Research Article

Titanium Hydride Nanoplates Enable 5wt% of Reversible Hydrogen Storage by Sodium Alanate below 80°C

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Sodium alanate (NaAlH₄) with 5.6 wt% of hydrogen capacity suffers seriously from the sluggish kinetics for reversible hydrogen storage. Ti-based dopants such as TiCl₄, TiCl₃, TiF₃, and TiO₂ are prominent in enhancing the dehydrogenation kinetics and hence reducing the operation temperature. The tradeoff, however, is a considerable decrease of the reversible hydrogen capacity, which largely lowers the practical value of NaAlH₄. Here, we successfully synthesized a new Ti-dopant, i.e., TiH₂ as nanoplates with ~50 nm in lateral size and ~15 nm in thickness by an ultrasound-driven metathesis reaction between TiCl₄ and LiH in THF with graphene as supports (denoted as NP-TiH₂@G). Doping of 7 wt% NP-TiH₂@G enables a full dehydrogenation of NaAlH₄ at 80°C and rehydrogenation at 30°C under 100 atm H₂ with a reversible hydrogen capacity of 5 wt%, superior to all literature results reported so far. This indicates that nanostructured TiH₂ is much more effective than Ti-dopants in improving the hydrogen storage performance of NaAlH₄. Our finding not only pushes the practical application of NaAlH₄ forward greatly but also opens up new opportunities to tailor the kinetics with the minimal capacity loss.

1. Introduction

Hydrogen storage, bridging hydrogen generation and hydrogen application, plays a crucial role in a future hydrogen energy society [1–4]. Distinct from the matured technologies of compressed and liquefied hydrogen, solid state hydrides can realize higher hydrogen density under moderate pressures and temperature. Metal complex hydrides have attracted tremendous attention as the most promising hydrogen storage candidates because of their high gravimetric and volumetric hydrogen densities [5–8]. Sodium alanate, NaAlH₄, is a typical complex hydride possessing 7.4 wt% of hydrogen capacity and favorable thermodynamics [9–12]. However, the sluggish kinetics results in high operation temperature and poor reversibility for hydrogen storage in NaAlH₄, therefore limiting its practical on-board applications.

Catalyst doping has been proved a feasible approach to help reducing the kinetic barriers of hydrogen storage reactions in metal hydrides. Transition metals and their compounds, especially Ti-based dopants, were found to have the ability to promote fast dissociation and recombination of hydrogen molecules [12–14]. In this respect, Bogdanović and Schwickardi contributed an important breakthrough by introducing a few millimoles of Ti(OBu)₄ or TiCl₃ into NaAlH₄, which enabled reversible hydrogen storage with NaAlH₄ at moderate conditions [15]. After that, a variety of Ti-based species have been explored and evaluated, including halides, oxides, nitrides, borides, carbides, hydrides, alloys, and elemental metals (Figure 1) [16–31]. In most cases, the
studies show that the in situ formed TiH2 is a catalytic active Ti-based compounds. More encouragingly, considerable be a better candidate of dopant in comparison with other valent state and containing hydrogen itself, is expected to phase in the Ti-based compound-modification. 

Figure 1: Comparison of hydrogen desorption (a) and absorption (b) performance of NaAlH4 doped with various Ti-based catalysts. 

Ti-species tends to react with NaAlH4 to form TiAlH4, which shows significant catalytic effect on the de-/rehydrogenation. Although most of the Ti-based species exhibit positive effects on the improvement of kinetics, the reduced hydrogen capacity becomes another important issue, especially for the heavy dopants [32]. More importantly, dopants with high valent Ti are readily reduced to the low valence and even to metal state of zero-valence during ball milling with NaAlH4, while the anions tend to combine with Na+ to form hydrogen inert compounds, consequently further lowering the available hydrogen capacity of the whole composite [16, 33, 34]. As a result, the reversible hydrogen capacity remains only 3-4 wt% for Ti-doped NaAlH4 system [35–37]. This is far from 5.6 wt% of theoretical value while NaAlH4 decomposes to NaH and Al. Therefore, it is in great need to tackle the abovementioned trade-off issue between reaction temperature and hydrogen capacity of NaAlH4-based hydrogen storage materials.

