Effect of carbon nanotubes on the microstructural evolution and hydrogen storage properties of $Mg(BH_4)_2$

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ABSTRACT

As an important member of complex hydrides, $Mg(BH_4)_2$ has a high gravimetric capacity (14.9 wt%). In this study, the $Mg(BH_4)_2$ was synthesized by the ion exchange method. Afterwards, the $Mg(BH_4)_2$ composites with different amounts (2, 5, 10, 25 and 50 wt%) of carbon nanotubes (CNTs) were prepared by mechanical milling. Effects of the CNTs on the microstructural evolution and hydrogen storage properties were investigated. The onset desorption temperature of the $Mg(BH_4)_2$-5 wt% CNTs is decreased to lower temperature around 120 °C from 275 °C. The desorption plateau of $Mg(BH_4)_2$-5 wt% CNTs is the highest, which ascribes that CNTs causes the reaction pathway change. Additionally, the $Mg(BH_4)_2$-5 wt% CNTs shows the best dehydriding kinetics properties, and can desorb 6.04 wt% hydrogen within 2000 s at 300 °C. The dehydrogenation activation energy of the $Mg(BH_4)_2$-5 wt% CNTs is decreased to 130.2 kJ/mol H_2, which is much lower than that of pure $Mg(BH_4)_2$.

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1. Introduction

Nowadays, the protection of resources and environment are two major problems to the mankind. Hydrogen is a feasible examinee as an energy carrier of the future due to its high capacity density, clean combustion and potentially renewable character [1–5]. Achieving safe and efficient hydrogen storage systems is the critical technical bottleneck for the wide use of hydrogen as a fuel [6–9].

Among the existing hydrogen storage materials, metallic boro-hydrides ($M(BH_4)_n$; M shows a metal element and the n depends on the valence of M) such as $LiBH_4$, KBH_4, and $NaBH_4$ with high gravimetric and volumetric hydrogen capacities have engaged much attention for solid-state hydrogen (H_2) storage applications [10]. For instance, $LiBH_4$ has a gravimetric capacity of 18.5 wt% and a highest volumetric capacity of 121 kg H_2/m^3, which outdistances the targets (6.5 wt% and 50 kg H_2/m^3 for gravimetric and volumetric capacities, respectively) of the US Department of Energy (DOE). However, $LiBH_4$ can desorb 13.8 wt% of hydrogen, far lower than the theoretical value, and its dehydriding temperature has been reported to be above 357 °C [11–16,33].

According to first-principles calculation, the Pauling electronegativity (χp) value shows the strength of ionic bonding, which affects their stability. Moreover, the strength of B–H bond has more important effect on their reversibility and stability. The higher the value of χp, the weaker the $M(BH_4)_n$. Mg has a bigger χp ($\chi p = 1.31$) than Na, Li, and Ca ($\chi p = 0.93$, 0.98, and 1.00, respectively) [17–19]. In the report, we can find that $Mg(BH_4)_2$ has a gravimetric capacity of 14.9 wt% and a highest volumetric capacity of 146.5 kg H_2/m^3, and starts to release hydrogen at the temperature of 275 °C and reaches its hydrogen release peak when the temperature is increased to 375 °C [11,20–23].

Unfortunately, the high desorption temperature and poor kinetics hinder its hydrogen storage applications. A series of methods have been adopted to improve the hydrogen storage performance of $Mg(BH_4)_2$ such as adding catalysts, reducing the particle size to nanoscale and multiphase complex [24,25]. Li et al. [15] and Shi et al. [26] studied the ball-milled $Mg(BH_4)_2$ with Ti-based catalysts such as TiO_2, Ti, and $TiCl_3$, and they reported that when $TiCl_3$ added into $Mg(BH_4)_2$, the hydrogen desorption temperature was significantly decreased to about 88 °C, but Ti, TiH_2, and TiB_2 were useless to the desorption properties of $Mg(BH_4)_2$. Although such a desorption temperature is the best achievement so far, it is still too high for hydrogen storage applications. As a result, it is extremely urgent to find a new method which can decrease the desorption temperature of $Mg(BH_4)_2$ to the temperature range within DOE suggestion.

