Enhanced hydrogen storage kinetics and air stability of nanoconfined NaAlH₄ in graphene oxide framework†

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With a growing concern over climate change, hydrogen offers a wide range of opportunities for decarbonization and provides a flexibility in overall energy systems. While hydrogen energy is already plugged into industrial sectors, a physical hydrogen storage system poses a formidable challenge, giving momentum for safe and efficient solid-state hydrogen storage. Accommodating such demands, sodium alanate (NaAlH₄) has been considered one of the candidate materials due to its high storage capacity. However, it requires a high temperature for hydrogen desorption and becomes inactive irreversibly upon air-exposure. To enhance sluggish reaction kinetics and reduce the hydrogen desorption temperature, NaAlH₄ can be confined into a porous nanoscaffold; however, nanoconfined NaAlH₄ with sufficient hydrogen storage performance and competent stability has not been demonstrated so far. In this work, we demonstrate a simultaneously enhanced hydrogen storage performance and air-stability for NaAlH₄ particles confined in a nanoporous graphene oxide framework (GOF). The structure of the GOF was elaborately optimized as a nanoscaffold, and NaAlH₄ was infiltrated into the pores of the GOF via incipient wetness impregnation. As a result of the nanoconfinement, both the onset temperature and activation energy for hydrogen desorption of NaAlH₄ are significantly decreased without transition metal catalysts, while simultaneously achieving the stability under ambient conditions.

Introduction

Hydrogen has emerged as a clean and sustainable energy source capable of fulfilling growing global energy demand and potentially substituting traditional fossil fuels.¹ Metal hydrides are suitable candidates for safe and high-density solid-state hydrogen storage, although several challenges in kinetic and thermodynamic requirements must still be overcome.² Among metal hydrides, sodium alanate (NaAlH₄) has been widely investigated owing to its high hydrogen storage capacity (7.4 wt%) and moderate decomposition temperature (~180 °C).³ However, its slow hydrogen desorption kinetics and limited reversibility must be addressed for practical applications, along with a stability issue under ambient conditions in which NaAlH₄ tends to lose its hydrogen storage capability similar to other metal hydrides. To overcome these issues, a variety of Ti- and Ce-based catalytic additives have been used to improve the hydrogen storage performance of NaAlH₄.⁴⁻⁸ Rapid hydrogen desorption at temperatures below 100 °C and superior cycling properties have been demonstrated using high-performance transition metal–carbon composite catalysts.⁹⁻¹⁰ In addition to such transition metal-based catalysts, nanoconfined metal hydrides into a variety of nanoporous scaffolds has been employed. By effectively confining the metal hydrides inside nanopores of the scaffold, it is possible to achieve nanoparticles with dimensions below 10 nm.¹¹⁻¹² Nanoconfinement shortens the diffusion length of hydrogen atoms while increasing the number of grain boundaries and surface area, thereby improving hydrogen storage performance of metal hydrides. A wide range of host materials for NaAlH₄ have been previously demonstrated, including mesoporous carbon,¹³⁻¹⁵ carbon aerogel,¹⁶ carbon nanofiber,¹⁷⁻¹⁸ carbon nanotube,¹⁹ mesoporous silica,²⁰ metal–organic framework,²¹⁻²² and porous aluminium scaffold.²³ Most of the prior works have focused on enhancing reaction kinetics and reversibility, and to our knowledge there have been no studies on increasing air stability of the nanoconfined NaAlH₄.

Here, we report a nanocomposite of NaAlH₄ confined into graphene oxide framework (NaAlH₄@GOF) via incipient wetness impregnation, and discuss its enhanced hydrogen desorption kinetics as well as air stability compared to those of bulk NaAlH₄. A GOF is an expansion of GO layers by pillar molecules, and it has been shown as a promising material for gas storage,²⁴ nanofiltration membrane,²⁵ and ion-selective

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protective layer for redox-flow batteries because of a high surface area and adjustable interlayer spacing, simultaneously taking advantage of robustness and chemical versatility of GO. By virtue of such characteristics, GOF with a three-dimensional framework structure is an ideal host material for complex metal hydrides. Also, a gas-selective property of GO layers is expected to function as a protective layer for the confined metal hydrides.

