

Hydrogen Storage Property on Nickel-Atom-Dispersed Organosilica Nanotubes

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Hydrogen, which can be readily produced from renewable energy sources, contains a much larger chemical energy per mass (142 MJ kg⁻¹) than any hydrocarbon fuel. For example, a hydrogen electric fuel cell car, where hydrogen in a fuel cell is burnt electrochemically with oxygen from air, needs to store only about 4 kg of hydrogen to cover the range (~300 miles) of a gasoline-powered car, while generating only environmentally clean water as a byproduct. Consequently, hydrogen is considered to be an ideal fuel for solving an energy crisis and helping alleviate the earth's environmental problems that result from using petroleum fuels. The U.S. Department of Energy has targeted a maximum weight percent (wt %) of reversibly adsorbed hydrogen of 6.5% and a maximum hydrogen capacity per volume of 62 kg m⁻³ for many applications, including vehicles and portable devices. However, a major problem is that there is no hydrogen-storage material as yet developed that can allow the release of 6.5 wt % (target of the Department of Energy, DOE) hydrogen at practical atmospheric temperatures and pressure conditions, which are the usual conditions for cars and the ideal conditions for many other practical applications.

Thus far, several hydrogen-storage methods such as carbon-fiber-reinforced high-strength containers,¹ liquid hydrogen,² chemical hydrides,³ and carbon nanotubes (CNTs)⁴ have been suggested. Hydrogen storage in a gas or liquid phase is a relatively unsuitable system for a vehicle because it is dangerous and expensive.⁵ Bearing this in mind, there is a high level of interest in storing hydrogen on lightweight metals and advanced carbons. Many metals are capable of absorbing large amounts of hydrogen in the interstitial sites of their lattices, where hydrogen molecules are dissociated to the atoms at the surface of the metal before absorption. Although metal hydride is a potential hydrogen-storage material, some problems have to be overcome before it can be put into practical use, such as the slow kinetics during hydride formation and decomposition.⁶ On the other hand,

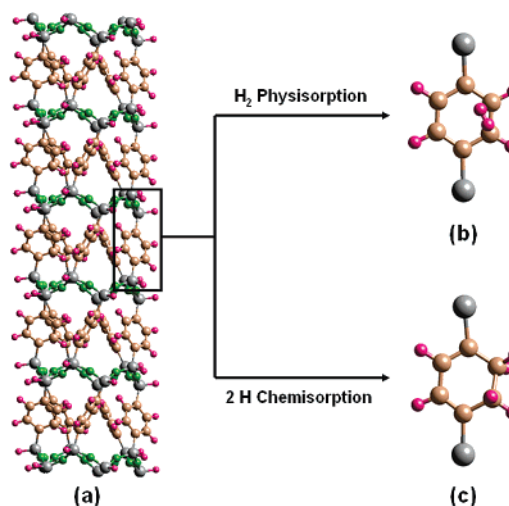


Figure 1. (a) PW91 optimized organosilica nanotube structure with the periodic boundary condition, (b) its magnified view after physisorption, and (c) its magnified view after chemisorption of two hydrogen atoms on a benzene ring. O, Si, C, and H atoms are shown in green, gray, light brown, and pink, respectively.

carbon nanotubes (CNTs) have been proposed as being a promising candidate for hydrogen storage since the first experimental study by Dillon et al.⁷ A CNT has a cylindrical structure and a high surface-to-volume ratio, which makes it ideal for the development of reversible hydrogen storage. However, recent studies show that the hydrogen content on a pristine CNT is releasable only in negligible amounts (<0.1 wt %) at practical conditions, thus not satisfying the 6.5 wt % target.^{8,9} Consequently, a pristine nanotube itself did not appear to be ideal as hydrogen-storage media for use in cost-effective hydrogen fuel cells operating in common atmospheric conditions.