Titanium hydride, TiH2, with Ti being already in low valent state and containing hydrogen itself, is expected to be a better candidate of dopant in comparison with other Ti-based compounds. More encouragingly, considerable studies show that the in situ formed TiH2 is a catalytic active phase in the Ti-based compound-modified NaAlH4 systems [38–43]. For example, Gross et al. observed the conversion of NaH/Al to NaAlH4 at 130°C and 82 atm H2 with the presence of TiH2, indicating a remarkable improvement of hydrogenation properties [38]. Kang et al. reported the in situ generation of TiH2 after mechanical milling of metallic Ti powder with NaH/Al mixture under H2 atmosphere [39]. A similar phenomenon was also observed during hydrogenation of the TiO2-modified NaAlH4 system [40]. Moreover, theoretical predications supported the creation of Ti-H bonds via extracting hydrogen atoms from the accessible AlH4/AlH3 groups [41–43]. However, introduction of commercial TiH2 into NaAlH4 seemed not very effective (only releasing 3.3 wt% H2 within 10 h at 150°C), which may be due to the large TiH2 particle, and thus, the catalytic interactions between TiH2 and NaAlH4 were limited [27]. It is therefore an open question to trigger the high catalytic activity of TiH2 that would reduce the reaction temperature and keep a high hydrogen capacity of NaAlH4 simultaneously.

In this work, we develop a novel facile sonochemical process for the fabrication of two-dimensional (2D) TiH2 nanoplates. Ultrasound was used to drive the formation of nanometer TiH2 on graphene by reacting TiCl4 with LiH in THF solution, thanks to the high solubility of LiCl. Well-defined TiH2 nanoplates with a lateral size of ~50 nm and thickness of ~15 nm on graphene (denoted as NP-TiH2@G) were successfully obtained. Outstanding catalytic activity for hydrogen storage reaction of NaAlH4 was found to be related to the significantly enhanced surface area and excellent dispersibility in comparison with commercial TiH2 in microscale. Full dehydrogenation and rehydrogenation were achieved, respectively, at 80°C and 30°C, with a practical capacity of 5 wt% for NaAlH4 doped with 7 wt% NP-TiH2@G. To the best of our knowledge, this is the first example that NaAlH4 can reversibly store hydrogen in the working temperature range of proton exchange membrane fuel cell (PEMFC) with the highest capacity (Figure 1). Such outstanding hydrogen storage performance of NaAlH4 meets the requirement for on-board hydrogen storage application.

2. Results

2.1. Preparation of TiH2 Nanoplates. The process for the preparation of TiH2 nanoplates was developed, as illustrated schematically in Figure 2, based on the following chemical reaction.

\[
\text{TiCl}_4 + 4\text{LiH} \xrightarrow{\text{THF}} \text{TiH}_2 + 4\text{LiCl} + \text{H}_2 \uparrow \tag{1}
\]

All sample handling was conducted in an Ar-filled glove box. Firstly, stoichiometric titanium tetrachloride (TiCl4)
and lithium hydride (LiH) along with a certain amount of graphene were added to tetrahydrofuran (THF) solution. Subsequently, the sonochemical process was conducted for 4 h at 40 kHz with continuous stirring. Finally, the solid-state product was obtained after filtration, washing, and drying.

Only a broad diffraction peak at around 25° with high background was observed in the X-ray diffraction (XRD) profile (Figure 3(a)), suggesting that the solid-state product was in amorphous or nanocrystalline state. Energy dispersive spectroscopy (EDS) analysis revealed that it was mainly composed of Ti and C in addition to a traced amount of Cl and O as impurities (Figure 3(b)). Further Raman characterization indicated that the C signal could reasonably be attributed to graphene from the characteristic D-band and G-band at 1340 and 1590 cm⁻¹, respectively (Figure S1, Supporting Information). More importantly, H₂ emission was detected by mass spectroscopy (MS) while heating the solid-state product (Figure 3(c)). A sample in the absence of graphene was prepared according to reaction (1) with the same process to determine exactly the H content. Thermogravimetric analysis (TGA) results indicated around 4 wt% of weight loss (Figure 3(d)), agreeing well with the H content in TiH₂. It is worth noting that the peak temperature for the hydrogen release of the solid product is around 120°C (Figure 3(c)), much lower than that of TiH₂ in microscale (>500°C) [44]. Suggesting the successful synthesis of graphene-supported TiH₂ nanoplats (denoted as NP-TiH₂@G hereinafter) by a newly developed sonochemical process. The thickness of the prepared TiH₂ nanoplats was determined as ~15 nm by atomic force microscope (AFM) measurement (Figure 4(d)).

