Graphene-wrapped reversible reaction for advanced hydrogen storage

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ABSTRACT

Here, we report the fabrication of a graphene-wrapped nanostructured reactive hydride composite, i.e., $2LiBH_4$-MgH_2, made by adopting graphene-supported MgH_2 nanoparticles (NPs) as the nanoreactor and heterogeneous nucleation sites. The porous structure, uniform distribution of MgH_2 NPs, and the steric confinement by flexible graphene induced a homogeneous distribution of $2LiBH_4$-MgH_2 nanocomposite on graphene with extremely high loading capacity (80 wt%) and energy density. The well-defined structural features, including even distribution, uniform particle size, excellent thermal stability, and robust architecture endow this composite with significant improvements in its hydrogen storage performance. For instance, at a temperature as low as 350 °C, a reversible storage capacity of up to 8.9 wt% H_2, without degradation after 25 complete cycles, was achieved for the $2LiBH_4$-MgH_2 anchored on graphene. The design of this three-dimensional architecture can offer a new concept for obtaining high performance materials in the energy storage field.

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1. Introduction

Lithium borohydride ($LiBH_4$) has been widely investigated as one of the most promising solid-state materials for hydrogen storage due to its high gravimetric (18.5 wt%) and volumetric hydrogen density (121 kg m^{-3}) [1,2]. Its practical applications, however, are significantly restricted by the high thermodynamic stability and sluggish reaction kinetics of $LiBH_4$, which are attributed to the strong ionic/covalent bonding between the constituent elements, which leads to a complete dehydrogenation only at temperatures exceeding 400 °C (Eq. (1)) and only partial rehydrogenation even under more extreme conditions of 600 °C and 35 MPa hydrogen [3,4].

$$LiBH_4 \leftrightarrow LiH + B + 3/2H_2 \qquad (1)$$

Developing reactive hydride composites (RHCs) by incorporating metal hydrides has been proven to be an effective strategy for lowering the reaction enthalpy, enhancing the kinetics, and improving the reversible capacity of $LiBH_4$, while preserving the high overall hydrogen density [5–10]. A prototypical RHC is the combination of $LiBH_4$ and MgH_2 in a 2:1 M ratio with a high theoretical hydrogen capacity of 11.4 wt% based on Eq. (2), as well as a more advantageous dehydrogenation enthalpy (42 kJ mol^{-1} H_2) due to

the formation of MgB_2 [5–7].

$$2LiBH_4 + MgH_2 \leftrightarrow 2LiH + MgB_2 + 4H_2 \qquad (2)$$
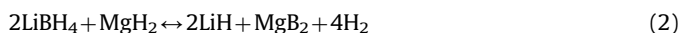
Nevertheless the $2LiBH_4$-MgH_2 composite still suffers from sluggish kinetics (as a temperature of over 400 °C is required for an appreciable dehydrogenation rate) and poor reversibility owing to grain growth, phase separation, and particle agglomeration during hydrogen sorption cycles at elevated temperature [6,11,12]. Downsizing materials to the nanometer scale has been extensively demonstrated to relieve the inherent limitations to the diffusion of elements in the solid state and facilitate destabilization induced by excess surface energy [13–15]. Due to the high reactivity of both $LiBH_4$ and MgH_2, the synthetic strategy of direct synthesis of the $2LiBH_4$-MgH_2 composite is limited to mechanical milling with uncontrollable size distribution, and, meanwhile, the performance of the mechanically milled composite is degraded during high-temperature cycling, mainly due to the uncontrolled particle growth and/or the aggregation during cycles of hydrogenation and dehydrogenation [16]. An alternative to synthesize and stabilize nanostructured hydrogen storage materials is nanoconfinement via encapsulation in porous scaffolds, leading to the formation of nanosized composite particles under steric confinement, which could effectively preserve the nanostructured morphology during thermal treatment and ensure the cycling stability [17–19]. Nonetheless, the inadequate efficiency, the tedious infiltration process, and a significant degradation of hydrogen capacity due to the massive "dead weight" introduced by inactive scaffolds, which

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is more obvious for the confinement of a binary composite, are major drawbacks for this strategy [19–21]. In terms of 2LiBH$_4$-MgH$_2$ composite, the loading capacity reported in the literature is less than 50 wt% (Table S1 in the Supporting Information). Moreover, in order to achieve the effective nanoconfinement of 2LiBH$_4$-MgH$_2$ composite, MgH$_2$ and LiBH$_4$ are required to be infiltrated in sequence, due to the lack of suitable solvents reported to dissolve both of them or their precursors in the previous literature [22,23]. Hence, the blocking of pores resulting from the preliminary infiltration of MgH$_2$ leads to the inhomogeneous distribution of LiBH$_4$ and prevents direct physical contact between LiBH$_4$ and MgH$_2$, which usually results in their individual decomposition and therefore, inferior dehydrogenation and hydrogenation kinetics and reversibility [23]. As a result, the practical hydrogen storage densities of the whole system for nanoconfined 2LiBH$_4$-MgH$_2$ composite reported in the literature is further reduced to lower than 4.5 wt% upon heating to 450 °C (Table S1). Therefore, the integration of both nanostructure engineering and high capacity to develop an efficient approach to the synthesis of high-performance reactive hydride composites is highly desirable, but remains a great challenge to date.