Experimental
Synthesis of graphene oxide framework (GOF)
To synthesize GOF, 200 mg of graphene oxide powder (GrapheneAll Co., Ltd) was first dispersed in 20 mL of methanol via sonication at room temperature for 1 h. The dispersion was then transferred into a Teflon-lined autoclave, and 400 mg of benzene-1,4-diboronic acid (B14DBA, Alfa Aesar, 96% purity) was added to the dispersion. The solvothermal reaction was performed at 100 °C for 48 h in an autoclave reactor. After cooling down to room temperature, the mixture was centrifuged at 10 000 rpm for 20 min and washed with methanol three times to remove the unreacted excess B14DBA linker molecules. The resulting GOF was dried under vacuum at 120 °C for 24 h and stored inside an Ar-filled glovebox for the subsequent NaAlH4 infiltration process.

Synthesis of NaAlH4 impregnated GOF (NaAlH4@GOF)
The infiltration of NaAlH4 into the GOF was performed under an Ar atmosphere. NaAlH4 was purified by dissolving the as-purchased NaAlH4 (Sigma-Aldrich, 93% purity, hydrogen storage grade) in anhydrous tetrahydrofuran (THF) and removing metallic impurities using a PTFE syringe filter (CHMLAB Group) with a pore size of 0.2 μm. The 1 M solution of NaAlH4 in THF was prepared using the purified NaAlH4. The 50–100 mg of GOF was added to 10 mL of the NaAlH4 solution, and the mixture was magnetically stirred at room temperature for 15 h. To collect NaAlH4 impregnated GOF composite, the mixture was centrifuged at 10 000 rpm for 20 min and washed with THF three times to remove bulk NaAlH4 that may have been recrystallized on the surface of the GOF. The resulting NaAlH4@GOF composite was vacuum-dried at room temperature overnight and stored in an Ar-filled glovebox until further analysis.

Material characterization
X-ray diffraction patterns for measuring interlayer spacing were acquired with a Rigaku SmartLab. N2 adsorption–desorption isotherms for specific surface area and pore size distribution were obtained with a Micromeritics 3Flex. Fourier-transform infrared spectroscopy (Bruker, Alpha), thermogravimetric analysis (Netzsch, TG 209 F1 Libra), and X-ray photoelectron spectroscopy (Thermo Scientific, K-Alpha) measurements were also performed to verify successful synthesis and characterize properties of the synthesized products. The NaAlH4 mass loading inside NaAlH4@GOF composite was measured via inductively coupled plasma-optical emission spectroscopy (Agilent, 720 ICP-OES).

Measurement of hydrogen desorption performance
The hydrogen desorption performance of bulk NaAlH4 and NaAlH4@GOF was measured by temperature programmed desorption mass spectrometry (TPD-MS) using a MicrotracBEL BELCAT II catalyst analyser and BELMass quadrupole mass spectrometer. Calibration was performed prior to the measurements using a mixture gas of H2 and Ar with a known H2 concentration. The 50–100 mg of NaAlH4@GOF composite was loaded into a quartz sample holder and purged with Ar for 30 min. The sample was ramped from room temperature to 500 °C with a heating rate of 2.5–20.0 °C min⁻¹ under a constant flow (30 mL min⁻¹) of Ar carrier gas, and the final temperature was held at 500 °C for 30 min to ensure a complete desorption.

Results and discussion
Synthesis and optimization of GOF
GOF was synthesized via solvothermal reaction of graphene oxide (GO) with benzene-1,4-diboronic acid (B14DBA) in methanol, as shown in Fig. 1a. B14DBA was chosen as the linker material based on good reactivity of boronic acids with hydroxyl functional groups of GO and relatively short length of the B14DBA molecule which is composed of a single phenyl ring unit connected to the boronic acids. Alternative choice of linkers may be considered to readily modify a physical property of the resulting GOF as necessary. For example, d-spacing of the GOF can be slightly increased by using a linker with a longer length (e.g. 4,4'-biphenyldiboronic acid). To optimize physical properties of the framework before NaAlH4 infiltration, we synthesized a series of GOFs by varying the ratio of GO and B14DBA – referred as GOF (1 : x) where x is the ratio of B14DBA relative to GO. Changes in d-spacing and Brunauer–Emmett–Teller (BET) specific surface area were measured via X-ray diffraction (XRD) and N2 adsorption–desorption isotherm experiments, respectively, to confirm successful synthesis of a three-dimensional nanoporous framework structure. Fig. 1b and S1† show a monotonic increase in the d-spacing of GOF with increasing linker concentration. As more linker molecules are intercalated into the GO structures, the overall alignment angle between the linker and GO moves closer to being perpendicular and the diffraction peak shifts to a lower angle. The corresponding interlayer distance between the GO sheets is expanded from 0.86 nm to 1.06 nm, reaching a maximum value beyond GO to B14DBA ratio of 1 : 2. Furthermore, the XRD patterns with a single diffraction peak indicate a well-defined layer structure for the GOF as well as full removal of unreac-

