Carbon 'grapevine' may store hydrogen

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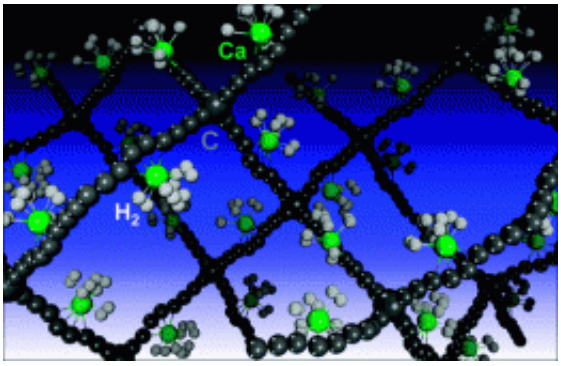

(PhysOrg.com) -- A nanoscale grapevine with hydrogen grapes could someday provide your car's preferred vintage of fuel.

Rice University researchers have determined that a lattice of calcium-decorated carbyne has the potential to store hydrogen at levels that easily exceed Department of Energy (DOE) goals for use as a "green" alternative fuel for vehicles.

The rise of nanoscale strategies for energy storage has been dramatic in recent years, as evidenced by labs worldwide suggesting various ways to use nanotubes and ribbons as a medium. But they may not be thinking small enough, according to new research by the lab of theoretical physicist Boris Yakobson that was published last week in the online journal *Nano Letters*. Yakobson is Rice's Karl F. Hasselmann Chair in

Engineering and a professor of materials science and mechanical engineering and of chemistry.

Carbyne is a chain of carbon atoms; it's what you'd get if you could pull a string from a slice of graphene the same way you'd pull a loose thread from a sweater. "A one-atom rod of carbon is as thin as it can ever get, way thinner than a carbon nanotube," Yakobson said.

Carbyne is considered an exotic material, but recent experiments show it can be synthesized and stabilized at room temperature, where the storage is mainly of interest. That's important, Yakobson said, because other nanoscale materials such as carbon nanotubes, graphene and even buckyballs are effective for hydrogen storage only at conditions that are too cold.

It's the calcium that serves as a bait and makes room-temperature storage possible for carbyne. Formed into a lattice, carbyne alone could theoretically store around 50 percent of its weight in hydrogen, far above the 6.5 percent capacity target set by the DOE for 2015. But the weak binding could work only at very low temperatures, Yakobson said.

Not so with calcium added. It allows the lattice to adsorb hydrogen with a binding energy favorable for effective room-temperature, reversible storage. Because calcium atoms don't cluster, they can be distributed along the carbyne strands like grapes on a vine and bind as many as six hydrogen atoms each; this would give the network a potential storage capacity of about 8 percent of its weight.

Because a scaffold of single-atom chains would be light and airy, there would be more room for the hydrogen to aggregate.

Yakobson and his colleagues suggested several scalable strategies for practical hydrogen storage. In one that resembles the so-called metal

organic frames recently studied by Yakobson's lab, a diamond-like lattice would allow five hydrogen atoms to be adsorbed at each calcium atom; the number of carbon atoms in each strand would determine the total capacity.

In the other, they suggested pulling calcium-decorated strands of atoms from graphene, which would serve as a frame for the array.

Yakobson said it is difficult to estimate when either of these or some other realization might happen. "But I am optimistic. From this theoretical concept, and based on experimental evidence of carbyne synthesis and experience with metal organic frame architectures, it may take two to three years to produce carbyne networks and, say, one to two years to tweak the calcium enrichment to obtain a material with good capacity for hydrogen," he said. "So in three to five years, one can have an industrial sample and then move to scale up -- that is, with intense work and some luck."

More information: Calcium-Decorated Carbyne Networks as Hydrogen Storage Media, *Nano Lett.*, Article ASAP DOI: 10.1021/nl200721v

Abstract
Among the carbon allotropes, carbyne chains appear outstandingly accessible for sorption and very light. Hydrogen adsorption on calcium-decorated carbyne chain was studied using ab initio density functional calculations. The estimation of surface area of carbyne gives the value four times larger than that of graphene, which makes carbyne attractive as a storage scaffold medium. Furthermore, calculations show that a Ca-decorated carbyne can adsorb up to 6 H2 molecules per Ca atom with a binding energy of 0.2 eV, desirable for reversible storage, and the hydrogen storage capacity can exceed 8 wt %. Unlike recently reported transition metal-decorated carbon nanostructures, which suffer from the

metal clustering diminishing the storage capacity, the clustering of Ca atoms on carbyne is energetically unfavorable. Thermodynamics of adsorption of H2 molecules on the Ca atom was also investigated using equilibrium grand partition function.

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