# Clustering of Sc on SWNT and Reduction of Hydrogen Uptake: *Ab-Initio* All-Electron Calculations

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Energies and kinetic barriers associated with transition metal (Sc) clustering on a single-walled carbon nanotube (SWNT) and graphene were studied by the all-electron density functional method. The analysis shows that the binding energy of Sc atom on SWNT is highly sensitive to the tube diameter and chirality. The metal atoms clustering on common SWNT, with diameters ∼1−2 nm, is energetically favorable and kinetically permitted. Although well-separated, lone Sc atoms on SWNT can enhance the hydrogen storage capacity, their aggregation into clusters significantly reduces the hydrogen uptake; e.g., a $Sc_4$ cluster has the same hydrogen uptake as a single Sc atom. Our analysis shows that, although indeed light transition metal decorated SWNT present potential material for the hydrogen storage, utter care should be taken to avoid the metal clustering on support material, to achieve and maintain higher hydrogen capacity.

Using hydrogen as the energy carrier instead of mineral fuels is a tantalizing way of having a sustainable energy supply and simultaneously saving our environment from pollution. Yet, there are still some important challenges to be addressed prior to possible actual spread of hydrogen-based energy infrastructure. One of the critical problems is the lack of suitable media for hydrogen storage with sufficiently high volumetric and gravimetric ratios at nearly ambient conditions. For more than a decade, carbon nanotubes (CNT) have been considered as promising hydrogen storage media due to their light weight and high surface to volume ratio.[1−3] Presently, however, an understanding emerges that due to weak physical adsorption of molecular hydrogen to the CNT walls (binding strength ∼0.03 eV),[4] the pure unmodified CNT are unlikely to be suitable for hydrogen storage and practical service.

Great efforts have been devoted to seeking materials that can immobilize hydrogen with binding strength of 0.2−0.4 eV, most promising among them being metal decorated carbon materials (e.g., fullerenes, carbon nanotubes, metal-organic frameworks).[5−11] It has been proposed that a single transition metal (e.g., Sc and Ti) atom supported on an organic molecule such as cyclopentadiene cation (Cp) or $C_{60}$ fullerene can bind 8−10 hydrogen atoms in nearly molecular form, with an average binding energy of about 0.2−0.5 eV/$H_2$.[5−7] Similar results were obtained in the case of a single Ti atom sitting on a CNT surface.[7] Different from the chemical binding of H to metal in metal hydrides, a lone transition metal atom binds hydrogen via the so-called "Kubas interaction",[5,12,13] where the H−H bond undergoes some elongation rather than a complete dissociation into atoms. Further studies show that, besides these transition metals, a single lithium or nickel atom on the CNT or $C_{60}$ surface can take up similar amounts of $H_2$ molecules.[11] CNTs or fullerenes decorated with these light metals are expected to store hydrogen up to 6−9 wt %,[5−9,11] which meets the DOE goals.

So far, the focus of the previous studies has been on hydrogen adsorption on single metal atom.[5−9,11] However, in real situations, the aggregation of the metal atoms on adsorption media may occur (e.g., at ambient and elevated operational temperature) and should be carefully considered before one can assess the actual potential of the material for hydrogen storage. It was suspected that metal clustering might reduce the area of hydrogen holding and thus reduce the hydrogen uptake.[14,15] However, the important questions on energetics, kinetics of metal aggregation, and the hydrogen uptake on the aggregated metal clusters remain unexplored. Here we present our studies on the Sc aggregation on single-wall CNT (SWNT) and the graphene surface as well as the hydrogen uptake on aggregated Sc clusters. We will show that the low diffusion barrier of the Sc atom on the SWNT leads to the high mobility of metal atoms and the large formation energy of Sc clusters drives the atomic aggregation. Furthermore, the hydrogen uptake on these aggregates gets significantly reduced due to dissociation of all incoming hydrogen molecules into atomic hydrogen, which forms a shielding layer on the metal cluster surface.

