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# Chemisorption on Nanoparticles: An Alternative Mechanism for Hydrogen Storage

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## Abstract

We present first principles, computational predictions of a porous, nano-structured semiconductor material that will reversibly store hydrogen for fuel cell applications. The material is competitive with current metal hydride storage materials, but contains only carbon and silicon, reducing both its cost and environmental impact. Additionally, unlike metal hydrides, the core skeleton structure of this material is unaltered when cycling from full hydrogen storage to full hydrogen depletion, removing engineering complications associated with expansion/contraction of the material.

Recent advances in fuel cell technologies have renewed interest in using hydrogen as a fuel. One of the main technological challenges to the widespread adoption of fuel cells is a secure, compact, lightweight and economic method of storing hydrogen[1]. Conventional approaches to hydrogen storage have focused on either physical storage of compressed hydrogen or storage in reversible metal hydrides[2, 3]. These approaches are typically limited by volume and weight constraints. It is estimated[1] that 5 kg of hydrogen will be required to power a fuel cell vehicle for 400 miles. Storing this quantity of gas in a reasonable volume would require pressures exceeding 10,000 psi. Alternatively, storing hydrogen in metal hydrides or alanates reduces the storage volume but the metallic elements significantly increase the weight[2].

In this Letter we propose an alternative material for hydrogen storage in which hydrogen is chemisorbed on the surfaces of a purpose built, porous, nano-structured, semiconductor material. Simulations are used first to design a nanoparticle building block that reversibly absorbs a maximal amount of hydrogen, while minimizing its total weight and volume. Additional simulations then predict how these nanoparticles will self-assemble into a macroscopic solid.

Unlike carbon nanotubes, in which it has been proposed that hydrogen is stored via physisorption with weak Van der Waals bonds[4], our proposed material stores hydrogen with stronger *covalent* bonds between hydrogen atoms and semiconductor surface atoms. The free energy of these bonds depends on the details of the atomic configuration at the surface and by utilizing the novel structure of highly curved nanoparticle surfaces it can be changed to favor either absorption or desorption of hydrogen.

While early studies of hydrogen terminated bulk silicon surfaces revealed hydrogen emission upon annealing[5], it has been calculated that these bulk surfaces would not be suitable for hydrogen storage as the surface structures with high H content are only meta-stable[6]. However, here we show that on a nanoparticle surface, the high degree of curvature dramatically reduces the repulsion between neighboring SiH<sub>2</sub> groups, increasing the opportunity for reversible absorption and emission of hydrogen and therefore hydrogen storage.

To design a hybrid carbon-silicon nanoparticle where the transition from Si-H<sub>2</sub> to Si-H surface groups can be used to reversibly store hydrogen the relative stabilities of these surface groups was determined by performing a series of first principles density functional calculations[7] of their lowest energy structures and the kinetic barrier to hydrogen

absorption/desorption[9]. Similar calculations have recently been used to examine the storage of hydrogen in carbon nanotubes[4, 10–12].

The formation energies,  $\Omega$ , of the structures with Si-H and Si-H<sub>2</sub> surfaces are given[6] by

$$\Omega = E^{tot} + E_{ZPE} - n_{Si}\mu_{Si} - n_H\mu_H \quad , \quad (1)$$

where  $E^{tot}$  is the total energy,  $E_{ZPE}$  is the zero-point Si-H vibrational energy ,  $n_{Si}$  is the number of Si atoms, and  $\mu_{Si}, \mu_H$  are the silicon and hydrogen chemical potentials.

The surface to volume ratio of a nanoparticle increases as its size decreases, therefore, in principle, maximum hydrogen storage will be achieved for the smallest nanoparticles. A prototype structure for 1 nm silicon nanoparticles has previously been proposed[13, 14] as the structure of nanoparticles synthesized by sonification of porous silicon. Figures 1(a) and (b) show the structure of these 1 nm particles, consisting of 29 Si atoms, with (100) facets containing SiH<sub>2</sub> dihydride groups and reconstructed SiH dimer groups. This particle contains 12 SiH<sub>2</sub> groups and upon reconstruction the H content is reduced from Si<sub>29</sub>H<sub>36</sub> to Si<sub>29</sub>H<sub>24</sub>. The critical hydrogen chemical potential,  $\mu_H^C$ , at which the most stable surface reconstructs and changes from dihydrides to dimers is given by  $\mu_H^C = \frac{1}{12}(E^{Si_{29}H_{36}} - E^{Si_{29}H_{24}})$ .