A time dependence of growth of TiH₂ nanoplats was also clearly observed by means of TEM (as shown in Figure 5). For comparison, the pristine graphene with a clean surface is shown in Figure S4 (Supporting Information). After 1 h of ultrasonic treatment, a large number of ~10 nm sized black sheets cover on the graphene (Figures 5(a) and 5(b)). Extending the time to 2 h, some nanoplats grew up to ~50 nm (Figures 5(c) and 5(d)). Further extending to 4 h, the ~50 nm-sized nanoplats were largely increased in quantity along with the disappearance of small nanosheets (Figures 5(e) and 5(f)). The loading amount of TiH₂ was determined to be ~70% in weight by inductively coupled plasma spectroscopy (ICP) examination, which is distinctly higher than that obtained previously by a solvothermal process (~46%) [44]. Thus, higher catalytic activity was expected. In a strong contrast, only coarse particles with ~500 nm in size were obtained via the same sonochemical process without graphene as support (Figure S5, Supporting Information). This fact unambiguously indicates the critical important role played by graphene as a hard template governing the morphology of TiH₂ nanoplate, attributed to the very similarity in lattice spacings (2.10 Å for the (002) planes of TiH₂ and 2.13 Å for the (100) planes of graphene) [44].

2.2. Catalytic Activity of TiH₂ Nanoplats. The 4 h-sonicated NP-TiH₂@G was selected to mix with NaAlH₄ by ball milling in order to evaluate its catalytic effectiveness because it took 4 h to complete the conversion of TiH₂ from TiCl₄ as indicated by the thorough disappearance of the characteristic reflections of LiH in the XRD profile after 4 h of sonification (Figure S6, Supporting Information). Six samples of interplanar spacing of 0.21 nm (Figure 4(c)), which corresponds to the (002) planes of TiH₂. The TEM observations, therefore, strongly prove the successful synthesis of graphene-supported TiH₂ nanoplats (denoted as NP-TiH₂@G hereinafter) by a newly developed sonochemical process. The thickness of the prepared TiH₂ nanoplats was determined as ~15 nm by atomic force microscope (AFM) measurement (Figure 4(d)).

![Figure 2: Schematic illustration for the preparation process of TiH₂ nanoplats.](image-url)
NaAlH$_4$-xNP-TiH$_2$@G with $x = 0, 1, 3, 5, 7$, and $9 \text{ wt}\%$ were examined. A remarkable reduction in the dehydrogenation temperature of NaAlH$_4$ was observed as NP-TiH$_2$@G increasing from 1 wt% to 7 wt% (as shown in Figure 6(a)). For the 7 wt% NP-TiH$_2$@G-containing sample, the release of hydrogen started from 80°C and completed at 160°C with an usable hydrogen capacity of 5 wt%. The on-set and end temperatures of dehydrogenation were reduced by 115 and 180°C, respectively, compared to those of the pristine NaAlH$_4$. Further increase of NP-TiH$_2$@G to 9 wt% caused an obvious loss of hydrogen capacity without obvious reduction in the dehydrogenation temperature. Therefore, 7 wt% was the optimal amount for NP-TiH$_2$@G by taking into account of the hydrogen capacity and the dehydrogenation temperature.

