

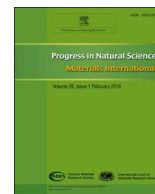
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Original Research

One-step uniform growth of magnesium hydride nanoparticles on graphene[☆]Yuqin Huang^{a,b}, Guanglin Xia^a, Jie Chen^a, Baoping Zhang^a, Qian Li^{b,c}, Xuebin Yu^{a,*}^a Department of Materials Science, Fudan University, Shanghai 200433, China^b State Key Laboratory of Advanced Special Steel & Shanghai Key Laboratory of Advanced Ferrometallurgy & School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China^c Materials Genome Institute, Shanghai University, Shanghai 200444, China

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ABSTRACT

A simple solvent-free method to synthesize MgH₂ nanoparticles (MgH₂ NPs) uniformly grown on graphene nanosheets (GNs) has been reported in this paper. Based on the formation of MgH₂ by di-n-butylmagnesium ((C₄H₉)₂Mg) thermal decomposition under hydrogen pressure, the GNs were added as matrix to hinder the agglomeration and growing of MgH₂ NPs. The fabricated MgH₂/GNs nanocomposites, in which MgH₂ NPs were homogeneously growing in the graphene matrix, have been synthesized by the favorable adsorption energy between (C₄H₉)₂Mg and GNs. Resulting from the one-step solvent-free route, the generated MgH₂ NPs shows high hydrogen capacity and steady hydriding and dehydriding properties, without the interference of the synthetic medium. At the same time, the size of the fabricated MgH₂ NPs can be controlled by adjusting the mass ratio of MgH₂ to graphene, the various hydrogen pressure and temperature. Attributed to smaller size effect, well uniform distribution of high density MgH₂ NPs, and the agglomeration blocking ability of graphene, the MgH₂/GNs-40 wt% exhibits the favorite hydrogen storage performance.

1. Introduction

Considered as a promising candidate for solid-state hydrogen storage, Magnesium hydride (MgH₂) has been widely investigated as a result of its high theoretical gravimetric density (7.6 wt% H₂), low cost and abundance [1–3]. However, the poor thermodynamics and slow kinetics hampered the application of the MgH₂ [4–6]. Due to high activation energies of hydrogenation (100 kJ mol⁻¹) and dehydrogenation (160 kJ mol⁻¹), the hydrogenation of Mg and the reversible dehydrogenation from MgH₂ are both slow [7–9], which means a temperature higher than 300 °C is required for hydrogen absorption and even higher temperature is needed for the reversible hydrogen release to proceed because of the stubborn thermodynamic. The sluggish kinetics is mainly ascribed to the low hydrogen diffusion coefficient (4×10⁻¹³ and 1.5×10⁻¹⁶ m² s⁻¹ for bulk Mg and MgH₂, respectively), the chemisorption of hydrogen at the magnesium surface (the energy to split molecule of hydrogen is 432 kJ mol⁻¹), and MgO layer formed outside the bulk magnesium, which impedes the hydrogen dissociation and the later hydrogen atom diffusion [10].

With larger specific surface area, shorter hydrogen diffusion distance, and more activated sites for the solid-gas reaction [11,12],

nanostructured MgH₂ has improved hydrogenation and dehydrogenation kinetics, thus nanostructuring is one of the most effective alternatives to enhance hydriding and dehydriding kinetics [13,14]. Theoretical calculations have proved that when the crystal size of Mg/MgH₂ comes to a few nanometers, the hydriding/dehydriding energy could sharply decreased [15–18]. For instance, via ab initio study, Wagemans et al. have figured out that the dehydrogenation enthalpy is 75 kJ mol⁻¹ and 63 kJ mol⁻¹ for bulk MgH₂ and Mg₉H₁₈ cluster (~0.9 nm), respectively. The temperature for hydrogen desorption of MgH₂ cluster significantly reduced to 200 °C, experimentally, the dehydrogenation enthalpy of MgH₂ nanowires with a diameter of ~0.7 nm down to 37.55 kJ mol⁻¹, half of the value for bulk counterpart [19]. Various research efforts have been made to synthesis nanoscaled MgH₂, which can be generally divided into three forms, that is nanoparticles/nanowires, nanoalloys and particles confined in nanostructured substrates [20]. In 2007, through vapor-transport approach, Li et al. have synthesized Mg nanowires with diameters ranging from 30 to 170 nm and clarified their size-controlled hydriding/dehydriding properties as well [21]. Although the synthesized 30 nm nanowires has much lower values of hydriding and dehydriding activation energies than that of bulk MgH₂, the nanowire topology collapsed after 3 cycles,

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* Corresponding author.