On the other hand, our recent experiment¹⁰ has shown that Ni-dispersed multiwalled CNTs (MWCNT) with an outer diameter of ~20 nm can release up to 2.8 wt % H₂ at practical conditions. On the other hand, as the Ni sizes dispersed became larger, it was also found that the hydrogen desorption temperature increased, which is not suitable for practical applications. However, unlike the CNT, benzene–silica hybrid materials, as shown in Figure 1a, always have their benzenes disconnected through SiO₂ networks; thus, it may be possible to disperse nickel on an atomic-scale size in principle because only the benzene ring unit structures of an organosilica material are favorable for incorporating Ni atoms. Consequently, benzene–silica materials are considered to be the ideal host structures for Ni dispersion to give optimal hydrogen desorption properties compared to that for CNTs.

Recently, we observed a hydrogen-storage capacity of 0.9 wt %¹¹ in the mesoporous organic silica at 2000 kPa and

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0.68 wt %¹² in the rodlike organic silica at 80 kPa. However, these results indicate that it is very hard to achieve a high hydrogen-storage capacity exceeding 1 wt % at practical pressure conditions on pristine benzene–silica materials. Here, we have explored the hydrogen adsorption properties of the organosilica nanotubes doped with the Ni metal, as it seems that the hydrogen-storage capacity of metal-doped benzene–silica materials could be higher than that on pristine materials because they are capable of modulating hydrogen-storage capacities.

Figure 1a shows the schematic surface structure of the benzene–silica materials. All atoms are displayed as a ball model. This organosilica structure is made of a covalently bonded network composed of $O_{1.5}Si-C_6H_4-SiO_{1.5}$ units, which is fully described in the previous work.¹³ In this study, our focus is on exploring hydrogen-adsorption and -desorption properties of pristine organosilica and Ni-atom-dispersed hybrid nanotubes. The calculations were mainly performed using the PW91¹⁴ method with the periodic condition.¹⁵ All atoms were described using nonlocal norm-conserving Vanderbilt scalar pseudopotentials,¹⁶ and a plane-wave basis was truncated to include only plane waves having kinetic energies less than 300 eV where the set of k -points used to expand the electronic wave function was based on the Monkhorst–Pack scheme.¹⁷ On the other hand, the self-consistent B3LYP¹⁸ and KMLYP¹⁹ density functional theories were used for determination of thermochemical and kinetic parameters involved in hydrogen adsorption on the pristine and the Ni-atom-doped organosilica structures.²⁰ The electronic wave function was expanded using the 6-31G-(d,p) valence double- ζ plus polarization²¹ basis set for all atoms. The frequency calculations to determine zero-point energy (ZPE) corrections are performed at the geometries obtained through full optimization.

The interaction between a hydrogen molecule and the carbon atoms in the exterior side of the nanotube is determined. It is found that the structure as shown in Figure

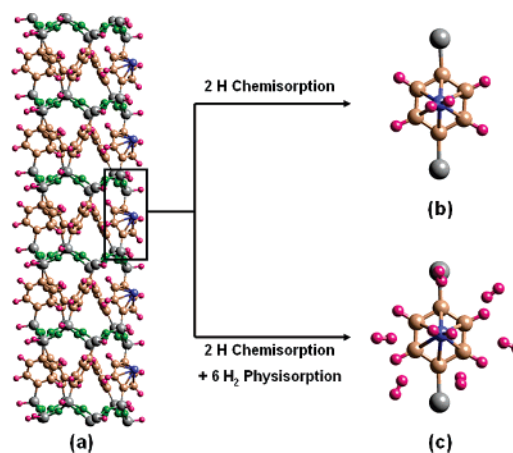


Figure 2. PW91 optimized structures: (a) Ni-atom-doped organosilica nanotube, (b) chemisorption of two hydrogen atoms on a Ni atom, (c) 6 H_2 are adsorbed through van der Waals interactions while one H_2 is dissociated into two H atoms on the Ni atom. O, Si, C, H, and Ni atoms are shown in green, gray, light brown, pink, and blue, respectively.