The dehydrogenated sample was subsequently subjected to hydrogenation with ramped temperatures under 100 atm of H$_2$ pressure (as shown in Figure 6(b)). The 7 wt% NP-TiH$_2$@G-containing sample showed superior rehydrogenation properties to those of pristine NaAlH$_4$ and NaAlH$_4$ doped with the commercial TiH$_2$. Specifically, 7 wt% NP-TiH$_2$@G-containing sample absorbed 5 wt% H$_2$ from 25°C to 105°C. It is worth emphasizing that the 7 wt% NP-TiH$_2$@G-containing sample started to absorb hydrogen at a temperature as low as 25°C, and more than 90% of the rehydrogenation can be completed below 90°C, which is close to the working temperature of PEMFC. Such significant improvement of the rehydrogenation by the addition of 7 wt% NP-TiH$_2$@G demonstrated for the first time that high reversible capacity coupled with the dehydrogenation temperature of NaAlH$_4$ can be achieved simultaneously by a proper dopant, which can be mainly attributed to the highly homogenous dispersion of the prepared NP-TiH$_2$@G (Figure 6(c)) than that of the commercial TiH$_2$ (Figure 6(d)) in NaAlH$_4$. The Ti-rich area was clearly observed in NaAlH$_4$ doped with the commercial TiH$_2$, probably due to the large particle size of TiH$_2$ (Figure S7, Supporting Information). More importantly, most of the NP-TiH$_2$ was converted to...
Al-Ti species after 24 h ball milling with NaAlH₄, whereas only small amount of Al-Ti species can be detected in the commercial TiH₂ (Figure S8, Supporting Information). This suggests that the reduced particle size of TiH₂ facilitates the formation of Al-Ti species, which possess high catalytic activity for the dehydrogenation and rehydrogenation of NaAlH₄ [9, 34, 40]. Further XRD characterization indicated that the reversible hydrogen capacity still originated from the decomposition and reformation of NaAlH₄ (as shown in Figure S9 (Supporting Information)).

Moreover, the dehydrogenation temperature was further reduced by ~10°C in the follow-up 2nd cycle (Figure S10, Supporting Information). It can be clearly seen that the particle size of Ti-containing species reduced largely to around 5 nm from the aberration-corrected scanning transmission electron microscope (STEM) observation and EDS mapping analyses (as shown in Figure 7). From the relative content analyses, the Al-Ti species changed from Al₈₅Ti₁₅ for the as-milled sample to Al₅₈Ti₄₂ for the cycled sample, close to Al₅₀Ti₅₀, suggesting the reconstruction or optimization of the local atomic structure of Al-Ti species during cycling. This is further evidenced by the slight low-angle shift of the characteristic reflection of Al-Ti species in the XRD profiles because of the incorporation of more Ti (Figure S11, Supporting Information). According to the density functional theory (DFT) calculation, the kinetic barrier of the transfer of H atom from NaAlH₄ to the surface of Al is largely reduced from 0.47 eV (Figure S12a, Supporting Information) to 0.14 eV (Figure S12b, Supporting Information) with the present of one Ti atom. This process can even proceed spontaneously when two Ti atoms are introduced into the surface of Al in the near-nearest-neighbor mode (Figure S12c, Supporting Information). This suggests that the Al-Ti species are of great importance for the significant improvement of dehydrogenation kinetics of NaAlH₄, which agrees well with the previous reports [40, 45].

### 2.3. Hydrogen Storage Kinetics of NP-TiH₂@G-Containing NaAlH₄

Figures 8(a) and 8(b) show the isothermal dehydrogenation behaviors of NaAlH₄-7 wt% NP-TiH₂@G sample after 1 dehydrogenation/rehydrogenation cycle, measured by volumetric and thermogravimetric (TG) methods, respectively. Isothermal volumetric dehydrogenation indicates that the full dehydrogenation of 5 wt% of hydrogen was achieved within 30 min at 140°C. At 120°C, it took around 200 min to complete. Even at 100°C, the major part of hydrogen (around 3.2 wt%) can be released within 30 min and the dehydrogenation completed within 500 min. The time for the full dehydrogenation was reduced to only 250 min at TG measurement (Figure 8(b)), which is attributed to the absence of blocking effect from hydrogen back pressure. More encouragingly, the full dehydrogenation can be achieved even at 80°C, which is the lowest dehydrogenation temperature for NaAlH₄ reported so far.

