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# Excellent catalysis of $\text{Mn}_3\text{O}_4$ nanoparticles on the hydrogen storage properties of $\text{MgH}_2$ : an experimental and theoretical study†

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Recently, transition metal oxides have been evidenced to be superior catalysts for improving the hydrogen desorption/absorption performance of  $\text{MgH}_2$ . In this paper,  $\text{Mn}_3\text{O}_4$  nanoparticles with a uniform size of around 10 nm were synthesized by a facile chemical method and then introduced to modify the hydrogen storage properties of  $\text{MgH}_2$ . With the addition of 10 wt%  $\text{Mn}_3\text{O}_4$  nanoparticles, the  $\text{MgH}_2$ - $\text{Mn}_3\text{O}_4$  composite started to release hydrogen at 200 °C and approximately 6.8 wt%  $\text{H}_2$  could be released within 8 min at 300 °C. For absorption, the completely dehydrogenated sample took up 5.0 wt%  $\text{H}_2$  within 10 min under 3 MPa hydrogen even at 100 °C. Compared with pristine  $\text{MgH}_2$ , the activation energy value of absorption for the  $\text{MgH}_2 + 10$  wt%  $\text{Mn}_3\text{O}_4$  composite decreased from  $72.5 \pm 2.7$  to  $34.4 \pm 0.9$  kJ mol<sup>-1</sup>. The catalytic mechanism of  $\text{Mn}_3\text{O}_4$  was also explored and discussed with solid evidence from X-ray diffraction (XRD), Transmission Electron Microscope (TEM) and Energy Dispersive X-ray Spectroscopy (EDS) studies. Density functional theory calculations revealed that the Mg-H bonds were elongated and weakened with the doping of  $\text{Mn}_3\text{O}_4$ . In addition, a cycling test showed that the hydrogen storage capacity and reaction kinetics of  $\text{MgH}_2$ - $\text{Mn}_3\text{O}_4$  could be favourably preserved in 20 cycles, indicative of promising applications as a solid-state hydrogen storage material in a future hydrogen society.

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## 1. Introduction

Faced with a global energy crisis and environmental issues, the world is crying out for sustainable clean energy sources.<sup>1-3</sup> Hydrogen, which can generate electricity *via* fuel cells with nearly no emission of pollutants, is regarded as one of the most promising substitutes for fossil fuels.<sup>4-6</sup> In order to store and transfer hydrogen conveniently, efficiently and safely, hydrogen storage materials with a moderate operating temperature, low cost, good dynamics and high hydrogen storage density are urgently required.<sup>7</sup> Among numerous materials, magnesium hydride ( $\text{MgH}_2$ ) with high mass hydrogen storage capacity (7.76 wt%), good reversibility, low cost and other outstanding performances (LIB anode) has attracted intense attention worldwide.<sup>8-11</sup> Nevertheless, two challenges (stable

thermodynamics and poor kinetics) still need to be conquered before the large scale application of  $\text{MgH}_2$ .<sup>12-14</sup> In the past few decades, extensive research has been conducted to overcome these challenges through diverse methods, such as catalyst doping,<sup>15-20</sup> alloying<sup>21-24</sup> and nanotechnology.<sup>25-27</sup>

According to previous reports, transition metals (TMs) and their compounds showed a quite effective influence on improving the hydrogen storage properties of  $\text{MgH}_2$ .<sup>28-31</sup> For example, Liu *et al.*<sup>32</sup> synthesized a Co@CNT nanocatalyst by carbonizing zeolitic imidazolate framework-67 and doped it into  $\text{MgH}_2$ . The experimental results showed that the onset temperature of  $\text{MgH}_2$  decreased to 267.8 °C with the addition of Co@CNTs and the dehydrogenation capacity of  $\text{MgH}_2$ -Co@CNTs could reach 6.89 wt% at 300 °C within 15 min. For absorption, the  $\text{MgH}_2$ -Co@CNTs could absorb 6.15 wt%  $\text{H}_2$  at 250 °C within 2 min. Cheng *et al.*<sup>33</sup> found that  $\text{Pd}_{30}\text{Ni}_{70}$ /CMK-3 could significantly improve the de/re-hydrogenation performance of  $\text{MgH}_2$  at low temperature. About 6 wt% hydrogen could be released below 290 °C and 4 wt% hydrogen could be absorbed at 70 °C under a hydrogen pressure of 3 MPa within 18 000 s. Besides pure metal, metal oxides, which can be easily synthesized, are preferred by scientists to improve the hydrogen storage performance of  $\text{MgH}_2$ .<sup>34-38</sup> Chen *et al.*<sup>39</sup> found that a  $\text{MgH}_2$ -Co/TiO<sub>2</sub> composite started to desorb hydrogen at about 190 °C with a low apparent activation energy of 77 kJ mol<sup>-1</sup>. In

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addition, the dehydrogenated sample could absorb about 4.24 and 1.0 wt% hydrogen within 10 min at 100 and 50 °C, respectively. Bhatnagar *et al.*<sup>40</sup> demonstrated that MgH<sub>2</sub> catalyzed by Fe<sub>3</sub>O<sub>4</sub>@GS offers improved hydrogen storage behaviour. The MgH<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub>@GS had an onset desorption temperature of about 262 °C and the dehydrogenated sample could absorb 6.20 wt% hydrogen in 2.5 min under 15 atm H<sub>2</sub> pressure at 290 °C. Mustafa *et al.*<sup>41</sup> discovered that a MgH<sub>2</sub>-5 wt% CeO<sub>2</sub> sample released about 3.6 wt% hydrogen in 30 min at 320 °C and the dehydrogenated sample could absorb approximately 3.95 wt% hydrogen within 5 min at 320 °C.

Apparently, both transition metals and their oxides can remarkably improve the hydrogen storage properties of MgH<sub>2</sub>. In our recent study,<sup>42</sup> ZrMn<sub>2</sub> was found to strikingly improve the hydrogen storage properties of MgH<sub>2</sub>; however, research on the catalytic effect of Mn based compounds on MgH<sub>2</sub> has rarely been reported in the literature. In this work, Mn<sub>3</sub>O<sub>4</sub> nanoparticles were successfully synthesized *via* a simple chemical method and adopted to enhance the comprehensive hydrogen storage properties of MgH<sub>2</sub>. To our knowledge, no studies have been conducted on doping Mn<sub>3</sub>O<sub>4</sub> as a catalyst into MgH<sub>2</sub>. Further, the significantly improved hydrogenation and dehydrogenation performance of MgH<sub>2</sub> catalyzed by Mn<sub>3</sub>O<sub>4</sub> was systematically studied and the catalytic mechanism was also explored and discussed in detail.

## 2. Experimental

### 2.1 Sample preparation

All the chemical reagents were of analytical grade. The nano-Mn<sub>3</sub>O<sub>4</sub> powder was prepared by decomposition of Mn(Ac)<sub>2</sub>·4H<sub>2</sub>O in diethylene glycol (DEG). Firstly, 2.45 g Mn(Ac)<sub>2</sub>·4H<sub>2</sub>O was dissolved into 100 ml DEG at a temperature of 80 °C. After this, the solution was heated to 160 °C in an oil bath pot and then kept for 8 h. After cooling to room temperature, the suspension was centrifuged and washed with deionized water and ethanol to remove the residual organic solvent. Finally, Mn<sub>3</sub>O<sub>4</sub> nanoparticles (nano-Mn<sub>3</sub>O<sub>4</sub>) can be obtained after vacuum-drying at 70 °C for 10 hours.