E-mail address: yuxuebin@fudan.edu.cn (X. Yu).<http://dx.doi.org/10.1016/j.pnsc.2016.12.015>

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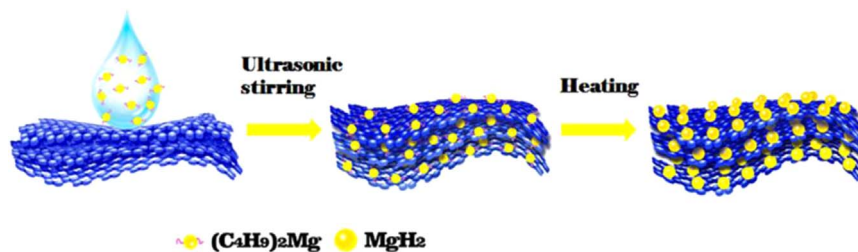


Fig. 1. Schematic illustration of the synthesis process of MgH_2 NPs on GNs.

and none of the nanowires could be regenerated. The structure synthesized by this route is fragile, due to the agglomeration of nanoscaled Mg. In addition, by electrochemical synthesis, Kondo-Franco and co-workers successfully compounded surfactant-stabilized magnesium nanoparticles with a diameter of 5 nm [21], with a relatively low onset dehydrogen temperature but the majority of hydrogen release still above the 350 °C. Adding nanostructured catalyst improves the hydrogen desorption properties. Shao et al. [22], has prepared nanocrystalline Ti-catalyzed MgH_2 , the desorption enthalphy of MgH_2 decreased to 77.7 kJ mol^{-1} .

Apparently, the structure and property stability of this nanostructured form is too far to meet the requirement of practical application. New structure and synthetic method are urgent to be developed. Thus much attention has been paid on nanoconfinement of Mg-based hydrides. By means of melt infiltration of molten Mg, de Jongh et al. firstly reported the preparation of Mg nanoparticles nanoconfined into nanoporous carbon [23]. No bulk magnesium could be detected if the loading capacity is lower than 15 wt% and, moreover, the size of Mg nanoparticles could be tuned by the pore size of carbon. It indicates molten infiltration is an effective way to generate nanoconfined Mg/ MgH_2 in a low hydrogen capacity. Subsequently, a suitable precursor to prepare MgH_2 was found, i.e., $(C_4H_9)_2Mg$, which could be dissolved in hexane and form MgH_2 according to Eq. (1) [24,25].



It provides a more convenient route to directly prepare MgH_2 nanoparticles via solution infiltration process. For instance, Nielsen et al. embedded MgH_2 nanoparticles into porous scaffold materials (carbon aerogel monoliths) through decomposition of $(C_4H_9)_2Mg$ and found that uptake of magnesium hydride was proportional to the pore volume of the aerogel material [26]. It was reported that the pore size distribution of the scaffold material exercised a great influence on the hydrogen desorption kinetics of nanoconfined MgH_2 , and the smaller pores led to faster desorption rate, probably caused by the decreased size of the space-confined hydride. Recently, Konarova et al. investigated the behavior to form MgH_2 /carbon mesoporous via decomposition of $(C_4H_9)_2Mg$ and wet infiltration in CMK3 [27]. Meanwhile, the roles of the high surface area host materials are also vital. The support materials act as a structure director, size controller and aggregation preventer [28,29]. In 2011, Jeon et al. synthesized an air-stable composite that consist of Mg nanocrystals (5 nm) in a gas-barrier polymer matrix, thus both the storage of a high density of hydrogen (4 wt% for the composite) and rapid kinetics (loading in < 30 min at 200 °C) were realized [30]. Au et al. deposited MgH_2 on carbon aerogels, lowering the dehydrogenating temperature by 140 °C, realizing the 1.3 wt% capacity and showing that the growth of the nanoparticles is effectively prevented by the carbon support [31]. Although dispersing MgH_2 into porous hosts improves hydriding/dehydrogenating property and stability to some extent [32,33], the emergence of a significant net loss of hydrogen capacity owing to the introduction of the “dead weight” of the scaffolds plagued this strategy.

