Tunable NaBH₄ Nanostructures Revealing Structure-Dependent Hydrogen Release

Muhammad Saad Salman, Aditya Rawal, and Kondo-Francois Aguey-Zinsou*

Borohydrides are promising candidates for hydrogen storage and generation assuming these can be tuned to reversibly deliver hydrogen under practical conditions. Nanostructuring of borohydrides has the potential to enable such control but this has remained elusive due to the lack of approaches to effectively prepare and stabilize borohydride nanostructures. Herein, a simple and straightforward method to assemble NaBH₄, as a model borohydride, into sphere, cube, and bar-like shapes using tetrabutylammonium bromide (TBAB), octadecylamine (ODA), and tridecanoic acid (TDA), respectively, is demonstrated. More importantly, the shape of the NaBH₄ nanostructures could be tuned from one morphology to another by simply adjusting the ratio of surfactants and this is found to lead to distinct hydrogen properties. In particular, remarkable shifts in the melting points and hydrogen desorption temperatures are observed depending on the NaBH₄ morphologies, i.e., spheres, cubes, or bars. For example, for the NaBH₄ spheres, hydrogen release starts at \(\approx 50^\circ \text{C}\) compared to the \(>500^\circ \text{C}\) of bulk NaBH₄ without any transition metal dopant or catalyst. Observation of such structure-dependent relationships finally enables new avenues to deliberately tune borohydrides toward nanostructures with specific hydrogen properties otherwise difficult to control.

1. Introduction

Hydrogen (H₂) is considered as the next energy carrier. However, its safe and efficient storage remains a technical challenge.[1] A range of materials, including metal alloys, carbons, metal–organic frameworks, and complex hydrides, has been proposed as promising candidates for storing hydrogen.[11–12] In particular, borohydrides have garnered great attention due to their higher gravimetric hydrogen content.[3] Among the borohydride family, sodium borohydride (NaBH₄) with \(\approx 10.6\ \text{wt}\% \ H₂ \) remains one of the most studied candidates for hydrogen generation and/or storage. NaBH₄ can generate hydrogen via hydrolysis; however, this approach suffers from significant drawbacks, including the recycling of the end products and the overall efficiency of the process.[4] Hydrogen can also be generated from NaBH₄ through direct heating. However, in this case, hydrogen is not released before 500 °C due to the thermodynamic stability of NaBH₄.[5]

Several methods have been proposed to improve the hydrogen properties of NaBH₄ and the reversibility of the hydrogen release upon its thermolysis, such as partial substitution,[6] reaction with another hydride,[7] and the use of transition metal catalysts.[8] However, hydrogen release still occurs at temperatures \(>300^\circ \text{C}\) and direct regeneration of NaBH₄ from the recombination of its thermally decomposed products (Na or NaH and B) with hydrogen is unfavorable even at temperatures and pressures of around 400 °C and 350 bar H₂, respectively.[14]

An alternative approach to improve the hydrogen properties of NaBH₄ is through its nanostructuring at 100 nm or below. Significant improvements in the hydrogen desorption and storage properties have been reported upon nanosizing hydrides.[1b,9] In this case, it is hypothesized that nanosized hydrides can display altered hydrogen properties due to their higher surface areas, shorter diffusion paths for hydrogen, interfacial reaction pathways, and/or new surface states.[9a,10] Nonetheless, controlling the properties of nanosized hydrides is challenging and remains elusive because of the lack of methods to effectively synthesize and stabilize such nanostructures. Contrary to transition metals or their oxides for which a plethora of nanosynthesis methods have been reported, hydrides are very reactive by nature and thus difficult to synthesize and stabilize at the nanoscale.[11]

The simplest method to obtain nanoscale hydrides is via nanocoating of the hydride within the pores of a scaffold.[10a,12] For example, the nanocoating of LiBH₄ and NaBH₄ borohydrides in CuS hollow spheres led to drastic improvements with desorption occurring from room temperature with up to 0.7 wt% reversible hydrogen storage at 300 °C.[13] Similarly, by
encapsulating NaBH₄ nanoparticles in graphene a net reversible hydrogen capacity of ≈7 wt% was achieved at 350 °C for a few cycles. However, these nanoconfinement approaches suffer from serious drawbacks such as the complex nature of the hydride−scaffold reactions and the dead weight and volume of the host scaffold, which drastically reduce the practical hydrogen storage capacity because the hydride is only 20−30 wt% of the nanofluidified systems. An alternative strategy to avert the dead weight of porous supports is to synthesize borohydride nanostructures via wet chemistry approaches using surfactants and/or ligands. In this context, early work was conducted by our group to obtain NaBH₄ nanoparticles in the presence of tetrabutylammonium bromide (TBAB) using a precipitation method where the surfactant is easily removed and/or replaced with a metallic shell. On one hand, after stabilizing NaBH₄ nanoparticles (<30 nm) with TBAB the melting point was decreased and the onset hydrogen desorption temperature was shifted to ≈400 °C; on the other hand, reversibility of up to 5 wt% H₂ was achieved from the core−shell NaBH₄@Ni nanostructure at 350 °C. This core−shell strategy gives clear evidence of improved hydrogen storage properties due to nanosize effects and stabilization within a metallic shell. In this approach, control over the borohydride core is essential to lead to improved hydrogen properties. Accordingly, the development of better synthetic methods that allow for tailoring the morphology and surface chemistry of borohydrides is important to further progress.

A much simpler way to obtain size-controlled borohydrides is through solvent evaporation−induced self-assembly. In this process, the nucleation and growth can facilely be controlled using different surfactants. Recently, using this technique we demonstrated that the size and morphology of the NaBH₄ and/or LiBH₄ nanostructures are highly dependent on the type of surfactant, their head groups, and chain lengths. From these preliminary studies focused on one surfactant to control the morphologies, it became apparent that better control should be possible using a combination of surfactants. Appropriate adjustment of surfactant systems can enable control over the nucleation and growth kinetics and final functional properties of nanocrystals due to the cooperative action of capping agents. For instance, the growth kinetics of the gold nanorods was found to be controllable by adjusting a mixture of surfactants, i.e., benzyltrimethylammonium chloride and cetyltrimethylammonium bromide, to produce long nanorods. Similar approaches have been adopted to obtain Pd nanoparticles of different shapes such as spheres, cubes, and octahedra, which are simple to synthesize, and these revealed structure-dependent hydrogen properties. The application of such a concept to the borohydride family is compelling as it may enable control over the hydrogen properties.

