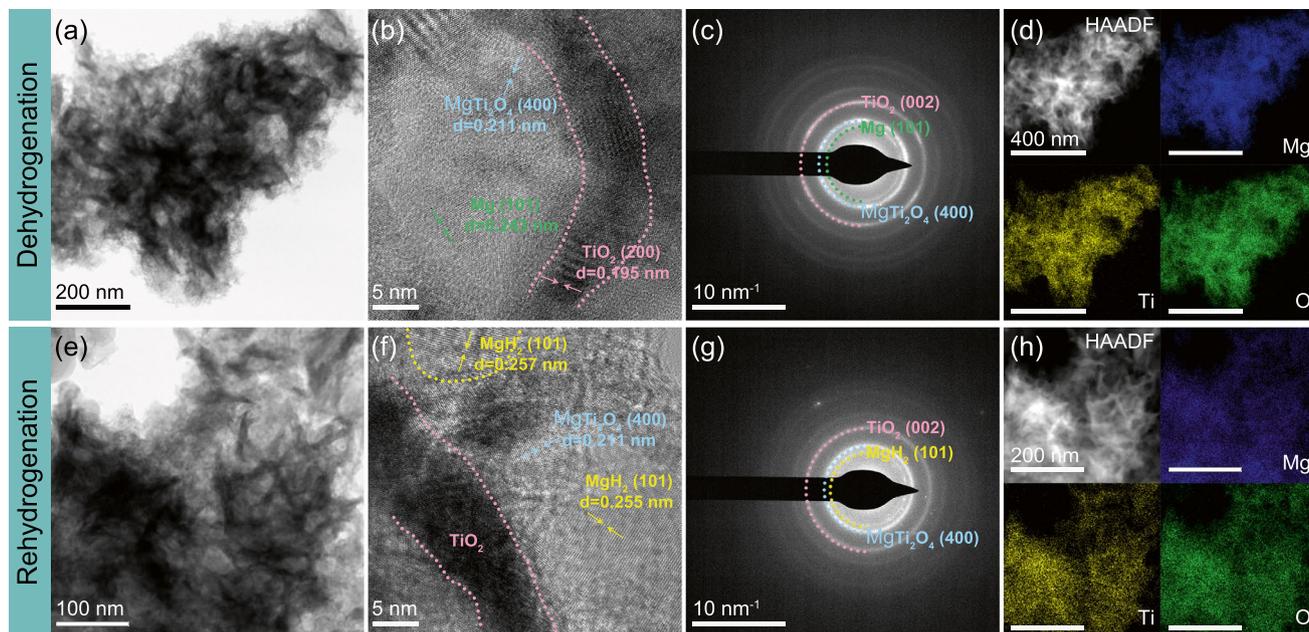


Fig. 5 BF, HRTEM, SAED, HAADF images as well as EDS elemental mapping results of dehydrogenated **a-d** and re-hydrogenated **e-h** 60MgH₂/TiO₂ heterostructure

for 1.5 min, a portion of MgH₂ react with TiO₂, generating a thin Mg-Ti oxide layer. After 2.5 min of irradiation, the MgH₂ near Mg-Ti oxide begins to release hydrogen to form Mg. The observed area releases hydrogen completely after 3 min. It can be seen that, unlike the neat MgO layer, the in-built ternary Mg-Ti oxide catalyst could act as a pathway to facilitate hydrogen diffusion, resulting in improved reaction kinetics. Through the pathways provided by Mg-Ti oxide, the hydrogen can diffuse into/out of Mg/MgH₂, possibly by a formation of metastable titanium hydride (TiH_x) species [19, 52], which coincides well with the XPS chemical state shifts discussed later. In addition, Mg-Ti oxide at the MgH₂/TiO₂ interfaces could also strongly anchor MgH₂ nanoparticles, which significantly inhibits the growth and agglomeration of MgH₂ particles during cycling. Moreover, the high ductility and flexibility of the Mg-Ti oxide [53] can significantly buffer the volume change of MgH₂ particles during de/re-hydrogenation cycles, preventing the detachment of MgH₂ from the TiO₂ substrate and thereby ensuring the excellent cyclic stability.

