ORIGINAL PAPER

Formation of Crystalline Sodium Hydride Nanoparticles Encapsulated Within an Amorphous Framework

**A. Sartbaeva · S. A. Wells · M. Sommariva ·
M. J. T. Lodge · M. O. Jones · A. J. Ramirez-Cuesta ·
G. Li · P. P. Edwards**

Abstract A major research theme to emerge in the science and technology of materials is the incorporation of nanostructure into the functionality of properties. Such nanostructured materials can offer distinct advantages over bulk materials, partly because the physical properties of the material itself can vary in a tunable, size-dependent fashion. Of course, in addition, nanoparticles offer a greatly increased surface area for chemical reaction. Typical methods for nanoparticle synthesis include: reaction in the liquid phase using the sol–gel approach and mechanical ball-milling of the bulk material; both of these approaches are somewhat problematic for the preparation of reactive nanostructured materials which are sensitive to air and/or moisture. We report here the formation of crystalline nanoparticles of sodium hydride encapsulated in a host amorphous silica gel matrix. These nanoparticles are formed by in situ hydrogenation of a precursor material— Na loaded silica gel—under mild conditions. The resulting material is considerably less pyrophoric and less air-sensitive than the bulk hydride. We anticipate that this

A. Sartbaeva · M. J. T. Lodge · M. O. Jones · P. P. Edwards (✉)
Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK
e-mail: peter.edwards@chem.ox.ac.uk

S. A. Wells
Department of Physics and Centre for Scientific Computing, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, UK

M. Sommariva · M. O. Jones · A. J. Ramirez-Cuesta
ISIS Facility, CCLRC Rutherford Appleton Laboratory, Chilton OX11 0QX, UK

G. Li
Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK

formation method of in situ modification of reactive precursor material may have wide applications.

Keywords Sodium hydride nanoparticles · Encapsulated · Silica gel framework · In situ hydrogenation

Introduction

Metal hydrides continue to attract interest as hydrogen storage materials [1, 2] and as reagents in organic synthesis [3–6]. Sodium hydride, in particular, is a powerful reducing agent used extensively as a reagent in organic chemistry [7–11]. Bulk sodium hydride is usually formed by the reaction of the liquid metal with hydrogen gas at temperatures above 200 °C, forming solid NaH: $2Na + H_2 = 2NaH$. This material is pyrophoric, and highly air- and moisture-sensitive. It is therefore generally stored and distributed as a suspension in mineral oil, which must be carefully removed with volatile solvents, such as pentane. This makes the use of sodium hydride inconvenient and environmentally unfriendly. An alternative, more stable and more easily handled formulation of sodium hydride would be of great practical use.

The crystal structure of NaH can be viewed as a cubic Na structure with the addition of interstitial hydride ions to give a rock salt structure. Notably, NaH has a smaller lattice parameter than the parent Na metal; importantly its formation involves a volume contraction rather than a volume expansion. The degree of volume contraction is considerable—approximately 10% (in fcc NaH $a = 4.89$ Å, while in bcc Na $a = 4.29$ Å). This suggested to us that NaH could be formed by direct treatment of sodium loaded into a porous host, e.g. silica gel with hydrogen, forming NaH in situ. Since the reaction proceeds with a volume contraction rather than volume expansion it bodes well that the reaction should not disrupt the silica matrix, and that the large pores within silica gel might allow for the growth of crystalline NaH nanoparticles. In addition, this might provide a route by which the continuous porosity of the host would be advantageous. Our starting material is silica gel loaded with sodium metal (32 wt%) provided by SiGNa Chem (this material is hereafter called Na-SG). The material is a coarse black powder and particulate sodium metal is dispersed in the nanoscale pores of the silica gel [12, 13]. SiGNa Chem produce Na-SG materials with various wt% of Na, 32 wt% being the highest currently available.

Results and Discussion

We have carried out both in situ hydrogenation and deuteration of Na-SG. The resulting material was characterised using Inelastic Neutron Spectroscopy (INS) [14] and neutron diffraction on TOSCA and GEM instruments at ISIS (Chilton, UK), Rietveld analysis, High-Resolution Transmission Electron Microscopy (HRTEM) and Electron Paramagnetic Resonance spectroscopy (EPR).

