

Silica Nanosprings – A Novel Nanostructured Material for Hydrogen Storage

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ABSTRACT

Hydrogen storage for transportation remains a major challenge because of the stringent requirements. Current approaches are still far short of achieving published goals, in particular in being able to operate at acceptable and viable temperatures. Physisorption, or non-dissociative approaches, where the hydrogen is stored on a solid substrate have largely focused on carbon-based materials and more recently metal oxide frameworks. However, both approaches suffer from significant drawbacks because of the low adsorption temperatures and the high pressures required. Silica nanosprings are a novel form of nanostructured glass that have the ability to store and release molecular hydrogen at room temperature. Our results using X-ray photoelectron spectroscopy suggest that multilayer adsorption of hydrogen on the nanospring surface may be possible, which is unique to this system - certainly, it does not occur with adsorption on carbon nanotubes.

Keywords: hydrogen storage, nanomaterials, nanosprings, glass, silica.

1 INTRODUCTION

Storage of hydrogen is required for stationary applications, such as residential heating and air conditioning and neighborhood electrical generation. It is critical for on-board automotive applications. The hydrogen storage systems for stationary applications can occupy a large area, employ multi-step charge/recharge cycles that operate at high pressures and temperatures, and compensate for slow kinetics by high capacity. On the other hand, the hydrogen storage systems required for transportation must operate with minimum weight and volume, supply enough hydrogen for a reasonable driving range, charge and recharge near room temperature, and provide hydrogen at a rate fast enough for fuel cell locomotion of cars, trucks and buses. A light-duty fuel cell vehicle must carry approximately 5-13 kg of hydrogen (depending on the size and type of vehicle) to allow a driving range of more than 300 miles [1]. For on-board hydrogen storage, vehicles need compact (high volumetric capacity), safe and

affordable (~\$4/kWh) containment. The material should be able to attain maximum storage capacity in the least amount of time (typically within 2-3 minutes) and at moderate temperatures.

Hydrogen has a very small specific volume as a gas. Hence, it requires pressurized tanks, liquefaction, or some kind of physical or chemical bonding for solid-state storage. Compressed hydrogen is a potential hazard because it is highly flammable. Liquid hydrogen is a commercial product and is used as a rocket fuel with oxygen. Cryogenic liquid hydrogen (cooled to -253°C) is stored in insulated cylinders at ambient pressure. Storing hydrogen in liquid form however, has two major disadvantages:

- 30% energy loss due to refrigeration
- 1% boil-off rate

Because of the energy losses in liquefaction of hydrogen and the hazard potential of compressed hydrogen, it is desirable to store hydrogen in the solid state.

Although, various solid-state storage materials have been identified, none has been developed so far that can fulfill all the criteria for on-board automotive applications. Based on the nature of absorption of hydrogen in the host material, solid-state hydrogen storage materials can be divided into two categories:

- Atomic hydrogen storage materials or dissociative materials that store hydrogen mainly by dissociation of hydrogen molecules and atomic absorption, i.e., chemisorption
- Molecular hydrogen storage materials or non-dissociative materials that store hydrogen primarily by physisorption

The storage properties of some solid-state hydrogen storage materials and their nanoscale modifications are briefly discussed below.

Metal organic frameworks (MOFs) are networks of transition metal atoms bridged by organic ligands that have been proposed as structured nanoporous materials for hydrogen storage [e.g., 2]. MOFs provide systems with large overall pore volumes and surface areas, adjustable pore sizes, and tunable framework-adsorbate interaction by ligand functionalization and metal choice. The most striking feature of MOFs is the total accessible bulk volume. Hydrogen can be inserted and then removed reversibly without any change in the storage medium,

unlike chemical bonding of hydrogen in metal hydrides. Of all available porous materials, MOFs show the highest surface area and therefore highest gravimetric uptake. However, the heat of adsorption of hydrogen on current MOFs is still quite low, typically 4-10 kJ/mol, which makes adsorption of any significant amount of hydrogen possible only at low temperatures (< 100 K).

The temperature dependence of hydrogen adsorption is a major consideration for storage applications. The adsorption capacity decreases rapidly with increase in temperature and is barely detectable above 193 K. Also, it is not clear from the results available to date that increasing the pressure will be sufficient to increase the adsorption capacity at ambient temperatures to a similar level as that achieved at 77 K.