In this work, we thus report on a simple strategy to obtain tailored NaBH₄ nanostructures using surfactants as stabilizers and shape-directing agents via the solvent evaporation method. Using that novel approach, the size and morphology of NaBH₄ nanostructures were tuned to spheres, cubes, and bars, and transformed to one another by simply adding a cosurfactant. The deliberately controlled NaBH₄ nanostructures showed varied hydrogen desorption behaviors, proving for the first time morphology-dependent hydrogen properties. Our strategy not only results in different shapes of NaBH₄ but also, depending on the type of morphology stabilized, triggers hydrogen desorption at low temperatures. Accordingly, this work is believed to have unprecedented potential as a first step toward hydrogen nanostructure−property relations in complex borohydrides.

2. Characterizations

2.1. Transmission Electron Microscopy (TEM)

Microscopic analysis was done by TEM on a Philips CM200 operated at 200 kV. The materials were dispersed in cyclohexane followed by short ultrasonication and then dropped onto a carbon-coated copper grid. The grids were enclosed in an argon-filled vial and then rapidly transferred to the TEM facility to minimize air exposure.

2.2. X-Ray Diffraction (XRD)

Crystalline phases were determined by XRD on an X′pert Multipurpose XRD system operated at 40 mA and 45 kV with monochromated Cu Kα radiation (λ = 1.541 Å) from 10° to 80°. The materials were protected against oxidation from the air by a Kapton foil.

2.3. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was conducted on a Bruker Vertex 70V. The materials were mixed with KBr and loaded in an air-tight chamber fitted on a Harrick-Scientific Praying Mantis diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) accessory. The spectra were collected at room temperature from 600 to 4000 cm⁻¹ over 124 scans with a resolution of 1 cm⁻¹.

2.4. Nuclear Magnetic Resonance Spectroscopy

Solid-state ¹¹B magic angle spinning NMR experiments were conducted on a wide-bore Bruker Biospin Avance III solids 300 MHz spectrometer with a 7 T superconducting magnet operating at a frequency of 96.18 and 300 MHz for the ¹¹B and ¹H nuclei, respectively. Approximately 30 mg of the material was center packed into 4 mm zirconia rotors fitted with Kel-f caps and spun in a double-resonance H-X probe head at rotation speeds of up to 12 kHz at the magic angle. The 1D ¹¹B spectra were acquired with a hard 4 μs radiofrequency pulse corresponding to a 90° tip angle. The recycle delay of 30 s was sufficient to ensure full relaxation of the ¹¹B signal and 4−16 signal transients were coadded to ensure sufficient signal to noise. The spectra were obtained at room temperature, with an acquisition time of 40 ms to acquire the full ¹¹B signal. The SpinA64 decoupling scheme with a field strength of 72 kHz was used for the ¹H heteronuclear decoupling. The 2D ¹H-¹¹B heteronuclear correlation (HETCOR) measurements were acquired with 4−16 transients in the indirect (F2) dimension and 128 increments of 68.25 μs each in the indirect (F1) dimension, and recycle delays of 5 s. Frequency switch Lee–Goldburg (FSLG) homonuclear decoupling at a field strength of 83 kHz was applied during the ¹H evolution to enable high-resolution ¹H spectra in the F1 dimension. After ¹H evolution, 100 ms of ¹H spin diffusion time was used to...
allow for sufficient signal of the protons from the surfactant layer to diffuse to the BH₄⁻ core, followed by 1 ms ¹H to ⁱ¹B cross-polarization. The ⁱ¹B chemical shifts were referenced to pure solid NaBH₄ at −42 ppm and the ¹H chemical shifts were referenced to adamantane at 1.8 ppm.

2.5. Thermal Stability and Hydrogen Release

The thermal decomposition of the surfactant-stabilized NaBH₄ structures was evaluated by thermal gravimetric analysis/differential scanning calorimetry (TGA/DSC) using a Mettler Toledo DSC 3 coupled to a Pfeiffer Omnistar mass spectrometer (MS). The samples were packed in standard aluminum pans (40 µL) and the TGA/DSC characterizations were conducted under a flow of argon of 20 mL min⁻¹ from 20 to 500 °C with a heating rate of 5 °C min⁻¹. The hydrogen desorption profiles of the materials were determined by MS.

3. Results and Discussion

3.1. Synthesis of Varied NaBH₄ Morphologies

Scheme 1 shows a simple synthetic approach that was developed to obtain various morphologies of NaBH₄. To form NaBH₄ into deliberately controlled morphologies, a set amount of high-purity NaBH₄ was dissolved in a low-boiling-point solvent (i.e., isoproplylamine (IPA)) containing the stabilizing surfactant. The mixture upon solvent evaporation was then found to lead to the sphere, cube, and bar-like NaBH₄ nanostructures depending on the type of surfactant used, i.e., TBAB, octadecylamine (ODA), and tridecanoic acid (TDA), respectively (Figure 1a and Figure S1, Supporting Information). The morphology of the NaBH₄ particles is thus directly linked to the nature of the surfactant used and in particular its head group. It is noteworthy that the evaporation of NaBH₄ in IPA in the absence of a surfactant also led to a cube-like morphology due to the interaction of amine groups from the solvent with NaBH₄ (Figure 1a). Indeed, recrystallization of NaBH₄ in amine-free solutions was found to lead to particles of undefined morphologies. For instance, evaporation of NaBH₄ dissolved in diglyme was found to only produce irregular morphologies.[20] It is thus apparent that amine-based functionalities favor the growth of cubic NaBH₄. Though the exact mechanism is unclear, we believe that this could be due to the preferential adsorption of amine on the [100] facet of NaBH₄.