On exposure to H_2 gas the material reacts under mild conditions (we have explored conditions of 1 to 3 bars of hydrogen pressure and temperatures of 100 to 300 °C), visibly changing colour from black to brown. We attribute this change in colour to the conversion of metallic Na to ionic NaH dispersed in the silica matrix. Interestingly, the texture of the material did not significantly change, remaining a coarse powder, indicating that the silica gel matrix is not significantly disrupted by the reaction of the dispersed sodium metal with hydrogen/deuterium. The material reacts vigorously with water, evolving hydrogen gas, and less vigorously with acetone. When this brown powder is exposed to air its colour slowly fades over several hours until the surface of the grains becomes almost white; it is not pyrophoric. We attribute this change in colour to the formation of NaOH, by a slow reaction with atmospheric moisture.

In Fig. 1 we show inelastic neutron spectroscopy data for the starting material, for the hydrogenated material and for bulk sodium hydride as a reference [15]. Our data were collected on the TOSCA instrument at ISIS (see "Method" section). The bare sample (Na-SG) was measured and later hydrogenated in situ at 473 K under 2 bars of hydrogen for 6 h. The raw INS spectra of bulk NaH exhibit a series of strong features (in the 50–125 meV range) related to the optical part of the phonon density of states (DoS), and mainly due to the H^- and Na^+ anti-phase motion in the lattice unit cell. The first overtones of optical bands are also clearly visible in the recorded spectra at about twice the energy transfer intervals, that is between 125 and 200 meV. The same features are clearly visible in our data for the hydrogenated material, which matches the spectrum of bulk NaH almost exactly. This confirms
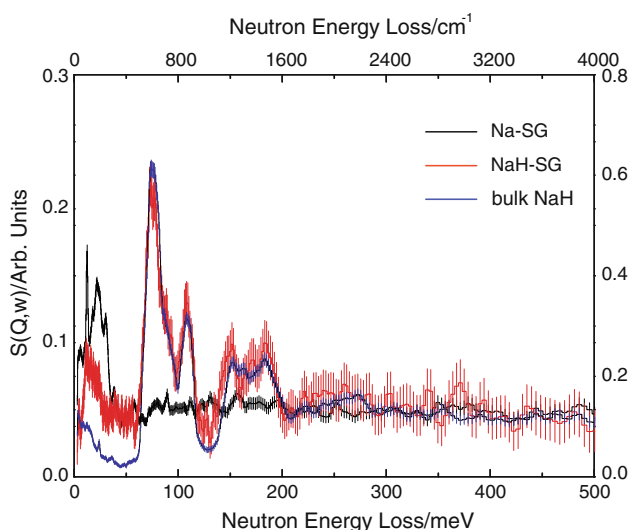

Fig. 1 Inelastic neutron spectroscopy data on sodium SG (*black*), hydrogenated NaH-SG (*red*) and bulk sodium hydride (*blue*, scaled to match the maximum height of the *red curve*). The scale on the *left* corresponds to Na-SG data (*black*), the scale on the *right* corresponds to NaH-SG and bulk NaH (*red and blue*). The features around 100 meV are the optical modes, the ratio 2:1 due to LO-TO splitting, their presence indicates the existence of NaH crystallites that are least larger than 15 nm [15]

that we have formed NaH and we will call the hydrogenated material NaH-SG from now on. Since the observed scattering is dominated by hydrogen, the scattering spectrum of the nanoparticulate NaH in SG is similar to bulk NaH. We calculated the degree of conversion of Na to NaH by integrating the area under the INS spectrum in the range 0–500 meV, obtaining a result of at least 54% conversion of the available Na to NaH, dispersed within the amorphous silica host.

We carried out EPR (Electron Paramagnetic Resonance) spectroscopy on silica gel (Davisil-646, Aldrich), the starting Na-SG material and a sample of NaH-SG material hydrogenated at 473 K under 2 bars of hydrogen pressure for 24 h; these data are shown on Fig. 2. The silica gel spectrum (black line) shows only a negligible background signal. In contrast, the Na-SG material (red line) shows a strong asymmetric resonance signal, typical of conduction electrons [16, 17]. After the reaction with hydrogen the NaH-SG material (blue line) shows a signal of greatly decreased intensity, consistent with the conversion of almost all the dispersed sodium metal to a diamagnetic hydride. We attribute the remaining weak signal to a small concentration of "dangling bond" states in the SiO_2 matrix, analogous to recent results on zeolite frameworks [18].