The thick black curve in Fig. 2 shows our calculated temperature dependence of the chemical potential of hydrogen atoms in an H<sub>2</sub> molecule,  $\mu_H(T)$  at 1 atmosphere pressure. The value of  $\mu_H^C$  for the Si<sub>29</sub>H<sub>36</sub> → Si<sub>29</sub>H<sub>24</sub> reconstruction is plotted as a red horizontal line in Fig. 2 The intersection between this line and the  $\mu_H(T)$  curve shows that  $\mu_H^C$  corresponds to a critical temperature  $T^C$  of approximately 580K. Temperatures lower than this will favor dihydride structures (hydrogen storage) and higher temperatures will favor dimer structures (hydrogen emission). We note that while bulk silicon surfaces with SiH dimers are too energetically stable to store hydrogen at room temperature ( $T^C < 300K$ ), the reduced SiH<sub>2</sub> repulsion on silicon nanoparticle surfaces favors surface SiH<sub>2</sub> dihydrides too strongly ( $T^C = 580K$ ). This increased stability of SiH<sub>2</sub> groups at the nanoscale arises from the ability of these groups to rotate away from each other [see Fig.1(a)] reducing the H-H repulsion.

An absorption/desorption switching temperature of 580 K is too high to be compatible with fuel cells which require operating temperatures below 400 K. We therefore explored how  $T^C$  varies when alloying with carbon. Replacing silicon atoms with carbon in the core produces three high symmetry clusters; SiC<sub>4</sub>Si<sub>24</sub>, C<sub>5</sub>Si<sub>24</sub> and SiC<sub>16</sub>Si<sub>12</sub>. In C<sub>5</sub>Si<sub>24</sub> the five center silicon atoms are replaced with carbon, while in SiC<sub>4</sub>Si<sub>24</sub> the center remains silicon,

but its four neighbors are replaced with carbon. The  $\text{SiC}_{16}\text{Si}_{12}$  particle represents a piece of the SiC cubic lattice.

The shorter C-C bond lengths in the core of these clusters pull in the Si atoms from the surface of the nanoparticle, reducing the separation between Si atoms on neighboring  $\text{SiH}_2$  groups. This reduced separation increases the repulsion between neighboring dihydrides, favoring reconstructions to the dimer structure, such that  $T^C$  for all three of these silicon/carbon clusters decreases to an almost ideal value of 340 K (see black horizontal line in Fig. 2). Therefore, individual silicon clusters with carbon cores are promising materials for storing  $\text{H}_2$ . Each cluster can reversibly store 6  $\text{H}_2$  molecules, yielding a maximum density of  $20 \text{ kg m}^{-3}$  of  $\text{H}_2$ .

While individual  $\text{C}_5\text{Si}_{24}$  nanoparticles will efficiently store hydrogen, it would be desirable to assemble them into a macroscopic solid, while maintaining their ability to store hydrogen. The connection of two nanoparticles is expected to proceed first by two H atoms detaching from the surface of each cluster forming an  $\text{H}_2$  molecule and leaving two dangling bonds. The dangling bonds on neighboring clusters then connect to form a new covalent bond between the clusters.

Examination of the structure of  $\text{C}_5\text{Si}_{24}$  particles shows that they contain 4 (111)-type facets representing the faces of a tetrahedron and 6 pairs of dihydrides/dimers on (100)-type facets, each pair making up an edge of the tetrahedron [see Fig.1(h)]. We therefore envisage three limiting cases by which the particles could self-assemble into a close packed array via the formation of new Si-Si bonds; (i) connecting the (111) facets face-to-face, (ii) connecting the edges of the tetrahedra via the (100) dihydrides/dimers, or (iii) connecting the clusters via a single bond on the (100) facet. These three cases are illustrated in Figs. 1(c)-(e).