The full isothermal rehydrogenation (~5 wt% of hydrogen) of dehydrogenated NaAlH₄-7 wt% NP-TiH₂@G completed within only 25 min at 100°C (as shown in
Figure 8(c). Amazingly, the full rehydrogenation was also achieved even at 30°C. This is the first complex hydride system that is able to work at the target temperature range proposed by US DOE with 5 wt% of reversible hydrogen capacity, although the dehydrogenation/rehydrogenation rates need to be further improved [46].

The apparent activation energy of dehydrogenation reactions of NaAlH₄-7 wt% NP-TiH₂@G was calculated based on the Kissinger’s plots (Figure 8(d)), in which the peak temperatures and the heating rates were obtained from temperature programmed desorption (TPD) curves shown in Figure S13 (Supporting Information). The apparent activation energies for each step are 80 ± 3 and 70 ± 2 kJ mol⁻¹, respectively. These values are reduced by ~40% compared to those of the pristine NaAlH₄ [47], and even remarkably lower than those of other catalyst-modified NaAlH₄ systems (Table S1) [48–54], indicating the significant reduction of the dehydrogenation kinetic barriers induced by the newly formed Al-Ti catalytic species. In contrast, the addition of 7 wt% NP-TiH₂@G did not affect much the thermodynamic properties of NaAlH₄ as indicated by the nearly unchanged desorption enthalpy change, which were determined to be approximately 36.5/47.4 and 36.3/47.0 kJ/mol-H₂ for pristine sample and 7 wt% NP-TiH₂@G-containing sample, respectively, by analyzing the differential scanning calorimetry (DSC) results (Figure S14, Supporting Information).

2.4. Dehydrogenation/Rehydrogenation Cycling of NP-TiH₂@G-Containing NaAlH₄. Dehydrogenation/rehydrogenation cycling performance of the NaAlH₄-7 wt% NP-TiH₂@G sample is shown in Figure 9(a). Here, dehydrogenation was operated at 140°C under initial vacuum and rehydrogenation at 100°C/100 atm H₂. No obvious degradation was observed after 50 cycles. The hydrogen capacity was 4.8 wt% at the 50th cycle, which means a capacity retention...
of 96% based on the initial capacity of 5.0 wt%. The cycling performance demonstrates a stable cyclability of the NP-TiH$_2$@G-containing NaAlH$_4$.

To shed light on the stable cycling behavior of NP-TiH$_2$@G-containing NaAlH$_4$, the particle size, distribution, and chemical states of catalytic species were examined and analyzed. TEM observation displayed that the catalytic species remained as ultrafine particles of ~5 nm in size without obvious agglomeration (Figure 9(b)). EDS mapping analyses (Figures 9(c) and 9(d)) indicated the homogenous distribution of Ti element on NaAlH$_4$ matrix even after 50 cycles. In addition, high-resolution XPS spectra of Ti 2p showed a stable chemical state from 2 to 50 cycles for the nearly unchanged $2p_{3/2} - 2p_{1/2}$ spin–orbit doublet at 453.2/458.1 eV (Figure 9(e)) [55]. As a result, we believe that the small particle size, homogenous dispersion, and stable chemical state are of critical importance for the long-term cyclability of NP-TiH$_2$@G-containing NaAlH$_4$. This finding provides important insights and greatly encourages the further development of the catalysis-promoted complex hydrides for practical on-board applications.