†tected linkers. Fig. 1c and S1b† show type I (microporous) isotherms with a maximum BET specific surface area of 200.5 m² g⁻¹ for GO to B14DBA ratio of 1 : 2, comparable to previously reported values and much higher than 4.6 m² g⁻¹ for as-received GO. Average pore diameter is calculated to be around 2 nm (Fig. S2†), confirming a nanoporous structure. Once the maximum BET specific surface area is reached for GOF (1 : 2),...
an additional increase in the linker concentration leads to a decrease in the BET specific surface area with negligible increase in the d-spacing. Based on these results, we chose GOF (1:2) as the optimal scaffold for NaAlH₄ impregnation.

To further verify the formation of chemical bonding between GO and B14DBA, Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA) were performed. The FT-IR spectra (Fig. 1d) of GOF (1:1), GOF (1:2), and GOF (1:4) exhibit characteristic B–O deformation at \( \tilde{v} \approx 680 \) cm\(^{-1}\), B–C vibration at \( \tilde{v} \approx 1080 \) cm\(^{-1}\), B–O stretch at \( \tilde{v} \approx 1340 \) cm\(^{-1}\), and C=C stretch at \( \tilde{v} \approx 1520 \) cm\(^{-1}\), which are clearly observed in B14DBA but not in GO. A broad O–H stretch around 3200 cm\(^{-1}\) is also observed, indicating that some functional groups of GO remain in GOF after the solvothermal process. Moreover, the TGA curves (Fig. 1e) of GOF show a rapid mass loss around 220 °C due to decomposition of oxygen-containing functional groups,\(^{29}\) compared to a lower decomposition temperature around 150 °C for both GO and B14DBA. Combined with the increased d-spacing, enhanced BET specific surface area, and FT-IR measurements, this improved thermal stability suggests that B14DBA forms new chemical bonds with GO to evolve into a nanoporous framework, rather than simply being intercalated between the GO sheets.

**Preparation of NaAlH₄@GOF nanocomposites**

NaAlH₄ was infiltrated into the nanoporous GOF via incipient wetness impregnation using solutions of purified NaAlH₄ in tetrahydrofuran (THF), as illustrated in Fig. 2a. Wetness impregnation was chosen over melt infiltration as the method for preparing NaAlH₄@GOF based on the thermal stability of GOF as well as the simplicity and low cost of the solution-based synthesis process. We used three different NaAlH₄ concentrations (0.25 M, 1 M, and 3 M) for the impregnation process to determine the optimal process condition. The resulting NaAlH₄...
infiltrated GOFs were referred to as NaAlH4@GOF (x M) where x is the concentration of NaAlH4 in THF.

As shown in the XRD patterns of bulk NaAlH4 and NaAlH4@GOFs (Fig. 2b), the sharp diffraction peaks from crystalline NaAlH4 are not observed for NaAlH4@GOFs. This implies a successful confinement of NaAlH4 inside the nanoporous scaffold resulting in nanocrystalline NaAlH4 and causing severe peak broadening, since amorphous NaAlH4 bulk phase has never been observed in NaAlH4 infiltrated nanoporous composites.25 Furthermore, a complete removal of recrystallized NaAlH4 that may have formed on the surface of the GOF is also verified from the XRD results. When a solution with a higher NaAlH4 concentration was used for wetness impregnation, the diffraction peak of NaAlH4@GOF is broadened and the d-spacing increases from 1.10 nm (0.25 M) and 1.17 nm (1 M) to 1.28 nm (3 M), suggesting that an extreme NaAlH4 loading may have a detrimental effect on the structural integrity of the framework (Fig. S3†). The surface morphology of GOF and NaAlH4@GOF from transmission electron microscopy (TEM) images do not show any significant differences upon NaAlH4 infiltration (Fig. S4†). In bright field scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy (BF-STEM-EDS) measurements, the images of NaAlH4@GOF indicate the coexistence of GOF and confined NaAlH4; Na and Al mapping originated from NaAlH4 coincide with carbon and oxygen from GOF, which presents a successful confinement of NaAlH4 into GOF (Fig. S5†).

