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Nanoconfinement of borohydrides in CuS hollow nanospheres: A new strategy compared to carbon nanotubes

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ABSTRACT

Herein, the nanoconfinement of $LiBH_4$ and $NaBH_4$ in a carbon (carbon nanotubes, MBH_4@CNT) and an inorganic support (CuS hollow nanospheres, MBH_4@CuS) is compared. Both led to drastic improvements in hydrogen storage properties, with hydrogen desorption occurring from room temperature, and the reversibility greatly enhanced. However, successive hydrogen desorption and absorption cycles for MBH_4@CNT led to a decrease in hydrogen storage capacity, most likely due to partial oxidation from oxygen-containing groups on the surface of the carbon nanotubes. In contrast, little to no decrease in capacity was observed for MBH_4@CuS, indicating that similar materials may be a more viable alternative for future nanoconfinement research.

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Introduction

Under the pressure of diminishing fossil fuel resources and the growing environmental concerns arising from carbon emissions, the use of renewable energy has gained increasing public attention. Energy storage plays a vital role, delivering continual supply from the variable output of renewables. Hydrogen is a highly favourable energy carrier, being clean and abundant with high energy density. However, its practical application has been limited due to the challenges in finding a method for its storage that is light, safe, compact and affordable. Traditional ways of storing hydrogen are liquefaction, compression of gas, physisorption and chemisorption. However, none of the current technologies can meet the 6.5 mass% hydrogen capacity target and reversible low temperature

hydrogen sorption conditions for them to be suitable for practical applications [1,2].

Lightweight complex borohydrides, such as $LiBH_4$ and $NaBH_4$, are among the most investigated and promising materials for the purpose of hydrogen storage [3,4]. They have high volumetric and gravimetric densities compared to most other solid hydrogen materials, theoretically storing 18.5 mass % and 10.8 mass% of hydrogen, respectively. The main challenges in using complex borohydrides in practice are the slow desorption kinetics and lack of reversibility of the materials [3–6]. The decomposition of $LiBH_4$ and $NaBH_4$ via thermolysis requires very high temperatures and activation energies due to the strong covalent bonds within the $[BH_4]^-$. This temperature is generally above the melting point of the materials, which may result in a decrease in surface area, limitations on the growth of product phase and further restriction of the

reversibility. The hydrogen desorption mechanism also tends to be complex. For example, bulk $LiBH_4$ exhibits multiple hydrogen desorption reactions with at least three intermediates. The stabilities of these intermediates make the release of the final hydrogen atom very difficult and full decomposition only occurs at temperatures above 727 °C [4].

In the past decade, nanoconfinement of complex hydrides within carbon scaffolds like activated carbon [7], carbon aerogels [8,9], mesoporous carbons [10], and carbon nanotubes [11] has been used to improve their hydrogen storage properties by introducing size-dependent effects. Unlike conventional approaches such as doping/catalyst addition or destabilization through partial cation substitution or reaction with another hydride, nanoconfinement can improve both the thermodynamic and kinetic properties of the materials [12,13]. The hydrides are destabilized due to excess surface energy and contributions from the interface, leading to improved thermodynamics, and diffusion distances are decreased, leading to improved kinetics [12,14]. However, the use of carbon supports for nanoconfinement tends to lead to only limited reversibility, most likely due to oxygen-containing groups on the surface of the carbon [15] that cause partial oxidation of the hydrides as they are heated [16]. In this study, the reversible behaviour of $LiBH_4$ and $NaBH_4$ was compared when nanoconfined in a carbon support (carbon nanotubes, CNT) and an inorganic support (hollow copper sulphide nanospheres, CuS) to determine whether inorganic materials that do not host oxygen-containing groups on their surface lead to improved reversibility. This could lead to new directions for nanoconfinement approaches in the future.

Material and methods

All operations were carried out under inert atmosphere in an Argon-filled LC-Technology glove box (<1 ppm O_2 and H_2O).