MgH<sub>2</sub> was prepared in our laboratory. The magnesium (purity 99.99%) used was purchased from Sinopharm Chemical Reagent. Mg powder was first hydrogenated at 380 °C and under a hydrogen pressure of 65 bar for 2 h. Then the sample was ball-milled at 450 rpm for 5 h and MgH<sub>2</sub> was synthesized by repeating the above hydrogenation treatment. The nano-Mn<sub>3</sub>O<sub>4</sub> powder and MgH<sub>2</sub> with mass ratios of 5 : 95, 10 : 90 and 15 : 85 were mixed by ball milling. Ball milling of the above samples was performed on a QM-3SP4 planetary ball mill (Nanjing) at 400 rpm for 2 h under 1 bar of Ar (the ball to material ratio is 40 : 1). To avoid contamination and oxidation, all samples were handled and transferred in an Ar-filled glove box (Mikrouna) where the water/oxygen concentration was less than 0.1 ppm.

### 2.2 Sample characterization

The phase composition was analyzed by X-ray diffraction (XRD), which was carried out on an X'Pert Pro X-ray diffractometer

(PANalytical, the Netherlands) with Cu K alpha radiation at 40 kV and 40 mA. A special container was used to prevent air and water contamination when samples were transferred and scanned. The morphology of samples was studied using scanning electron microscopy (SEM, Hitachi SU-70) and transmission electron microscopy (TEM, Tecnai G2 F20 STWIN) with energy dispersive spectroscopy (EDS). The hydrogen absorption and desorption results were obtained using Sieverts-type apparatus. Approximately 75 mg sample was heated to 430 °C at a heating rate of 2 °C min<sup>-1</sup> in a stainless steel container during testing of the non-isothermal hydrogen desorption properties. Isothermal measurements were performed by quickly heating the sample to the target temperature and then keeping the temperature constant throughout the whole test. In addition, the isothermal absorption performance was measured at various temperatures under a hydrogen pressure of 30 bar while the isothermal desorption performance was tested at different temperatures under a hydrogen pressure below 0.01 bar.

### 2.3 Theoretical methods

All calculations were carried out within the DMol<sup>3</sup> code.<sup>43,44</sup> The generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) functional was used to describe the exchange and correlation effects.<sup>45</sup> The DFT semi-core pseudopotential (DSPP) core treatment method was used for relativistic effects and replaces the core electrons with an effective potential and introduces a degree of relativistic correction into the core.<sup>46</sup> The double numerical atomic orbital augmented by a polarization function (DNP) was chosen as the basis set.<sup>47</sup> To achieve the calculation convergence, a smearing of 0.005 Ha (1 Ha = 27.21 eV) to the orbital occupation was applied. In the geometry structural optimization, the convergence tolerances of energy, maximum force and displacement were 1.0 × 10<sup>-5</sup> Ha, 0.002 Ha Å<sup>-1</sup> and 0.005 Å, respectively.

## 3. Results and discussion

### 3.1 Characterization of the prepared Mn<sub>3</sub>O<sub>4</sub> nanoparticles

The structure and morphologies of the prepared Mn<sub>3</sub>O<sub>4</sub> nanoparticles were analysed *via* XRD and TEM measurements, as shown in Fig. 1. Fig. 1a exhibits the TEM image of the Mn<sub>3</sub>O<sub>4</sub> sample prepared by the simple chemical method. It can be clearly seen from the picture that the particle size of the as-prepared Mn<sub>3</sub>O<sub>4</sub> ranged from 5 nm to 20 nm. Besides, the corresponding SAED image in Fig. 1b reveals that the diffraction rings correspond to the (211)/(220) of Mn<sub>3</sub>O<sub>4</sub>. In addition, it can be clearly seen from the particle size distribution curve that the size of prepared Mn<sub>3</sub>O<sub>4</sub> was mainly concentrated in the range of 7 to 15 nm. The magnified TEM image of the marked part in Fig. 1c is shown in Fig. 1d, where the lattice planes corresponding to the (220) plane of Mn<sub>3</sub>O<sub>4</sub> can be observed. The XRD examination result shown in Fig. 1e also indicates that the diffraction peak of Mn<sub>3</sub>O<sub>4</sub> (PDF# 24-0734) can be clearly identified. Based on the TEM and XRD results, Mn<sub>3</sub>O<sub>4</sub> nanoparticles were successfully synthesized and an outstanding catalytic