We additionally confirmed a successful infiltration of NaAlH4 inside the GOF through N2 adsorption–desorption isotherm and FT-IR measurements. Subsequent to the impregnation process, BET specific surface area of NaAlH4@GOF (1 M) is reduced to 6.6 m² g⁻¹, compared to 200.5 m² g⁻¹.
for as-synthesized GOF (Fig. 2c). The FT-IR spectra of NaAlH₄@GOF (1 M) shown in Fig. 2d clearly display Al–H bending modes at ~670 cm⁻¹ and 890 cm⁻¹, and Al–H stretching modes at ~1650 cm⁻¹,⁷⁸ which are not observed in GOF. A FT-IR spectrum of GOF treated with THF for 15 h without NaAlH₄ was also measured as a control, which shows no change compared to before the THF treatment. Finally, NaAlH₄ mass loading inside the NaAlH₄@GOF composite was calculated for each NaAlH₄ solution concentration (Fig. 2e) using Al content determined from inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements. The resulting NaAlH₄ loadings were 6.7 wt% for NaAlH₄@GOF (0.25 M), 20.0 wt% for NaAlH₄@GOF (1 M), and 27.6 wt% for NaAlH₄@GOF (3 M), demonstrating a comparable or higher mass loading of active materials relative to other existing porous scaffolds.¹²

Hydrogen desorption performance and air-stability of NaAlH₄@GOF

The hydrogen desorption reaction of NaAlH₄ consists of three steps, as shown in Fig. 3a. Hydrogen desorption properties of NaAlH₄@GOF (1 M) were measured using temperature programmed desorption mass spectrometry (TPD-MS) and compared with those of bulk NaAlH₄. The TPD-MS profiles at different heating rates and the corresponding Kissinger plots for bulk NaAlH₄ and NaAlH₄@GOF (1 M) are shown in Fig. 3b–e. The TPD-MS curves of bulk NaAlH₄ (Fig. 3b) present an onset desorption temperature at 180 °C, close to the melting point of NaAlH₄. However, NaAlH₄@GOF (1 M) starts to release hydrogen at room temperature, in agreement with the previous reports that hydrogen desorption starts at ambient temperature for nanoconfined NaAlH₄ with particle size below 10 nm.¹⁸,¹⁹,³¹
The three desorption peaks for bulk NaAlH₄, which correspond to the desorption reaction of NaAlH₄, Na₃AlH₆, and NaH, were 282 °C, 311 °C, and 401 °C, respectively, measured at a heating rate of 10.0 °C min⁻¹. Above 400 °C, the dehydrogenation of NaAlH₄@GOF occurs at a higher temperature than bulk NaAlH₄. The redox reaction between oxygen in the remained THF and NaAlH₄ – which likely make AlₓOᵧ nanoclusters – also releases hydrogen, and this is revealed as dehydrogenation at a higher temperature and higher activation energy of dehydrogenation in step 3 [Fig. 3a]. We focused our investigation on the first two reaction steps, which are of interest for practical applications as these desorption reactions proceed at relatively lower temperatures and are known to be reversible. In the TPD-MS profile of NaAlH₄@GOF (1 M) [Fig. 3d], the desorption temperatures for the first and second reaction step measured at a heating rate of 10.0 °C min⁻¹ are significantly reduced to 108 °C and 231 °C, respectively. As some amount of confined NaAlH₄ directly reacts with oxygen elements from GOF and THF, leading to the early decomposition of NaAlH₄, it diminishes the hydrogen capacity in the first step compared to bulk NaAlH₄.¹¹

We calculated the activation energy for the hydrogen desorption of both bulk and nanoconfined NaAlH₄ using the Kissinger equation,¹³ and the results from each step are presented in Fig. 3a. The Kissinger plots corresponding to bulk NaAlH₄ and NaAlH₄@GOF (1 M) are shown in Fig. 3c and e, respectively. The activation energy of the hydrogen desorption process can be determined according to the following equation:

