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Short Communication

Direct mechanochemical formation of alkali metal borohydrides nanocrystals exhibiting kinetic and thermodynamic destabilizations

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ARTICLE INFO

Article history:

Received 9 November 2015

Received in revised form

15 December 2015

Accepted 15 December 2015

Available online 7 January 2016

Keywords:

Hydrogen storage

Mechanical milling

Nanostructure

Metal borohydrides

ABSTRACT

The NaBH_4 nanocrystals (NCs) were successfully synthesized by mechanically driven anion metathesis between LiBH_4 and NaCl where the newly formed NaBH_4 has an approximately 10 nm in size being *in situ* embedded in the buffering matrix of LiCl byproduct. These NaBH_4 NCs obtained show significantly enhanced desorption properties with a reduction in onset temperature by 30%, over 6 times faster kinetics and nearly 4 times higher equilibrium pressure than those of micro- NaBH_4 . This novel mechanochemical approach can also be employed to prepare other borohydrides NCs such as KBH_4 .

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Introduction

The key challenge for use of hydrogen in portable electronic and transport sectors is the compact and safe storage in solid-state [1]. Alkali metal borohydrides MBH_4 ($M = \text{Li}, \text{Na}, \text{K}$) are regarded as one of the most promising candidates for their high capacity with a gravimetric density up to 18 wt% and reversible hydrogen storage, relative to the reported metal hydrides, complex aluminum hydrides and carbonaceous adsorbents [2–9]. However, the application of alkali metal borohydrides is blocked by larger enthalpies for desorption (e.g., ΔH° value for LiBH_4 is ~ 74 kJ/mol H_2) and higher kinetic barrier to regenerate borohydrides, indicating that an

unacceptably high pressure and/or temperature are required for H_2 -release and uptake in borohydrides (e.g., over 300 °C for desorption and over 35 MPa for LiBH_4 regeneration) [10,11]. Thus many methods such as catalytic doping, cation/anion substitution, hydride additives and size effects are employed to improve the kinetics and thermodynamics of complex borohydrides [10–16]. Among them, one effective strategy is to reduce the particle size to nanoscale [15–19].

Generally, mechanical milling, as a top-down approach, was directly adopted to crush micron-sized borohydrides into smaller pieces. However, it is difficult to produce dramatic size effects due to the inhomogeneous size distribution ranging from 2 nm to 10 μm [20,21]. The second approach is infiltration of borohydrides into a nanoscaffold via impregnation that the

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<http://dx.doi.org/10.1016/j.ijhydene.2015.12.094>

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particle size can be controlled by the uniform nano-channels. Unfortunately, this technique is basically applicable for laboratory-scale preparation, but the fastidious loading process precludes a scale-up by this route [18,22]. Later, a bottom-up self-assembly route was proposed to reorganize borohydrides from solution [16,19], which is recognized as a facile route to obtain intriguing structures, but their dissipative structures are often randomly organized without controlled regularity, especially that their particle sizes below 20 nm are difficult to be achieved. Recently, the mechanochemical method has been demonstrated to be an effective route of synthesis borohydrides NCs such as $\text{Mg}(\text{BH}_4)_2$, $\text{V}(\text{BH}_4)_3$, $\text{La}(\text{BH}_4)_3$, $\text{Mn}(\text{BH}_4)_2$, etc [23–26]. However, the preparation of alkali metal borohydrides NCs by mechanochemical is rarely reported up to now, and the formation mechanisms for these borohydrides NCs above are still unclear, which would block the expansion of this prepared method for other hydrides NCs. Here, we demonstrate for the first time the direct, solvent-free synthesis of NaBH_4 nanocrystals (NCs) with approximately 10 nm size by mechanochemical processing, and study its formation mechanisms and decomposition properties by using X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and pressure-composition-temperature (PCT) Sieverts-type apparatus. In addition, this mechanochemical approach can also be employed to prepare other borohydrides NCs such as KBH_4 .