1b is the lowest-energy structure for a hydrogen physisorbed organosilica nanotube, where a hydrogen molecule is adsorbed above two adjacent carbon atoms of a benzene ring and the axis of the molecule is same as that of the nanotube. The distance between the adsorbed hydrogen atom and the carbon atom is in the range of 3.21–3.24 Å, and the molecular hydrogen adsorption energy is determined to be -23.0 kJ/mol. Also, it is found that two hydrogen atoms are chemisorbed on C atoms of the benzene ring forming the CH_2 unit. This dissociative chemisorption energy of hydrogen is -12.6 kJ/mol, and the activation barrier of the chemisorption is 424.7 kJ/mol. Although the enthalpy for the dissociative hydrogen chemisorption is thermodynamically exothermic, it is considered that the high activation barrier of 424.7 kJ/mol hinders kinetically the reaction. From these results, it is considered that only two hydrogen molecules adsorb on the pristine organosilica materials without the dissociative chemisorption of H_2 , and the calculated hydrogen storage capacity is 2.2 wt %.

Figure 2 shows hydrogen storage properties of the Ni-doped benzene–silica hybrid nanotubes. The nickel adsorption energy on the nanotube is -178.7 kJ/mol, which indicates that the nickel-doped organosilica material is a very stable structure. When one hydrogen molecule comes to the nickel-adsorbed benzene ring, the hydrogen molecule is dissociated into the atoms and then chemisorbed on the nickel atom, as shown in Figure 2b. The distance between two hydrogen atoms is elongated to 0.94 Å from 0.75 Å, and the distance between the hydrogen atom and the nickel atom is 1.52 Å. The hydrogen chemisorption energy is -137.2 kJ/mol. After two hydrogen atoms are chemisorbed, the next-coming hydrogen molecules are physisorbed above the nickel atom. We determine the H_2 adsorption energies until the number of hydrogen molecules around the nickel atom reaches seven, at which point one hydrogen molecule is dissociatively chemisorbed and six H_2 are physisorbed on a Ni atom (see Figure 2c). The physisorption energy per molecule of hydrogen is -12.6 kJ/mol, and the distance between the physisorbed hydrogen molecule and the nickel atom is in the range of 3.21–3.34 Å. Hydrogen adsorption is 10.4 kJ/mol more exothermic in the pristine structure than in the Ni-atom-dispersed organosilica nanotube. However,

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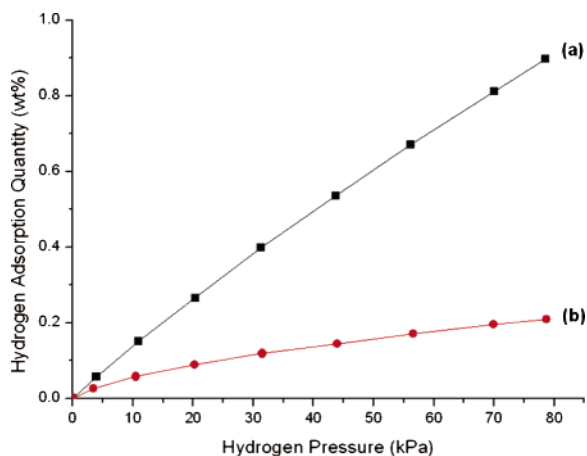


Figure 3. Hydrogen adsorption isotherms for the (a) 10 and (b) 15 wt % nickel-doped organosilica nanotubes at 78 K.

the maximum number of adsorbed hydrogen molecules is 3.5 times larger when the hybrid material is doped by the nickel. In this respect, the expected hydrogen storage capacity is capable of exceeding the 6 wt % at moderate pressure conditions.

We have also synthesized 10 and 15 wt % nickel-doped benzene–silica nanotubes using 1,4-bis(triethoxysilyl)-benzene for the precursor (see the Supporting Information), and TEM images of Ni-doped organosilica nanotubes indicate that the metal particles of 10 wt % Ni doped structure are much smaller than that of the 15 wt % Ni loading as shown in Figure S1 of the Supporting Information. Figure 3 shows the correlation between the hydrogen-storage capacities and the sizes of dispersed Ni nanoparticles at pressures ranging from 0 to 80 kPa. The higher hydrogen-adsorption capacity of 0.9 wt % on smaller Ni nanoparticles, compared to the 0.2 wt % on larger sizes of Ni nanoparticles, indicates that the hydrogen-adsorption capacity on the nanotube having smaller Ni particles is higher than that having larger metal particles. Consequently, these preliminary results show that attachment of agglomerated Ni cluster atoms instead of one Ni atom on the benzene ring unit could significantly reduce the maximum hydrogen-storage capacity obtained when one Ni atom is attached on each benzene unit. This is because H_2 molecules around each Ni on agglomerated clusters could involve more chemisorption processes than physisorption processes because of geometric constraints. In this respect, it is considered that the development of reversible hydrogen-storage media with high H_2 storage capacity using Ni-coated organosilica nanotubes requires the ingenious methodology to disperse one Ni atom on each benzene ring unit of an organosilica nanotube.