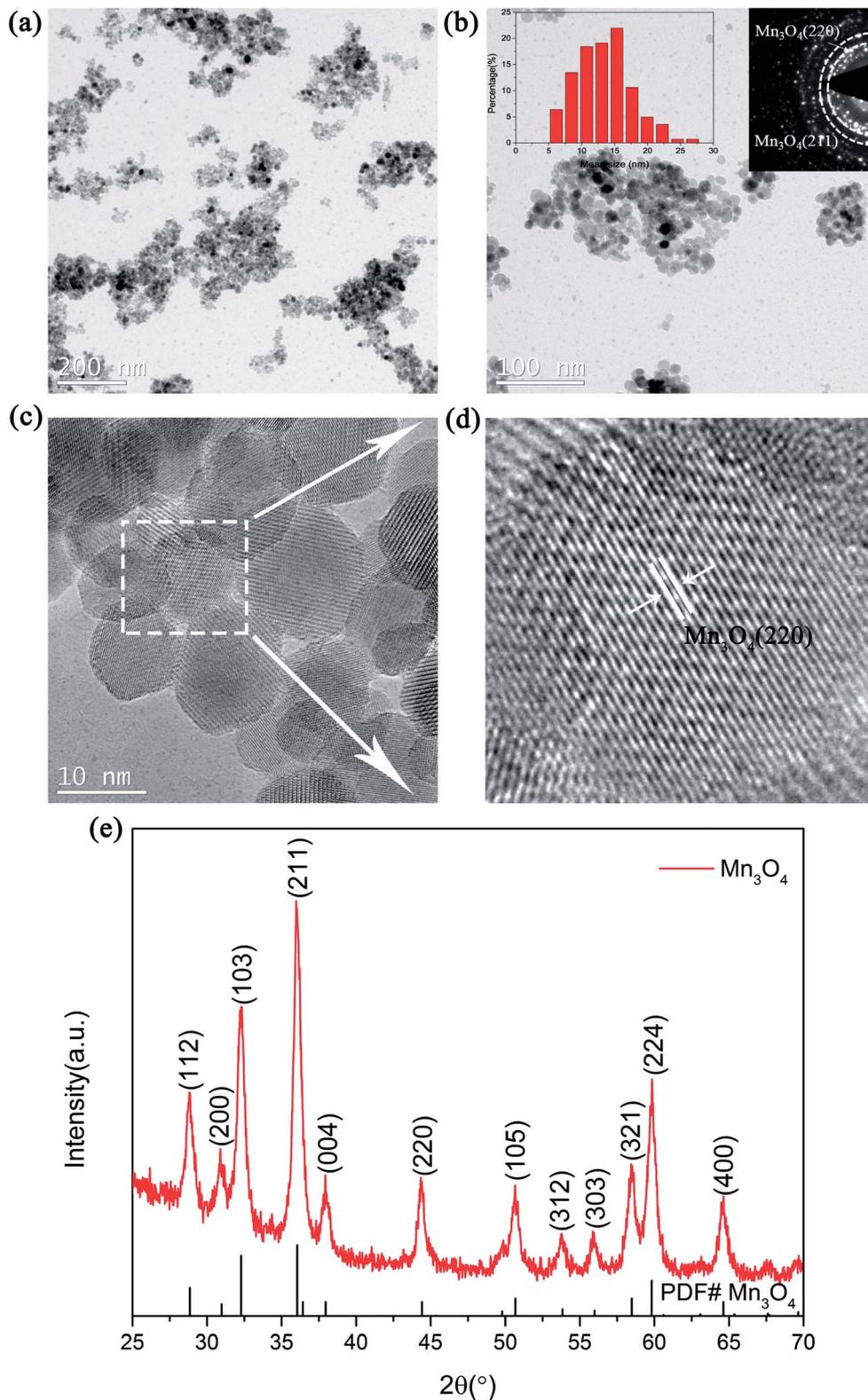


Fig. 1 TEM images (a and c), TEM image with SAED patterns and particle size distribution curve (b), magnified TEM image (d) and XRD pattern (e) of the as-prepared  $\text{Mn}_3\text{O}_4$  nanoparticles.



effect on improving the hydrogen storage properties of  $\text{MgH}_2$  was expected.

### 3.2 Catalytic effect of the $\text{Mn}_3\text{O}_4$ nanoparticles on the hydrogen storage properties of $\text{MgH}_2$

To examine the catalytic effect of  $\text{Mn}_3\text{O}_4$  on the hydrogen desorption properties of  $\text{MgH}_2$ , various amounts of  $\text{Mn}_3\text{O}_4$  (5, 10 and 15 wt%) were doped into the  $\text{MgH}_2$  powders by ball-milling under a 1 bar Ar atmosphere for 2 h. The composites composed of  $\text{MgH}_2$  and  $x$  wt%  $\text{Mn}_3\text{O}_4$  nanoparticles ( $x = 5, 10$  and 15) were denoted as  $\text{MgH}_2 + 5$  wt%  $\text{Mn}_3\text{O}_4$ ,  $\text{MgH}_2 + 10$  wt%  $\text{Mn}_3\text{O}_4$  and  $\text{MgH}_2 + 15$  wt%  $\text{Mn}_3\text{O}_4$ , respectively. All of these milled composites were collected for structural characterization and property tests. Fig. 2a exhibits the XRD patterns of the  $\text{Mn}_3\text{O}_4$ -doped composites. Clearly, the  $\text{MgH}_2$  phase still dominated the XRD profiles and no obvious reacted phases occurred after ball milling. In addition, quite weak peaks of Mg can be seen in this pattern, which could be attributed to the unreacted Mg during synthesis.<sup>15</sup> TPD (Temperature Programmed Desorption) analyses of different amounts of  $\text{Mn}_3\text{O}_4$  nanoparticle doped  $\text{MgH}_2$  samples were also performed. Fig. 2b

depicts the TPD curves of the above three composites and undoped  $\text{MgH}_2$  sample, revealing a single step of hydrogen release. It can be observed that the volumetric release curves of  $\text{MgH}_2 + \text{Mn}_3\text{O}_4$  composites shifted towards lower temperatures with the increasing added amount of  $\text{Mn}_3\text{O}_4$ . The as-synthesized  $\text{MgH}_2$  began to desorb hydrogen at 340 °C and released about 7.4 wt% hydrogen. With the addition of  $\text{Mn}_3\text{O}_4$  nanoparticles, the initial desorption temperatures of the  $\text{MgH}_2 + 5$  wt%  $\text{Mn}_3\text{O}_4$ ,  $\text{MgH}_2 + 10$  wt%  $\text{Mn}_3\text{O}_4$  and  $\text{MgH}_2 + 15$  wt%  $\text{Mn}_3\text{O}_4$  composites decreased to 230 °C, 200 °C and 200 °C, respectively. To further explore the hydrogen storage properties of the modified  $\text{MgH}_2$  systems, isothermal desorption measurements were carried out at 300 °C, as shown in Fig. 2c. The results show that the doping of  $\text{Mn}_3\text{O}_4$  could significantly improve the hydrogen desorption kinetics of  $\text{MgH}_2$ . The  $\text{MgH}_2 + 5$  wt%  $\text{Mn}_3\text{O}_4$ ,  $\text{MgH}_2 + 10$  wt%  $\text{Mn}_3\text{O}_4$  and  $\text{MgH}_2 + 15$  wt%  $\text{Mn}_3\text{O}_4$  composites could desorb 6.9 wt%, 6.7 wt% and 6.2 wt% hydrogen in 8 min, while the pure  $\text{MgH}_2$  released only 0.038 wt%  $\text{H}_2$  in the same duration. From a comprehensive perspective of the dehydrogenation temperature and capacity, the  $\text{MgH}_2 + 10$  wt%  $\text{Mn}_3\text{O}_4$  composite was chosen for further