Nanostructured carbon materials such as carbon nanofibers (CNFs) or graphite nanofibers (GNFs) [e.g., 3], carbon nanotubes (multi wall, MWNT and single wall, SWNT) [e.g., 4], and carbon nanoscrolls (CNS) [e.g., 5] exhibit novel properties and have been the subject of various investigations for hydrogen storage. Carbon materials adsorb hydrogen non-dissociatively on the surface and hydrogen storage capacity is proportional to their specific surface area and the volume of micropores. The linear dependence of the storage capacity on specific surface area of carbon materials is independent of the nanostructure [6]. In 2000, Pinkerton *et al.* from General Motors [7] measured hydrogen absorption in K- and Li-doped graphite, and Li doped MWNT. The maximum hydrogen uptake of 1.3 wt % was observed in K-doped graphite. The other materials did not show any significant hydrogen uptake. Moreover, weight gain was also observed in an argon atmosphere containing no hydrogen and most of the weight gain observed in thermogravimetric analysis was due to moisture. Hence, they concluded that these materials are not capable of storing hydrogen in any “technologically useful form”.

Nanostructured oxide ceramics may represent an alternative to MOFs and carbon-based nanomaterials. Theoretical studies have indicated that certain ceramics, in particular oxide glasses, exhibit suitable surface properties for H₂ storage [8]. In this paper, we show that a novel nanostructured form of glass, silica nanosprings, represents a viable approach for hydrogen storage.

2 EXPERIMENTAL

Silica nanosprings were synthesized in a standard tubular furnace that is operated at temperatures as low as 325°C (more typically in the temperature range 350-1000°C) and atmospheric pressure [9]. The nanosprings grow via the vapor liquid solid (VLS) mechanism, which is facilitated by the presence of the nanoparticle catalysts [10]. The nanosprings can be grown on a variety of substrates, including polymers such as polyimide. The only requirement is that the substrate can withstand the process temperature. In this present study, the nanosprings were

grown on single-crystal Si substrates. A cross section view of an as-grown silica nanospring mat is shown in Fig. 1.

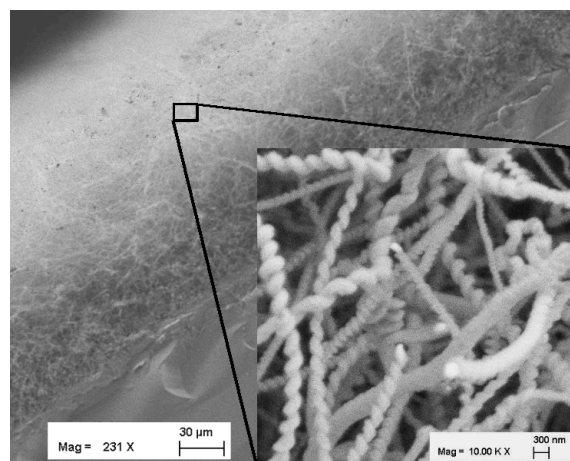


Figure 1: Secondary electron image of a silica nanospring mat.

X-ray photoelectron spectroscopy (XPS) was performed in conjunction with H₂ adsorption in order to determine whether H₂ adsorbs dissociatively, or molecularly, and if so, is the process one of chemisorption or physisorption. Since hydrogen cannot be measured directly with XPS, the chemical shifts of the Si 2p and O 1s core levels of the SiO₂ can be used to characterize the H₂ adsorption mechanism. The XPS data were acquired in a vacuum chamber, with a base pressure of 5×10^{-10} torr, using the Mg K α emission line (1253 eV) and a hemispherical energy analyzer with a resolution of 0.025eV. An electron flood gun was used to eliminate sample charging during XPS acquisition. Sample could be heated or cooled *in situ* and the temperature was determined using a thermocouple in direct contact with the sample. Ultra high purity H₂ (99.9999%) was leaked into the vacuum chamber at a pressure of 1×10^{-8} torr, where the exposure is given in units of Langmuirs (1L= 10^{-6} torr-s). A series of H₂ adsorption studies were carried out at room temperature and at liquid N₂ (LN₂) temperature (77 K). At each temperature XPS spectra were acquired after each exposure to H₂. Adsorption sequences for the two temperatures were obtained from two different regions of the sample, with 2L dosing steps in the first region and 5L dosing steps in the second region.