Images a and b of Figure 4 show the charge densities of the Ni-dispersed organosilica nanotube and the seven- H_2 -adsorbed, Ni-doped organosilica nanotube, respectively. It is interesting to note that the charge density between the nickel atom and the nickel-adsorbed benzene ring is different because of the presence of the hydrogen molecules. In Figure 4a, the charge density continuously exists from the benzene ring to the Ni atom, indicating that a strong bond forms between the benzene ring and the Ni atom. On the other hand, when the hydrogen molecules are adsorbed on the nickel atom, the charge density around the nickel atom is slightly moved in the direction of the chemisorbed hydrogen

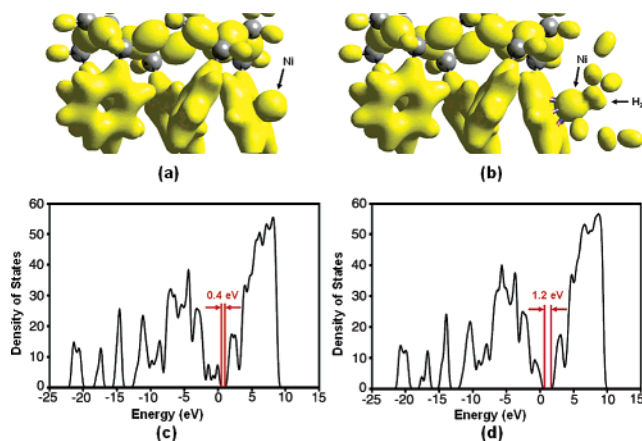


Figure 4. Charge densities for (a) the Ni-dispersed organosilica nanotube, (b) the Ni-dispersed organosilica nanotube with 7 H_2 adsorbed around the nickel atom. The yellow contour is the charge density, whereas blue and gray indicate the nickel and silicon atoms, respectively. Electron density of states for (c) the Ni-doped organosilica nanotube and (d) the 7 H_2 adsorbed Ni-doped organosilica nanotube.

molecule, which results in the small charge vacancy between the nickel atom and the benzene ring, as shown in Figure 4b. We also explore the effect of hydrogenation on the density of states (DOS) of the nickel-doped organosilica material. Figure 4c shows the DOS of the Ni-doped hybrid material. Because of the existence of the band gap, it is determined that the organosilica structure with nickel is not a metallic material. Changes in the DOS for the nickel-doped hybrid material after the hydrogen adsorption are presented in Figure 4d. The contours of the two DOS graphs are fairly similar, and the changes in the three band gaps in the low-energy ranges are negligible after the hydrogen molecules are adsorbed on the organosilica material. However, the band gap located slightly above the Fermi level is increased from 0.4 to 1.2 eV by the hydrogenation. This may be attributed to the formation of the charge vacancy when the hydrogen molecules are adsorbed on the nickel atom.

In summary, it is demonstrated that 2 H_2 molecules could be adsorbed on the benzene ring of the pristine organosilica material, but this is not sufficient for practical usage as a hydrogen storage system. However, when the nickel atom is adsorbed on the benzene ring, 6 H_2 molecules could be physisorbed around each nickel atom after one H_2 molecule is dissociatively chemisorbed on the nickel atom, where the slight movement of charge density around the nickel atom to the adsorbed hydrogen stabilizes the hydrogen adsorption up to 7 H_2 . In this light, we conclude that nickel-atom-dispersed organosilica nanotubes could provide viable alternatives to reversible hydrogen-storage materials with high hydrogen capacities exceeding the 6 wt % at moderate pressure conditions.

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Supporting Information Available: Synthesis procedures, structure of **1**, and TEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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