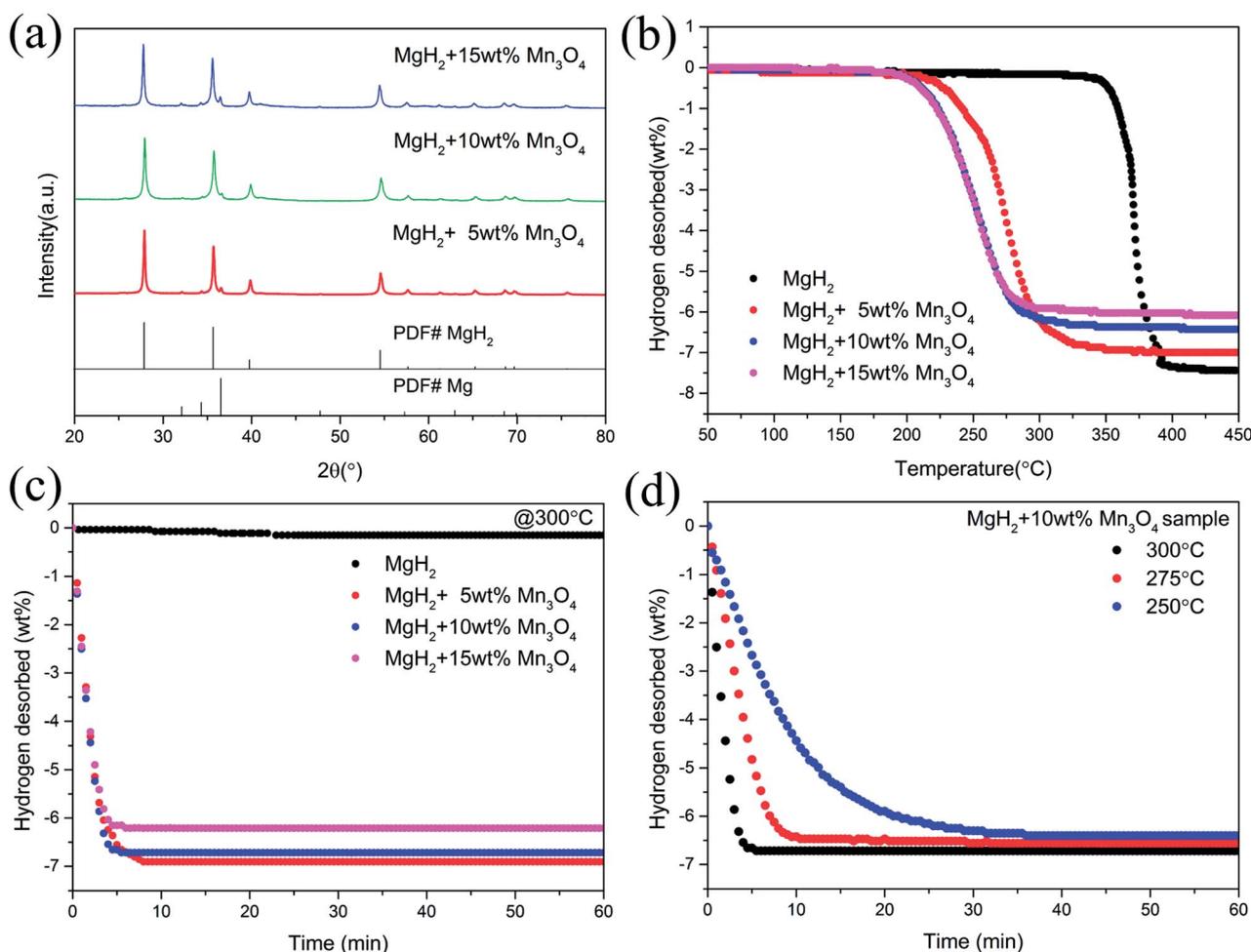


Fig. 2 XRD patterns (a), volumetric release curves (b), and isothermal dehydrogenation curves (c and d) of  $\text{MgH}_2$ ,  $\text{MgH}_2 + 5$  wt%  $\text{Mn}_3\text{O}_4$ ,  $\text{MgH}_2 + 10$  wt%  $\text{Mn}_3\text{O}_4$ , and  $\text{MgH}_2 + 15$  wt%  $\text{Mn}_3\text{O}_4$  samples.



study. Fig. 2d illustrates the isothermal desorption profiles of the  $\text{MgH}_2 + 10 \text{ wt\% Mn}_3\text{O}_4$  composite at different temperatures (250, 275 and 300 °C). The composite could release 6.4 wt% hydrogen (nearly 94% of the theoretical hydrogen storage capacity) within 10 min at 275 °C and about 6.3 wt% hydrogen could be desorbed in 30 min even at 250 °C.

Apart from the significantly improved desorption performance, we also focused on the absorption behaviour of the  $\text{MgH}_2 + 10 \text{ wt\% Mn}_3\text{O}_4$  composite. The isothermal and non-isothermal hydrogen absorption curves are shown in Fig. 3. Fig. 3a depicts the non-isothermal hydrogenation curves of the prepared  $\text{MgH}_2$  and  $\text{MgH}_2 + 10 \text{ wt\% Mn}_3\text{O}_4$  samples. The dehydrogenated  $\text{MgH}_2 + 10 \text{ wt\% Mn}_3\text{O}_4$  sample started absorbing hydrogen from room temperature, and about 5.4 wt% hydrogen could be taken up before 250 °C. However, the dehydrogenated  $\text{MgH}_2$  dilatorily absorbed hydrogen from 183 °C, which was approximately 160 °C higher than that for the dehydrogenated  $\text{MgH}_2 + 10 \text{ wt\% Mn}_3\text{O}_4$ . Further isothermal absorption measurements of the as-prepared  $\text{MgH}_2$  and the  $\text{MgH}_2 + 10 \text{ wt\% Mn}_3\text{O}_4$  composite were conducted and the results are presented in Fig. 3b and c. At 50 °C, the

dehydrogenated  $\text{MgH}_2 + 10 \text{ wt\% Mn}_3\text{O}_4$  sample exhibited a hydrogen absorption capacity of 2.5 wt% within 20 min. When heated to 75 °C, the hydrogen uptake of the  $\text{Mn}_3\text{O}_4$  containing sample amounted to 4.1 wt% in 20 min. Within an identical time period, the hydrogen absorption capacity was increased to 5.1 wt% when the temperature was increased to 100 °C. Obviously, the  $\text{MgH}_2 + 10 \text{ wt\% Mn}_3\text{O}_4$  sample showed faster hydrogen absorption kinetics than pure  $\text{MgH}_2$  (Fig. 3b). Besides, the  $E_a$  values of the hydrogen absorption reaction were calculated to further explore the improved hydrogenation kinetics. Fig. 3d reveals the isothermal hydrogenation data of  $\text{MgH}_2$  and the  $\text{MgH}_2 + 10 \text{ wt\% Mn}_3\text{O}_4$  composite simulated using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation,<sup>48,49</sup> which can be written as:

$$\ln[-\ln(1 - \alpha)] = n \ln k + n \ln t \quad (1)$$

where  $\alpha$  is the fraction of Mg transformed into  $\text{MgH}_2$  at a particular time,  $k$  is an effective kinetic parameter, and  $n$  is the Avrami exponent. The values of  $n$  and  $n \ln k$  obtained by fitting the JMAK plots are shown in Fig. S1.† The  $E_a$  values for the