Comparing the total energy of  $\text{C}_5\text{Si}_{24}\text{H}_{22}$  clusters where an  $\text{H}_2$  molecule has been removed from a (111) and (100) facet, we find it is 0.5 eV more favorable to leave a dangling bond on a (111) facet than on a (100) facet (see Methods). From kinetic considerations this suggests that  $\text{C}_5\text{Si}_{24}\text{H}_{22}$  clusters will connect as in Fig. 1c. As none of the (100)  $\text{SiH}_2/\text{SiH}$  groups required for hydrogen storage are involved in these connections between nanoclusters, the hydrogen storage properties of the assembly are unaffected.

The calculated value of  $\mu_H^C$  for reconstructing surface dihydrides on two clusters connected by (111) facets (Fig. 1c),  $\text{C}_{10}\text{Si}_{48}\text{H}_{66} \rightarrow \text{C}_{10}\text{Si}_{48}\text{H}_{42}$  corresponds to a  $T^C$  of approximately 340 K, the same as a single  $\text{C}_5\text{Si}_{24}$  cluster, i.e. the small structural changes introduced when

two nanoparticles are connected by their (111) facets do not affect the relative energies of their  $\text{SiH}_2$  and  $\text{SiH}$  surface groups. Extending the structure further by joining 5 and 20  $\text{C}_5\text{Si}_{24}$  clusters to form a  $\text{C}_{25}\text{Si}_{120}$  ring structure and a  $\text{C}_{100}\text{Si}_{480}$  dodecahedron (see Figs. 1f and g) we find that the dihydride to dimer reconstruction is still unchanged with a  $T^C$  of approximately 340 K.

Currently, the synthesis of large quantities of  $\text{SiC}_4\text{Si}_{24}\text{H}_{36}$  and  $\text{C}_5\text{Si}_{24}\text{H}_{36}$  is not as routine as synthesizing pure silicon clusters. We hope that the potential applications of these material for hydrogen storage will stimulate the synthetic chemistry community to develop such synthesis techniques. We note that the reduction of tetrachlorosilane is a standard growth method for pure Si clusters and suggest that a similar reduction approach might be used to generate these hydrogen terminated silicon carbide nanoparticles. The core could be generated from the commercially available dimethyl propane or tetramethyl silane after halogenation of all the C-H bonds and the Si shells could be generated from partially halogenated disilanes.

Utilizing the total hydrogen content, the  $\text{C}_5\text{Si}_{24}\text{H}_{36}$  nanoparticle solids store  $40 \text{ kg m}^{-3}$  of  $\text{H}_2$ , which is equivalent to storing  $\text{H}_2$  gas at  $\sim 20,000$  psi pressure. This corresponds to 3.2 wt%  $\text{H}_2$  which is significantly higher than the theoretical limit of 1.4 wt% achieved by  $\text{LaNi}_5\text{H}_6$ , currently one of the most promising metal hydride storage systems. If however, only the  $\text{H}_2$  stored via the dihydride/dimer reconstruction mechanism is considered then the active hydrogen content decreases to 1.6 wt%. In addition to vehicular applications, another promising application of fuel cells is in portable consumer electronic devices. In these devices the benchmark for energy storage is Lithium ion batteries. Hydrogen stored in the above nano-material and combined with oxygen in a fuel cell has an energy density of  $4.3 \text{ MJ kg}^{-1}$ . This is approximately an order of magnitude higher than Li batteries ( $0.5 \text{ MJ kg}^{-1}$ ), while the two media have similar weights and volumes.