Figure 1 displays typical TEM images of the surfactant-stabilized NaBH₄ nanostructures obtained via solvent evaporation. Relatively small NaBH₄ particles (≈10–50 nm) were observed in the presence of TAB as compared to the cubes (≈800 nm) and bars (≈1.5 μm) imaged in the presence of the ODA and TDA surfactants, respectively (Figure 1b–d). This is due to the stronger interaction of the ammonium head group (R₄N⁺) of TAB with NaBH₄ as compared to the amine (–NH₂) of ODA and/or carboxylic (–COOH) of TDA, and the greater steric hindrance of the tetrabutyl chains in TAB resulting in the formation of smaller micelles and accordingly small NaBH₄ nanoparticles.[11b,21] However, as shown in Scheme 1b and Figure S1, Supporting Information, the size of the NaBH₄ nanoparticles was also found to depend upon the evaporation rate, and thus the rate of nucleation and growth. This can be understood as fast evaporation of IPA leads to smaller particles due to minimized Ostwald ripening and low surface tension.[22]

It is thus apparent that the type of surfactants, their interactions with the growing seeds of NaBH₄, and the evaporation rate are equally important in controlling the size and shape of NaBH₄ nanostructures. The formation of the distinctive nanostructures of NaBH₄ is possibly due to the different functional groups of the surfactants R₄N⁺ (for TAB), –NH₂ (for ODA), and –COOH (for TDA), which can selectively coordinate with the surface planes of the growing seeds[11b,c] and modify the surface energy and define the final structures of NaBH₄. Further analysis by XRD revealed that all the materials crystallized in the common α-NaBH₄ cubic phase (Figure 2a and Figure S2, Supporting Information). For NaBH₄-TBAB-10 and NaBH₄-ODA-10, additional diffraction peaks (below 24°) related to their respective surfactants were observed (Figure S3, Supporting Information). The emergence of diffraction peaks related to the surfactants could be due to layer-by-layer adsorption onto the NaBH₄ surface as
surfactant packing as multilayers would exhibit some crystalline domains.\cite{23} Notably, the surfactant-modified NaBH₄ nanostructures showed reduction in the crystallite sizes compared to the bulk NaBH₄ (Table S1, Supporting Information, and Figure 1).

As expected,\cite{24} the surfactant concentration was also found to control the nucleation and growth process of the NaBH₄ particles. Therefore, when the concentration of TBAB was varied, the initial particle size ≈50 nm for NaBH₄-TBAB-2.5 reduced to ≈5 nm for NaBH₄-TBAB-20 (Figure 2b and Figure S4, Supporting Information). In contrast, an increase in ODA concentration was found to increase the size of the NaBH₄ cubes (from 300 to 950 nm), and loss of the cubic morphology was observed at higher ODA concentration (Figure 2c and Figure S5, Supporting Information). This could be due to the formation of excessive borohydride–amine complexes upon the reaction of $\text{─NH}_2$ with BH₄⁻ at a higher concentration of amine.\cite{25}

For the TDA-stabilized NaBH₄, the undefined morphologies of NaBH₄-TDA-2.5 evolved into bar-like morphologies of increasing length for TDA concentration above 5 mM (Figure 2d and Figure S6, Supporting Information). Only spherical NaBH₄ nanoparticles were previously observed at a TDA concentration as low as 100 μM,\cite{11b,15} and this indicates that TDA has two critical micelle concentrations (CMCs), which direct the growth of NaBH₄ into the sphere and/or bar-like nanostructures.\cite{11b,26}

Considering this, we propose that the formation of bar-like nanostructures is a result of a side-to-side attachment of the NaBH₄ nuclei.\cite{27} Notably, in this case, the growth mode of the NaBH₄ bars may occur along the [100] direction as previously observed in the case of cubic NaCl crystals elongated as needles.\cite{28}

The crystal structure of NaBH₄ is isomorphous to NaCl; therefore, the nucleation and growth of NaBH₄ can also be explained based on the studies on NaCl crystals.\cite{28,29a} Wang et al.\cite{29d} argued that the formation of cubic morphology of NaCl is due to the fast diffusivity of Na⁺ and Cl⁻ ions and a nondirectional growth in aqueous solutions. In the presence of glycerol, a medium of higher viscosity than water, the crystal growth conditions can be changed where Na/Cl diffusion is slower and NaCl can nucleate along rhombic decahedron, octahedron, and submicron-cubic structures.\cite{29a} The fact that we have observed cubic morphologies of NaBH₄ in IPA and with ODA (both with $\text{─NH}$ functionalities) could be due to the fast ionic diffusivity of Na⁺/BH₄⁻ ions at the IPA/ODA interface and this may lead to the thermodynamically favorable growth of cubes enclosed by [100] facets. The deviation from the cubic morphology of NaBH₄ could be due to the limited diffusivity of Na⁺/BH₄⁻ and/or incomplete/restricted growth of NaBH₄ in the presence of TBAB and/or TDA.

### 3.2. Interactions between NaBH₄ and the Surfactants

The interaction between the surfactants and the NaBH₄ nanostructures was investigated by FTIR (Figure 3) and NMR (Figure 4) in solid state. The FTIR spectra of NaBH₄-IPA
displayed the typical $\text{B}─\text{H}$ stretching and bending peaks between 2400 and 2220 cm$^{-1}$ and at 1120 cm$^{-1}$, respectively. All the surfactant-stabilized nanomaterials show similar vibrations in addition to the peaks between 3000 and 2840 cm$^{-1}$ corresponding to the $\text{C}─\text{H}$ stretching modes of the surfactants (Figure 3 and Figure S7, Supporting Information). For $\text{NaBH}_4$-TBAB, an additional peak at 2129 cm$^{-1}$ was observed due to the interaction of the $\text{BH}_4^-$ anions with the $\text{R}_4\text{N}^+$ cations.$^{[30]}$ For $\text{NaBH}_4$-ODA-10, the sharp stretching vibrations between 3360 and 3200 cm$^{-1}$ and the bending at 1590 cm$^{-1}$ are from the $\text{─NH}_2$ groups of the ODA surfactant. For $\text{NaBH}_4$-TDA-10, a new peak at 1557 cm$^{-1}$ attributed to $\text{C}─\text{O}$ vibration was observed due to the interaction of $\text{NaBH}_4$ with $\text{─COOH}$ in TDA (Figure 3).