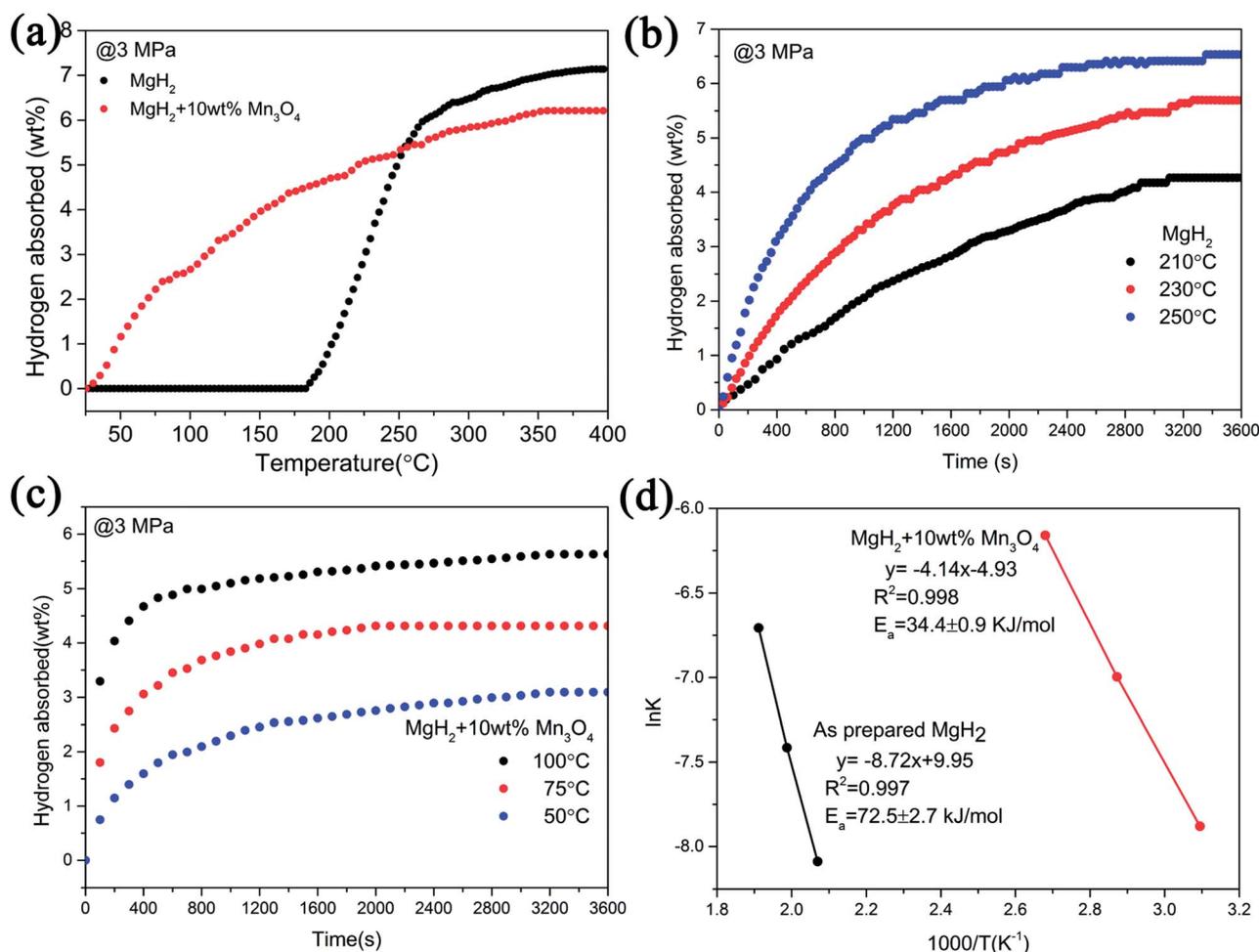


Fig. 3 Non-isothermal hydrogenation curves (a), isothermal hydrogenation curves (b and c) and the corresponding Arrhenius plots (d) of  $\text{MgH}_2$  with and without 10 wt%  $\text{Mn}_3\text{O}_4$ .



hydrogenation reactions were calculated according to the Arrhenius equation:<sup>50</sup>

$$k = A \exp(-E_a/RT) \quad (2)$$

According to the plots in Fig. 3d, the calculated  $E_a$  value of the absorption process for the dehydrogenated  $\text{MgH}_2 + 10 \text{ wt}\% \text{ Mn}_3\text{O}_4$  was  $34.4 \pm 0.9 \text{ kJ mol}^{-1}$ , which was much lower than that of the dehydrogenated  $\text{MgH}_2$  ( $72.5 \pm 2.7 \text{ kJ mol}^{-1}$ ) and other  $\text{MgH}_2$ -based systems published recently.<sup>15,16</sup> The  $E_a$  for hydrogenation was distinctly decreased by 52.6%, indicating that the energy barrier for the absorption of hydrogen is remarkably reduced due to the addition of  $\text{Mn}_3\text{O}_4$ , which is reasonably responsible for the enhanced hydrogenation kinetics of the  $\text{MgH}_2 + 10 \text{ wt}\% \text{ Mn}_3\text{O}_4$  composite.

To achieve the practical application of hydrogen storage materials, preserving long-term kinetics is considered one of the key technology indicators. Although favourable hydrogen absorption and desorption properties of  $\text{Mn}_3\text{O}_4$  doped  $\text{MgH}_2$  were evidenced, the cycling performance of the  $\text{MgH}_2\text{-Mn}_3\text{O}_4$  composite still needs to be explored. The cycle behaviour of the  $\text{MgH}_2 + 10 \text{ wt}\% \text{ Mn}_3\text{O}_4$  composite was tested at  $300 \text{ }^\circ\text{C}$  for 20

cycles. As revealed in Fig. 4, the hydrogen storage capacity of the  $\text{MgH}_2 + 10 \text{ wt}\% \text{ Mn}_3\text{O}_4$  composite reached 6.6 wt% in the first dehydrogenation process. When exposed to a 30 bar hydrogen atmosphere, the dehydrogenated sample could quickly absorb 6.4 wt%  $\text{H}_2$  at  $300 \text{ }^\circ\text{C}$ . After 20 cycles, a high reversible capacity of 6.1 wt% was still maintained, which corresponds to 95.3% of the original capacity. Generally,  $\text{MgH}_2$  particles tend to grow and aggregate during pyrolysis, leading to the degradation of cycling performance.<sup>51,52</sup> In one of our previous studies,<sup>15</sup> the cycling results showed that the capacity of Fe doped  $\text{MgH}_2$  was obviously decreased after 20 cycles. It is evident that the hydrogen storage capacity of the  $\text{MgH}_2 + 10 \text{ wt}\% \text{ Mn}_3\text{O}_4$  composite remained stable without significant decline after 20 cycles, revealing remarkable enhancement due to the catalytic activity of  $\text{Mn}_3\text{O}_4$  nanoparticles.

### 3.3 De/hydrogenation mechanism

As mentioned above,  $\text{Mn}_3\text{O}_4$  showed a superior catalytic effect on improving the hydrogen absorption and desorption properties of  $\text{MgH}_2$ . For a better understanding of the catalytic mechanism of the  $\text{Mn}_3\text{O}_4$  modified  $\text{MgH}_2$  system, a deeper investigation was conducted. It can be seen in the TEM image (Fig. 5a) that the average size of the  $\text{MgH}_2 + 10 \text{ wt}\% \text{ Mn}_3\text{O}_4$  composite after 20