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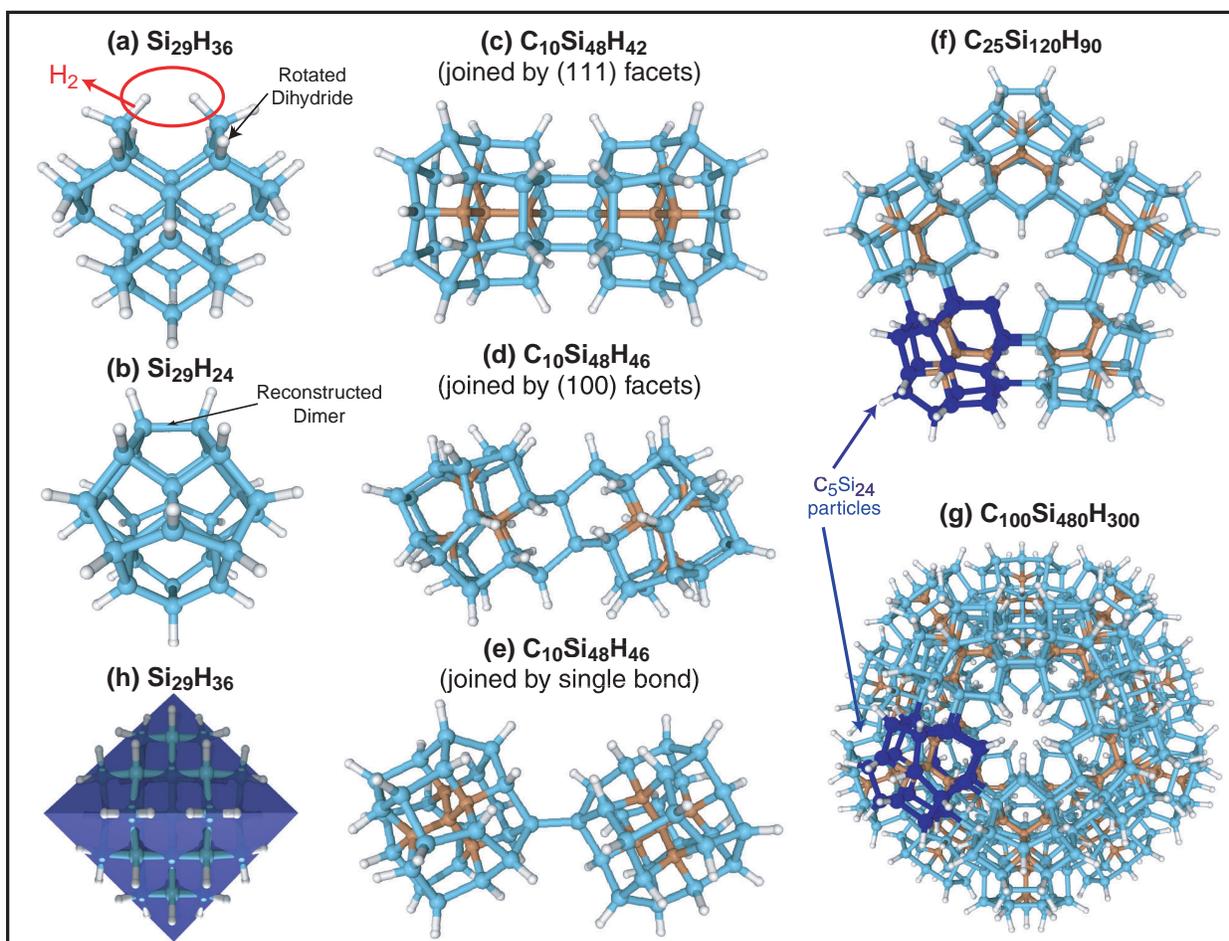


FIG. 1: Calculated atomic structures of single, double, 5-fold and 20 nanoparticles structures. Si, C and H atoms are colored blue, brown and white. In (f) and (g) atoms in a single  $\text{C}_5\text{Si}_{24}$  particle are highlighted in dark blue.