Fig. 4 Hydrogen desorption performance of bulk NaAlH₄ and NaAlH₄@GOF (1 M) upon air exposure, and XPS spectra of GOF and NaAlH₄@GOF (1 M). (a) Normalized hydrogen capacity of bulk NaAlH₄ and NaAlH₄@GOF exposed to air for 0 h, 3 h, 1 d, 3 d, and 7 d. (b) TPD-MS profiles of air-exposed bulk NaAlH₄ at a heating rate of 10.0 °C min⁻¹. (c) TPD-MS profiles of air-exposed NaAlH₄@GOF (1 M) at a heating rate of 10.0 °C min⁻¹. (d) C 1s XPS spectra of as-synthesized GOF. (e) C 1s XPS spectra of as-synthesized NaAlH₄@GOF (1 M).
where $\beta$ is the heating rate, $T_p$ is the peak temperature obtained from the TPD-MS profile, $E_a$ is the activation energy, $R$ is the universal gas constant, and $A$ is a pre-exponential factor. Therefore, activation energy can be estimated from the slope in the Kissingler plot of $\ln \left( \frac{\beta}{T_p^2} \right)$ versus $\frac{1}{T_p}$. The activation energy for the first and second desorption reaction is 124.30 kJ mol$^{-1}$ and 148.76 kJ mol$^{-1}$ for bulk NaAlH$_4$, agreeing with the prior reports (Table S1†). Upon the confinement inside the nanoporous GOF, the activation energy decreases to 47.13 kJ mol$^{-1}$ for the first reaction and 108.45 kJ mol$^{-1}$ for the second reaction, demonstrating a remarkable improvement in the hydrogen desorption performance. The activation energy values for NaAlH$_4$@GOF are comparable to or even smaller than the relative peak area for NaAlH$_4$@GOF are comparable to or even smaller than the

Conclusions

In summary, this work demonstrates the viability of utilizing GOF as a nanoscaffold for confining hydrogen storage material for the first time. The framework structure with an optimized d-spacing results in a noticeable nanoconfinement effect for NaAlH$_4$ in which both the onset hydrogen desorption temperature and the activation energy for the first two reversible hydrogen desorption reactions of NaAlH$_4$ are significantly reduced without transition metal catalysts.

However, hydrogen capacity loss is observed in the nanocomposite, possibly caused by the detrimental reaction between NaAlH$_4$ and oxygen functional groups in the GOF. At the same time, the air stability of the confined NaAlH$_4$ is dramatically improved as a result of the formation of surface-reduced GOF during NaAlH$_4$ infiltration acting as a barrier layer. Although we focused our study on NaAlH$_4$, the beneficial effect of GO as a nanoporous host for confinement may be extended to other metal hydrides. Future work will involve optimizing the synthesis process to increase active NaAlH$_4$ content, and studying the possible catalytic effect of boron atoms inside the GOF on the hydrogen storage behaviour of the GOF-based nanocomposites.

Conflicts of interest

There are no conflicts to declare.