The wavenumber of the $\text{─CH}_2$ asymmetric and symmetric peaks can also be used to assess the level of the order of the surfactants at the surface of the $\text{NaBH}_4$ nanoparticles.$^{[31]}$ As compared with the FTIR of the pure surfactants (Figure S7, Supporting Information), all the $\text{─CH}_2$ stretching vibrations slightly shifted to higher wavenumbers for $\text{NaBH}_4$-TBAB-10 (from 2872 and 2957 to 2875 and 2960 cm$^{-1}$), $\text{NaBH}_4$-ODA-10 (from 2847 and 2914 to 2849 and 2916 cm$^{-1}$), and $\text{NaBH}_4$-TDA-10 (from 2847 and 2911 to 2849 and 2925 cm$^{-1}$). This shift to higher wavenumbers indicates the formation of a disordered layer of surfactants at the surface of the $\text{NaBH}_4$ nanoparticles due to enhanced Gauche defects of the surfactants’ carbon chain.$^{[11b,32]}$

To further probe the interaction of surfactants with $\text{NaBH}_4$ at the molecular level, 2D $^{11}\text{H}─^{13}\text{B}$ HETCOR analyses by solid-state NMR were performed (Figure 4). For all the materials, the primary $^{13}\text{B}$ signal is of the $\text{NaBH}_4$ site at $-40.8$ ppm, showing a correlation to the $\text{BH}_4^-$ protons at $-1$ ppm. In addition, multiple correlation peaks of the borohydride $^{13}\text{B}$ species with the surfactant protons were observed (Figure 4b–d). In the case of $\text{NaBH}_4$-TBAB-10 (Figure 4b), strong correlation signals were observed between the $\text{CH}_2/\text{CH}_3$ protons of the TBAB and the $^{13}\text{B}$ borohydride species in the $\text{NaBH}_4$, whereas two secondary $^{13}\text{B}$ borohydride signals centered at $-36$ and $-37$ ppm show strong correlations to the $\text{CH}_2/\text{CH}_3$ as well as the $\text{NCH}_2$ protons.

This indicates that these secondary sites are likely molecular $\text{BH}_4^-$ species embedded within the surfactant layer, rather than a distinct borohydride phase. In the case of $\text{NaBH}_4$-ODA-10 and $\text{NaBH}_4$-TDA-10, correlation signals between the $\text{NaBH}_4$ and the surfactant $\text{CH}_2$ protons were also observed, but these are relatively weak compared to the observation made in $\text{NaBH}_4$-TBAB-10 (Figure 4d). The stronger interaction observed for the TBAB surfactant as compared to ODA or TDA can also be evidenced from the $^{13}\text{B}$ linewidth (Figure 4d). Thus, although the overall presence of correlation peaks indicates that in all cases the surface of the $\text{NaBH}_4$ core is occupied by the surfactant molecules, this interaction varies in strength. The line broadening

---

Figure 2. a) XRD patterns of $\text{NaBH}_4$-IPA, $\text{NaBH}_4$-TBAB-10, $\text{NaBH}_4$-ODA-10, and $\text{NaBH}_4$-TDA-10. “Ref. PDF” denotes the XRD pattern of $\text{NaBH}_4$ from the reference powder diffraction file. The change in the particle sizes of b) $\text{NaBH}_4$-TBAB (c) $\text{NaBH}_4$-ODA, and (d) $\text{NaBH}_4$-TDA with an increase in the concentration of TBAB, ODA, and TDA from 2.5 to 20 mM.
in the case of NaBH₄-TBAB-10 shows that NaBH₄ was effectively encapsulated within TBAB as compared to NaBH₄-ODA-10 and NaBH₄-TDA-10. The TBAB system is intrinsically charged, and therefore the resulting ionic interaction with the NaBH₄ species could result in a suppression of the crystal growth along specific planes in favor of a “spherical” stabilization of the NaBH₄ nanoparticles.

3.3. The Interplay of Surfactants in Directing Shape Tunable NaBH₄ Nanostructures

Although using a single surfactant is sufficient to control the size and shape of the NaBH₄ nanostructures to some extent, we found that an additional level of control and tunability in morphology was possible by cosurfactant addition. For example,
starting with NaBH₄-TDA-20, when TBAB was added as a cosurfactant during the solvent evaporation, the original bar-like assembly gradually transformed into smaller bars with an ≈75% and ≈58% reduction in length (l) and width (d), respectively, as the concentration of TBAB was increased from 5 to 20 mM (Figure 5b–e). At a higher concentration of TBAB (Figure 5d,e), spherical particles of size ≈25 nm were also observed and this suggests a stronger interaction of TBAB/NaBH₄ compared to TDA/NaBH₄ as confirmed by NMR, and thus a progressive displacement of TDA at the NaBH₄ surface in favor of TBAB.

In contrast, cubes in the case of NaBH₄-ODA-2.5 (Figure 5f) were transformed into spherical (Figure 5g–j) and bar-like nanostructures (Figure 5k–n) by varying the concentration of TBAB and TDA cosurfactants at (g,k) 2.5 mM, (h,l) 5 mM, (i,m) 10 mM, and (j, n) 20 mM, respectively. All the scale bars are 500 nm except in (i) and (j), which are 100 nm. The letters “l” and “d” denote length and width.

**Figure 5.** Morphological evolution of surfactant-directed formation of NaBH₄ nanostructures of controlled morphologies. The TDA-directed NaBH₄ bars in the case of a) NaBH₄-TDA-20 are transformed into smaller bars and a mixture of bar and spheres with an increase in the concentration of TBAB as a cosurfactant b) 2.5 mM, c) 5 mM, d) 10 MM, and e) 20 mM. In contrast, the NaBH₄ cubes in the case of f) NaBH₄-ODA-2.5 are transformed into g–j) spherical nanoparticles and k–n) bars upon increasing the concentration of TBAB and TDA cosurfactants at (g,k) 2.5 mM, (h,l) 5 mM, (i,m) 10 mM, and (j, n) 20 mM, respectively. All the scale bars are 500 nm except in (i) and (j), which are 100 nm. The letters “l” and “d” denote length and width.
and TDA surfactants, respectively. As the concentration of TBAB as a cosurfactant increased from 5 to 20 mM (Figure 5g–j), an ≈74% reduction on both sides of the cubes was observed for NaBH₄-ODA/TBAB-1/8, ultimately leading to spherical particles of size ≈60 nm (Figure 5j). Interestingly, the initial cubic morphology can still be observed during the whole process of transformation, highlighting the combined action of the surfactants on the growth of NaBH₄ particles. This again suggests a progressive displacement of ODA by TBAB, which enables a stronger stabilization of NaBH₄ surface planes as compared to ODA. Similarly, when TDA was added to NaBH₄-ODA-2.5 as a cosurfactant, the initial cube-like structure progressively evolved into a bar-like nanostructure (Figure 5k). In this case of shape evolution, an increase in the aspect ratio was observed (Figure 5k–n). This indicates that at a high concentration (20 mM) of TDA the diffusion of the Na⁺/BH₄⁻ ions in IPA may be greatly restricted and the initially grown cubes (with 2.5 mM ODA) elongated in the direction of [100] as bars.