Preparation of materials

CNT were purchased from Shenzen Nanotech Port Co. Ltd (purity > 90%, CNT 60%, outer diameter < 2 nm). Copper (II) sulphate ($CuSO_4$, anhydrous) and sodium hydroxide (NaOH) were purchased from Ajax Finechem. Polyvinylpyrrolidone (PVP K30, MW ~ 40,000) was purchased from Fluka Analytical. Hydrazine hydrate ($N_2H_4.H_2O$, 80%) and lithium borohydride ($LiBH_4$, 95%) were purchased from Merck. Thioacetamide ($CH_3C(S)NH_2$) was purchased from BDH. Sodium borohydride ($NaBH_4$, 99%) and Diethylene glycol dimethyl ether (diglyme) were purchased from Sigma–Aldrich. Tetrahydrofuran (THF) was purchased as HPLC grade from Fisher Scientific and dried using a LC Technology SP-1 Solvent Purification System. All other chemicals were used without further purification.

Impregnation of borohydrides in CNT (MBH$_4$@CNT)

CNT were purified as previously described [11]. The pore-volume of the resulting CNT was measured by BET using a Micromeritics TriStar 3000 Analyzer from Micrometrics Instrument Corporation and was determined to be 0.486 $cm^3\,g^{-1}$ 100 mg of purified CNT was lightly ground with a mortar and

pestle to break up large agglomerates, and evacuated on a Schlenk line for 6 h at 100 °C. In an Ar-filled glove box, 50 mg $LiBH_4$ was dissolved in 5 mL THF. Using a syringe, 0.2 mL $LiBH_4$ solution was injected into the flask containing evacuated CNT (enough to fill pore volume with small excess). The resulting material was dried under vacuum overnight. The process was repeated twice more. According to elemental analysis, the Li content was 2.4 ± 0.2 mass% and the B content was 3.7 ± 0.3 mass%. This corresponds to an overall $LiBH_4$ content of 7.5 ± 0.3 mass% in the material. An analogous method was used to incorporate $NaBH_4$ into CNT, using a solution of 50 mg $NaBH_4$ in 5 mL diglyme. Due to the high boiling point of diglyme (162 °C at ambient pressure), drying was performed under vacuum at 50 °C. According to elemental analysis, the Na content was 4.3 ± 0.4 mass% and the B content was 1.9 ± 0.2 mass%. This corresponds to an overall $NaBH_4$ content of 7.4 ± 0.6 mass % in the material.

Synthesis of CuS hollow spheres

CuS hollow spheres were synthesized through a sacrificial template method based on Kirkendall diffusion, scaled up from the procedure by Zhu et al. [17] A solution of $CuSO_4$ was prepared by dissolving 0.3192 g $CuSO_4$ in 150 mL milli-Q water. 19.2 g PVP was added to act as a surfactant. 150 mL NaOH solution with pH of 10 and 0.2 mL 4 M $N_2H_4.H_2O$ solution were then added to oxidize the copper ions to copper oxide. 0.7996 g thioacetamide was added to the solution and aged for 1 h to react with copper oxide and form copper sulfide hollow spheres. The resulting solution was centrifuged to obtain a black precipitate, which was washed with distilled water three times to remove the solvent residue, then washed with absolute ethanol three times to remove the remaining water. The solid was then dried under vacuum at room temperature for at least 12 h. The pore-volume of the resulting CuS hollow spheres was measured by BET to be 0.128 $cm^3\,g^{-1}$, and the surface area was 14 $m^2\,g^{-1}$.

Impregnation of borohydrides in CuS spheres (MBH$_4$@CuS)

The borohydrides were introduced inside the hollow nano-spheres by a similar wet impregnation approach to that used for CNT (Scheme 1). $LiBH_4$ (1.5 M) and $NaBH_4$ (0.5 M) was suspended in 5 mL THF and diglyme, respectively. The CuS spheres were further dried under vacuum at 100 °C. The desired solution (0.2 mL for $LiBH_4$ and 0.1 mL for $NaBH_4$) was then added to 20 mg of evacuated CuS spheres and dried under vacuum at room temperature for at least 18 h to allow impregnation of the borohydrides. The resulting powders were black ($LiBH_4$@CuS) or dark grey ($NaBH_4$@CuS). After impregnation, the pore volume decreased to 0.022 $cm^3\,g^{-1}$ and the surface area decreased to 3 $m^2\,g^{-1}$ as determined by BET measurements.

Characterization

The size, morphology and EDS analysis and elemental mapping of the particles were characterized by Transmission Electron Microscopy (TEM) using a Philips CM200 operated at 200 keV. TEM samples were dispersed in cyclohexane,