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# Fe<sub>3</sub>O<sub>4</sub> nanoclusters highly dispersed on a porous graphene support as an additive for improving the hydrogen storage properties of LiBH<sub>4</sub>†

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Fe<sub>3</sub>O<sub>4</sub> nanoclusters anchored on porous reduced graphene oxide (Fe<sub>3</sub>O<sub>4</sub>@rGO) have been synthesized by a one-step hydrothermal route, and then ball milled with LiBH<sub>4</sub> to prepare a hydrogen storage composite with a low onset dehydrogenation temperature, and improved dehydrogenation kinetics and rehydrogenation reversibility. The LiBH<sub>4</sub>-20 wt% Fe<sub>3</sub>O<sub>4</sub>@rGO composite begins to release hydrogen at 74 °C, which is 250 °C lower than for ball-milled pure LiBH<sub>4</sub>. Moreover, the composite can release 3.36 wt% hydrogen at 400 °C within 1000 s, which is 2.52 times as high as that of pure LiBH<sub>4</sub>. Importantly, it can uptake 5.74 wt% hydrogen at 400 °C under 5 MPa H<sub>2</sub>, and its hydrogen absorption capacity still reaches 3.73 wt% after 5 de/rehydrogenation cycles. The activation energy (*E<sub>a</sub>*) of the hydrogen desorption of the composite is decreased by 79.78 kJ mol<sup>-1</sup> when 20 wt% Fe<sub>3</sub>O<sub>4</sub>@rGO is introduced into LiBH<sub>4</sub> as a destabilizer and catalyst precursor, showing enhanced thermodynamic properties. It could be claimed that not only the destabilization of Fe<sub>3</sub>O<sub>4</sub>, but also the active Li<sub>3</sub>BO<sub>3</sub> species formed *in situ*, as well as the wrapping effect of the graphene, synergistically improve the hydrogen storage properties of LiBH<sub>4</sub>. This work provides insight into developing non-noble metals supported on functional graphene as additives to improve the hydrogen storage properties of LiBH<sub>4</sub>.

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## 1. Introduction

Hydrogen is considered to be a promising energy carrier capable of solving global energy and environmental crises on account of its clean combustion and high energy density.<sup>1</sup> However, the major barrier for realizing its large-scale utilization is the shortage of safe hydrogen storage and transportation techniques.<sup>2</sup> Extensive efforts have been centered on developing safe and efficient solid hydrogen storage materials with high hydrogen density, low dehydrogenation temperature, and favorable reversibility.<sup>3</sup> Lithium borohydride (LiBH<sub>4</sub>) has been regarded as one of the materials with the most potential in solid state hydrogen storage systems due to its high gravimetric hydrogen capacity (18.4 wt%).<sup>4</sup> However, it is too thermodynamically stable and kinetically slow at releasing hydrogen under moderate conditions, and high temperature and pressure are required for its rehydrogenation.<sup>5</sup> To overcome the poor

thermodynamic and slow kinetic properties of LiBH<sub>4</sub>, several strategies have been adopted to reduce its dehydrogenation temperature and improve its sorption rate, as well as its reversibility under benign conditions.<sup>6</sup>

One conventional strategy is doping with appropriate additives or catalysts, such as transition metals,<sup>7,8</sup> transition metal oxides<sup>9</sup>, or halides,<sup>10,11</sup> which can effectively improve the hydrogen storage properties of LiBH<sub>4</sub>. Among them, iron-based compounds have been found to be a class of additives with high catalytic activity. Yu *et al.*<sup>12</sup> investigated the effects of various oxides on the dehydrogenation behavior of LiBH<sub>4</sub>, wherein Fe<sub>2</sub>O<sub>3</sub> showed the best destabilization effect among the studied oxides (TiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, and SiO<sub>2</sub>). The LiBH<sub>4</sub>-2Fe<sub>2</sub>O<sub>3</sub> mixture started to release hydrogen below 100 °C, and 6 wt% hydrogen could be released after heating to 200 °C. Zhang *et al.*<sup>13</sup> found that the dehydrogenation temperature of LiBH<sub>4</sub> was significantly reduced by doping with small amounts of FeCl<sub>2</sub>, and the complete hydrogen desorption of LiBH<sub>4</sub> could be achieved due to the formation of metal boride. Recently, a superior destabilization effect of LiBH<sub>4</sub> was realised through the addition of nano-sized nickel ferrite NiFe<sub>2</sub>O<sub>4</sub>, and the *in situ*-formed Fe<sub>3</sub>O<sub>4</sub>, NiB, and Fe<sub>3</sub>B from the reaction between LiBH<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub> acted as the actual destabilization agents in accelerating the dehydrogenation properties of LiBH<sub>4</sub>.<sup>14</sup> More recently, boron-based compounds like H<sub>3</sub>BO<sub>3</sub>,<sup>15</sup> HBO<sub>2</sub>, and B<sub>2</sub>O<sub>3</sub><sup>16</sup> have been reported to effectively promote the

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dehydrogenation of  $\text{LiBH}_4$  due to the interactions between protonic and hydridic hydrogen. Cai *et al.*<sup>17</sup> found that nano-sized metal borides  $\text{MB}_x$  ( $\text{M} = \text{Mg}, \text{Ti}, \text{Fe}, \text{and Si}$ ) played an important catalytic role in enhancing the hydrogen storage performance of  $\text{LiBH}_4$ , and the catalytic effects of  $\text{MB}_x$  were influenced largely by the Pauling electronegativity of  $\text{M}$  in  $\text{MB}_x$  and the interfacial contact character between  $\text{LiBH}_4$  and  $\text{MB}_x$ .

Of particular interest is the fact that porous and nano-structured carbon materials as efficient catalysts or nanoscale frameworks can effectively lower the hydrogen evolution temperature and ameliorate the rehydrogenation conditions of  $\text{LiBH}_4$ .<sup>18</sup> In the case where  $\text{LiBH}_4$  was ball milled with various carbons (graphite, single-walled carbon nanotubes, and activated carbon), all the carbon additives could improve the H-exchange kinetics and H-capacity of  $\text{LiBH}_4$  due to heterogeneous nucleation and micro-confinement effects.<sup>19</sup> Besides this, other carbon hosts like activated carbon nanofibers,<sup>20</sup> fluorographite,<sup>21</sup> and nitrogen-doped hierarchically porous carbon<sup>22</sup> have also been used as substrates to destabilize or catalyze  $\text{LiBH}_4$ . Nevertheless, relying solely on this method still makes it difficult to achieve rapid reversible hydrogen absorption and desorption processes under mild conditions. Furthermore, nearly (or even more than) a 50 wt% capacity loss in the first dehydrogenation and rehydrogenation cycle was repeatedly observed in the carbon-added systems due to the addition of plenty of carbon materials to disperse or confine  $\text{LiBH}_4$ .<sup>23,24</sup>