To study the crystal structure of the resulting material, we performed neutron diffraction on the starting Na-SG and on a deuterated sample (NaD-SG). Importantly, the Na-SG material did not display any sharp diffraction peaks, consistent with the findings of Shatnawi et al. [13] (see Supplementary Materials), which emphasises the intrinsic amorphous nature of the host silica gel. Data for NaD-SG are shown in Fig. 3. The material now clearly displays sharp diffraction peaks. We carried out Rietveld refinement using phases of NaD, NaOD, Na_2O, Si, SiO_2 and Na_2SiO_3. The diffraction data were well fitted only to NaD (98%) with no other significant crystalline phases present. Fitting to peak profile widths [19] indicated a typical nanoparticle size of 44 nm. This is consistent with the formation of nanoparticles of crystalline NaD from the reaction of D_2 gas with the amorphous dispersion of sodium initially present in the Na-SG material.
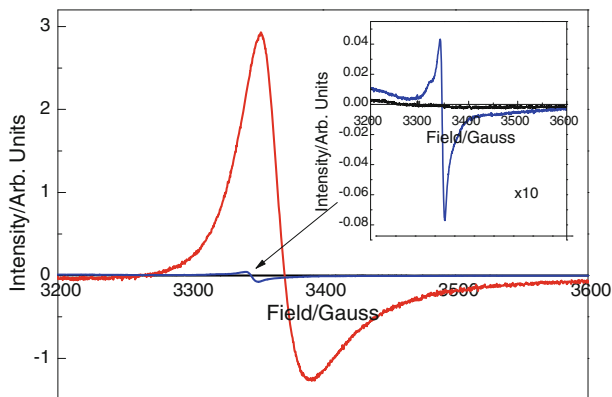

Fig. 2 Electron paramagnetic resonance spectra of silica gel Davisil (*black*), Na-SG (showing the presence of particulate sodium) (*red*) and NaH-SG (*blue*), showing conversion from metallic sodium and a very small concentration of dangling bonds
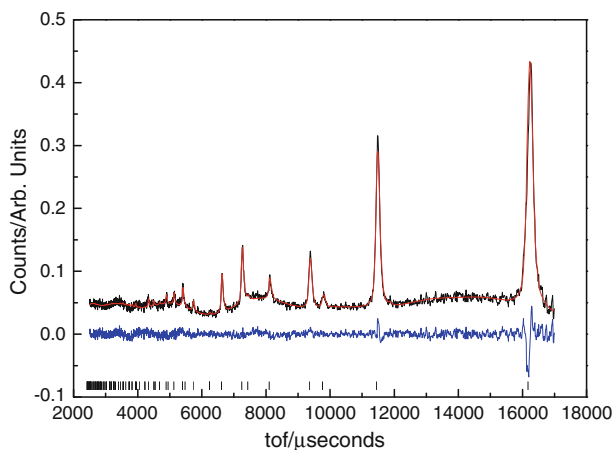
Fig. 3 Diffraction data on deuterated sodium SG material, showing bank 5 from GEM instrument at ISIS. *Black*—data points, *red*—fit, *blue*—difference between the data and the fit. *Black tick marks* indicate the positions of peaks for NaH phase

Fig. 4 High resolution transmission electron microscopy image of NaH-SG sample showing three distinguishable NaH nanoparticles (on the *left*) of approximately 50 nm in size. EDX was performed to confirm presence of Na
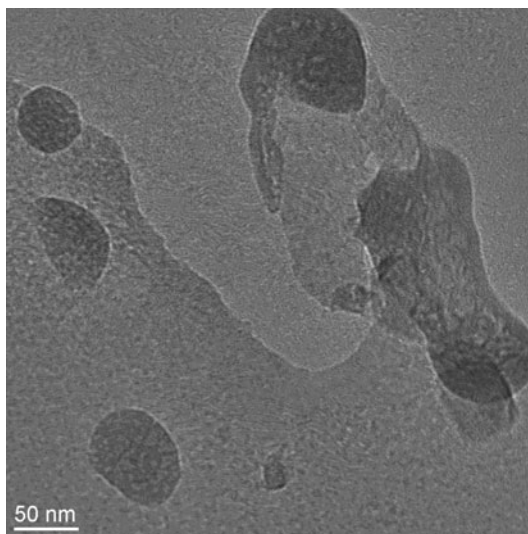
To examine the details of the nanoparticle morphology we used HRTEM (High-Resolution Transmission Electron Microscopy) in Department of Materials at Oxford University. Energy dispersive X-ray analyses (EDX) were performed in the TEM to confirm the presence of Na in the nanoparticles. In the Na-SG precursor material, we could detect the presence of Na dispersed in the framework by EDX, but we did not observe identifiable nanoparticles, consistent with our neutron diffraction data and with the findings of Shatnawi et al. In the NaH-SG, by contrast, we could observe (Fig. 4) distinct, isolated nanoparticles typically of a size between 20 and 50 nm, consistent with our findings from neutron diffraction.