Moreover, XPS analyses were employed to explore the evolution of the bonding state of Ti in the process of de/re-hydrogenation and the results are shown in Fig. 6d. XPS survey spectrum indicates the coexistence of Mg, O, and Ti

elements (Fig. S11), well coincident with the EDS mapping results. As shown in the high-resolution Ti 2*p* XPS spectra, the signals of Ti⁴⁺ species (458.8 eV for 2*p*_{3/2} and 464.5 eV for 2*p*_{1/2}) can be detected in all samples at different states, indicating that TiO₂ nanosheets still exist in the MgH₂/TiO₂ heterostructure during hydrogen ab/de-sorption process. Additionally, the typical doublets located at 456.8 and 462.5 eV of Ti³⁺ for as-synthesized MgH₂/TiO₂ composites further confirm the successful introduction of oxygen vacancies. Moreover, it can be seen that the Ti 2*p* signals of Ti²⁺ appear in the dehydrogenated samples and Ti²⁺ peaks shift to higher binding energies in the re-hydrogenated samples. The presence of Ti²⁺ peaks testifies the formation of low-valence Ti-H active species. The slight change of the peak position of Ti²⁺ demonstrates that Ti-H active species could act as the intermediates to promote the transportation of electrons and hydrogen [19], further proving that the Mg-Ti oxide acts as a pathway to promote hydrogen diffusion. It is well known that the electronegativity of Ti (1.54) is between Mg (1.31) and H (2.2) [21, 54]. Variable valence of Ti could also facilitate the electron transfer between Mg²⁺ and H⁻, providing a favorable condition for weakening the Mg-H bond. In addition, numerous multi-phase interfaces composed of MgH₂ and multivalence Ti promote the diffusion