Graphene has attracted great interest and has been applied in various areas, such as energy storage, sensors, and catalysis, on account of its unique characteristics.<sup>25</sup> The addition of functional graphene to  $\text{LiBH}_4$  could result in a high hydrogen storage capacity, rapid kinetics, and excellent reversibility. Xu *et al.*<sup>26,27</sup> reported that precious metal ( $\text{Pt}$  and  $\text{Pd}$ ) nanoparticles anchored onto graphene sheets could greatly improve the hydrogen desorption behavior and uptake reversibility of  $\text{LiBH}_4$ . The artful combination of catalysis and nanoconfinement has become a promising way to improve the dehydrogenation and rehydrogenation performance of  $\text{LiBH}_4$ . More recently, the hydrogen storage properties of  $\text{LiBH}_4$  have been shown to be improved tremendously by ball milling with graphene-supported highly-dispersed nickel nanoparticles at a low addition amount.<sup>28</sup> Zhang *et al.*<sup>29</sup> reported that a remarkable improvement in the hydrogen sorption, thermodynamic, and kinetic performances of  $\text{LiBH}_4$  could be realized by modification with three-dimensional porous fluorinated graphene.

Based on the previous studies, it is anticipated that Fe-based compounds can weaken the B–H bond and thus improve the hydrogen storage properties of  $\text{LiBH}_4$ .  $\text{Fe}_3\text{O}_4$  has attracted considerable attention due to its low cost, eco-friendliness, and natural abundance, which are widely applicable in energy storage, environmental governance, and photocatalytic fields.<sup>30,31</sup> In this work,  $\text{Fe}_3\text{O}_4$  nanoclusters assembled on porous reduced graphene oxide sheets ( $\text{Fe}_3\text{O}_4@\text{rGO}$ ) have been prepared successfully by a facile one-step hydrothermal route, and then were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, *etc.* Subsequently, the composite was employed as a destabilizer and catalytic additive for improving the dehydrogenation and

rehydrogenation behavior of  $\text{LiBH}_4$ . The  $\text{LiBH}_4$ –20 wt%  $\text{Fe}_3\text{O}_4@\text{rGO}$  composite prepared by high-energy ball milling showed an enhanced hydrogen desorption performance and uptake reversibility compared with ball-milled pure  $\text{LiBH}_4$ . The catalytic effects of  $\text{Fe}_3\text{O}_4@\text{rGO}$  on the hydrogen storage properties of  $\text{LiBH}_4$  were investigated and discussed in detail.

## 2. Experimental section

### 2.1 Materials

Commercially available  $\text{LiBH}_4$  (95%, Aladdin),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (AR, Aladdin), ascorbic acid (AR, Sinopharm Chemical Reagent Beijing Co., Ltd),  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  (99%, Aladdin), and  $\text{Fe}_3\text{O}_4$  (AR, Aladdin) were used as received, without further purification.

### 2.2 Synthesis of $\text{Fe}_3\text{O}_4$ nanoclusters supported on porous reduced graphene oxide sheets ( $\text{Fe}_3\text{O}_4@\text{rGO}$ )

The graphene oxide (GO) used in this work was prepared according to Hummer's method.<sup>32</sup>  $\text{Fe}_3\text{O}_4@\text{rGO}$  was synthesized on the basis of the reported procedure by Hu *et al.*<sup>33</sup> with a slight modification. Typically, 0.12 g GO was dispersed in 60 mL distilled water under ultrasound at room temperature, followed by slowly adding 0.90 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 1.76 g of ascorbic acid. Then, 10 mL  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  was quickly added into the solution under vigorous stirring. Subsequently, the mixture was transferred to a 100 mL Teflon-lined autoclave and heated at 180 °C for 8 h. After filtration, washing, and freeze drying, the final product was designated as  $\text{Fe}_3\text{O}_4@\text{rGO}$ . For comparison, the reduced graphene oxide (rGO) was obtained by a simple hydrogen thermal reduction method. In brief, the GO was heated from room temperature to 500 °C under 1 MPa hydrogen with a heating rate of 5 °C min<sup>−1</sup>, and held for 5 h in a home-made temperature programmed apparatus.

### 2.3 Preparation of the hydrogen storage composites

$\text{LiBH}_4$  was ball milled with the as-prepared  $\text{Fe}_3\text{O}_4@\text{rGO}$  nano-hybrid with a mass ratio of 4 : 1 at 500 rpm for 10 h under an Ar atmosphere using a planetary Fritsch-P6 mill. The weight ratio of the ball to powder mixture was about 40 : 1. The ball-milling procedure was carried out by alternating 15 min of milling and 15 min of resting to avoid the temperature of the sample container rising. For comparison, pure  $\text{LiBH}_4$  or the  $\text{LiBH}_4$  composites with the addition of  $\text{Fe}_3\text{O}_4$  and rGO were prepared following the same procedure. It should be pointed out that before the ball milling of  $\text{Fe}_3\text{O}_4@\text{rGO}$ , rGO, and  $\text{Fe}_3\text{O}_4$  with  $\text{LiBH}_4$ , they were all dried at 120 °C for 12 h in a vacuum oven to remove any possible absorbed water on their surfaces, and were then stored in an Ar-filled glove box. The samples are hereafter labeled as  $\text{LiBH}_4$ ,  $\text{LiBH}_4\text{--Fe}_3\text{O}_4$ ,  $\text{LiBH}_4\text{--rGO}$ , and  $\text{LiBH}_4\text{--Fe}_3\text{O}_4@\text{rGO}$ . All the sample handling was performed in an Ar-filled glove box. The amounts of oxygen and water vapour inside the glove-box were kept below 1 ppm.