Experimental section

The borohydride MBH_4 ($M = \text{Na}, \text{K}$) nanocrystals (denoted as MBH_4 -NCs hereafter) was prepared by solid-phase metathesis reaction according to Eq. (1) using LiBH_4 (95% purity, Sigma-Aldrich), NaCl or KCl (anhydrous, 99.9% purity, Sigma-Aldrich) as starting materials without purification. The procedure of MBH_4 -NCs preparation involved mechanical milling of LiBH_4 and NaCl (or KCl) mixture in a 1:1 M ratio at ambient temperature under an argon (Ar) atmosphere for 10 h at a speed of 400 rpm. These borohydrides NCs were gradually obtained via mechanically triggered metathesis, trapping and confinement in chlorides (i.e. the byproducts), which enabled the NCs to be relatively fine and homogeneous existing. All operations were handled entirely in an Ar-filled glove box.



To reveal the phase component evolutions, XRD patterns were carried out on a Rigaku D/max 2400 with $\text{Cu K}\alpha$ radiation at 50 kV and 30 mA and further analyzed with a Rietveld refinement program RIETAN-2000 [27]. During XRD measurements, the surface of samples was covered with Scotch tape to prevent any possible reaction with water and oxygen. HRTEM and SEM observations were respectively carried out on JEOL JEM-2100 F and Shimadzu SUPERSAX-550 equipped with an energy dispersive X-ray spectrometer (EDX). Decomposition behaviors were studied using thermogravimetry (TG) by Netzsch STA 409 PC with a ramping rate of 5 °C/min under a flowing Ar atmosphere. The thermodynamics and kinetics in desorption were measured using an automated Sieverts-type

apparatus (Suzuki, made in Japan). The pressures in the reactor and gas reservoir were monitored using high-precision pressure transducers. The evolved hydrogen was quantified by calculating the pressure changes in the reactor using the equation of state. For the purpose of comparison, the by-product of LiCl masses were excluded in the determination of the hydrogen amount released from the samples.

Results and discussion

Fig. 1a shows the XRD pattern of starting materials of LiBH_4 and NaCl (1: 1 in molar) after 10 h ball-milling. It can be seen that the Bragg peaks can be indexed as NaBH_4 , LiCl and residual NaCl , while the absence of LiBH_4 phase is most likely due to its mechanical-induced amorphous and/or nanocrystalline nature [28]. This indicates the occurrence of the metathesis reaction between LiBH_4 and NaCl , being also supported by the micrographic changes in Fig. 1(b,c) where the milled sample exhibits smooth and connective features, being significantly different from the initially cubic and independent shape before ball-milling. Its qualitative phase analysis yields 43 wt% NaBH_4 , close to the theoretic value of 47 wt% according to Eq. (1), which clearly means that the metathesis between LiBH_4 and NaCl approach to completion after 10 h ball milling. Note that these peaks from the newly generated NaBH_4 are obviously broader and weaker, strongly suggesting its fine crystalline in size. Using Debye–Scherrer equation [29], the average grain size for NaBH_4 is further estimated to be about 13.6 ± 0.1 nm. The HRTEM images of the ball-milled products in Fig. 1(d,e) show that the approximately 10 nm-sized NaBH_4 NCs individually embeds in matrix of LiCl byproduct. To further validate this embedding structure, the ball-milled products were washed three-times by tetrahydrofuran (THF) under ultrasonic wave. The sample after THF washing as shown as Fig. 1(f,g) exhibits a nanoporous structure in the connective LiCl matrix, which is probably due to dissolution of the embedded NaBH_4 into THF. All above observations demonstrate that the NaBH_4 -NCs with ~10 nm in size can be successfully synthesized by direct mechanochemical route.

To reveal intrinsic formation mechanisms of NaBH_4 -NCs, the phase evolution of starting materials including $\text{LiBH}_4/\text{NaCl}$ (1: 1 in molar) with different milling times were determined by XRD technique. As can be seen from Fig. 2a that as the milling time increasing from 2 h to 5 h and to 10 h, the intensity of NaCl phase significantly decreases while that of NaBH_4 phase increases, indicating that the mechanical force-driven metathesis between LiBH_4 and NaCl starts and highly depends on the milling time. This metathesis would further cause misfit of elemental ratio of starting materials such as NaCl , which was indeed demonstrated by line EDX element analysis in Fig. 2b. It shows that in the connective structure, the molar content of Na and Cl elements distinctly disagrees with each other, i.e., the intensity of Cl element is much higher than the Na one in light gray region while a slightly high intensity of elemental Na than Cl can be observed in dark grey region (see insert in Fig. 2b).

Most interestingly, an obvious peak-shift can be observed in the Bragg d -spacings (i.e. 2θ values) of the NaCl phase after

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