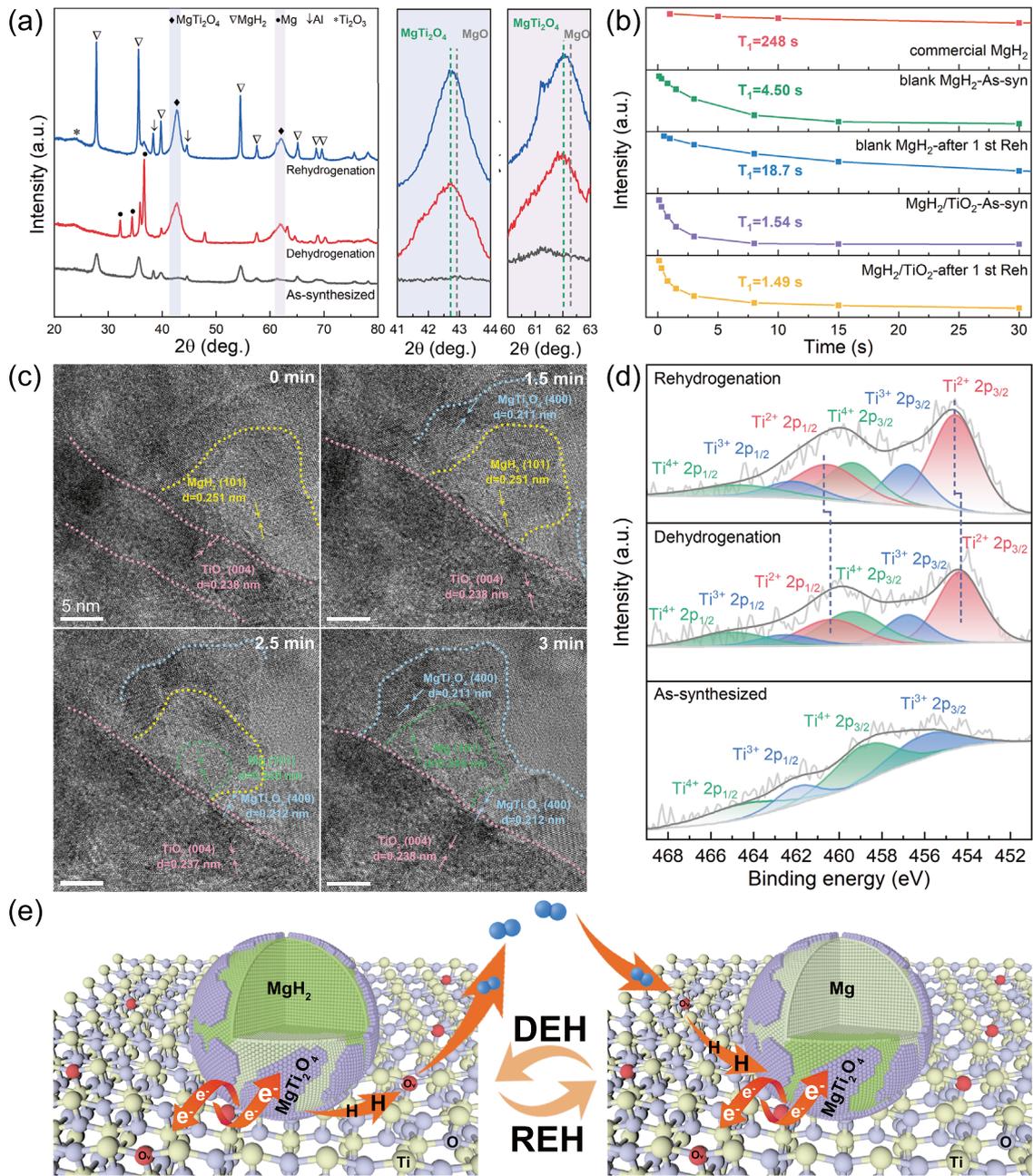


Fig. 6 **a** XRD patterns of the as-synthesized, dehydrogenated, and re-hydrogenated $60\text{MgH}_2/\text{TiO}_2$ heterostructure. **b** NMR spin lattice relaxation times of $60\text{MgH}_2/\text{TiO}_2$, commercial MgH_2 , and blank MgH_2 . **c** In situ HRTEM images showing the microstructure evolution of the hydrogenated $60\text{MgH}_2/\text{TiO}_2$ during the hydrogen desorption process. **d** High-resolution Ti 2p spectra of $60\text{MgH}_2/\text{TiO}_2$ at different states. **e** Schematic diagram showing the hydrogenation and dehydrogenation mechanisms of $\text{MgH}_2/\text{TiO}_2$ heterostructure

of hydrogen and electron and provide more nucleation sites for MgH_2/Mg . Thus, the existence of multivalence Ti-based catalysts accounts for the significantly enhanced hydrogen storage performances of the $\text{MgH}_2/\text{TiO}_2$ heterostructure.

Based on the experimental results and analyses, it is concluded that the superior hydrogen storage performances of the $\text{MgH}_2/\text{TiO}_2$ heterostructure can be attributed to the intrinsic and extrinsic synergistic effects, as illustrated in Fig. 6e: (1) Graphene-like 2D TiO_2 nanosheets with a high

specific surface area provide the unimpeded channels for the rapid diffusion of hydrogen and more nucleation sites for MgH_2/Mg , thereby improving the kinetics of de/re-hydrogenation. (2) Nano-sized MgH_2 are uniformly confined on TiO_2 nanosheets to form a flower-like heterostructure, which significantly suppresses the growth and agglomeration of MgH_2 during the hydrogen ab/de-sorption processes, ensuring the excellent cycling stability. Meanwhile, the restacking of TiO_2 nanosheets can be hampered in turn. (3) Abundant oxygen vacancies introduced by the "one-stone-two-birds" strategy significantly enhance the electrical conductivity of TiO_2 NS and provide additional active sites for transportation of electrons and hydrogen, leading to greatly enhanced hydrogen sorption kinetics. (4) The ternary Mg-Ti oxide catalyst located at the interface of MgH_2 and TiO_2 acts as the pathway to facilitate hydrogen diffusion, resulting in improved hydrogen storage properties. In addition, Mg-Ti oxide possesses better ductility and flexibility than pure MgO. Thus, due to the stable interfacial bonding strength between oxide layers and the MgH_2 nanoparticles, Mg-Ti oxide may exhibit a long-term confinement effect on MgH_2 nanoparticles and significantly buffer successive expansion and contraction of MgH_2 particles during de/re-hydrogenation cycles, improving reversible cycling performance. (5) Multi-valence Ti-based catalysts favor the electron transfer between Mg^{2+} and H^- , weakening the Mg-H bond. Additionally, numerous multi-phase interfaces composed of Mg^{2+} and multi-valence Ti containing species could provide more diffusion pathways for hydrogen and more nucleation sites for MgH_2/Mg .

4 Conclusion

In the present work, a flower-like $\text{MgH}_2/\text{TiO}_2$ heterostructure has been successfully synthesized using oxygen vacancy-rich 2D TiO_2 NS as the functional scaffold. Benefitting from the intrinsic (nano-sized MgH_2) and extrinsic (catalytic activity of Mg-Ti oxide at interfaces) effects as well as the incorporation of oxygen vacancies, the prepared $\text{MgH}_2/\text{TiO}_2$ heterostructure exhibits superior hydrogen storage performances. Specifically, the composite shows excellent desorption performances with a low onset desorption temperature down to 180 °C and a rapid initial dehydrogenation rate at 300 °C (2.116 wt% min⁻¹), surpassing those of the state-of-the-art MgH_2 systems catalyzed by TiO_2 . Meanwhile, the

$\text{MgH}_2/\text{TiO}_2$ heterostructure displays an excellent cycling stability with a capacity retention of 98.5% after 100 cycles at 300 °C. This work offers a promising approach for applying graphene analogues to the construction of advanced hydrogen storage materials with 0D/2D heterostructures.

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