### 2.4 Characterization

The crystal structure and morphology of the samples were characterized by scanning electron microscopy (SEM, Hitachi



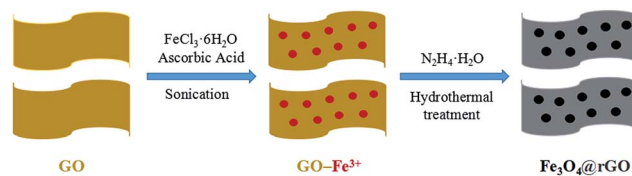
SU8010), transmission electron microscopy (TEM, Hitachi HT7700), X-ray diffraction (XRD, D/Max-2500/PC, Cu K $\alpha$  radiation), and X-ray photoelectron spectrometry (XPS, Thermo Scientific K-Alpha+, Al K $\alpha$  radiation). For the XRD studies, all the samples were smeared on a glass slide in the Ar-filled glove box, and then were covered by a layer of plastic film to avoid moisture and oxygen contact during measurement. This resulted in a scattering peak at  $2\theta = 22^\circ$  in the XRD pattern attributed to the plastic film coverage. The specific surface area and porosity of the  $\text{Fe}_3\text{O}_4@\text{rGO}$  nanohybrid were measured by nitrogen adsorption-desorption at 77 K using a Micromeritics TriStar II 3020 Analyzer. Fourier transform infrared (FTIR) spectra were obtained by a Nicolet 6700 FTIR spectrometer equipped with a MCT detector to record the features of the chemical bonding states of the samples. For the FTIR studies, the samples were milled with dry KBr with a mass ratio of 1 : 100 and pressed into one thin slice in the Ar-filled glove box, and then they were placed into a lab-built Ar-filled container to protect the samples from air and moisture during the transfer process. The thermodynamic analysis of the samples was carried out using a simultaneous thermal analyzer (DTG-60A) in air from room temperature to 900  $^\circ\text{C}$ , at a heating rate of 10  $^\circ\text{C min}^{-1}$ . Differential scanning calorimetry (DSC) measurements for the dehydrogenation of the samples were carried out using a Mettler Toledo TGA/DSC1 system at heating rates of 5, 10, 15, and 20  $^\circ\text{C min}^{-1}$  from 50 to 500  $^\circ\text{C}$  under an Ar flow (50 mL  $\text{min}^{-1}$ ).

The hydrogen desorption and absorption properties were investigated using a Sievert-type apparatus manufactured by the General Research Institute for Nonferrous Metals. Temperature-programmed-desorption (TPD) experiments were carried out in a temperature range from room temperature to 620  $^\circ\text{C}$ , at a heating rate of 5  $^\circ\text{C min}^{-1}$ . The isothermal dehydrogenation and rehydrogenation measurements were performed at the desired temperature under initial hydrogen pressures of 0.01 MPa and 5 MPa, respectively. For the rehydrogenation measurement of the samples, the samples were first evacuated continuously until they did not release any more hydrogen, in order to make sure that they had completely released their hydrogen. Then, the isothermal rehydrogenation was performed at the desired temperature with an initial hydrogen pressure of 5 MPa for 1 h. In this work, the hydrogen contents of all the samples are presented based on the total weight of the composites, in order to make a comparison with the as-milled  $\text{LiBH}_4$ .

### 3. Results and discussion

#### 3.1 Synthesis and characterization of as-prepared $\text{Fe}_3\text{O}_4@\text{rGO}$

The schematic synthesis procedure of the  $\text{Fe}_3\text{O}_4@\text{rGO}$  nanohybrid is illustrated in Scheme 1. Firstly, GO was sonicated in water to obtain nanosheets of a few layers, and the liquid was brown-yellow. Then, iron(III) chloride hexahydrate and ascorbic acid were added to the liquid under continuous stirring, so that the  $\text{Fe}^{3+}$  ions were thoroughly dispersed onto the GO surface by electrostatic interaction. Later, hydrazine hydrate was added



Scheme 1 Schematic illustration of the synthesis of the  $\text{Fe}_3\text{O}_4@\text{rGO}$  nanohybrid.

dropwise into the liquid under vigorous stirring. After the liquid became dark, it was transferred into a Teflon-lined container and reacted at 180  $^\circ\text{C}$  for 8 h. Lastly, the black product was isolated, washed, and freeze-dried.

The microstructure of the as-prepared  $\text{Fe}_3\text{O}_4@\text{rGO}$  nanohybrid was studied using SEM and TEM. From the SEM image shown in Fig. 1a, it is clearly observed that tiny  $\text{Fe}_3\text{O}_4$  nanoparticles are evenly distributed onto the surface of the large, disordered, and over-lapped graphene sheets. Fig. S1a† shows the typical morphology of GO, revealing the wrinkled sheet-like structure, and large, smooth surface. After the hydrogen thermal treatment, rGO with abundant wrinkles and defects is obtained (Fig. S1b†). Fig. 1b shows the TEM image of the  $\text{Fe}_3\text{O}_4@\text{rGO}$  nanohybrid, in which it can be found that the snowflake-like  $\text{Fe}_3\text{O}_4$  nanoclusters consist of plentiful small particles of 5–6 nm in size, which are anchored uniformly onto the reduced graphene surface. The resultant  $\text{Fe}_3\text{O}_4@\text{rGO}$  nanohybrid is mainly composed of Fe, O, and C elements, according to the EDS analysis (Fig. S2†).  $\text{N}_2$  adsorption-desorption isotherms and the corresponding pore size distribution curve of the nanohybrid are exhibited in Fig. 1c and d. Its specific surface area is calculated to be 119.3  $\text{m}^2 \text{g}^{-1}$  based on the BET method. The pore volume is 0.374  $\text{cm}^3 \text{g}^{-1}$ , with major pores located at about 3.7 nm and 14.7 nm in diameter, indicating the mesoporous characteristics of the as-prepared  $\text{Fe}_3\text{O}_4@\text{rGO}$  nanohybrid.

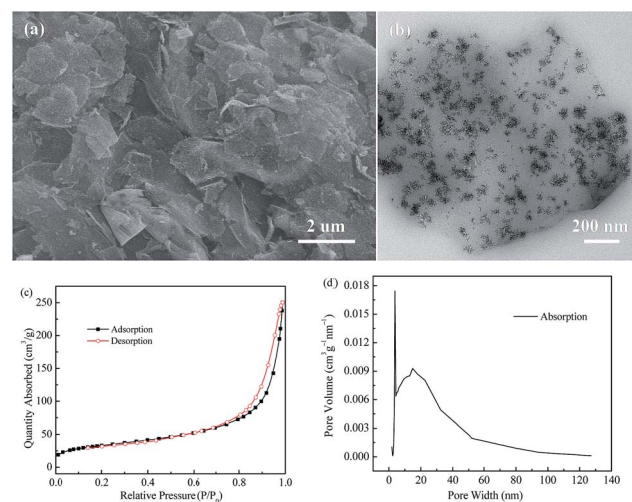


Fig. 1 (a) SEM image, (b) TEM image, (c) nitrogen adsorption-desorption isotherms, and (d) BJH pore-size distribution pattern of the as-prepared  $\text{Fe}_3\text{O}_4@\text{rGO}$  nanohybrid.