3 RESULTS AND DISCUSSION

The initial rationale for using silica nanosprings as a hydrogen storage medium was their large surface area, which is clearly demonstrated in Fig. 1. However, examination of the nanosprings with XPS quickly revealed that their electronic structure is unique relative to other forms of silica. Displayed in Fig. 2 are XPS spectra of the Si 2p core level states of linear silica nanowires and silica nanosprings. The binding energy of the Si 2p core level state of nanowires is at 103.70 eV, which is almost

equivalent to SiO_2 and corresponds to Si^{4+} [11]. In contrast, the binding energy of the Si 2p core level of the nanosprings is 102.8 eV, which is indicative of an intermediate ionization state between Si^{3+} (100.02 eV) and Si^{4+} . Relative to SiO_2 films and linear nanowires, the surface stoichiometry of the nanosprings results in a unique ionization state of the Si sites. The relevance of this intermediate ionization state of Si sites to hydrogen adsorption is addressed below.

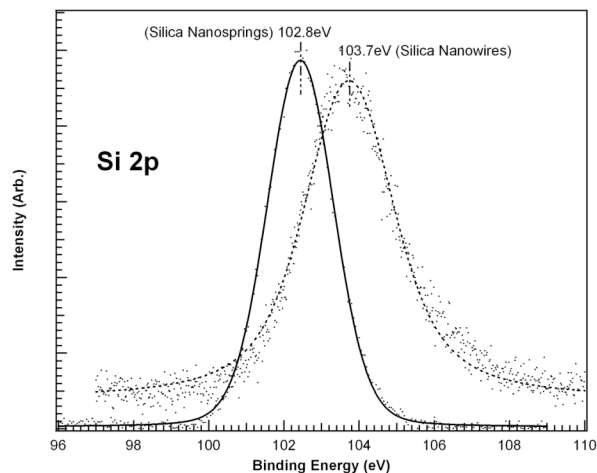


Figure 2: XPS spectra of the Si 2p level state.

The binding energy shifts of the Si 2p and O 1s core levels have been used as a qualitative measure of H_2 adsorption capacity, as well as to determine the adsorption sites, i.e., Si, O or both sites. Thermally stimulated desorption of H_2 from the surface of the nanosprings was used in conjunction with the core level shifts to determine if H_2 is chemi- or physisorbed onto the nanospring surface. Figure 3(a) is a montage of the XPS spectra of the Si 2p core level as a function of room temperature exposures to H_2 . The dots represent the experimental data and the solid lines are fits to the data using a Voigt function convoluted with a Lorentzian. From examination of Fig. 3(a) it can be seen that H_2 adsorption shifts the Si 2p to lower binding energies, which is indicative of electron charge redistribution. While the ionization state is still mixed, the shift is towards the Si^{3+} state, which suggests that surface charge redistribution favors Si. The largest single shift of the Si 2p state occurs with the first exposure of 2L H_2 (230 meV) and continues at a slower rate upon subsequent exposures until a maximum shift of 380 meV at 8L H_2 . The Si 2p core level shifts back to higher binding energies at 10L of H_2 , which suggests the completion of a monolayer and the formation of a second layer. The average value of the binding energy of the O 1s as function of exposure is 530.99 ± 0.01 eV. Other than an anomalous shift at 8L, the O 1s core level state is unaffected by H_2 adsorption. This, in conjunction with the shift of the Si 2p core level state, suggests that charge redistribution is due to the interaction of the adsorbed H_2 with the Si surface sites. However, we cannot preclude the participation of the O surface sites in

redistribution of surface charge. This observation is consistent with a theoretical prediction that hydrogen bonds to silicon atoms if silica is negatively charged [12].

To determine if H_2 dissociatively adsorbs at room temperature, as well as to determine the desorption energy from the surface of the nanosprings, the sample exposed to 10L H_2 was annealed at 373 K. After annealing, the Si 2p core level state shifts by 160 meV from 102.49 eV (10L H_2) to 102.65 eV, but does not return to the initial value of 102.8 eV. This result suggests that the majority of the hydrogen desorbs, but residual amounts remain. Annealing at temperatures up to 673 K did not remove all the remaining hydrogen, which would indicate that H_2 is initially dissociatively adsorbed and that subsequent adsorption is molecular. Repeated cycling with 5L dosing step between 10L of H_2 exposure followed by annealing resulted in Si 2p core level shifts between 102.5 eV and 102.65 eV. The low desorption H_2 temperature of 373 K is 500 K lower than the reported desorption temperature of H_2 from single walled carbon nanotubes (SWNT). Furthermore the full width at half maximum (FWHM) of the Si 2p core level spectrum upon annealing (hydrogen desorption) is effectively equivalent to that of the pristine nanosprings.