Methods

INS

INS spectra were measured using the crystal-analyser inverse-geometry time of flight (ToF) spectrometer, TOSCA at ISIS pulsed spallation neutron source. Na-SG sample was placed in a stainless steel can. We first collected a background spectrum at temperature below 20 K. In situ hydrogenation was performed under following conditions—473 K and 1 bar of hydrogen for 6 h. The resulting spectrum was collected over the range of 0–500 meV (0–4,000 cm^{-1}) at temperature below 20 K again and compared to bulk NaH.

EPR

The data were collected on a Bruker EMX spectrometer (University of Oxford, Inorganic Chemistry Laboratory) using a continuous wave (CW) in the X-Band at a frequency of 9.418 GHz. Samples were loaded into quartz ESR tubes (3 mm) under inert atmosphere.

HRTEM

The data were collected at University of Oxford, Department of Materials. Samples of Na-SG and NaH-SG were dispersed in cyclohexane using an ultrasound bath to form a suspension and deposited on a standard 200 mesh TEM Cu grid covered with a thin holey amorphous carbon film. Images of the materials were obtained in a JEOL 3000F field emission gun TEM operating at 300 kV and equipped with a Gatan slow scan 1k × 1k pixel CCD camera.

Concluding Remarks

We find that a new phase of NaH, in the form of distinct crystalline NaH nanoparticles, can be readily formed within an amorphous silica gel matrix by in situ transformation of nanodisperse Na in the silica framework, by treatment with hydrogen gas under mild conditions. The formation of the nanoparticles appears to occur without significant disruption of the host silica gel matrix, so that nanoparticles remain encapsulated within the silica gel. The nanoparticles react slowly when exposed to ambient air and retain their reactivity to water and acetone. We anticipate that our new approach of in situ transformation of a precursor material may have wide applicability to produce other reactive nanoparticles stabilized within a silica framework.

References

1. W. Grochala and P. P. Edwards (2004). *Chem. Rev.* **104**, (3), 1283–1315.
2. A. Zuttel (2004). *Naturwissenschaften* **91**, (4), 157–172.
3. W. M. Mueller, J. P. Blackledge, and G. G. Libowitz *Metal Hydrides* (Academic Press, New York, 1968).
4. B. Schmidt and M. Pohler (2003). *Org. Biomol. Chem.* **1**, (14), 2512–2517.
5. Y. H. Fan, et al. (2006). *J. Nanopart. Res.* **8**, (6), 935–942.
6. Z. Wang, W. Zhou, and G. Lin (1985). *Tetrahedron Lett.* **26**, (50), 6221–6224.
7. L. Paquette (ed.) *Encyclopedia of Reagents for Organic Synthesis* (Wiley, New York, 2004).
8. P. Caubere (1983). *Angew. Chem. Int. Ed. Engl.* **22**, (8), 599–613.
9. M. A. Hayward and M. J. Rosseinsky (2003). *Solid State Sci.* **5**, (6), 839–850.
10. P. A. A. Klusener, et al. (1986). *Angew. Chem. Int. Ed. Engl.* **25**, (5), 465–466.
11. R. Pi, et al. (1987). *J. Org. Chem.* **52**, (19), 4299–4303.
12. J. L. Dye, et al. (2005). *J. Am. Chem. Soc.* **127**, (26), 9338–9339.
13. M. Shatnawi, et al. (2007). *J. Am. Chem. Soc.* **129**, (5), 1386–1392.
14. P. C. H. Mitchell, et al., *in* J. L. Finney and D. L. Worcester (eds.), *Vibrational Spectroscopy with Neutrons with Applications in Chemistry, Biology, Materials Science and Catalysis*. Series on neutron techniques and applications (World Scientific, Singapore, 2005), p. 642.
15. G. Auffermann, et al. (2004). *J. Phys. Condens. Matter* **16**, (32), 5731–5743.
16. J. A. Weil, J. R. Bolton, and J. E. Wertz *Electron Paramagnetic Resonance: Elementary Theory, Practical Applications* (Wiley, New York, 1994).
17. R. N. Edmonds, et al. (1984). *J. Phys. Chem.* **88**, (17), 3764–3771.
18. L. Li, et al. (2009). *Angew. Chem. Int. Ed.* **48**, (36), 6678–6682.
19. H. M. Rietveld (1969). *J. Appl. Crystallogr.* **2**, 65–71.