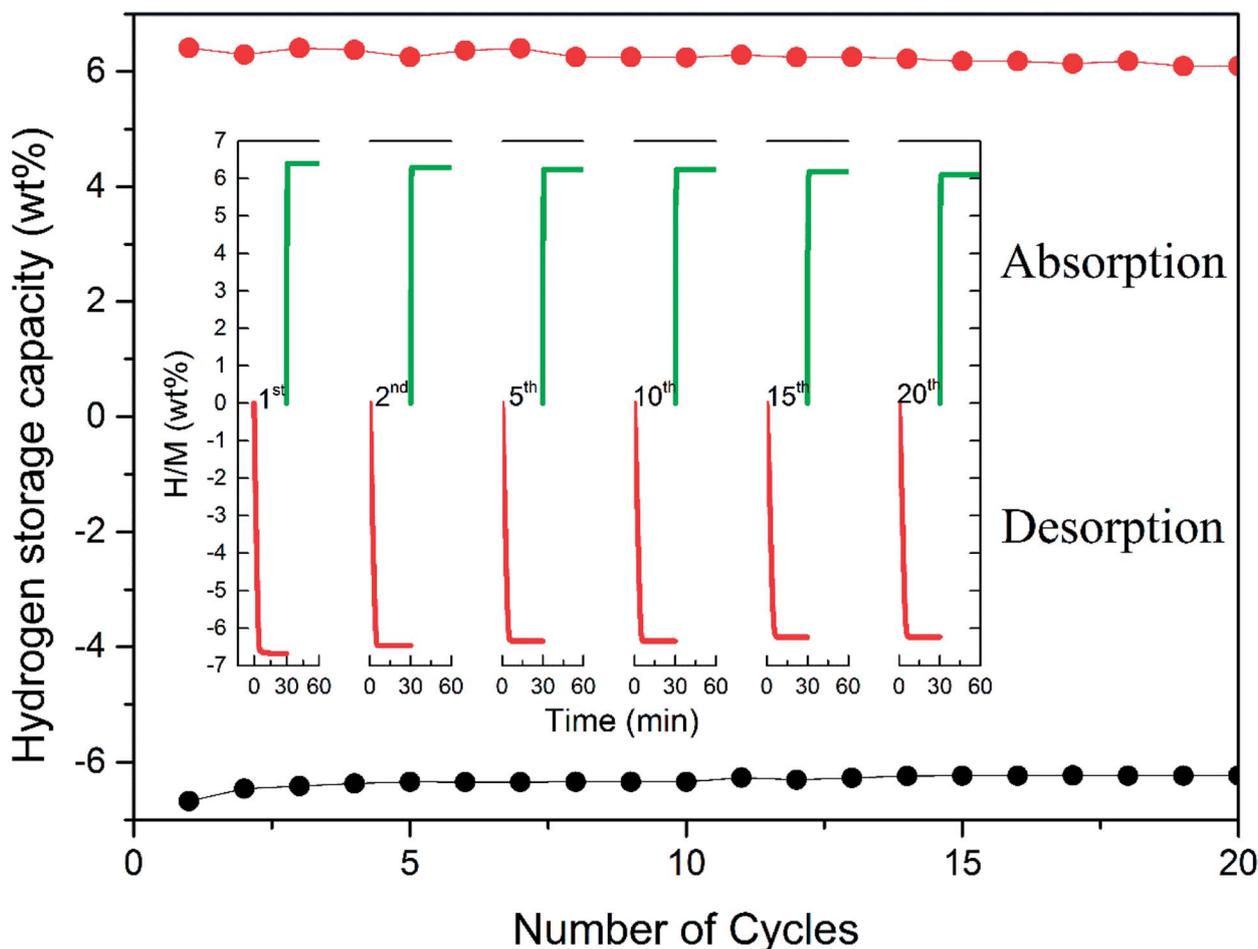


Fig. 4 Non-isothermal dehydrogenation/hydrogenation curves and hydrogen storage capacity of the  $\text{MgH}_2 + 10 \text{ wt}\% \text{ Mn}_3\text{O}_4$  composite.



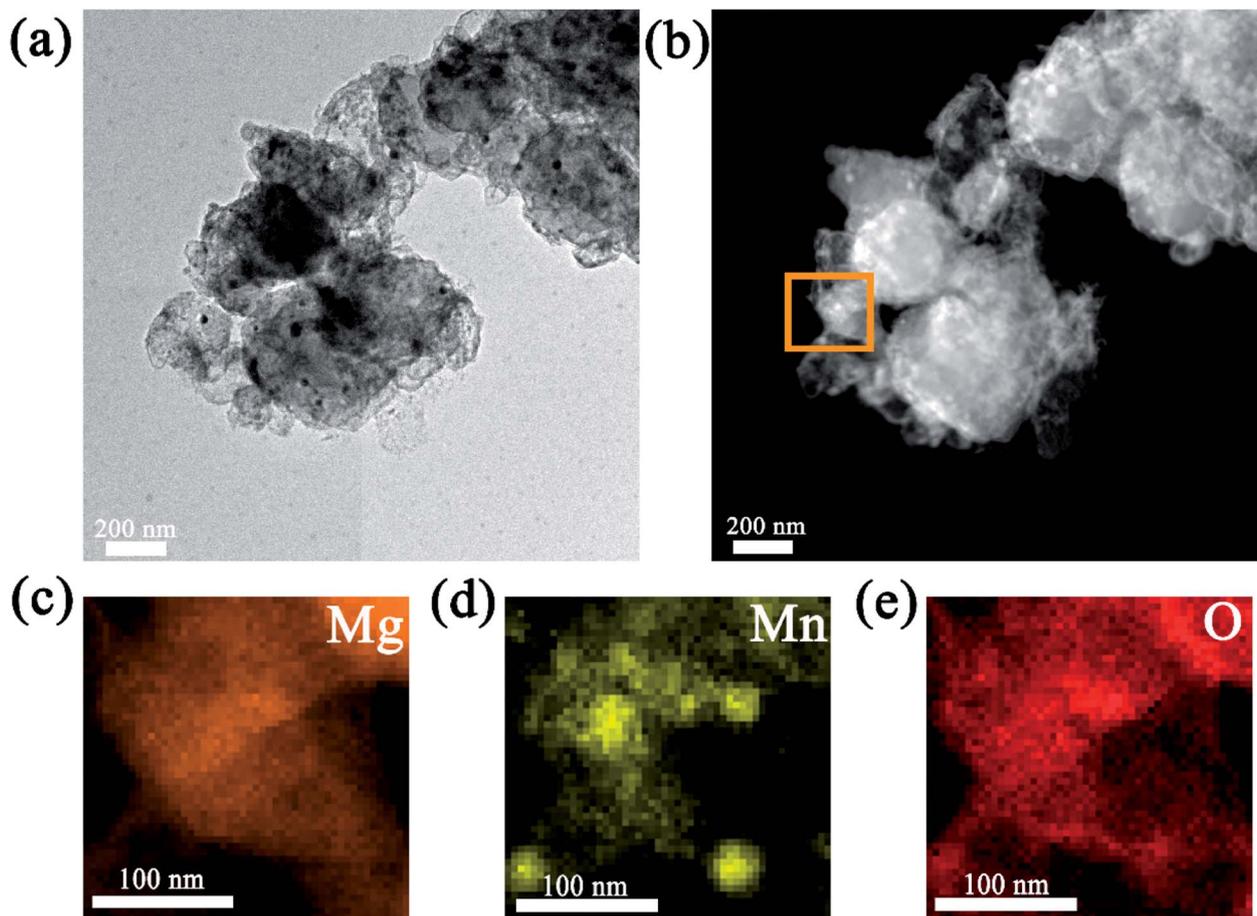


Fig. 5 TEM image (a); STEM-HAADF image (b); corresponding EDS maps (c, d and e) of the  $\text{MgH}_2 + 10 \text{ wt\% Mn}_3\text{O}_4$  composite after 20 cycles.

cycles approached 300 nm, which is much smaller than that of ball-milled  $\text{MgH}_2$  (over 800 nm) as shown in Fig. S2.† Moreover, the HAADF-STEM image in Fig. 5b shows that numerous bright nanoparticles were homogeneously distributed on the surface of  $\text{MgH}_2$ . Corresponding EDS mapping demonstrated that Mn and O covered almost the whole surface of the  $\text{MgH}_2 + 10 \text{ wt\% Mn}_3\text{O}_4$  composite after 20 cycles.<sup>53</sup>