In the theoretical studies of these systems, energies generally depend, quite sensitively, on the choice of the methods. To draw reliable conclusions, a greater degree of care should be taken for the choice of the method. Most of the previous theoretical studies on such systems were performed using density functional (DFT) methods with pseudopotential.[5−8,11] It is well-known that pseudo-potential based methods are less accurate than an all-electron calculation. Therefore, we use the all-electron based DFT method using the generalized gradient approximation of type Becke98[16] for exchange and correlation functional, with the Gaussian basis set 6-31G as implemented in Gaussian03 package.[17]

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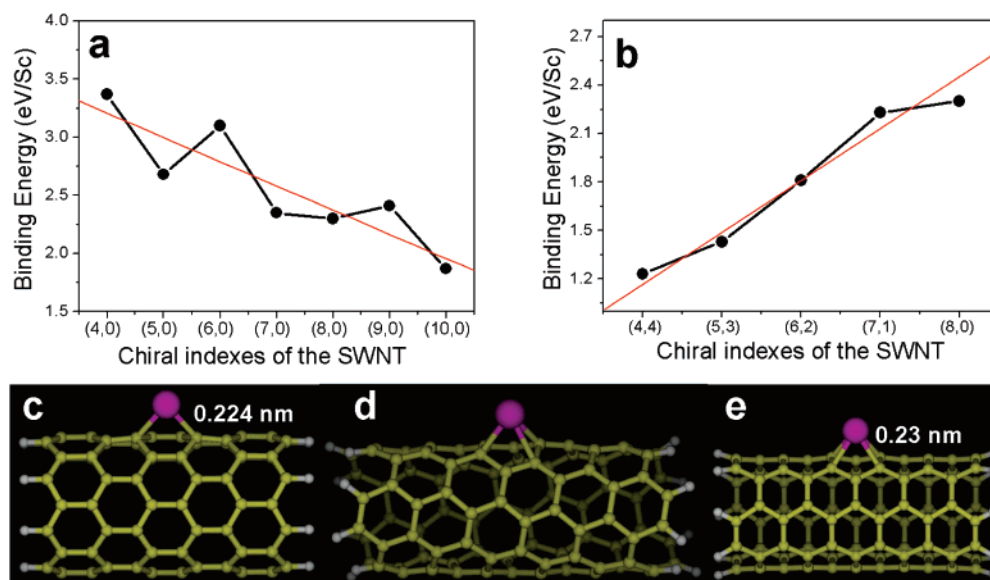† P.O.K. and F.D. contributed equally to this work.

**Figure 1.** (a) Diameter and (b) chiral angle dependence of binding energies of a single Sc atom on SWNTs. Red lines are the linear fit of the energies. (c)−(e) show the optimized structure of Sc@(8,0), (6,2), and (4,4) SWNTs.
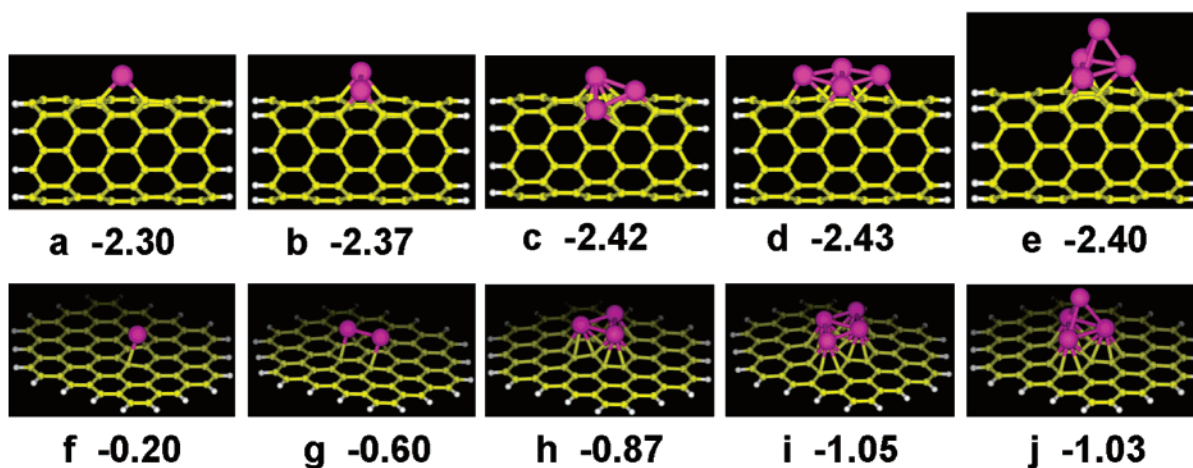


**Figure 2.** Optimized structures of the nanotube (8,0) with (a) one, (b) two, (c) three, and (d) and (e) four Sc atoms. The corresponding structures of graphene are shown in (f)−(j), respectively. The formation energies of the $Sc_n$ clusters are listed in electronvolts.

