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# Solid-state synthesis of amorphous TiB<sub>2</sub> nanoparticles on graphene nanosheets with enhanced catalytic dehydrogenation of MgH<sub>2</sub>

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## ARTICLE INFO

## Article history:

Received 19 October 2013

Received in revised form

2 December 2013

Accepted 21 December 2013

Available online 29 January 2014

## Keywords:

Hydrogen storage

Magnesium hydride

Bi-component catalyst

Synergistic effect

## ABSTRACT

A bi-component catalyst TiB<sub>2</sub>/GNSs (GNSs is the abbreviation of graphene nanosheets) is synthesized by a solid-state method. Microstructural characterizations based on SEM (scanning electron microscopy), TEM (transmission electron microscopy) and N<sub>2</sub> physisorption show that the size of TiB<sub>2</sub>/GNSs catalyst is at nanoscale (20–30 nm) with a surface area of 84.69 m<sup>2</sup> g<sup>-1</sup>. The TiB<sub>2</sub>/GNSs nanoparticles ball milled with MgH<sub>2</sub> and exhibit enhanced catalytic effects on the dehydrogenation properties of MgH<sub>2</sub> compares to TiB<sub>2</sub> and GNSs individually. DSC (differential scanning calorimetry) measurements confirm that the peak desorption temperature of MgH<sub>2</sub>-5 wt%TiB<sub>2</sub>/GNSs composites can be lowered more than 44 °C than the pure as-milled MgH<sub>2</sub>. And the dehydrogenation kinetics of TiB<sub>2</sub>/GNSs-doped MgH<sub>2</sub> is severalfold acceleration compares to the pure as-milled MgH<sub>2</sub>. It is proposed that the TiB<sub>2</sub>/GNSs nanoparticles could significantly enhance the intimate interface between TiB<sub>2</sub>/GNSs and hydride, therefore, provide more active “catalytic sites” and H “diffusion channels” to reduce the dehydrogenation temperature and improve the dehydrogenation kinetics of MgH<sub>2</sub>. The synergistic effect of nano-GNSs and TiB<sub>2</sub> nanoparticles contributes to the highly efficient for dehydrogenation of MgH<sub>2</sub>-5wt%TiB<sub>2</sub>/GNSs composites.

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## 1. Introduction

Magnesium hydride (MgH<sub>2</sub>) has attracted much attention for hydrogen storage applications because of its high gravimetric (7.6 wt%) and volumetric (110 kg/m<sup>3</sup>) capacity [1,2]. However, the high hydrogen desorption temperature >300 °C and

sluggish sorption kinetics of MgH<sub>2</sub> have limited its practical application [3,4]. The origin of high operational temperatures and sluggish kinetics is mainly due to the strongly endothermic dehydriding reaction (about 75 kJ/mol) and slow diffusivity of H atoms through MgH<sub>2</sub>/Mg [5,6].

To overcome these two drawbacks, numerous strategies have been developed involving alloying [7–10], catalyzing

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[11–15] and nanosizing [16–20]. As part of this research, a wide range of metals [21–24], transition metal compounds [25–30] have been studied. Among these metals and transition metal compounds tested, titanium compounds such as  $\text{TiF}_3$ ,  $\text{TiCl}_3$ ,  $\text{TiO}_2$ ,  $\text{TiN}$  and  $\text{TiC}$  have attracted considerable interest as high effective catalysts due to the high affinity of titanium cation toward hydrogen in  $\text{MgH}_2$  [27,28,30–32], thus to destabilize the Mg–H bonds and promote  $\text{MgH}_2$  dissociation. Wang et al. [27] investigated the effects of typical titanium compounds ( $\text{TiF}_3$ ,  $\text{TiCl}_3$ ,  $\text{TiO}_2$ ,  $\text{TiN}$  and  $\text{TiH}_2$ ) on hydrogen sorption kinetics of  $\text{MgH}_2$  systematically, it was found that  $\text{TiF}_3$  exhibited the most enhanced catalytic activity on  $\text{MgH}_2$ , and it was also proposed F anion in the catalytic function plays an important role. Similarly, small addition of  $\text{TiC}$  significantly improved absorption and desorption kinetics of  $\text{MgH}_2$  [28,31]. In particular, it was found that decreased the particle size of  $\text{TiC}$  led to significant dehydrogenation kinetic improvement [31]. In addition, the influence of milling with 50 wt% $\text{TiB}_2$  for  $\text{MgH}_2$  decomposition has been investigated by Dobrovolsky et al. [32] and the dissociation temperature of  $\text{MgH}_2$  was reduced by about 50 °C. Furthermore, crystalline  $\text{TiB}_2$  as an efficient catalyst for synthesis and dehydrogenation/hydrogenation properties of  $\text{NaAlH}_4$  system has already been studied in our previous work [33], and the maximum decreasing temperature of hydride decomposition was reduced to 90 °C for  $\text{NaAlH}_4/4$  mol% $\text{TiB}_2$  mixture obtained by ball milled 70 h under 1 MPa  $\text{H}_2$  pressure. Thus, it is proposed that less quantity addition of  $\text{TiB}_2$  nanoparticles maybe improve the hydrogen sorption properties of  $\text{MgH}_2$  under more mild conditions.