To elucidate the evolution of  $\text{Mn}_3\text{O}_4$  nanoparticles in the de/hydrogenation process, the  $\text{MgH}_2 + 10 \text{ wt\% Mn}_3\text{O}_4$  sample in the ball-milled, dehydrogenated and re-hydrogenated states was collected and examined by XRD measurements (Fig. 6). Although the diffraction peaks of  $\text{Mn}_3\text{O}_4$  were unclear in the XRD patterns, TEM measurements (Fig. S3†) demonstrated that small particles of  $\text{Mn}_3\text{O}_4$  can be observed to be evenly distributed on the surface of  $\text{MgH}_2$ . Compared with that of pure  $\text{MgH}_2$ , the particle size of  $\text{MgH}_2 + 10 \text{ wt\% Mn}_3\text{O}_4$  in Fig. S3† was much smaller. Clearly,  $\text{MgH}_2$  or Mg still dominated the XRD patterns in Fig. 6 after the doping of  $\text{Mn}_3\text{O}_4$ . However, it is interesting that Mn and  $\text{Mg}_{0.9}\text{Mn}_{0.1}\text{O}$  phases occurred in both the dehydrogenated and rehydrogenated samples, as shown in Fig. 6b and c. In addition, the TEM image (Fig. S4†) reveals that Mn particles were uniformly dispersed on the surface of  $\text{MgH}_2$ . It should be pointed out that  $\text{Mn}_3\text{O}_4$  in contact with Mg can readily form Mn and  $\text{Mg}_{0.9}\text{Mn}_{0.1}\text{O}$  under conditions of high

temperature.<sup>40</sup> The XRD and TEM results indicate that the added  $\text{Mn}_3\text{O}_4$  nanoparticles were reduced to metallic Mn during the de/hydrogenation process. Therefore, we believe that metallic Mn is the key active catalytic species which enhance the hydrogen release/uptake for  $\text{MgH}_2/\text{Mg}$ .

The impact of Mn metal on the catalytic performance was further investigated by DFT calculations, where the Mn (330) surface was modeled, as shown in the TEM picture. The bond length and the Mulliken population (MP) are described in Fig. 7b. As presented, due to the presence of the Mn support, the Mg–H bonds were dramatically elongated and the average bond length is 2.48 Å, much longer than the pristine one (1.72 Å). Besides, the partial density of states (PDOS) in Fig. 7c shows that the ss-orbital overlap of the Mg–H bond was obviously weakened and the s electrons of Mg and H were mainly distributed at  $-5 \sim 0 \text{ eV}$  and  $-5 \sim -6 \text{ eV}$ , respectively. This reduced orbital interaction corresponds to the faint bond strength, which benefits the de/hydrogenation kinetics.<sup>54</sup> Therefore, the presence of Mn plays an important role in improving the hydrogen storage properties of the  $\text{MgH}_2$  molecule.

Based on the XRD, TEM and calculation results, the whole synthesis and de/hydrogenation process is illustrated in Fig. 8.  $\text{Mn}_3\text{O}_4$  nanoparticles prepared by a facile chemical method



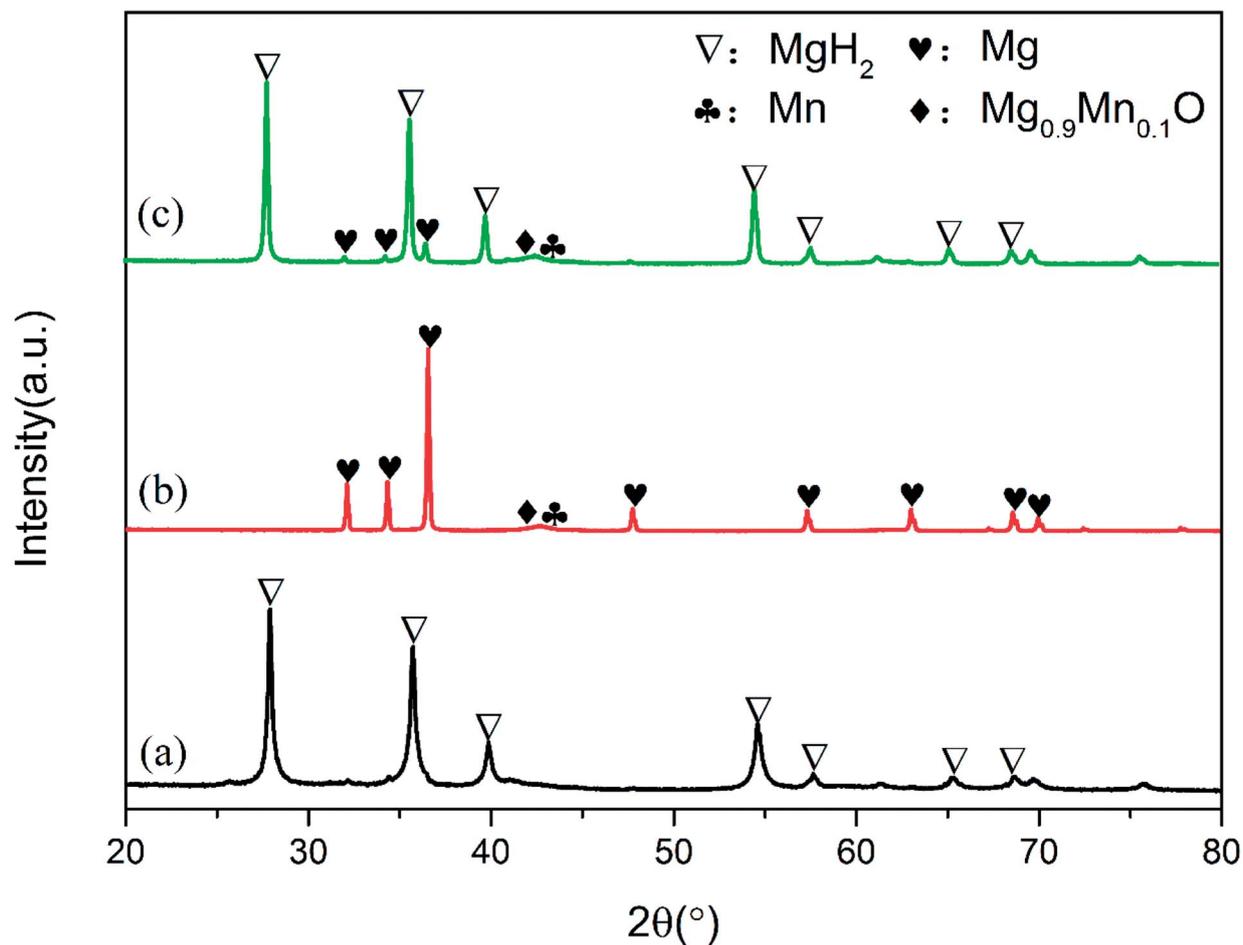


Fig. 6 XRD patterns of ball-milled (a), dehydrogenated (b) and hydrogenated (c)  $\text{MgH}_2$  + 10 wt%  $\text{Mn}_3\text{O}_4$  samples.

were evenly decorated on the surface of  $\text{MgH}_2$  during ball milling. In the de/hydrogenation process,  $\text{Mn}_3\text{O}_4$  was reduced to metallic Mn. The Mn “coating”, on one hand, will promote

the fracture of the Mg–H bond in  $\text{MgH}_2$  and reduce the de/hydrogenation temperature. On the other hand, it will help to separate the  $\text{MgH}_2$  particles and prevent them from growing