Upon XRD analysis, however, no discernible changes in the position of the diffracting planes were observed with or without cosurfactants (Figure S8–S10, Supporting Information), although notable changes in the intensity of the high-surface-energy crystal planes of NaBH₄ were visible. This could be due to the structural changes induced by surfactants. For example, for NaBH₄-TDA/TBAB, it is apparent that the intensity of the (311), (331), and/or (111) crystal planes of TBAB-stabilized NaBH₄ gradually decreased with the increasing TBAB concentration (Figure S8, Supporting Information). Similar trends were observed when TBAB was used as a cosurfactant in the case of NaBH₄-ODA/TBAB (Figure S9, Supporting Information). In contrast, slight changes in the peak intensities of (111) and (331) planes were noted in the case of NaBH₄-ODA/TDA (Figure S10, Supporting Information). Also, all the NaBH₄ nanostructures showed reduction in the crystallite sizes with the increase in surfactant concentration compared to the bulk NaBH₄ (Table S1, Supporting Information). For instance, the crystallite size ≈32 nm was reduced to ≈18 nm for NaBH₄-ODA-2.5 and NaBH₄-ODA/TBAB-1/8, respectively. Similarly, the crystallite size ≈30 nm was reduced to ≈21 nm for NaBH₄-TDA-20 and NaBH₄-TBAB/TDA-1, respectively. Once again, the cosurfactant provides an additional barrier to the growth of particles and therefore restricts the size in the nanoregime. These calculations are also aligned with the particle sizes determined by TEM (Figure 5).

The changes in the intensity of crystalline planes (Figure S8–S10, Supporting Information) with increasing concentration of all the cosurfactants indicate changes in particle shape and corroborate well with the TEM results (Figure 5). Our observations are also consistent with the reports on the shape control of other nanomaterials such as gold,[31] where significant changes in the crystallographic planes and overall morphology of the gold nanoparticles were observed with an increase in the concentration of CTAB. It can thus be concluded from our results that the surfactants preferentially interact with the facets of NaBH₄ and this ultimately results in tunable morphologies. However, attempts to determine specific surface plane/surfactant interaction by high-resolution TEM and selected area electron diffraction (SAED) were difficult due to the sensitive nature of NaBH₄ under the electron beam even at cryogenic temperatures.[34]

A proposed mechanism based on the microscopic observations for the shape transformation is summarized in Scheme 2. For cube-to-sphere shape evolution, it is possible that TBAB displaces the ODA molecules and preferentially adsorbs at the sides of the cube (Scheme 2a). A gradual increase in the TBAB concentration could then displace ODA and trigger a surface reconstruction toward spherical morphologies. For cube-to-bar shape evolution, the adsorption of TDA could occur on the side of the cube and in a similar manner induce the growth of NaBH₄ particles along [100], and this would favor the crystallization of NaBH₄ along thinner and longer bars (Scheme 2b). Such an elongated growth along the [100] direction in contrast to the enclosed [100] facets for cubes was previously observed in the case of NaCl nanoneedles.[28]

For the bar-to-sphere shape evolution, the TBAB molecules may adsorb on the end of the bars and suppress their elongated growth toward shorter lengths and width, and ultimately these would evolve into a sphere-like morphology (Scheme 2c). Our proposed mechanism on the shape transformation is consistent with previous studies,[15] but herein it is observed for the first time with a common material NaBH₄ for hydrogen storage and thus provides new avenues to potentially modify the hydrogen storage properties of materials by simply tuning their morphology.

3.4. Hydrogen Desorption Properties

The selected NaBH₄ nanostructures were further investigated using DSC and MS to evaluate their thermal behavior and in particular the temperature at which they start to release hydrogen (Figure 6). All the NaBH₄ nanostructures showed notable shifts in their melting points (Tᵥm) and hydrogen release temperature compared to the unmodified NaBH₄ (Figure 6 and Figure S11 and S12, Supporting Information). The Tᵥm for NaBH₄-TBAB-20, NaBH₄-ODA-2.5, and NaBH₄-TDA-20 appeared at ≈200, 455, and 405 °C, which is 300, 40, and 100 °C lower than the unmodified NaBH₄, respectively (Figure 6). Similar trends were observed in the case of the mixed surfactant (Figure S13, Supporting Information). For all the NaBH₄ nanomaterials, the shift in Tᵥm toward lower temperatures can be due to the reduction in particle size and/or increase in specific surface areas consistent with the studies on the size-dependent shifts for the nanoparticles.[36] Notably, the lowest Tᵥm in the case of NaBH₄-TBAB-20 could be due to the NaBH₄ nanoparticles of size less than 50 nm (Figure 5). The shifts in Tᵥm can also be due to the different coordination strengths between the surfactants and NaBH₄, which may destabilize NaBH₄ and alter its melting and/or decomposition.