The SWNTs are modeled as clusters, by taking a tube section of ∼1.2 nm with all the dangling bonds on the tube ends terminated by hydrogen atoms (e.g., three samples shown in Figure 1c−e). To minimize the finite size effects, the Sc atoms were placed at the center of the SWNT segments. A polycyclic aromatic hydrocarbon cluster, $C_{66}H_{20}$, was used to model the graphene (Figure 2b). Due to the odd number of electrons on the Sc atoms, we performed spin-polarized calculations to obtain the correct magnetic ground state. The total spin of the systems in the ground state with one Sc atom is found to be $1/2$. The addition of Sc atoms further increases the total spin in the ground state according to the formula $1/2n$, where $n$ is the number of Sc atoms. We also calculated other spin states, which were found higher in energy.

For the aggregation of metals on the SWNTs the major driving force is metal−metal attraction. A stronger metal−SWNT interaction may compensate for this attraction, essentially preventing the aggregation. Therefore, the metal−SWNT interaction is critical for prohibiting the metal aggregation. A systematic study was performed to estimate the binding strength between a single Sc atom and the SWNT and its dependence on the diameter and chirality angle. A wide range of zigzag type SWNTs with diameters ranging from 0.31 to 0.78 nm [(*m*,

0), where $m = 4, 5, ..., 10$] and SWNTs with chirality angles from 0° to 30° [(*n*, 8 − *n*), where $n = 4, 5, ..., 8$]) were considered in this study.

Figure 1a shows the diameter dependence of binding energies of single Sc atom on zigzag nanotubes. It can be seen that the binding energy of a single Sc on small diameter SWNT is very strong (e.g., 3.37 eV on (4,0) SWNT) but decreases fast with increasing tube diameter (e.g., decrease to 1.83 eV on (10,0) SWNT). This is due to the decrease in chemical reactivity of the nanotubes with decreasing curvature. On the other hand the binding energy of a Sc atom on graphene, which represents a limiting case of large diameter SWNT, is only 0.2 eV. It is worth noticing that such a decrease in the binding energy with increasing diameter is not monotonous, e.g., in Figure 1a two peaks appear for (6,0) and (9,0) SWNTs, whose binding energies actually increase. This is not surprising, as unlike other nanotubes, which are semiconducting, these two nanotubes are metallic. A similar trend can be found in Figure 1b, where the binding energies of the two of the metallic SWNTs with chirality indexes (4,4) and (7,1) lie above the fitted line. Dependence of binding energy on chirality of the nanotubes can be seen from Figure 1b. Interestingly, going from (4,4)-armchair to (8,0)-zigzag SWNT, the binding energy increases by almost a factor

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of 2. A similar trend is also observed for the (5,5) and (10,0) tubes with the BE of the latter (1.87 eV) about twice that of the former (0.95 eV). These results clearly indicate that the zigzag SWNT bind Sc atom much stronger as compared with armchair SWNT of similar diameter.

Our results show a very strong dependence of binding energies on the diameter and chirality angle of SWNT. Although very small diameter SWNTs bind Sc atoms strongly, binding energy is very sensitive to the tube chirality angle and tube type and decreases fast with increasing SWNT diameter. For SWNTs of 1−2 nm, which is the typical diameter of experimental SWNTs, the binding energy should be significantly lower (e.g., less than 1.0 eV). Compared to the ∼3.90 eV/atom cohesive energy of Sc bulk,[18] such a binding energy is too weak to prevent the Sc atom aggregation.

As a next step we consider the interaction between the metal atoms by systematically studying the interactions of 1−4 Sc atoms on the surface of (8,0) SWNTs and graphene by computing the corresponding energies. The optimized structures are shown in Figure 2. The formation energy of the supported cluster $Sc_n$ is defined as

$$E(Sc_n) = [E(Sc_n@Support) - E(Support) - nE(Sc)]/n$$

where $E(Sc_n@SWNT)$, $E(support)$, and $E(Sc)$ are the total energies of the whole system, supporting material ((8,0) SWNT or graphene), and a single Sc atom, respectively. With increasing number of atoms (from $Sc_1$ to $Sc_4$), $E$ decreases very quickly (from −0.2 to −1.05 eV) on graphene but very slowly (from −2.3 to −2.43 eV) on the (8,0) SWNT, which implies that the isolated Sc atoms may be more stable on small SWNTs with diameters less than 0.6 nm but aggregation on large SWNTs is almost inevitable unless the supported Sc atoms are immobile. It is important to note that, on (8,0) SWNT, although the formation energy of $Sc_4$ is almost same as that of four isolated single Sc atoms, large Sc clusters may have much lower energy than the isolated Sc atoms due to the increase in the Sc−Sc coordination. An example of 12 Ti atoms aggregation on the $C_{60}$ surface was shown in ref 14.