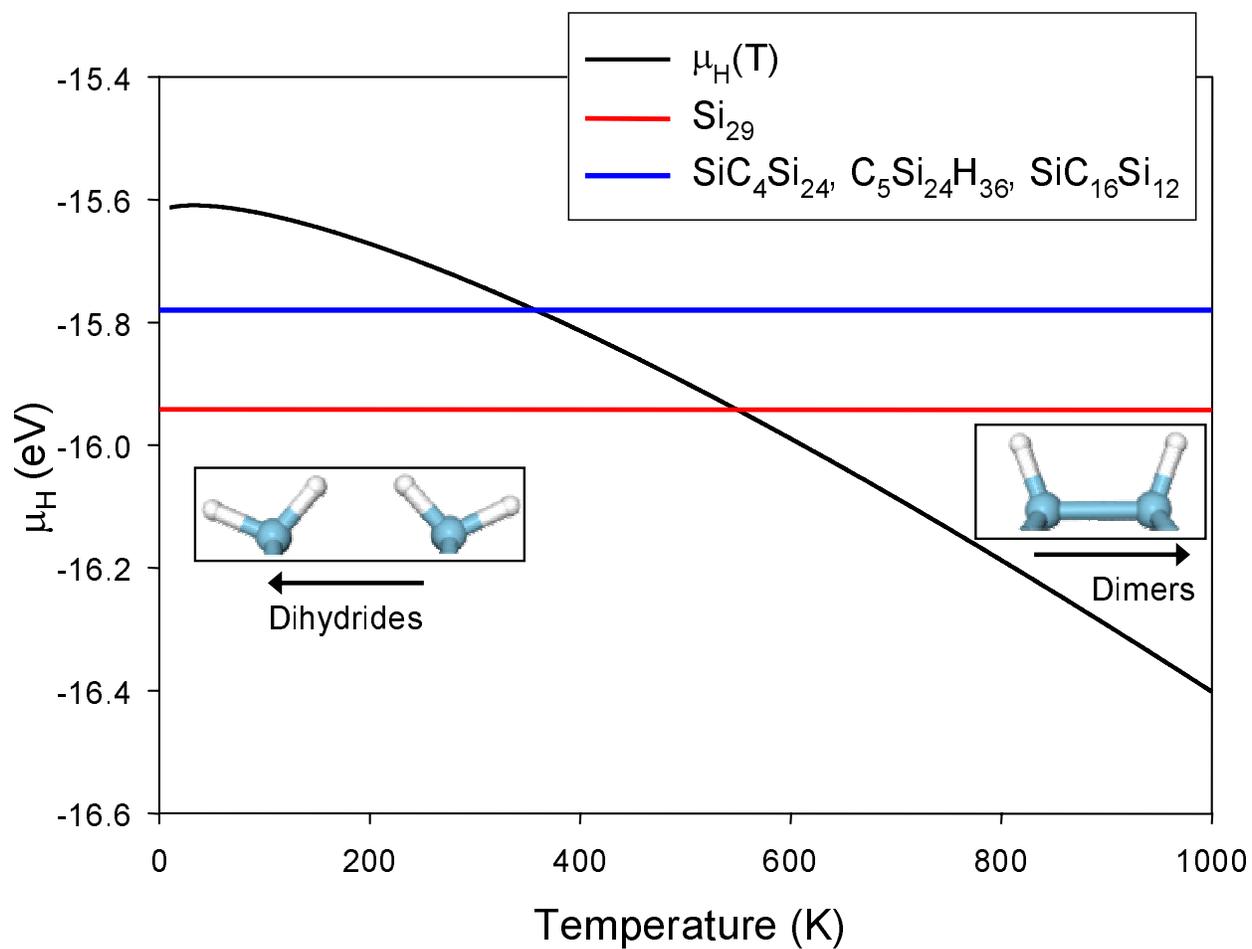


FIG. 2: The temperature dependence of the chemical potential of hydrogen. The solid black curve shows  $\mu_H$  in  $H_2$  gas at 1 atmosphere. Red and black horizontal lines mark the value of  $\mu_H$  at which  $Si_{29}$  and  $C_5 Si_{24}$  nanoparticle surface reconstruct from 36 to 24 H atoms.