Furthermore, the hydrogen release profile of these NaBH₄ nanostructures as determined by MS revealed that hydrogen was the sole gaseous product from the NaBH₄ nanostructures (Figure 6 and Figure S14, Supporting Information). All the nanostructures showed improved hydrogen release compared to the unmodified NaBH₄. For instance, NaBH₄-TBAB-20, NaBH₄-ODA-2.5, and NaBH₄-TDA-20 started to release hydrogen at a temperature as low as ≈50 °C, respectively. In comparison, unmodified NaBH₄ does not show any hydrogen release before 500 °C (Figure S14, Supporting Information). The materials
NaBH₄-TBAB-20, NaBH₄-ODA-2.5, and NaBH₄-TDA-20 also released a significant amount of hydrogen at ≈200, 400, and 100 °C, respectively. Overall, the hydrogen release profiles of the NaBH₄ nanostructures suggest a combined effect of unique morphologies and/or nanosizing as these trends on the hydrogen release from the NaBH₄ nanostructures corroborate well with their corresponding Tₘ (Figure 6 and Figure S11, Supporting Information). Nonetheless, the synthesized nanostructures still require a temperature ≥400 °C for major hydrogen release. This could be due to severe and inevitable agglomeration of the nanostructures upon thermal decomposition of the surfactants at elevated temperatures.

To confirm whether the differences in hydrogen release were due to the varied morphologies of NaBH₄ or a premature decomposition of the surfactant leading to a loss in morphology, we further examined the NaBH₄ nanostructures after heat treatment at 250 °C, that is, near the decomposition temperature of the surfactants (Figures S13, Supporting Information). All the selected NaBH₄ nanostructures either stabilized with a surfactant or surfactant mixture exhibited good thermal stability without a significant loss in their morphologies except for NaBH₄-TDA-20 (Figure S16, Supporting Information). In this case, the loss in morphology may be due to the relatively weaker interaction of TDA with NaBH₄ as compared to TBAB or ODA evidenced by NMR (Figure 4). Overall, the preservation of the NaBH₄ nanostructures near the decomposition temperature of the surfactants indicates that the melting and/or decomposition of these organic entities (Figure S15, Supporting Information) does not significantly compromise the structural stability of the NaBH₄ nanostructures. Therefore, these results strongly suggest the
existence of shape-dependent hydrogen release properties. From these observations, it is also apparent that with further improvements to effectively stabilize NaBH₄ nanostructures, e.g., with a more stable coating, low hydrogen release temperatures should be achievable.

To further verify if the hydrogen release was dependent on the particle size, we selected NaBH₄-ODA/TBAB-1/2, NaBH₄-ODA/TBAB-1/4, and NaBH₄-ODA/TBAB-1/8 with particle sizes ≈ 250, 90, and 70 nm (Figure 5 and 7). The desorption profiles of these materials indicated that hydrogen was released in multiple steps. All the nanomaterials started to release a significant amount of hydrogen at ≈ 150 °C (Figure S17, Supporting Information). Notably, the initial hydrogen release at 200 °C shifted to ≈ 180 °C upon increasing the ODA/TBAB ratio from 1/2 to 1/8, as a mean to decrease the average particle size from 250 to 70 nm (Figure 7 and 5h–i). In this process, it is noteworthy that the peak at ≈ 215 °C remains unaltered upon particle size reduction (Figure 7). The hydrogen peak at 215 °C is believed to be due to the \( \text{H}^+ / \text{H}^0 \) interaction between the surfactant (ODA) and the surface of NaBH₄, and subsequent destabilization as previously reported. Accordingly, such interaction would be insensitive to any morphological changes.

The decrease in the initial hydrogen release temperature observed was thus corroborated with the reduction in the particle sizes. A similar trend was also observed at higher temperatures (≥ 300 °C). For example, the peak at ≈ 445 °C corresponding to the full decomposition of the borohydride shifted to ≈ 438 °C upon reducing the particle size of NaBH₄ from ≈ 250 to ≈ 70 nm (Figure 7). Collectively, this corresponds to a temperature difference of ≈ 70 °C from ≈ 505 °C. Therefore, it is apparent that concomitant effects of particle morphology and size can lead to the improved hydrogen release properties for NaBH₄. Notably, our observations demonstrate that “simple” control of NaBH₄ morphology and particle size is comparable and, in some cases, better than current state-of-the-art approaches reported for improving the hydrogen release properties of NaBH₄ through catalyst doping, destabilization with reactive hydrides, and confinement in porous inorganic and/or carbon hosts (Table S2, Supporting Information). Given the simplicity of our approach, we believe that it finally provides grounds for designing intricate hydride nanostructures with hydrogen that can be fully tuned and further improved by modifying the synthetic parameters and replacing the surfactant with a stable metallic shell allowing for full reversible hydrogen uptake and release. For this, further investigations are underway.

4. Conclusion

In summary, we have demonstrated a facile solution–based synthesis for the growth of NaBH₄ into deliberately controlled shapes. Increasing the evaporation rate induced the formation of smaller sized particles. The as-synthesized NaBH₄ nanostructures exhibited distinctive nanostructures induced by the surfactants. Moreover, for the first time, the nanostructures of NaBH₄ were transformed into the desired assemblies either as spheres, cubes, or bars using an appropriate cosurfactant. By tuning the size and/or shapes of NaBH₄ using the surfactants, the melting points were shifted, and hydrogen started to release at a lower temperature than the bulk NaBH₄. The \( T_m \) for the NaBH₄ spheres, cubes, and bars appeared at ≈ 200, 455, and 405 °C, which are ≈ 300, 40, and 100 °C lower than for the unmodified NaBH₄, respectively. Remarkably, all the nanostructures started to release hydrogen at a temperature as low as 50 °C. Our approach is expected to provide guidelines to tune the structures and further explore the structure–property relations in the complex hydride materials on the nanoscale for hydrogen storage and generation applications.

5. Experimental Section

Materials: All the experiments were performed under an inert atmosphere in an argon-filled LC-Technology glove box (\( \text{O}_2 \) and \( \text{H}_2 \text{O} < 1 \text{ppm} \)). NaBH₄ (99.99%), IPA (≥ 99.5%), 1-ODA (≥ 95%), tetra-n-butylammonium bromide (≥ 98%, TBAB) dried at 100 °C for 6 h, and TDA (≥ 98%) were purchased from Sigma-Aldrich.

