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Enhanced hydrogen storage properties of MgH_2 catalyzed with carbon-supported nanocrystalline TiO_2

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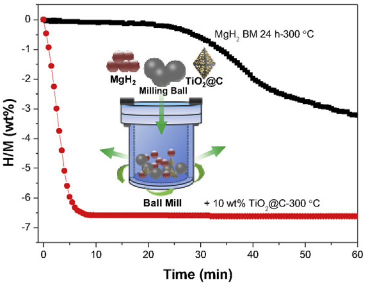
HIGHLIGHTS

- Nanocrystalline TiO_2@C is used to improve hydrogen storage kinetics of MgH_2.
- The onset desorption temperature of MgH_2-10 wt% TiO_2@C sample is only 205 °C.
- The MgH_2-10 wt% TiO_2@C sample releases 6.5 wt% H_2 within 7 min at 300 °C.
- The dehydrogenated TiO_2@C-doped sample absorbs 6.6 wt% H_2 in 10 min at 140 °C.
- The weakened Mg-H bond is responsible for the reduced desorption temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon-supported nanocrystalline TiO_2 (TiO_2@C) shows good catalytic activity in the hydrogen storage reaction of MgH_2. Adding a small amount of carbon-supported nanocrystalline TiO_2 remarkably reduces the dehydrogenation operating temperatures because the MgH_2-10 wt% TiO_2@C sample starts releasing H_2 at 205 °C, which is 95 °C lower than that of pristine MgH_2. At 300 °C, the 10 wt% TiO_2@C-containing sample rapidly releases 6.5 wt% hydrogen within 7 min. More importantly, the dehydrogenated 10 wt% TiO_2@C-containing sample takes up hydrogen even at room temperature and under a hydrogen pressure of 50 bar, and approximately 6.6 wt% hydrogen is absorbed within 10 min at 140 °C. Kinetic measurements reveal a 30% and 50% reduction in the apparent activation energy of the dehydrogenation and hydrogenation of MgH_2, respectively, with the presence of 10 wt% TiO_2@C additive. Density functional theory calculations present the extended bond lengths and the reduced bond strengths for Mg-H bonding when MgH_2 adsorbs on the TiO_2 clusters, which is responsible for the reduced de-/hydrogenation temperatures of the TiO_2@C-containing MgH_2.

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1. Introduction

Increasing air pollution and global warming problems have stimulated the development of clean renewable energy technologies. Hydrogen energy is regarded as one of the most promising options to replace traditional energy because it does not produce any harmful gases [1]. Materials-based solid-state storage of hydrogen has attracted intense interest for mobile applications due to its high hydrogen density and safety [2,3]. Substantial efforts have been conducted in developing solid-state hydrogen storage systems, including the use of metal hydrides and complex hydrides [4–9]. Among them, magnesium hydride (MgH_2) has attracted considerable attention because of its high hydrogen storage capacity (7.6 wt%), good reversibility, and low cost [10–14]. However, its practical application is still hindered by its high thermodynamic stability and slow dehydrogenation kinetics.

There have been various attempts to improve the hydrogen storage performance of MgH_2, including catalyst addition [15–38], nanostructuring [39–41] and composition modification (destabilization systems) [42–44]. In particular, many experiments have proven that adding catalysts is quite effective at reducing the operating temperature and improving the dehydrogenation kinetics of MgH_2 [15–38]. A wide variety of catalysts, ranging from transition metals [15–33] to rare earth metals [34–36] to carbon-based materials [37,38], have been studied and developed. Of these, transition metals (Ti, Zr, V, Nb, Ni, Co, etc.) and their compounds have shown remarkable catalytic activities in improving the hydrogen storage performance of MgH_2. For example, Oelerich et al. [15] studied the catalytic properties of different transition metal oxides on the hydrogen storage performance of MgH_2, and found that while Cr_2O_3 exhibited the highest activity on hydrogen absorption of MgH_2, doping with V_2O_3 and Fe_3O_4 led to the fastest hydrogen desorption from MgH_2. A metal oxide, with a large number of structural defects, low stability, high valence state and great affinity of the transition-metal ion to hydrogen, usually offered high catalytic activity on the hydrogenation reaction of Mg [16–18]. Hanada et al. [18] reported that the Nb_2O_5-doped MgH_2 absorbed ~4.5 wt% H_2 at room temperature under 10 bar of hydrogen pressure within 15 s. Chen et al. [19] observed a 197 °C reduction in the onset dehydrogenation temperature of Ni nanofiber-doped MgH_2, and the MgH_2-4 wt% Ni sample released 7.05 wt% H_2 within 11 min at 325 °C in the isothermal mode. Liang et al. [20] compared the catalytic performances of metallic Ti, V, Mn, Ni, Fe, and found that the order of catalytic activity for hydrogen storage in MgH_2 was Ti > V > Fe > Ni > Mn. Cui et al. [21] demonstrated that a multivalent Ti-doped MgH_2 system started releasing H_2 at approximately 175 °C and resulted in 5 wt% H_2 within 15 min at 250 °C. Our recent results also revealed that the 5 wt% Ti_3C_2-MgH_2 sample released 6.2 wt% H_2 within 1 min at 300 °C and re-absorbed 6.1 wt% H_2 within 30 s at 150 °C, exhibiting remarkably improved hydrogen desorption and absorption kinetics [22].