Carbon nanotubes (CNTs), one of the carbon allotropes, has been

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used for nanoconfinement, catalysis and reducing the strength of bond in the field of hydrogen storage. It can be utilized for improving the hydrogen storage properties of complex hydrides owing to its unique electrical, thermal and mechanic properties [8,27–31]. In previous research studies, adding CNTs into materials have shown that it can catalyse the hydrogen storage of NaAlH$_4$. As a result, CNTs can reduce the strength of Al—H bond and thus enhance the hydrogen desorption. Recently, Han et al. [30] synthesized the hybrids of Mg(BH$_4$)$_2$-CNTs with Mg(BH$_4$)$_2$ loadings of 25, 50 and 75 wt% through a solvent method and reported that the Mg(BH$_4$)$_2$-CNTs with 50 wt% Mg(BH$_4$)$_2$ started to release hydrogen at 76 °C and the dehydrogenated Mg(BH$_4$)$_2$-CNTs could absorb 2.5 wt% of H$_2$ at 350 °C under the hydrogen pressure of 10 MPa. Furthermore, CNTs have shown the properties of both accomplishing nanoconfinement and catalysing the performance of hydrogen desorption [29–31].

Up to now, there were few reports about the research on the Mg(BH$_4$)$_2$ doped with trace of CNTs. In this study, combining the advantage of high activity of ball milling and the catalytic effect of CNTs in Mg(BH$_4$)$_2$ hydrogen storage materials, the hydrogen storage performance of Mg(BH$_4$)$_2$-x CNTs (x = 2, 5, 10, 25 and 50 wt%) is studied by focusing on the microstructural evolution and the improvement of hydrogen desorption properties.

2. Experimental

The raw materials of NaBH$_4$ (98%, Aladdin), MgCl$_2$ (99%, Aladdin) and multi-wall carbon nanotubes (>97 wt% in purity and >60 nm in externaldiameter) were obtained commercially. Mg(BH$_4$)$_2$ was synthesized by NaBH$_4$ and MgCl$_2$ based on the reaction (1) and diethyl ether was used as a solvent [32,33].

$$2NaBH_4 + MgCl_2 \rightarrow Mg(BH_4)_2 + 2NaCl \qquad (1)$$
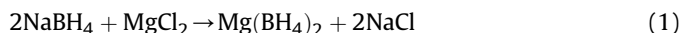
All the synthesis work was carried out in glove box (MBRAUN) that was filled with high purity argon and the water and oxygen concentrations were kept below 0.1 ppm. A mixture of NaBH$_4$ and MgCl$_2$ (in a molar ratio of 2:1) was ball-milled at a rate of 500 rpm for 12 h and then ball-milled in diethyl ether at a rate of 400 rpm for another 24 h. After ball milling, the product was lautered by a fine-grade glass frit to remove NaCl. A further desolvation dried under vacuum at 230 °C for 3 h in order to remove the diethyl ether from the Mg(BH$_4$)$_2$ completely.

The surface of CNTs was treated to ensure functionalization. The concentrated nitric acid of 50 ml was added to CNTs under stirring in an oil bath with the temperature heated to 140 °C. And then, it was refluxed and stirred for 6 h to remove impurities. After that, the mixture was washed with distilled water untill the pH value is closed to 7, and finally dried under vacuum at the temperature of 80 °C.

Mg(BH$_4$)$_2$ with different CNTs additives (2, 5, 10, 25 and 50 wt%) were mechanically milled for 10 h in a stainless steel vial. The ball to powder ratio was approximately 40:1 and the stainless steel balls were 6 mm and 10 mm in diameter. The milling was performed at 350 rpm, and was interrupted for 6 min after 6 min milling, in order to reduce the temperature and inhibit the decomposition reaction.

The hydrogen storage properties of the samples with a typical amount of around 100 mg were examined by a Sieverts'-type apparatus using the volumetric method. The amount of hydrogen desorbed from the sample was calculated from the pressure changes in a certain volume. The sample temperature was gradually raised to 500 °C for dehydrogenation at a heating rate of 10 °C/min. A primary vacuum of 10^{-3} bar was applied for dehydrogenation.