Synthesis of Surfactant-Modified NaBH₄ Nanostructures: To a solution of NaBH₄ (100 mM in IPA), a set concentration (2.5–20 mM, final) from a TBAB, ODA, and TDA surfactant stock solution (200 mM in IPA) was
added while stirring the mixture at 500 rpm and room temperature. After stirring for 1 h, the homogenized mixture was dried under vacuum at 2, 50, 100, 250, and/or 500 mbar, 30 °C. For comparison, a control sample without any surfactant was also prepared. The NaBH₄ materials prepared were denoted as NaBH₄-X-N (where X = TBA, ODA, or TDA, N = 2.5, 5, 10, or 20 is the concentration in mM).

**Synthesis of Cosurfactant-Modified and Shape-Transformed NaBH₄ Nanostructures:** For the shape-transformed NaBH₄ nanostructures, stock solutions of the selected cosurfactants were prepared beforehand and appropriate concentrations were mixed with the solutions containing NaBH₄. Briefly, for transforming NaBH₄ cubes to bar-like morphologies, the concentrations of ODA and NaBH₄ were 2.5 and 100 mM, respectively, and the concentration of the TDA cosurfactant was varied from 2.5 to 20 mM. For bar to sphere shape, the concentrations of ODA and NaBH₄ were 20 and 100 mM respectively, and the concentration of the cosurfactant TBA was varied from 2.5 to 20 mM. Similarly, for cube to sphere, the concentrations of ODA and NaBH₄ were 5 and 200 mM respectively, and the concentration of the cosurfactant was changed from 2.5 to 20 mM. The solutions were mixed and stirred for 1 h at room temperature and dried at 2 mbar, 30 °C. All other the synthetic parameters remained unaltered. The NaBH₄ materials prepared with cosurfactants are denoted as NaBH₄-X/Y-N (where X and Y denote TBA, ODA, TDA surfactants and N is the molar ratio of X and Y).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

The authors gratefully acknowledge financial support by the UNSW Internal Research Grant program. The authors appreciate the use of instruments in the Mark Wainwright Analytical Centre at UNSW as well as equipment funded by the Australian Research Council (ARC)–Linkage Infrastructure, Equipment and Facilities (LIEF). M.S.S. also acknowledges the financial support from the Australian Government.

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

hydrogen storage, nanosize, size effects, sodium borohydride

![Image](https://www.advancedsciencenews.com/)

[1] a) Q. Lai, M. Paskevicius, D. A. Sheppard, C. E. Buckley, A. W. Thornton, M. R. Hill, Q. Gu, J. Mao, Z. Huang, H. K. Liu, Z. Guo, A. Banerjee, S. Chakraborty, R. Ahuja, K.-F. Aguey-Zinsou, ChemSusChem **2015**, 8, 2789; b) Q. Lai, Y. Sun, T. Wang, P. Modi, C. Cazorla, U. B. Demirci, J. R. Ares Fernandez, F. Leardini, K.-F. Aguey-Zinsou, Adv. Sustainable Syst. **2019**, 3, 1900043.

[2] a) Q. Yao, Z.-H. Lu, R. Zhang, S. Zhang, X. Chen, H.-L. Jiang, J. Mater. Chem. A **2018**, 6, 4386; b) Q. Yao, K. Yang, W. Nie, Y. Li, Z.-H. Lu, Renewable Energy **2020**, 147, 2024.

[3] a) S. Thangviriya, R. Utke, Int. J. Hydrogen Energy **2015**, 40, 4167; b) S. S. Muir, X. Yao, Int. J. Hydrogen Energy **2011**, 36, 5983.

[4] U. B. Demirci, O. Akdim, P. Miele, Int. J. Hydrogen Energy **2009**, 34, 2638.

[5] P. Martelli, R. Caputo, A. Remhof, M. Mauron, A. Borgschulte, A. Züttel, J. Phys. Chem. C **2010**, 114, 7173.

[6] I. Llamas-Jansa, N. Alivouane, S. Deletada, J. E. Fonnløp, C. Frommen, T. Humphries, K. Lieutenant, S. Sartori, M. H. Sorby, B. C. Hauback, J. Alloys Compd. **2012**, 530, 186.

[7] a) J. F. Mao, X. B. Yu, Z. P. Guo, H. K. Liu, Z. Wu, J. Ni, J. Alloys Compd. **2009**, 479, 619; b) J. Mao, Z. Guo, X. Yu, H. Liu, J. Phys. Chem. C **2011**, 115, 9283.

[8] T. D. Humphries, G. N. Kalantzopoulos, I. Llamas-Jansa, J. E. Olsen, B. C. Hauback, J. Phys. Chem. C **2013**, 117, 6060.

[9] a) A. Schneemann, J. L. White, S. Kang, S. Jeong, L. F. Wan, E. S. Cho, T. W. Heo, D. Prendergast, J. J. Urban, B. C. Wood, M. D. Allendorf, V. Stavila, Chem. Rev. **2018**, 118, 10775; b) Y. Sun, C. Shen, Q. Lai, W. Liu, D.-W. Wang, K.-F. Aguey-Zinsou, Energy Storage Mater. **2018**, 10, 168; c) Q. Lai, T. Wang, Y. Sun, K.-F. Aguey-Zinsou, Adv. Mater. Technol. **2018**, 3, 1700298; d) P. E. de Jongh, M. Allendorf, J. J. Vajo, C. Zlotek, MRS Bull. **2013**, 38, 488.

[10] a) T. K. Nielsen, F. Besenbacher, T. R. Jensen, Nanoscale **2011**, 3, 2086; b) L. H. Wagner, E. H. Majzoub, M. D. Allendorf, J. C. Grossman, Phys. Chem. Chem. Phys. **2012**, 14, 6611.

[11] a) Y. Pang, Y. Liu, M. Gao, L. Ouyang, J. Liu, H. Wang, M. Zhu, H. Pan, Nat. Commun. **2014**, 5, 3519; b) T. Wang, K.-F. Aguey-Zinsou, Int. J. Hydrogen Energy **2020**, 45, 2054; c) T. Wang, K.-F. Aguey-Zinsou, Energy Technol. **2019**, 7, 1801159.

[12] P. Ngene, R. van den Berg, M. H. W. Verkuijlen, K. P. de Jong, P. E. de Jongh, Energy Environ. Sci. **2011**, 4, 4108.

[13] Q. Lai, M. Christian, K.-F. Aguey-Zinsou, Int. J. Hydrogen Energy **2014**, 39, 9339.