In addition, the presence of carbon structures facilitates the further enhancement of the catalytic activity of transition metal compounds by increasing the diffusion of hydrogen within bulk MgH_2 resulting from an increase in transfer channels [27–33]. Chuang et al. [27] synthesized an Nb_2O_5/SWCNT-doped MgH_2 composite in situ by ball milling Nb_2O_5 and carbon nanotubes (SWCNT) with Mg under 30 bar of H_2. The authors found that its apparent activation energy for dehydrogenation was only half of that of pristine MgH_2. Luo et al. [29] revealed that NbF_5/SWNTs co-catalyzed MgH_2 exhibited superior hydrogenation properties and cycle stability, compared with the sample catalyzed by NbF_5 alone.

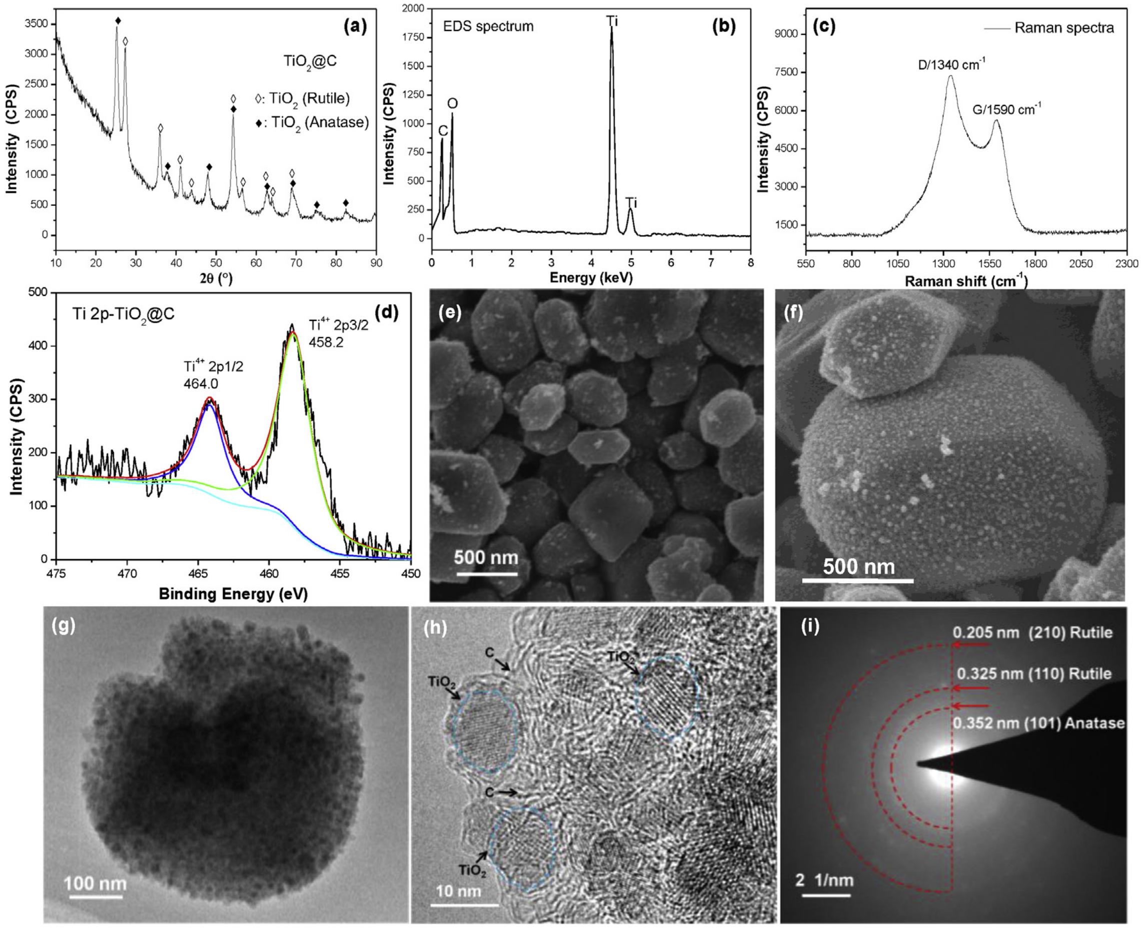

Fig. 1. The XRD pattern (a), EDS spectrum (b), Raman spectra (c), Ti element XPS spectrum (d), SEM images (e and f), TEM images (g and h), and fast Fourier transform image (i) of the as-synthesized TiO_2@C composite.