We also find that the planar $Sc_4$ cluster is more stable than the 3D tetrahedral $Sc_4$ cluster both on SWNT and graphene (Figure 2d,e,i,j), which may indicate the possibility of wetting of SWNT by light transition metals (e.g., Sc or Ti) by formation of single transition metal layer on SWNT surface. Experimentally, also it has been observed that Ti atomic layers on the surface of SWNT are very stable.[19]

Considering most experimentally produced SWNTs have larger diameters than the (8,0) SWNT and Sc binds more weakly on larger SWNTs, the above calculation shows that the aggregation of Sc atoms on SWNT is energetically preferable. However, once these atoms are on the surface they must move toward each other to form the aggregate, this will involve overcoming the barriers on potential energy surfaces. An estimate of this mobility or the diffusion barrier of Sc atoms on SWNT could give a clearer picture on the possibility of the aggregation. Previous molecular dynamics simulation shows that isolated Sc atoms are quite stable on the $C_{60}$ surface up to the temperature of 1000 K.[5] However, the SWNT surface is different from $C_{60}$, where 12 isolated pentagons can bind 12 Sc atoms stronger. Here migration barriers of the Sc atom on the SWNT and graphene surface were calculated using the SQT2 method with the Gaussian03 package.[17] These calculations are computationally very expensive; therefore we considered two relatively small representative systems, which are two extreme cases of
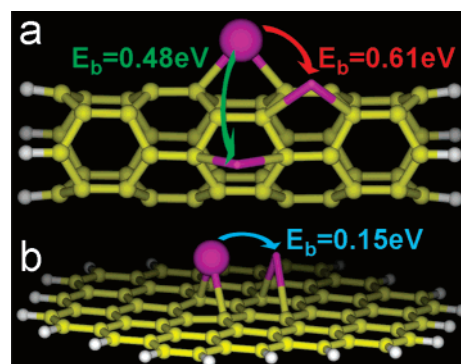


**Figure 3.** Possible paths and barrier of Sc diffusion along SWNT (4,0) (up) and graphene layer (down) and corresponding barriers.

not only curvature but also the binding strength of the Sc atom namely, (4,0) SWNT and graphene.

On the (4,0) nanotube there are two possible directions for the migration of the Sc atom: (i) along the circumference direction (from one 6-fold ring to the other across a carbon−carbon bond that is parallel to the tube axis as shown by green arrows in Figure 3a) and (ii) along the off-tube axis (shown by the red arrow in Figure 3a), with the corresponding barrier of 0.48 and 0.61 eV, respectively (for details of transition states see also Supporting Information Figures S1 and S2). However, on the graphene the migration barrier is only 0.15 eV (Figure 3b, also see Supporting Information Figure S3). Among all the SWNTs studied here (4,0) SWNT and graphene bind Sc atom most strongly and weakly, respectively; therefore we can conclude that the diffusion barrier, $E^*$, of a single Sc atom on larger diameter SWNT surfaces will be less than that on (4,0) SWNT and higher than that on graphene and will lie in the range 0.15−0.48 eV. We also estimated the diffusion frequencies of these two extreme cases at room temperature ($T = 298$ eV) using transition state theory:

$$f = 10^{13} \exp[-E^*/k_B T]$$

where $E^*$ is the diffusion barrier, $k_B$ is the Boltzmann constant, and $T$ is the temperature. The calculated diffusion frequency in this energy range is ∼$10^5$−$10^{10}$ s$^{-1}$, which is very fast implying that the single Sc atoms will be extremely mobile on both SWNT and graphene.

We can conclude from the above analysis that the Sc aggregation on SWNT is both energetically and kinetically probable. Irrespective of the initial configurations, the Sc atoms on SWNT will aggregate into clusters at ambient condition. Therefore the hydrogen uptake on the supported metal clusters is the key to determine the hydrogen storage capacity of the hybrid materials.