Fig. S3† shows the XRD patterns of the GO and rGO. For the GO, a well-defined peak is located at  $2\theta = 10.8^\circ$  with 0.87 nm  $d$ -spacing, indicating the presence of abundant oxygen-containing functional groups on the sides of the GO nano-sheets.<sup>34</sup> However, the rGO has only a very low intensity peak around  $25.8^\circ$ , which indicates a distorted graphite structure and hence suggests the formation of rGO sheets.<sup>35</sup> The XRD pattern of the as-prepared  $\text{Fe}_3\text{O}_4@\text{rGO}$  nanohybrid is displayed in Fig. 2a. Some diffraction peaks occur at  $30.1^\circ$ ,  $35.6^\circ$ ,  $43.1^\circ$ ,  $57.0^\circ$ , and  $62.7^\circ$ , which are in good agreement with the characteristic peaks of pure cubic  $\text{Fe}_3\text{O}_4$  (JCPDF 65-3107). To further verify the surface chemical composition of  $\text{Fe}_3\text{O}_4@\text{rGO}$ , XPS analysis was carried out. Two typical characteristic peaks situated at the binding energies of 709.81 and 723.46 eV are attributed to the  $\text{Fe } 2p_{3/2}$  and  $\text{Fe } 2p_{1/2}$  of  $\text{Fe}_3\text{O}_4$  (Fig. 2b).<sup>36</sup> The peak at 530.27 eV in the O 1s spectrum (Fig. 2c) can be assigned to the Fe–O bonds of  $\text{Fe}_3\text{O}_4@\text{rGO}$ .<sup>37</sup> TGA was used to quantify the loading amount of  $\text{Fe}_3\text{O}_4$  in the  $\text{Fe}_3\text{O}_4@\text{rGO}$  nanohybrid, and was conducted from room temperature to  $900^\circ\text{C}$  in air, at a heating rate of  $10^\circ\text{C min}^{-1}$ . The TGA curves of  $\text{Fe}_3\text{O}_4@\text{rGO}$  and pure  $\text{Fe}_3\text{O}_4$  are shown in Fig. 2d. There are two stages of weight loss for  $\text{Fe}_3\text{O}_4@\text{rGO}$ . The weight loss below  $150^\circ\text{C}$  is ascribed to the evaporation of absorbed moisture. The abrupt weight loss from  $192^\circ\text{C}$  to  $425^\circ\text{C}$  is due to the burning of graphene in air. Based on the weight loss, 51.4 wt% graphene and 48.6 wt%  $\text{Fe}_3\text{O}_4$  are estimated for the  $\text{Fe}_3\text{O}_4@\text{rGO}$  nanohybrid.

### 3.2 Hydrogen sorption, thermodynamic, and kinetic properties of the composites

It is well-known that the hydrogen storage properties of  $\text{LiBH}_4$  can be altered by varying the amount of catalyst added. The preliminary experiments of  $\text{LiBH}_4$  with different rGO addition amounts were performed and the results are shown in Fig. S4 and S5.† It can be seen that all the  $\text{LiBH}_4$ - $x$  wt% rGO composites

( $x = 11, 20$ , and  $33$ ) exhibit improved dehydrogenation performances with respect to the ball-milled pure  $\text{LiBH}_4$ . The three composites have almost the same initial dehydrogenation temperature, being able to release hydrogen at  $220.5^\circ\text{C}$ , but their final dehydrogenation capacity is different. With an increase in the addition amount, the final dehydrogenation capacity decreases gradually. Furthermore, the isothermal hydrogen desorption profiles at  $400^\circ\text{C}$  of the as-milled  $\text{LiBH}_4$  with and without the rGO composites are presented in Fig. S5.† The  $\text{LiBH}_4$ -20 wt% rGO composite exhibits the quickest hydrogen desorption rate among the  $\text{LiBH}_4$ - $x$  wt% rGO composites, and it can release 3.46 wt% hydrogen after 3600 s, which is twice as large as the dehydrogenated capacity of ball-milled pure  $\text{LiBH}_4$  under identical conditions. Taking the dehydrogenation temperature and kinetics into account, the addition of 20 wt% carbon materials is regarded as the best choice and  $\text{LiBH}_4$ -20 wt%  $y$  composites ( $y = \text{Fe}_3\text{O}_4$ , rGO, and  $\text{Fe}_3\text{O}_4@\text{rGO}$ ) are prepared and further investigated in the later work.

Fig. 3 illustrates the TPD performances of ball-milled pure  $\text{LiBH}_4$ ,  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$ ,  $\text{LiBH}_4$ -20 wt% rGO, and  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4@\text{rGO}$  composites from room temperature to  $620^\circ\text{C}$ . The pure  $\text{LiBH}_4$  starts to slowly release hydrogen at  $324^\circ\text{C}$ . However, the  $\text{LiBH}_4$ - $\text{Fe}_3\text{O}_4$  and  $\text{LiBH}_4$ -rGO samples can release hydrogen at  $78^\circ\text{C}$  and  $220.5^\circ\text{C}$ , which are  $246^\circ\text{C}$  and  $103.5^\circ\text{C}$  lower than that of pure  $\text{LiBH}_4$ , respectively. The initial dehydrogenation temperature of the  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4@\text{rGO}$  sample is as low as  $74^\circ\text{C}$ , and a total dehydrogenation capacity of 8.88 wt% is obtained. It is also found that the  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$  and  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4@\text{rGO}$  samples showed quicker dehydrogenation rates than the pure  $\text{LiBH}_4$  and  $\text{LiBH}_4$ -20 wt% rGO samples below 70 min, indicating that the destabilization effect of  $\text{Fe}_3\text{O}_4$  is predominant. However, the  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4@\text{rGO}$  and  $\text{LiBH}_4$ -20 wt% rGO samples showed quicker dehydrogenation rates than  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$  and pure  $\text{LiBH}_4$  after 70 min. The improvement of the dehydrogenation rate is attributed to the wrapping effect of the rGO and the catalytic effect of the *in situ*-formed  $\text{Li}_3\text{BO}_3$ . However, the formation of the stable species of  $\text{Li}_5\text{FeO}_4$  in the  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4@\text{rGO}$  composite may affect the dehydrogenation of

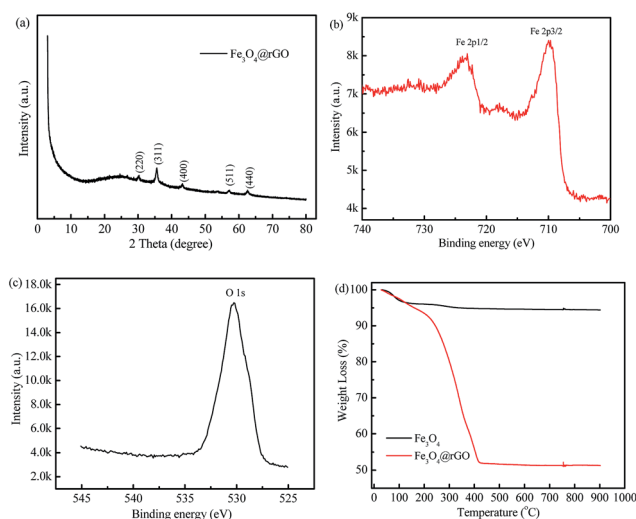


Fig. 2 (a) XRD pattern, (b) Fe 2p and (c) O 1s XPS spectra of the as-prepared  $\text{Fe}_3\text{O}_4@\text{rGO}$  nanohybrid, (d) TGA curves of  $\text{Fe}_3\text{O}_4@\text{rGO}$  and  $\text{Fe}_3\text{O}_4$  in air ranging from room temperature to  $900^\circ\text{C}$ .