3. Discussion

Two-dimensional TiH$_2$ nanoplates with a lateral size of 50 nm and a thickness of 15 nm were successfully synthesized by using graphene as support, based on a novel facile sonochemical process. The graphene played a critical role in the nucleation and growth of TiH$_2$ nanoplates. The prepared TiH$_2$ nanoplates displayed superior catalytic activity than the commercial TiH$_2$ of microscale for hydrogen storage in NaAlH$_4$. The 7 wt% NP-TiH$_2$@G-containing NaAlH$_4$ started releasing hydrogen at 80°C, which was lowered by 115°C in comparison with pristine sample. In TG measurement, full dehydrogenation was achieved with 5.0 wt% of practical hydrogen capacity even at 80°C. It is worth emphasizing that the rehydrogenation can complete at 30°C under 100 atm of H$_2$. Operating at 140°C/initial vacuum for
dehydrogenation and 100 °C/100 atm H₂ for rehydrogenation, a stable cyclability was confirmed, as only 0.2 wt% of capacity loss after 50 cycles. Mechanistic studies revealed the active catalytic species was converted from TiH₂ to Al₈₅Ti₁₅ during ball milling and further to near Al₅₀Ti₅₀ after the first de-/hydrogenation cycle, which remained stable in the subsequent cycling. DFT calculations reveal that the kinetic barrier of the transfer of H atom from NaAlH₄ to the surface of Al is largely reduced by the formation of Al-Ti species. The small particle, homogenous dispersion and stable chemical state of active catalytic species are responsible for the long-term cyclability of NP-TiH₂@G-containing NaAlH₄. The findings presented in this work make NaAlH₄ step closer towards practical on-board hydrogen storage applications.

4. Materials and Methods

4.1. Materials Synthesis. All reagents and solvents were purchased and used as received without further purification. TiH₂ nanoplates supported on graphene (NP-TiH₂@G) were synthesized by a newly developed sonochemical process [56] under argon atmosphere using titanium chloride (TiCl₄, 99.9%, Aladdin), lithium hydride (LiH, 99.4%, Alfa Aesar), and graphene (97%, Aladdin) as the raw materials. In a typical procedure, TiCl₄ (2 mmol), LiH (8 mmol), and graphene (20 mg) were sequentially added to 70 mL THF in a flask-3-neck which was irradiated by ultrasonic waves (40 kHz, W-600D, Shanghai Ultrasonic Instrument, Shanghai, China) for 4 h under mechanical stirring. A black precipitate of NP-TiH₂@G was separated from the THF solution by filtration, washed twice with THF and finally dried at 70 °C under dynamic vacuum. The obtained NP-TiH₂@G was mixed with NaAlH₄ on a planetary ball mill (Nanjing, China). The ball milling was conducted at 500 rpm for 24 h in the milling jar filled with 50 atm H₂ at the ball-to-sample weight ratio of approximately 120:1. The doping amounts of NP-TiH₂@G were set to be x = 0, 1, 3, 5, 7, and 9 wt%.

4.2. Characterization. The structure information was collected on a MiniFlex 600 X-ray diffractometer (XRD) (Rigaku, Japan) with Cu Kα radiation (λ = 0.15406 nm) operated at 40 kV and 15 mA. The 2θ range was set at 10-90° with a 0.05° step increment. A custom-designed container with a window covered by Scotch tape was used to prevent air and moisture exposure of the sample. The sample morphology and microstructure were observed with scanning electron microscope (SEM) (Hitachi S-4800), aberration-corrected scanning transmission electron microscope (STEM) (Titan G² 80-200 Chemi STEM FEI, 200 kV), and TEM (Tecnai G² F20 S-TWIN FEI, 200 kV). For SEM observation, the sample was transferred quickly to the SEM facility under Ar protection. For STEM and TEM examinations, the sample was protected with a double-tilt vacuum transfer holder (Gatan 648, USA). Atomic force microscope (AFM) characterization was performed on Bruker Dimension Icon under the tapping mode, with samples prepared by dropping freshly diluted sample solutions onto silicon substrates. X-ray photoelectron spectroscopy (XPS) analyses were carried out using a Thermo Scientific ESCALAB 250Xi spectrometer with a monochromatic Al Ka X-ray source at a base pressure of 6.8 × 10⁻⁹ Torr. The Ti content of samples were determined by inductively coupled plasma (ICP) spectroscopy on a PE Optima 8000 instrument.