The morphology and structure of the samples were analyzed using a scanning electron microscope (SEM, NOVA NANOSEM 450). The phase structures and compositions of the Mg(BH$_4$)$_2$-CNTs mixtures, protected by Scotch tape to prevent rapid oxidation and hydration, were analyzed by X-ray diffraction (XRD, D8 Discover) with Cu-Kα ($\lambda_1 = 1.54056$ Å, $\lambda_2 = 1.5444$ Å) radiation operated at 40 mA and 40 kV. 2θ scans were acquired from 10°~ 90° with a step size of 0.02° and an exposure time of 1 s per step. The XRD data were processed by Jade 5.0 software to obtain the structure and content of the phases in the sample.

3. Results and discussion

Fig. 1 shows the XRD patterns of pure Mg(BH$_4$)$_2$ and Mg(BH$_4$)$_2$ with different CNTs additives (2, 5, 10, 25 and 50 wt%) after ball milling for 10 h. The structure of the as-synthesized Mg(BH$_4$)$_2$ is β-Mg(BH$_4$)$_2$ [6]. There is no other crystal phase detected by XRD in Fig. 1(a). The β-Mg(BH$_4$)$_2$ exhibits the diffraction peaks at 2θ ≈ 17.12, 17.84, 18.78, 19.08, 20.26 and 21.22°. The pattern deriving from the blend obtained after ball-milling treatment appears as a superposition of those of Mg(BH$_4$)$_2$ and CNTs. The diffraction peaks of Mg(BH$_4$)$_2$ are drastically weakened and broadened to form into the nanocrystalline and amorphous state due to grain size reduction and lattice stress. The typical peaks of the CNTs at 2θ ≈ 25.64 and 42.69° are stronger with an increase of the CNTs amount. It is suggested that the as-milled products with different CNTs contents have a smaller average grain size, a larger amount of defects as well as amorphous structure, which are favored by hydrogen storage property.

To study the effect of the amount of additive CNTs on the B—H bonds, the FTIR spectra of pure Mg(BH$_4$)$_2$ and Mg(BH$_4$)$_2$-xCNTs (x = 2, 5, 10, 25 and 50 wt%) are shown in Fig. 2. In Fig. 2(a), there are three bands at 2386, 2291 and 2223 cm^{-1}, which correspond to stretching vibrations of bridged and terminal B—H bonds. The deformation vibration bands of B—H bonds in Mg(BH$_4$)$_2$ locate at 1267, 1126 and 1003 cm^{-1}. With the addition of CNTs, two peaks at 2386 and 2223 cm^{-1} of B-H stretching vibration disappear and the peak shape of the deformation vibration changes. Increasing the amount of CNTs, the typical band of B-H stretching vibration moves to a low frequency region. This indicates that a strong electronic interaction between CNTs and B—H bond exists and the strength of the B—H bonds is weakened by CNTs.
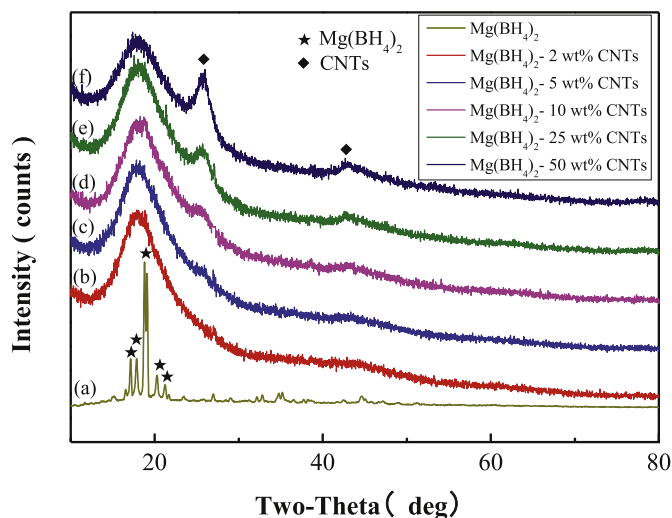

Fig. 1. XRD patterns of (a) pure Mg(BH$_4$)$_2$ and Mg(BH$_4$)$_2$-xCNTs composites: (b) x = 2, (c) x = 5, (d) x = 10, (e) x = 25 and (f) x = 50 wt%.