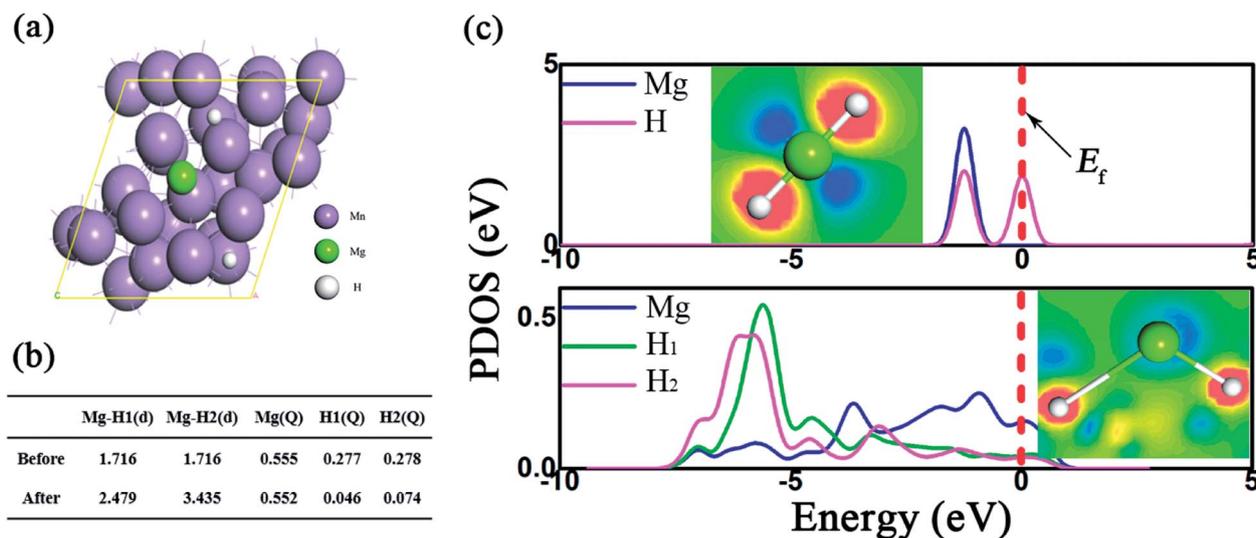


Fig. 7  $\text{MgH}_2$  absorption on the surface of Mn (330). The absorption configuration (a), the bond length, the Mulliken population of Mg–H before and after absorption on the Mn (330) surface (b) and the corresponding partial density of states (c). Inset: the deformation density of  $\text{MgH}_2$  where blue or orange denotes the charge depletion or accumulation.



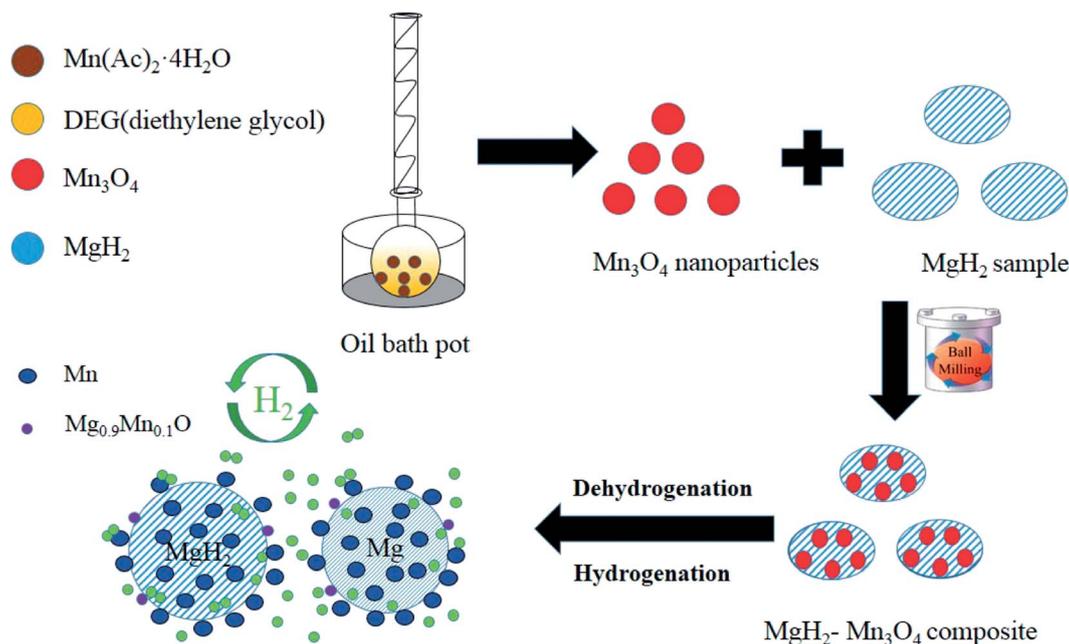


Fig. 8 Schematic summary of the synthesis and de/hydrogenation process in MgH<sub>2</sub>-Mn<sub>3</sub>O<sub>4</sub> composites.

and aggregating, thus preserving the stable cycling properties. As a result, the  $E_a$  value of the hydrogen absorption reaction was greatly decreased and the hydrogen storage properties of the Mn<sub>3</sub>O<sub>4</sub>-doped MgH<sub>2</sub> were significantly enhanced.

## 4. Conclusion

In summary, Mn<sub>3</sub>O<sub>4</sub> nanoparticles around 10 nm were successfully synthesized by a simple chemical method and a series of experiments proved that Mn<sub>3</sub>O<sub>4</sub> can remarkably improve the hydrogen storage properties of MgH<sub>2</sub>. During the process of the non-isothermal mode, the MgH<sub>2</sub> + 10 wt% Mn<sub>3</sub>O<sub>4</sub> composite released approximately 6.4 wt% hydrogen from 200 °C to 300 °C. Moreover, the MgH<sub>2</sub> + 10 wt% Mn<sub>3</sub>O<sub>4</sub> composite desorbed 6.7 wt% hydrogen within 8 min under the isothermal conditions of 300 °C. The dehydrogenated MgH<sub>2</sub> + 10 wt% Mn<sub>3</sub>O<sub>4</sub> sample could absorb hydrogen under 3 MPa H<sub>2</sub> pressure even at room temperature, and about 5.4 wt% hydrogen could be charged before 250 °C. The  $E_a$  of rehydrogenation of the MgH<sub>2</sub>-10 wt% Mn<sub>3</sub>O<sub>4</sub> composite was calculated to be  $34.4 \pm 0.9$  kJ mol<sup>-1</sup>. In addition, this sample exhibited favourable cycling stability with no significant fading over 20 cycles. Further XRD, TEM and theoretical calculations revealed that the *in situ* formed Mn weakened the Mg-H bond, and thus greatly promoted the de/hydrogenation reaction and preserved the cycling performance. This study combined experimental results with DFT calculations to investigate the catalytic effect of Mn<sub>3</sub>O<sub>4</sub> on improving the hydrogen storage properties of MgH<sub>2</sub>, which will be a good reference for developing a new composite hydrogen storage system.

## Conflicts of interest

There are no conflicts to declare.

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