To address these issues, graphene (GNs) has been paid much attention [34]. Not only serve as a support for anchoring well-dispersed NPs, but also effectively prevent the aggregation and growth of MgH_2

during de-/rehydrogenation, GNs is believed to be a suitable substrate with its light mass, large specific surface area and catalytic action toward hydrogen dissociation/recombination [35–37], not to mention its significantly influence on the heat transfer characteristics of nanostructured MgH_2 [37–41], thus leading to greatly advanced loading/unloading dynamics and hydrogen storage performance of MgH_2 [41]. Recently, Xia et al. successfully prepared GNs supported ultrafine MgH_2 NPs with both homogeneous distribution and high loading percent via solvothermal method, which exhibited advanced hydrogen storage performance and significantly enhanced cycling stability [42]. In spite of the tremendous hydrogen storage performance improvement, the synthesis process, which is time-consuming and inconvenient with solvent-washing procedure, remains to be simplified.

Here, we report a one-step, solvent-free synthetic method for the high loading and size controllable MgH_2 NPs uniformly growing on GNs (Fig. 1). GNs-supported MgH_2 NPs are formed by the decomposition of $(C_4H_9)_2Mg$ which is well dispersed on GNs by ultrasonic treatment. During the temperature-rise period and the process of heat preservation, the MgH_2 starts to nucleating and growing on the GNs via the hydrogenolysis of $(C_4H_9)_2Mg$. Taking advantage of the favorable adsorption energy between $(C_4H_9)_2Mg$ and GNs [43], the fabricated MgH_2 NPs can be firmly anchored on the GNs with well dispersion. As a result, adding graphene plays a vital role in the effective stabilization of MgH_2 nanoparticles against self-agglomeration, sintering and degradation of any nanometric effects upon hydrogen cycling.

2. Experimental section

2.1. Reagents and synthesis

$(C_4H_9)_2Mg$ (1.0 M in heptanes) was obtained from Sigma Aldrich. High purity hydrogen gas (99.999%) was used throughout the experiments. All material handling, weighing, loading and washing were performed in a glove box filled with high purity argon (O_2 and H_2O < 1 ppm) from Mikrouna.

MgH_2 were synthesized via the hydrogenolysis of $(C_4H_9)_2Mg$. Different loading capacities of MgH_2 on GNs of 40, 60, and 70 wt% were synthesized by changing the ratio between $MgBu_2$ and GNs, which were denoted as MgH_2 /GNs-60 wt%, MgH_2 /GNs-40 wt%, MgH_2 /GNs-30 wt%, respectively. In a typical synthesis of MgH_2 /GNs-40 wt%, 1.6 mL $MgBu_2$ solution and 0.02 g graphene were mixed in a pressure reactor vessel with a volume of 5 mL. The vessel was stirred for 1 h with ultrasonic stirring. The hydrogenolysis of $MgBu_2$ was then carried out at 200 °C under a hydrogen pressure of 2 atm for 20 h, with a heating rate of 2 °C min^{-1} . Subsequently, the product was dried at room temperature via dynamic vacuum on a Schlenk line, leading to the formation of MgH_2 /GNs-40 wt%. Pure MgH_2 NPs was synthesized as the same steps without grapheme.

2.2. Instrument and analysis

Thermogravimetric analysis (TG; Netzsch STA449 F3) connected to a mass spectrometer (MS; Hiden HPR 20) was conducted in a glove

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