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References

1 A. Sartbaeva, V. L. Kuznetsov, S. A. Wells and P. P. Edwards, *Energy Environ. Sci.*, 2008, 1, 79–85.
2 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 and V. Stavila, *Chem. Rev.*, 2018, 118, 10775–10839.
3 I. P. Jain, P. Jain and A. Jain, J. Alloys Compd., 2010, 503, 303–339.
4 B. Bogdanović and M. Schwickardi, J. Alloys Compd., 1997, 253–254, 1–9.
5 C. P. Balde, H. A. Stil, A. M. J. van der Eerden, K. P. de Jong and J. H. Bitter, J. Phys. Chem. C, 2007, 111, 2797–2802.
6 B. Bogdanović, M. Felderhoff, A. Pommerin, F. Schüth and N. Spielkamp, Adv. Mater., 2006, 18, 1198–1201.
7 Q. Gao, G. Xia and X. Yu, Nanoscale, 2017, 9, 14612–14619.
8 Z. Yuan, Y. Fan, Y. Chen, X. Liu, B. Liu and S. Han, Int. J. Hydrogen Energy, 2020, 45, 21666–21675.
9 X. Zhang, Y. Liu, K. Wang, Y. Li, M. Gao and H. Pan, ChemSusChem, 2015, 8, 4180–4188.
10 Y. Liu, X. Zhang, K. Wang, Y. Yang, M. Gao and H. Pan, J. Mater. Chem. A, 2016, 4, 1087–1095.
11 P. E. de Jongh and P. Adelhelm, ChemSusChem, 2010, 3, 1332–1348.
12 T. K. Nielsen, F. Besenbacher and T. R. Jensen, Nanoscale, 2011, 3, 2086–2098.
13 Y. Li, G. Zhou, F. Fang, X. Yu, Q. Zhang, L. Ouyang, M. Zhu and D. Sun, Acta Mater., 2011, 59, 1829–1838.
14 C. L. Carr, W. Jayawardana, H. Zou, J. L. White, F. El Gabaly, M. S. Conradi, V. Stavila, M. D. Allendorf and E. H. Majzoub, Chem. Mater., 2018, 30, 2930–2938.
15 U. Jeong, H. Kim, S. Ramesh, N. A. Dogan, S. Wongwilawan, S. Kang, J. Park, E. S. Cho and C. T. Yavuz, Angew. Chem., Int. Ed., 2021, 60, 22478–22486.
16 T. K. Nielsen, M. Polanski, D. Zasada, P. Javadian, F. Besenbacher, J. Bystrzycki, J. Skibsted and T. R. Jensen, ACS Nano, 2011, 5, 4056–4064.
17 C. P. Balde, B. P. C. Hereijgers, J. H. Bitter and K. P. de Jong, J. Am. Chem. Soc., 2006, 45, 3501–3503.
18 C. P. Balde, B. P. C. Hereijgers, J. H. Bitter and K. P. de Jong, J. Am. Chem. Soc., 2008, 130, 6761–6765.
19 M. Christian and K.-F. Aguey-Zinsou, Nanoscale, 2010, 2, 2587–2590.
20 S. Zheng, F. Fang, G. Zhou, G. Chen, L. Ouyang, M. Zhu and D. Sun, Chem. Mater., 2008, 20, 3954–3958.
21 R. K. Bhakta, J. L. Herberg, B. Jacobs, A. Highley, R. Behrens Jr, N. W. Ockwig, J. A. Greathouse and M. D. Allendorf, J. Am. Chem. Soc., 2009, 131, 13198–13199.
22 V. Stavila, R. K. Bhakta, T. M. Alam, E. H. Majzoub and M. D. Allendorf, ACS Nano, 2012, 6, 9807–9817.
23 E. Ianni, M. V. Sofianos, M. R. Rowses, D. A. Sheppard, T. D. Humphries and C. E. Buckley, Int. J. Hydrogen Energy, 2018, 43, 17309–17317.
24 J. W. Burress, S. Gadjnelli, J. Ford, J. M. Simmons, W. Zhou and T. Yildirim, Angew. Chem., Int. Ed., 2010, 49, 8902–8904.
25 Y. Zhang, S. Zhang and T.-S. Chung, Environ. Sci. Technol., 2015, 49, 10235–10242.
26 S. Kim, J. Choi, C. Choi, J. Heo, D. W. Kim, J. Y. Lee, Y. T. Hong, H.-T. Jung and H.-T. Kim, Nano Lett., 2018, 18, 3962–3968.
27 E. S. Cho, A. M. Ruminski, S. Aloni, Y.-S. Liu, J. Guo and J. J. Judge, Nat. Commun., 2016, 7, 1804.
28 K. Severin, Dalton Trans., 2009, 27, 5254–5264.
29 G. Srinivas, J. W. Burress, J. Ford and T. Yildirim, J. Mater. Chem., 2011, 21, 11323–11329.
30 S. Gomes, G. Renaudin, H. Hagemann, K. Yvon, M. P. Sulic and C. M. Jensen, J. Alloys Compd., 2005, 390, 305–313.
31 S. Chumphongphan, U. Filso, M. Paskevicius, D. A. Sheppard, T. R. Jensen and C. E. Buckley, Int. J. Hydrogen Energy, 2014, 39, 11103–11109.
32 E. H. Majzoub, J. L. Herberg, R. Stumpf, S. Spangler and R. S. Maxwell, J. Alloys Compd., 2005, 394, 265–270.
33 H. E. Kissinger, Anal. Chem., 1957, 29, 1702–1706.
34 S. Pei and H.-M. Cheng, Carbon, 2012, 50, 3210–3228.
35 M. H. W. Verkuijlen, R. de Gelder, P. J. M. van Bentum and A. P. M. Kentgens, J. Phys. Chem. C, 2011, 115, 7002–7011.
36 D. E. Dedrick, R. Behrens and R. J. S. N. L. Bradshaw, Sandia Report, 2007, 4960, pp. 1–57.
37 E. S. Cho, A. M. Ruminski, Y.-S. Liu, P. T. Shea, S. Kang, E. W. Zaia, J. Y. Park, Y.-D. Chuang, J. M. Yuk, X. Zhou, T. W. Heo, J. Guo, B. C. Wood and J. J. Urban, Adv. Funct. Mater., 2017, 27, 1704316.
38 D. J. Han, S. Kim and E. S. Cho, J. Mater. Chem. A, 2021, 9, 9875–9881.