Besides physical and chemical adsorption, hydrogen molecules could also be adsorbed on the supported metal on the surface of CNTs via the so-called Kubas interaction. The Kubas interaction is in between physical binding and the chemical bond.[5,12,13] Because the normal DFT method cannot be used to describe the physical interaction (mostly Van der Waals type) correctly, the method used in this calculation should be tested for its appropriation for the Kubas interaction. To test the validity of the method, two small systems, a single Sc atom sitting on a cyclopentadiene cation ($C_5H_5$) and on a benzene molecule ($C_6H_6$), are studied with both B98/6-31G and MP2/6-31G** (see Supporting Information S4). Although the results from B98/6-31G are different from those calculated in ref 5, it is in very good agreement with those calculated by MP2/6-
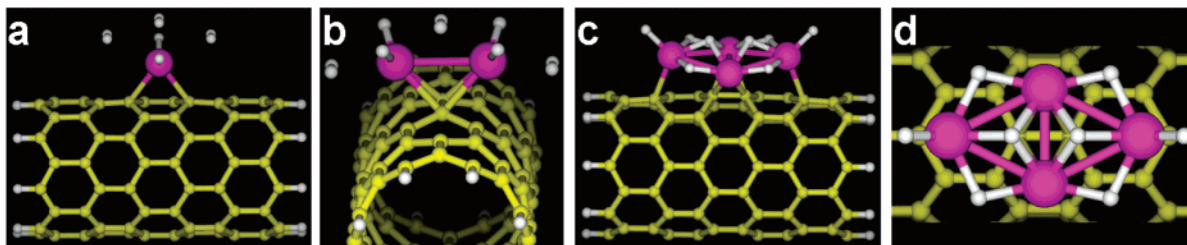
**Figure 4.** Hydrogen uptake on aggregated $Sc_n$ ($n = 1, 2, 4$) clusters on (8,0) SWNT. (d) is the top view of (c).

31G\*\*. These calculations are computationally very expensive; hence, we study the hydrogen uptake on only the (8,0) SWNT with single Sc atom and $Sc_n$ clusters with $n = 2$ and 4 on the surface.

The optimized structures of one, two, and four Sc atoms saturated with hydrogen on (8,0) SWNT are shown in Figure 4. Unlike the previous study,[5] where each metal atom could bind up to five $H_2$, our results (both by MP2/6-31G\*\* and B98/6-31G method) show that the maximum number of adsorbed $H_2$ on a single Sc atom is 4 (Figure 4a). The first two $H_2$ bind strongly (0.88, 0.11 eV, respectively) and the next two $H_2$ bind very weakly (0.03 and 0.04 eV, respectively) to the supported Sc atom. The addition of the second Sc atom to the neighboring six-member ring of the (8,0) nanotube cluster leads to metal−metal attraction, eventually decreasing the space available for $H_2$ molecules to be adsorbed. Figure 4b shows the saturated hydrogen uptake on a $Sc_2$ cluster, 2 of the 5 adsorbed hydrogen molecules are completely dissociated and another three $H_2$ are in nearly molecular form. Although the number of Sc atoms is doubled, the hydrogen uptake increases only 25% (from 4 to 5). It again shows the importance of having Sc atoms well separated to achieve higher weight percentage of adsorbed $H_2$ molecules.

The hydrogen uptake on a planar $Sc_4$ cluster is shown in Figure 4c,d. It is surprising that all the adsorbed hydrogens are dissociated into atomic form, which means the hydrogen interacted with the supported $Sc_4$ cluster via chemical bonds instead the Kubas interaction as for the interaction between hydrogen and a single metal atom or Sc dimer. After the uptake of 4 $H_2$, the Sc cluster cannot take any more hydrogen because the chemically adsorbed H layer shields the cluster from taking any more $H_2$ (Figure 4d). The eight H atoms bind tightly to the $Sc_4$ cluster with an average binding strength of 0.74 eV/H (in excess to the binding in molecular $H_2$). The strong binding of the chemically dissociated hydrogen indicates its chemisorption on the metal "surface" and is not suitable for hydrogen storage, as desorption would be very difficult. We observe that, in addition to important and detrimental reduction of steric accessibility of metal caused by clustering,[14] the latter also changes the nature of binding from easily reversible Kubas type to rather strong dissociative mode, as one could expect on increasingly larger metal catalyst particle.

In summary, our results show that metal decorated SWNTs are good candidate for the hydrogen storage material only if the metal atom aggregation can be prevented efficiently (e.g., on very small SWNT surface). However, due to lower migration barriers and the strong metal−metal attraction, aggregation of metal atoms in the form of a metallic layer or clusters on typical experimental SWNT (diameter of 1−2 nm) seems inevitable. The hydrogen storage capacity of these metallic layers and clusters is very poor due to the transition from Kubas interaction to chemical bonds and is not suitable for hydrogen storage.

Therefore, experimentally great care is required during the growth of these materials to ensure the proper separation between and anchoring of the metal atoms. Possibly, the heptagons inevitably present in the zeolite-like carbon foams[20,21] may help immobilizing the metal atoms.

**Supporting Information Available:** Detailed information (figures) about the Sc atom diffusion barrier in (4,0) SWNT and graphene and hydrogen uptake on single Sc atom supported on cyclopentadiene-cation (Cp) b) and benzene molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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