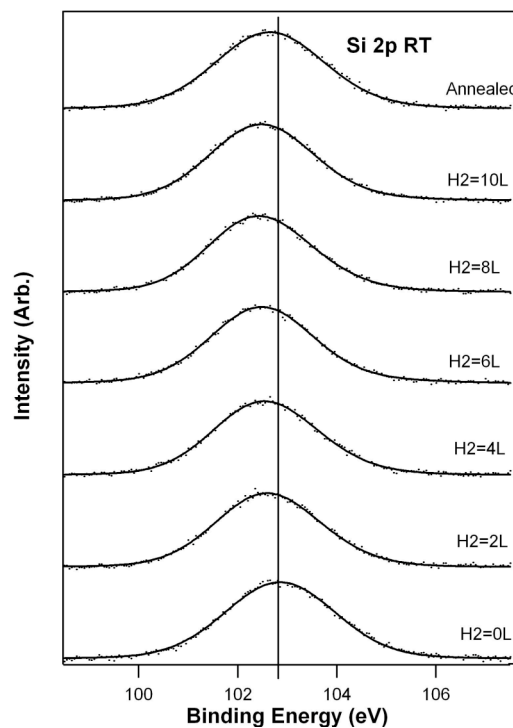


Figure 3: Silicon XPS spectra as a function of H_2 exposure at room temperature.

The preceding observations suggest that the H_2 adsorption rate is larger for initial exposures and decreases with subsequent exposures. The minimum binding energy of the Si 2p core occurs at an exposure of 8L, and then shifts by 30 meV from 102.47 eV to a binding energy of 102.50 eV with two more Langmuirs exposure, for a total

exposure of 10L H₂. This result suggests that the completion of a monolayer of H₂ occurs with an exposure of 8L. Furthermore, the shift of the Si 2p core level to higher binding energies for exposures exceeding 8L is indicative of the formation of a second monolayer of H₂. This conclusion is supported by studies of H₂ adsorption on porous Vycor glass, another form of high-purity SiO₂ glass [13], where it was found that the first monolayer was very strongly bonded to the glass surface, while the adsorption energy between the second monolayer and the first monolayer was relatively weaker.

In order to demonstrate the temperature dependence of isobaric adsorption of H₂ onto the nanosprings, samples were cooled to 77 K and H₂ adsorption experiments were conducted using the procedure used for room temperature adsorption. Comparing the data obtained at the two different temperatures one finds that the shift of the Si 2p core level states with H₂ adsorption exhibit similar trends. However, for adsorption at 77 K the binding energy shift of the Si 2p is significantly larger. For example, at 8L H₂ exposure the shift is 510meV, compared to 380meV at room temperature, where 2L dosing steps were used for both experiments. Physisorption is typically enhanced at lower temperatures due to decreased phonon-adsorbate interactions. With a subsequent H₂ exposure of 2L, for a total of 10L, the binding energy of Si 2p shifts back by 190meV to a higher binding energy. A similar shift of 30meV was observed at 10L of H₂ at room temperature. Thus, at room temperature and 77 K a second monolayer of H₂ begins to form, where the sticking coefficient for the second monolayer increases with decreasing temperature.

The behavior of the O 1s core level state as a function of H₂ adsorption at 77 K is equivalent to room temperature adsorption, there is no obvious effect on the O1s binding energy. The average values are 530.99 ± 0.01 eV for O1s at room temperature and 531.00 ± 0.04 eV at 77 K. These observations further indicate that hydrogen is most likely associated with the Si sites on the nanospring surface.

Thermal annealing of the nanosprings with 10L of H₂ to 373 K causes a shift of the Si 2p core level state back to the original binding energy (102.5 eV) prior to H₂ exposure. Once again we can conclude that the adsorbed hydrogen molecularly desorbs. This desorption temperature is approximately 400% higher than that of carbon (80 K). It is practical for applying nanosprings as storage media for H₂ since the heat required for releasing H₂ can be obtained from the heat generated by the exhaust of a combustion engine. Furthermore, our process allows for very large quantities of nanosprings to be formed at very low cost.

4 CONCLUSIONS

In conclusion, glass nanosprings offer a superior alternative to nanostructured forms of carbon for hydrogen storage both at room and liquid nitrogen temperatures. Multilayer physisorption of hydrogen on Si sites at the nanospring surface was verified by XPS. Multilayer

adsorption is critical to the use of nanostructured materials for hydrogen storage. Without this capability required storage capacities will not be attainable. In addition, the low (100°C) desorption temperature of H₂ from the surface of the nanosprings is superior to that reported for carbon nanotubes and favors quick release of stored hydrogen. Collectively, these observations lead to the conclusion that silica nanosprings, a unique form of nanostructured glass, shows promise as the next generation material for hydrogen storage.

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