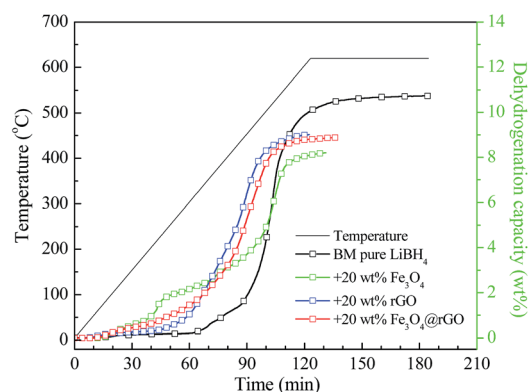


Fig. 3 TPD curves of ball-milled pure  $\text{LiBH}_4$ ,  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$ ,  $\text{LiBH}_4$ -20 wt% rGO, and  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4@\text{rGO}$  composites.



LiBH<sub>4</sub>, leading to the slightly reduced dehydrogenation performance when comparing it with the LiBH<sub>4</sub>-20 wt% rGO composite. The significantly decreased initial dehydrogenation temperature and improved dehydrogenation rate of LiBH<sub>4</sub> indicate that the addition of Fe<sub>3</sub>O<sub>4</sub>@rGO by ball milling can clearly improve the desorption properties of LiBH<sub>4</sub>.

To further study the desorption kinetics of the LiBH<sub>4</sub>-20 wt% y composites (y = Fe<sub>3</sub>O<sub>4</sub>, rGO, and Fe<sub>3</sub>O<sub>4</sub>@rGO), DSC tests at different heating rates were performed to evaluate the activation energy ( $E_a$ ) of these composites using Kissinger's method:<sup>38</sup>

$$\frac{d \left[ \ln \left( \frac{\beta}{T_m^2} \right) \right]}{d \left[ \frac{1}{T_m} \right]} = -\frac{E_a}{R}$$

in which  $\beta$  is the heating rate,  $T_m$  is the peak temperature, and  $R$  is the ideal gas constant. In this work,  $T_m$  is calculated using the DSC results obtained under the diverse heating rates of 5, 10, 15, and 20 °C min<sup>-1</sup>. The DSC curves of the LiBH<sub>4</sub>-20 wt% Fe<sub>3</sub>O<sub>4</sub>@rGO composite are shown in Fig. 4a. Fig. S6† presents the DSC curves of the LiBH<sub>4</sub>-20 wt% Fe<sub>3</sub>O<sub>4</sub> and LiBH<sub>4</sub>-20 wt% rGO composites. The dependence of  $\ln(\beta/T_m)$  vs.  $1/T_m$  of the composites is shown in Fig. 4b. The value of  $E_a$  is calculated to be 102.02 kJ mol<sup>-1</sup> for the LiBH<sub>4</sub>-Fe<sub>3</sub>O<sub>4</sub>@rGO composite, which is much smaller than that of ball-milled pure LiBH<sub>4</sub> (181.80 kJ mol<sup>-1</sup>).<sup>39</sup> This suggests that the  $E_a$  is significantly

affected when using Fe<sub>3</sub>O<sub>4</sub>@rGO as a destabilizer and catalytic additive, which effectively decreases the energy barrier of LiBH<sub>4</sub> in the dehydrogenation process and thus causes the rapid dehydrogenation behavior of the composite.

Isothermal dehydrogenation measurements were carried out to explore the effect of Fe<sub>3</sub>O<sub>4</sub>@rGO on the dehydrogenation kinetics of LiBH<sub>4</sub>. Fig. 5a shows the isothermal dehydrogenation curves of the LiBH<sub>4</sub>-20 wt% y composites (y = Fe<sub>3</sub>O<sub>4</sub>, rGO, and Fe<sub>3</sub>O<sub>4</sub>@rGO) at 400 °C, under an initial hydrogen pressure of 0.01 MPa. The LiBH<sub>4</sub>-20 wt% Fe<sub>3</sub>O<sub>4</sub>@rGO sample shows a faster hydrogen desorption rate than the other three hydrogen storage materials, and it can release 3.84 wt% hydrogen within 3600 s, whereas the pure LiBH<sub>4</sub>, LiBH<sub>4</sub>-20 wt% Fe<sub>3</sub>O<sub>4</sub>, and LiBH<sub>4</sub>-20 wt% rGO samples can release 1.71, 2.04, and 3.47 wt% hydrogen under the same conditions, respectively. In addition, the dehydrogenation curves of the LiBH<sub>4</sub>-20 wt% Fe<sub>3</sub>O<sub>4</sub>@rGO composite at different temperatures are shown in Fig. 5b. The composite is capable of releasing 2.28, 3.84, and 5.93 wt% hydrogen at 350, 400, and 450 °C, respectively. Remarkably, Fe<sub>3</sub>O<sub>4</sub>@rGO has a superior catalytic effect on the dehydrogenation kinetics and capacity of LiBH<sub>4</sub> compared with Fe<sub>3</sub>O<sub>4</sub> or rGO alone. The improvement in the hydrogen storage performance not only comes from the destabilization of the Fe<sub>3</sub>O<sub>4</sub> NPs, but also from the confinement of the rGO.<sup>18,40</sup> It is speculated that their synergistic effects will assist in improving the dehydrogenation performance of LiBH<sub>4</sub>. The newly formed structural defects and the close contact between the

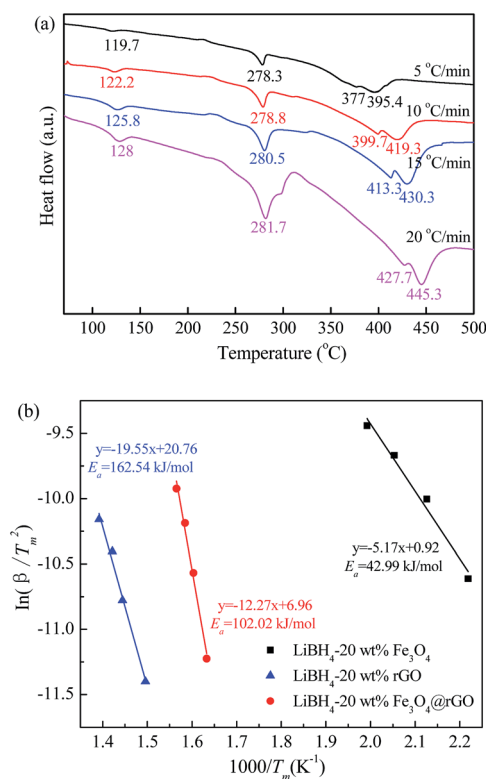


Fig. 4 (a) DSC curves for the LiBH<sub>4</sub>-20 wt% Fe<sub>3</sub>O<sub>4</sub>@rGO composite at various heating rates and (b) Kissinger's plots of  $E_a$  for the LiBH<sub>4</sub>-20 wt% y composites (y = Fe<sub>3</sub>O<sub>4</sub>, rGO, and Fe<sub>3</sub>O<sub>4</sub>@rGO).