Apart from transition metal compounds, some non-metal elements such as carbon materials (graphite, carbon nanotubes, activated carbon, fullerene and graphene) were also employed to function as efficient catalysts to improve the sorption kinetics of  $\text{MgH}_2$  [14,15,34–36]. These carbon materials can also act as excellent anti-sintering agents towards  $\text{MgH}_2$  powder during ball milling and hydrogenation/dehydrogenation reaction. Especially for graphene nanosheets (GNSs), as new member of the carbon materials group, can facilitate the hydrogenation/dehydrogenation kinetics due to its high surface area, special microstructure and high defective edge sites, which inhibits the particles agglomeration, benefits hydrogen atoms diffusion and stimulated  $\text{H}_2$  dissociation during hydrogen sorption reaction of hydride [37,38]. Recently, many researchers reported that the effects of carbon-supported catalysts were more efficient for hydrogen sorption kinetics compared with doping the identical carbon and metal/metal compounds directly [39–42]. It was found that such catalysts can not only control the particles size of supported materials at nanoscale to exhibit excellent catalytic effect, lower the addition amount of catalyst without reduction of the catalytic effect, but also decrease the milling time due to easier contact of hydride surface by nanosizing of carbon-supported catalysts. Therefore, GNSs-based nanocomposites are becoming increasingly recognized for their application in promoting performance of hydrogen storage. Furthermore, the cost to process and use GNSs-based catalysts for hydrogen storage can be suppressed by the advanced preparation technology and large mass of green wood sources on the world.

Herein, we select  $\text{TiB}_2$  as the transition metal compound due to its high catalytic activity, highly crumpled GNSs was employed as the support of  $\text{TiB}_2$  because of its high surface area and defective edge sites. The synthesis of amorphous  $\text{TiB}_2$  nanoparticles on GNSs (denoted as  $\text{TiB}_2/\text{GNSs}$ ) by a solid-state approach and the excellent catalytic effects of  $\text{TiB}_2/\text{GNSs}$  on  $\text{MgH}_2$  dehydrogenation kinetics and hydrogen storage capacity are reported. The fundamental mechanism responsible for the improved hydrogen sorption properties of  $\text{MgH}_2\text{-TiB}_2/\text{GNSs}$  system is also presented.

## 2. Experimental

### 2.1. Sample preparation

#### 2.1.1. Synthesis of $\text{TiB}_2/\text{GNSs}$

GNSs was prepared by thermal exfoliation of graphene oxide (GO) at 900 °C in a quartz tube under  $\text{Ar-H}_2$  (9:1 v/v) flow for 30 min.  $\text{TiB}_2/\text{GNSs}$  catalyst was prepared from GNSs-supported  $\text{Ti}(\text{OH})_4$  and  $\text{KBH}_4$  by a solid-state reaction as described in our previous work [33]. Meanwhile, individual  $\text{TiB}_2$  nanoparticles were synthesized separately following the same procedure.

#### 2.1.2. Synthesis of Mg-based nanocomposites

Typically, the  $\text{MgH}_2$  powder (Alfa Aesar, 98%) was mixed with 5 wt% as-prepared  $\text{TiB}_2/\text{GNSs}$ , then the mixture was loaded in a 100 mL stainless steel milling vessel containing steel balls, the ball-to-powder mass ratio equal to 40:1. Planetary ball mill model was employed and the milling detail was as follows: ball milling the mixture for 5 h under 0.5 MPa  $\text{H}_2$  pressure at room temperature with a rotational speed of 450 rpm, after every 12 min of milling there was a 30 s pause and the rotation was automatically reversed. For reference,  $\text{MgH}_2\text{-5wt}\%\text{TiB}_2$ ,  $\text{MgH}_2\text{-5wt}\%\text{GNSs}$  and  $\text{MgH}_2$  composites were also prepared in the same conditions. All the materials handling was performed in a glovebox filled with purified argon (99.999%), in which the  $\text{H}_2\text{O}$  and  $\text{O}_2$  levels were below 1 ppm.

### 2.2. Characterization techniques

The synthesized materials were characterized by powder X-ray diffraction (XRD, Rigaku MiniFlexII,  $\text{Cu K}\alpha$  radiation), X-ray photoelectron spectrometer (XPS, PHI 5000 Versaprobe, ULVAC PHI), scanning electron microscopy (SEM, JEOL JSM7500), transmission electron microscopy (TEM, JEOL JEM-2010FEF, 200KV), and nitrogen adsorption and desorption isotherms (NOVA 2200e, Quantachrome Instruments). The composition of  $\text{TiB}_2/\text{GNSs}$  was quantified by inductively coupled plasma optical emission spectrometry (ICP-OES) (ICP-9000). Decomposition performance of the hydrogen storage materials was measured by differential scanning calorimetry (DSC, Q20P, TA Instruments), the heating rate was 5 °C  $\text{min}^{-1}$  and the temperature ranged from 110 to 440 °C. Hydrogen desorption properties were determined using a homemade Sievert's apparatus. Desorption measurements were performed at 300, 270, and 240 °C with an initial pressure of 5 KPa, respectively.

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