[14] L. Chong, X. Zeng, W. Ding, D.-J. Liu, J. Zou, Adv. Mater. **2015**, 27, 5070.

[15] M. L. Christian, K.-F. Aguey-Zinsou, ACS Nano **2012**, 6, 7739.

[16] Y. Li, Q. Zhang, F. Fang, Y. Song, D. Sun, L. Ouyang, M. Zhu, RSC Adv. **2014**, 4, 983.

[17] a) S.-J. Jeon, G.-R. Yi, S.-M. Yang, Adv. Mater. **2008**, 20, 4103; b) L. Qi, Coord. Chem. Rev. **2010**, 254, 1054; c) S. Bandypadhyay, G. Singh, W. R. Glomm, Mater. Today Chem. **2017**, 3, 1.

[18] a) J. Xiao, L. Qi, Nanoscale **2011**, 3, 1381; b) M. Uota, H. Arakawa, N. Kitamura, T. Yoshimura, J. Tanaka, T. Kijima, Langmuir **2005**, 21, 4724; c) D. Li, W. Zhao, L. Cao, Y. Gao, Y. Liu, W. Wang, T. Qi, ChemSusChem **2019**, 12, 4412; d) B. Sohrabi, H. Gharibi, S. Javadian, M. Hashemianzadeh, J. Phys. Chem. B **2007**, 111, 10069; e) C. M. Payne, D. E. Tsentalovich, D. N. Benoit, L. J. Anderson, W. Guo, V. L. Colvin, M. Pasquali, J. H. Hafner, Chem. Mater. **2014**, 26, 1999.

[19] a) E. A. Crespo, M. Ruda, S. Ramos de Debiaggi, E. M. Bringa, F. U. Braschi, G. Bertolino, Int. J. Hydrogen Energy **2012**, 37, 14831; b) G. Li, H. Kobayashi, S. Dekura, R. Ikeda, Y. Kubota, K. Kato, M. Takata, T. Yamamoto, S. Matsumura, H. Kitagawa, J. Am. Chem. Soc. **2014**, 136, 10222; c) A. Klinkova, P. V. Cherepanov, I. G. Ryabinin, M. Ho, M. Ashokkumar, A. F. Ismyakov, D. V. Andreeva, E. Kurnacheva, Small **2016**, 12, 2450.

[20] a) M. Ozerova, O. V. Komova, S. A. Mukha, V. I. Simagina, G. V. Odegova, S. S. Arzumanov, O. A. Bulavchenko, O. V. Netskina, Int. J. Hydrogen Energy **2020**, 45, 30756.

[21] C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, Chem. Rev. **2005**, 105, 1025.
[22] H.-K. Chan, P. C. L. Kwok, Adv. Drug Delivery Rev. 2011, 63, 406.
[23] a) T. Zhang, C. Xu, J. Puckette, F. D. Blum, J. Phys. Chem. C 2012, 116, 11626; b) H. J. Perera, R. Latifi, F. D. Blum, J. Phys. Chem. C 2019, 123, 19005.
[24] A. P. LaGrow, B. Ingham, M. F. Toney, R. D. Tilley, J. Phys. Chem. C 2013, 117, 16709.
[25] a) J. Mao, Q. Gu, Z. Guo, H. K. Liu, J. Mater. Chem. A 2015, 3, 11269; b) J. Chen, T. He, G. Wu, Z. Xiong, L. Liu, X. Ju, P. Chen, J. Phys. Chem. C 2014, 118, 13451.
[26] A. González-Pérez, L. M. Varela, M. García, J. R. Rodríguez, J. Colloid Interface Sci. 2006, 293, 213.
[27] T. K. Sau, C. J. Murphy, Langmuir 2005, 21, 2923.
[28] E. R. Townsend, W. J. P. van Enckevort, P. Tinnemans, M. A. R. Blijlevens, J. A. M. Meijer, E. Vlieg, Cryst. Growth Des. 2018, 18, 755.
[29] a) Q. Chen, Z. D. Hood, J. Qiu, B. Guan, Y. Xia, ChemNanoMat 2019, 5, 1131; b) E. R. Townsend, W. J. P. van Enckevort, J. A. M. Meijer, E. Vlieg, Cryst. Growth Des. 2015, 15, 5375; c) Y. Qin, D. Yu, J. Zhou, CrystEngComm 2017, 19, 5356; d) B. Wang, P. Jin, Y. Yue, S. Ji, Y. Li, H. Luo, RSC Adv. 2015, 5, 5072.
[30] L. V. Titov, L. A. Gavrilova, E. R. Eremin, S. S. Mishchenchuk, V. Y. Rosolovskii, Bull. Acad. Sci. USSR Div. Chem. Sci. 1971, 20, 1266.
[31] a) Z. Wei, H. Matsui, Nat. Commun. 2014, 5, 3870; b) B. Nikoobakht, M. A. El-Sayed, Langmuir 2001, 17, 6368.
[32] M. J. Hostetler, J. J. Stokes, R. W. Murray, Langmuir 1996, 12, 3604.
[33] S. Y. Moon, T. Kusunose, T. Sekino, Mater. Lett. 2009, 63, 2038.
[34] J. Hadernann, A. Abakumov, S. Van Rompaey, T. Perkisas, Y. Filinchuk, G. Van Tendeloo, Chem. Mater. 2012, 24, 3401.
[35] X. Kou, S. Zhang, Z. Yang, C.-K. Tsung, G. D. Stucky, L. Sun, J. Wang, C. Yan, J. Am. Chem. Soc. 2007, 129, 6402.
[36] a) T. P. Martin, U. Näher, H. Schaber, U. Zimmermann, J. Chem. Phys. 1994, 100, 2322; b) J. Zhang, Q. Fu, Z. Cui, Y. Xue, CrystEngComm 2019, 21, 430; c) R. A. Varin, T. Czujko, Z. Wronski, Nanotechnology 2006, 17, 3856.
[37] L. Lombardo, H. Yang, A. Züttel, Mater. Today Energy 2018, 9, 391.
[38] M. Christian, K.-F. Aguey-Zinsou, Chem. Commun. 2013, 49, 6794.