In this paper, we have adopted a bottom-up self-assembly strategy to controllably synthesize three-dimensional (3D) MgH$_2$@Graphene (MH@G) porous structure via solvothermal treatment with the assistance of H$_2$ (Fig. 1). By taking advantage of MH@G as the "smart nanoreactor", in which flexible and 3D-structured graphene serves as the flexible structure support and MgH$_2$ nanoparticles homogeneously distributed on graphene serve as favorable heterogeneous nucleation sites to uniformly adsorb the solution containing LiBH$_4$ and hence, construct LiBH$_4$ around MgH$_2$ nanoparticles, monodisperse 2LiBH$_4$-MgH$_2$ nanocomposite (LBMH@G) with a particle size of ∼10.5 nm was controllably fabricated on graphene. On the one hand, the nanostructuring of 2LiBH$_4$-MgH$_2$ composite could significantly decrease the phase boundaries between LiBH$_4$ and MgH$_2$, and improve the solid-state diffusion pathways for mass transport during hydrogen storage, alleviating the low mobility of atoms and ions. On the other hand, the resultant 3D architecture can not only provide accessible channels for fast transportation of hydrogen, but is also conductive to preserving the high thermal conductivity of the overall composite for rapid heat transfer during the hydrogen storage cycling, which is induced by the homogeneous distribution of flexible graphene. Moreover, the flexible graphene can prevent the growth and agglomeration of particles, and also can accommodate the stress caused by the large volume changes during consecutive cycles of hydrogen uptake and release, resulting in prolonged cycling lifetime. Altogether, the as-prepared graphene-supported 2LiBH$_4$-MgH$_2$ nanocomposite with a sandwich-type structure exhibits greatly improved hydrogen storage performance compared to other forms of 2LiBH$_4$-MgH$_2$, with high energy density, remarkable rate performance, and excellent cycling stability.

2. Results and discussion

The growth of homogeneous MgH$_2$ NPs anchored *in situ* on graphene was obtained by a hydrogenation induced solvothermal reaction of dibutyl magnesium at 200 °C for 24 h [24]. Field-emission scanning electron microscope (FE-SEM) (Fig. 2) and transmission electron microscope (TEM) (Fig. 3) images clearly show that homogeneous MgH$_2$ NPs with an average particle size of ∼ 5 nm are immobilized on large single graphene sheets with loading of 20% for the sample denoted as MH20@G. This homogeneous anchoring is attributed to the favorable absorption of dibutyl magnesium and MgH$_2$ on graphene (Figs. 2a and 3a). Cross-sectional SEM images show the nanostructures, consisting of alternating layers of MgH$_2$ NPs and graphene stacks in the composite, contains large out-of-plane macropores, afforded by the assembly of graphene sheets, and small mesopores from adding "spacers", *i.e.*, MgH$_2$ NPs, between the graphene sheets (Fig. 2b). It is worth noting that the weight fraction of MgH$_2$ NPs in the as-prepared 3D architectures could be easily controlled by adjusting the concentration of the reactants. With increasing loading from 20% to 60% (MH60@G), no aggregation was observed due to the high surface area of graphene as the structural support (Figs. 2d and 3d). The observation of out-of-plane pores in MH@G agrees well with the N$_2$ adsorption-desorption analysis (Fig. S1a), which exhibits the prominent characteristic of type-IV isotherms with a distinct H2 hysteresis loop in the P/P_o range of 0.4–1.0, suggesting the presence of relatively large macropores and mesopores in the framework. The mesopore size calculated by the Barrett-Joyner-Halenda (BJH) method is around 3.710 nm (Fig. S1b), and the hybrid features a Brunauer-Emmett-Teller (BET) surface area of up to 794.7 m^2 g^{-1} and pore volume of 1.368 cm^3 g^{-1}. Combining these results with the SEM observations, it is clear that the porous structure of macropores and mesopores could provide easy pathways for the transportation of LiBH$_4$ solution to facilitate adsorption and nucleation on MgH$_2$ NPs. They also facilitate the transportation of hydrogen during reversible storage, while tolerating the volume changes during hydrogen absorption and desorption. High-magnification images reveal that the MgH$_2$ NPs are isolated from one another within the layer and separated from each other by the graphene stacks, which

🟡 **MgH₄**   💧 **LiBH₄ in THF**   ☁ **LiBH₄**
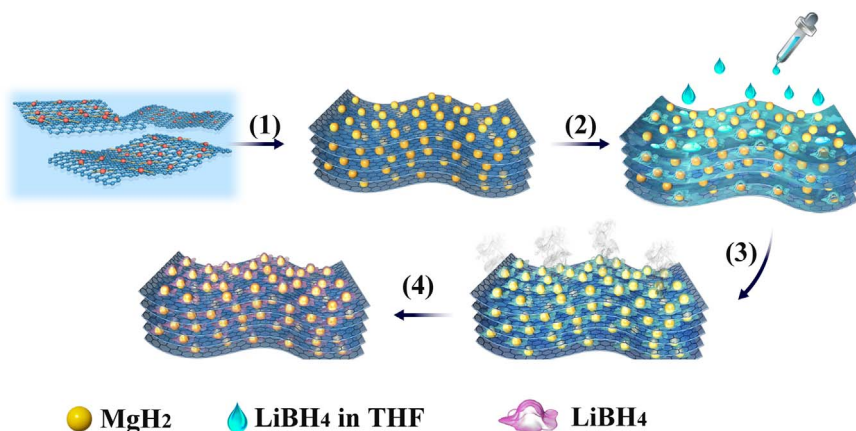
Fig. 1. Schematic illustration of the fabrication of graphene-supported 2LiBH$_4$-MgH$_2$ nanocomposite: (1) self-assembly of uniform MgH$_2$ NPs on graphene via solvothermal treatment; (2) infiltration of LiBH$_4$ solution; (3, 4) removal of solvent and heterogeneous nucleation of LiBH$_4$ on MgH$_2$ NPs.