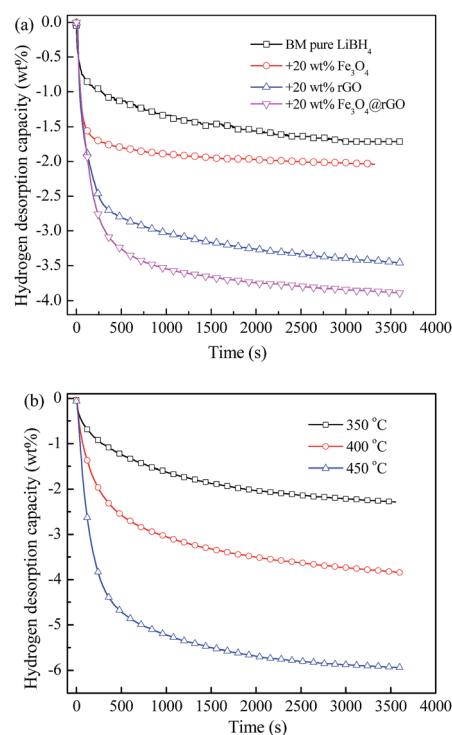


Fig. 5 Isothermal dehydrogenation curves of ball-milled (a) pure LiBH<sub>4</sub> and LiBH<sub>4</sub>-20 wt% y composites (y = Fe<sub>3</sub>O<sub>4</sub>, rGO, and Fe<sub>3</sub>O<sub>4</sub>@rGO) at 400 °C, and (b) the LiBH<sub>4</sub>-20 wt% Fe<sub>3</sub>O<sub>4</sub>@rGO composite at different temperatures.



$\text{Fe}_3\text{O}_4$ @rGO and  $\text{LiBH}_4$  during the ball milling process will also help achieve an enhanced dehydrogenation performance of  $\text{LiBH}_4$ .

Fig. 6a demonstrates the isothermal rehydrogenation curves at 400 °C for ball-milled pure  $\text{LiBH}_4$  and the  $\text{LiBH}_4$  composites with 20 wt%  $\text{Fe}_3\text{O}_4$ , rGO, and  $\text{Fe}_3\text{O}_4$ @rGO, under an initial hydrogen pressure of 5 MPa. The  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$ @rGO composite can absorb 5.45 wt% hydrogen within 3600 s. However, the pure  $\text{LiBH}_4$ ,  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$ , and  $\text{LiBH}_4$ -20 wt% rGO composites can only absorb 2.36, 4.18, and 4.86 wt% hydrogen under the same conditions, respectively. Therefore, it is concluded that adding  $\text{Fe}_3\text{O}_4$ @rGO into  $\text{LiBH}_4$  can result in a higher hydrogen storage capacity and quicker ab/desorption kinetics. In order to study the reversible hydrogen storage performance, the  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$ @rGO composite is rehydrogenated at 400 °C under 5 MPa  $\text{H}_2$  for 1 h after its complete dehydrogenation, and the cyclic rehydrogenation curves are shown in Fig. 6b. The composite exhibits superior rehydrogenation behavior and an absorption capacity of 3.73 wt% after 5 cycles of hydrogen de/absorption is achieved, which is up to 69.1% of the initial hydrogen absorption capacity for the composite. However, pure  $\text{LiBH}_4$  requires extremely harsh conditions of 600 °C and 35 MPa hydrogen pressure to rehydrogenate.<sup>41</sup> Obviously, the  $\text{LiBH}_4$ - $\text{Fe}_3\text{O}_4$ @rGO composite shows a higher hydrogen absorption capacity than the composites with  $\text{Fe}_3\text{O}_4$  or rGO. Thus,  $\text{Fe}_3\text{O}_4$ @rGO can simultaneously ameliorate the hydrogen release and uptake

reversibility for the  $\text{LiBH}_4$  system under moderate conditions, which is largely attributed to the combined effects of the reduced graphene oxide and  $\text{Fe}_3\text{O}_4$  NPs.

### 3.3 Discussion and deduction of the reaction mechanism

To investigate the effect of morphology on the improvement of the hydrogen storage properties of the  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$ @rGO composite, microstructural analysis of the composite was performed using SEM techniques. Fig. 7a shows that the composite has many defects and pores on its surface, with some particles, in the range of several tens of nanometers to several microns, encapsulated by graphene sheets. A high resolution SEM image is shown in Fig. S7† to further demonstrate the pores and particles of the as-milled  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$ @rGO sample. It can be observed that many small particles are wrapped tightly by the rGO sheets. After dehydrogenation at 400 °C (Fig. 7b), numerous wrinkles and channels randomly scattered on the sample surface appear. Furthermore, the dehydrogenated sample is still wrapped tightly by the rGO sheets. It is speculated that  $\text{Fe}_3\text{O}_4$ @rGO might play the role of a heterogeneous nucleation site for the  $\text{LiBH}_4$  decomposition by providing more hydrogen diffusion pathways and it may also prevent agglomeration during the dehydrogenation process. The uniform dispersion and smaller particle size will benefit the hydrogen desorption and absorption behavior of  $\text{LiBH}_4$ .<sup>42</sup>