4.3. Property Measurements. A home-built temperature programmed desorption (TPD) system attached to a mass spectrometer (MS) was employed to characterize the temperature-dependent dehydrogenation behavior using Ar...
as a carrier gas with a flow rate of 20 mL min\(^{-1}\). For each test, approximately 40 mg sample was heated up from room temperature to desired temperatures at 2°C min\(^{-1}\). Quantitative dehydrogenation/hydrogenation properties were measured using a Sieverts-type apparatus under isothermal and nonisothermal conditions, and the sample loading was approximately 70 mg sample. The nonisothermal data were acquired by gradually heating the sample from room temperature to a preset temperature at an average rate of 2°C min\(^{-1}\) under primary vacuum (-10\(^{-3}\) Torr) for dehydrogenation and 1°C min\(^{-1}\) with 100 atm H\(_2\) for hydrogenation. The isothermal measurements were conducted by rapidly heating the sample to a desired temperature and then dwelling during the entire test. The temperature and pressure were monitored and recorded simultaneously, and the amounts of hydrogen released/uptaken were calculated based upon the ideal gas law. Thermogravimetric analysis (TGA) was carried out on a Netsch TG 209 F3 instrument under an argon atmosphere at a ramping rate of 2°C min\(^{-1}\). Differential scanning calorimetry (DSC) experiments were performed with a NETZSCH DSC 200F3 unit at 2°C min\(^{-1}\) of heating rate. Approximately 2 mg of sample was placed in an Al\(_2\)O\(_3\) crucible for measurement.

4.4. Theoretical Calculation. Density functional theory (DFT) calculations were conducted in the Vienna Ab initio Simulation Package (VASP). The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE)
model was taken as the exchange-correlation functional [57]. Projector augmented wave pseudopotentials (PAWs) were employed to model the ionic potentials [58]. The precession setting of "PREC = Accurate" was used. All atoms were fully relaxed until the force on them was less than 0.05 eV Å\(^{-1}\). The Brillouin zone integration was performed with gamma-centred sampling of \(3 \times 3 \times 1\). The minimum-energy pathway was computed using the climbing-image nudged elastic
band (CI-NEB) method [59]. Al(111) surface was selected because it has the lowest surface free energy and then is most likely exposed. A six-layer slab containing 96 atoms was constructed to simulate the surface with the lowest two layers fixed to represent the bulk. The thickness of vacuum layer was set as 20 Å to avoid interaction between neighbouring images.

**Data Availability**

The data used to support the findings of this study are included within the article and supplementary information files and/or may be requested from the authors.

**Conflicts of Interest**

The authors declare no competing financial interest.

**Authors’ Contributions**

Z.H.R. and X.Z. contributed equally to this work.

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**Supplementary Materials**

Figure S1: Raman spectrum of as-prepared solid product after sonochemical reaction between TiCl₄ and LiH in THF. Figure S2: MS signal of gaseous product of reaction of TiCl₄ with LiH in THF under ultrasonic treatment. Figure S3: XRD profile of the solid obtained by drying the filtrate of reaction of TiCl₄ with LiH in THF under ultrasonic treatment. Figure S4: TEM image of pristine graphene. Figure S5: SEM image of TiH₂ prepared by sonochemical reaction of TiCl₄ and LiH without graphene as support. Figure S6: XRD profiles of NaAlH₄ doped by 7 wt% NF-TiH₂@G prepared by different ultrasonic times. Figure S7: SEM image of commercial TiH₂. Figure S8: Ti 2p XPS spectra of NaAlH₄ mixed with commercial TiH₂ and TiH₂ nanoplates. Figure S9: XRD profiles of 7 wt% NF-TiH₂@G-containing NaAlH₄ after different treatments. Figure S10: the volumetric dehydrogenation curves of activated NaAlH₄-7 wt% NP-TiH₂@G sample. Figure S11: XRD profiles of NaAlH₄-7 wt% NP-TiH₂@G sample after ball milling and 1st de/rehydrogenation cycle (2Θ: 39-44°). Figure S12: energy barriers of H atom transferring from NaAlH₄ molecule to Al surface (a) and single-Ti-substituted Al surface (b) and relaxed geometry of NaAlH₄ molecule placed on two-Ti-substituted Al surface (c). Figure S13: TPD curves of activated NaAlH₄-7 wt% NP-TiH₂@G sample with different heating rates. Figure S14: DSC curves of pristine NaAlH₄ and NaAlH₄-7 wt% NP-TiH₂@G samples. Table S1: comparison of activation energy (E_a) of NaAlH₄ doped with different catalysts. (Supplementary Materials)

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