In order to further analyze the effect of  $\text{Fe}_3\text{O}_4$ @rGO on the hydrogen storage properties of  $\text{LiBH}_4$ , the  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$ @rGO composite in different states was assessed using XRD and FTIR techniques. In order to investigate the effects of rGO and  $\text{Fe}_3\text{O}_4$  on  $\text{LiBH}_4$  individually, XRD patterns of the  $\text{LiBH}_4$ -20 wt% rGO and  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$  composites were also obtained (Fig. S7 and S8†). As shown in Fig. S8a,† the intense characteristic peaks of  $\text{LiBH}_4$  can be clearly seen after ball milling, and the  $\text{LiBO}_2$  phase is formed due to the reaction between  $\text{LiBH}_4$  and the O in the rGO. After it dehydrogenates at 400 °C (Fig. S8b†),  $\text{LiBH}_4$  can completely decompose, the  $\text{LiBO}_2$  converts to  $\text{Li}_3\text{BO}_3$ , and the  $\text{Li}_3\text{BO}_3$  exists in the later hydrogenation process (Fig. S8c†). As for the ball-milled  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$  composite (Fig. S9a†), apart from the characteristic peaks of  $\text{LiBH}_4$  and  $\text{Fe}_3\text{O}_4$ ,  $\text{LiBO}_2$  and  $\text{Li}_5\text{FeO}_4$  peaks are also detected. For its dehydrogenated sample (Fig. S9b†),  $\text{Li}_5\text{FeO}_4$  still exists.  $\text{LiBH}_4$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{LiBO}_2$  disappear, while  $\text{LiH}$  and  $\text{Li}_3\text{BO}_3$  phases appear, which indicates there are some reactions between  $\text{LiBH}_4$  and  $\text{Fe}_3\text{O}_4$  during the dehydrogenation reaction. Similar results are observed for the  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$ @rGO

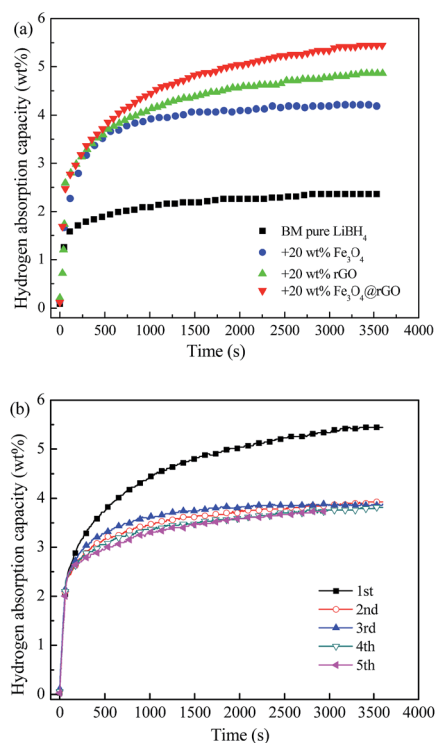


Fig. 6 (a) Isothermal rehydrogenation curves of the pure  $\text{LiBH}_4$  and  $\text{LiBH}_4$ -20 wt%  $y$  composites ( $y = \text{Fe}_3\text{O}_4$ , rGO, and  $\text{Fe}_3\text{O}_4$ @rGO), and (b) the rehydrogenation cycling stability of the  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$ @rGO composite at 400 °C under 5 MPa  $\text{H}_2$ .

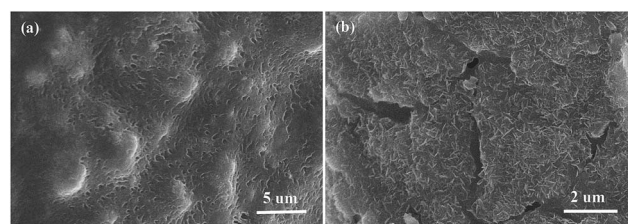
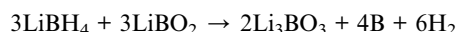


Fig. 7 SEM images of the  $\text{LiBH}_4$ -20 wt%  $\text{Fe}_3\text{O}_4$ @rGO composite: (a) as-milled and (b) after desorption at 400 °C.



composite (Fig. 8a and b). The characteristic peaks of the  $\text{LiBH}_4$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{LiBO}_2$ , and  $\text{Li}_5\text{FeO}_4$  species are verified for the ball-milled  $\text{LiBH}_4\text{-Fe}_3\text{O}_4\text{@rGO}$  sample, confirming that  $\text{LiBH}_4$  can react with  $\text{Fe}_3\text{O}_4$  during the ball milling process. It is believed that  $\text{Fe}_3\text{O}_4$  can react with  $\text{LiBH}_4$  to form  $\text{LiBO}_2$  and  $\text{Li}_5\text{FeO}_4$ . After dehydrogenation at  $400^\circ\text{C}$ , the formed  $\text{LiBO}_2$  can react further with the remaining  $\text{LiBH}_4$  to generate  $\text{Li}_3\text{BO}_3$ .<sup>43</sup> The  $\text{Li}_3\text{BO}_3$  and  $\text{Li}_5\text{FeO}_4$  still exist in the hydrogenation reaction (Fig. 8c), wherein  $\text{Li}_3\text{BO}_3$  acts as the actual active species for improving the reversible hydrogen storage properties of  $\text{LiBH}_4$ .<sup>44</sup> However, the formation of thermodynamically stable compounds like  $\text{Li}_3\text{BO}_3$  and  $\text{Li}_5\text{FeO}_4$  is an important reason for the reduced rehydrogenation capacity. The possible hydrogen desorption reactions of the  $\text{LiBH}_4\text{-20 wt\% Fe}_3\text{O}_4\text{@rGO}$  composite may be expressed as follows:



Although  $\text{LiBH}_4$  can reform in the rehydrogenation reaction, the existence of  $\text{LiH}$  in this state indicates that the rehydrogenation reaction is incomplete, which may be another reason for the degradation of the cyclic hydrogen absorption capacity of the  $\text{LiBH}_4\text{-Fe}_3\text{O}_4\text{@rGO}$  composite.

To further prove that  $\text{LiBH}_4$  is generated again after rehydrogenation, FTIR analysis of the as-milled, dehydrogenated, and rehydrogenated  $\text{LiBH}_4\text{-20 wt\% Fe}_3\text{O}_4\text{@rGO}$  samples was carried out. From Fig. 9a, characteristic peaks of B–H stretching bands at  $2227$ ,  $2292$ , and  $2387\text{ cm}^{-1}$  and B–H bending bands at  $1127\text{ cm}^{-1}$  are revealed. For the dehydrogenated sample (Fig. 9b), these characteristic bands of B–H are absent, indicating the complete decomposition of  $\text{LiBH}_4$  in the hydrogen desorption process. In contrast, the characteristic peaks of the B–H bands are visible in the spectrum of the rehydrogenated sample (Fig. 9c). The disappearance and re-emergence of the B–H bands are strong evidence for the reversibility of the

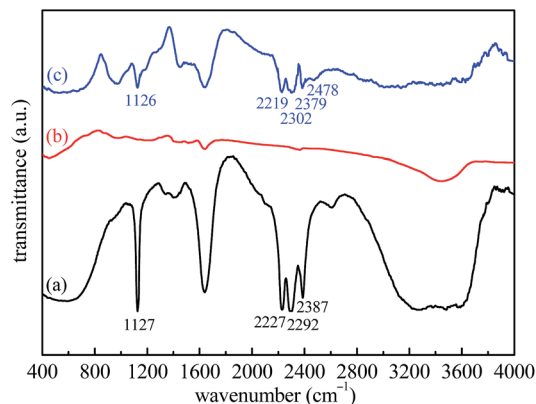


Fig. 9 FTIR spectra of the  $\text{LiBH}_4\text{-20 wt\% Fe}_3\text{O}_4\text{@rGO}$  composite: (a) as-milled, (b) after desorption at  $400^\circ\text{C}$ , and (c) after absorption at  $400^\circ\text{C}$ .

hydrogen desorption/absorption reactions. However, we also observe a new absorption peak at  $2478\text{ cm}^{-1}$ , which can be assigned to  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ .<sup>45</sup> Although  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  can react with  $\text{LiH}$  to generate  $\text{LiBH}_4$ , this reaction requires harsh conditions of  $500^\circ\text{C}$  and  $100\text{ MPa H}_2$  for  $72\text{ h}$ .<sup>46,47</sup> In our work, the rehydrogenation was carried out under the moderate conditions of  $400^\circ\text{C}$  and  $5\text{ MPa H}_2$  for  $1\text{ h}$ . Therefore, some  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  and  $\text{LiH}$  still remained in the rehydrogenated state for the  $\text{LiBH}_4\text{-20 wt\% Fe}_3\text{O}_4\text{@rGO}$  sample, suggesting that the reaction between  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  and  $\text{LiH}$  was not complete, thus affecting its cyclic rehydrogenation behavior. Furthermore, FTIR spectra of the  $\text{LiBH}_4\text{-20 wt\% rGO}$  composite in different states were also obtained and are shown in Fig. S10.† The  $\text{LiBH}_4$  can decompose and regenerate likewise after the dehydrogenation and rehydrogenation of the  $\text{LiBH}_4\text{-20 wt\% rGO}$  composite (Fig. S10b and c†). The peak of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  at  $2477\text{ cm}^{-1}$  is also detected in the rehydrogenated  $\text{LiBH}_4\text{-rGO}$  sample. The surface morphology of the  $\text{LiBH}_4\text{-20 wt\% Fe}_3\text{O}_4\text{@rGO}$  composite after the first hydrogenation changed greatly, as shown in Fig. S11.† Although the rehydrogenated sample is still wrapped tightly by the rGO nanosheets, the amount of wrinkles and channels on its surface apparently decreases. The morphology change can be another reason for the degradation of the cyclic hydrogen absorption capacity of the  $\text{LiBH}_4\text{-20 wt\% Fe}_3\text{O}_4\text{@rGO}$  composite, but its rehydrogenation performance is still superior to that of pure  $\text{LiBH}_4$ .

Based on the above analyses, we conclude that some  $\text{LiBH}_4$  can be confined in the pores of the reduced graphene oxide sheets, while the remaining  $\text{LiBH}_4$  spreads evenly over the surface after ball milling due to the loose porous structure of the sheets.  $\text{Fe}_3\text{O}_4\text{@rGO}$  acts as a destabilization agent by reacting with  $\text{LiBH}_4$  to decrease its onset dehydrogenation temperature. The *in situ*-formed active  $\text{Li}_3\text{BO}_3$  species during the dehydrogenation process has an actual catalytic effect on improving the dehydrogenation kinetics and rehydrogenation reversibility of  $\text{LiBH}_4$ . Simultaneously, abundant structural defects and channels are created during this process. The wrapping effect of the rGO nanosheets is proven to be able to effectively prevent the

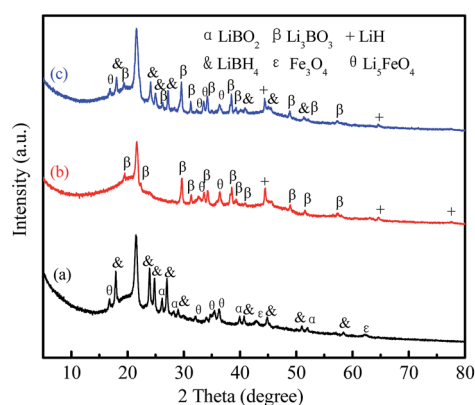


Fig. 8 XRD patterns of the  $\text{LiBH}_4\text{-20 wt\% Fe}_3\text{O}_4\text{@rGO}$  composite: (a) as-milled, (b) after desorption at  $400^\circ\text{C}$ , and (c) after absorption at  $400^\circ\text{C}$ .





nucleated particles from agglomerating during the dehydrogenation and rehydrogenation cycles.<sup>48</sup> In this regard, the destabilization, catalysis, and wrapping effect of the Fe<sub>3</sub>O<sub>4</sub>@rGO nanohybrid contribute jointly to the improved hydrogen storage performance of LiBH<sub>4</sub>.

## 4. Conclusions

In this study, porous reduced graphene oxide sheets decorated with Fe<sub>3</sub>O<sub>4</sub> nanoclusters were synthesized by a facile hydrothermal method. The Fe<sub>3</sub>O<sub>4</sub>@rGO nanohybrid, serving as a destabilizer and catalyst precursor, is added to LiBH<sub>4</sub>, resulting in the improvement of its hydrogen storage properties. The onset dehydrogenation temperature is reduced to 74 °C for the LiBH<sub>4</sub>-20 wt% Fe<sub>3</sub>O<sub>4</sub>@rGO composite, which is 250 °C lower than that of ball-milled pure LiBH<sub>4</sub>. Rehydrogenation with a promoted cycling stability is achieved at 400 °C under 5 MPa H<sub>2</sub>. The addition of Fe<sub>3</sub>O<sub>4</sub>@rGO also decreases the *E*<sub>a</sub> of the dehydrogenation reaction of LiBH<sub>4</sub> to 102.02 kJ mol<sup>-1</sup>, suggesting excellent desorption kinetics, and it can release 3.89 wt% hydrogen at 400 °C after 3600 s, which is 2.27 times as high as pure LiBH<sub>4</sub>. The significantly enhanced hydrogen storage properties of the composite are not only attributed to the destabilization derived from Fe<sub>3</sub>O<sub>4</sub>, but also the *in situ*-formed active Li<sub>3</sub>BO<sub>3</sub> species in the decomposition process, as well as the wrapping of the rGO sheets. This work may provide insight into new applications of Fe<sub>3</sub>O<sub>4</sub>@rGO and the addition of other functional graphenes decorated with non-noble metals into LiBH<sub>4</sub>, in order to fabricate hydrogen storage materials of desirable performance.

## Conflicts of interest

The authors declare no competing financial interest.

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