Theoretical Simulation of Deformed Carbon Nanotubes with Adsorbed Metal Atoms: Enhanced Reactivity by Deformation

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Abstract

Simulations adopting the generalized gradient approximation in the density functional theory were performed to investigate the reaction of carbon nanotubes with adsorbed metal atoms. Mechanical modification of the structure of carbon nanotubes enhances their chemical reactivity. Adsorption of W, Ta, or Nb on a (5,0) nanotube with a Stone–Wales defect was shown to have characteristically strong chemisorption. Bond-breaking in the C–C network and formation of a local metal–carbon complex were observed during the simulation. The adsorption of W, Ta, Nb, or Mo on a twisted (5,0) nanotube showed a preferred breaking of several bonds, even creating an opening in the wall. The enhanced chemical reactivity of deformed nanotubes is characterized by the formation of a metal–carbon complex. Applications of the reaction are suggested.

1. Introduction

Investigating the chemical nature of carbon nanotubes, especially the reactivity against metal species, is important for understanding the physical properties of nanotubes. When carbon nanotubes are placed in an environment with metallic elements, C atoms can react with metal atoms. This environment is found in various situations. In the catalyzed synthesis of nanotubes, the formation of metal–carbon complexes is known to be essential. Once the nanotube synthesis of nanotubes, the formation of metal–carbon complexes is found in various situations. In the catalyzed reaction, metallic elements, C atoms can react with metal atoms. This reaction is the temperature effect, by which the tube walls are disturbed and become reactive. Another is local deformation of a metal on the wall of a carbon nanotube at an interface has been studied by both experimental and theoretical approaches. The selection of metal elements is key to controlling the reaction. This important issue has been under considerable discussion.

Generally, when a theoretical simulation is applied, the reactivity of a metal atom on a pristine carbon nanotube with a perfect wall does not always appear reactive. In contrast, real experiments often show high reactivity. One reason is the temperature effect, by which the tube walls are disturbed and become reactive. Another is local deformation from a perfect wall. Insertion of defects and creation of strained structures are typical examples of local deformation. The origin of the enhancement of chemical reactivity can be investigated effectively by employing microscopic simulation of deformed nanotubes. This idea has been utilized in the above-mentioned studies. If we further add information on the chemical trends of elements, we should be able to open a new avenue for research.

In this study, we focus on the chemical reactivity of specified nanotubes with metal atoms. We selected a pristine (5,0) tube as a starting point for our discussion. Comparison among late transition elements shows that W and Ta could exhibit reactivity qualitatively different from those of other elements. To investigate this hypothesis, we considered deformed nanotubes. One is a tube with a Stone–Wales defect (SWD). The other is a twisted tube, prepared by employing a computer simulation. Certain late transition elements behave differently from the noble metal elements in reactivity on deformed nanotubes. We will focus on the formation of metal–carbon complexes to understand this chemical trend.

2. Calculation Conditions

To determine the high chemical reactivity in mechanically deformed nanotubes, we performed an electronic structure calculation of the nanotube using methods in density functional theory. We searched for enhanced reactivity in simulations to optimize the atomic structure of a metal-adsorbed nanotube. To determine this optimized structure, we applied the Born–Oppenheimer dynamics realized in the Quantum Espresso package. A generalized-gradient approximation (GGA) was applied for the description of the exchange–correlation energy functional, and each ionic pseudopotential was given by the ultrasoft pseudopotential.

The major parameters in the simulation are summarized here. The energy cut-off $E_c$ in the plane-wave expansion for the wave function is 20 Ry or higher. The $k$-mesh size is $1 \times 1 \times 10$ for all simulation cells with the $z$-direction parallel to the tube axis. A criterion to stop the simulation is to check for convergence when the total absolute value of the interatomic force becomes less than $F_z = 1.0 \times 10^{-4}$ Ry/a.u. The length of a nanotube was optimized by finding the energy minimum with respect to the simulation cell size along the tube axis.

3. Preparation of Defects and Deformation of the Nanotube

The defects of carbon nanotubes may be classified into three categories: i) topological defects, ii) rehybridization defects, and iii) incomplete bonding. Among these defects, the SWD attracts much attention. Carbon atom motion to form an SWD has been observed, demonstrating that the defect exists in real nanotubes. Strain release and bending deformation are often explained as being the results of the formation of an SWD because an SWD may create an essential dislocation center in the tube wall. Thus the topological defect is relevant when we consider the mechanical deformation of tubes.

These defects or defective sites modify the electronic structure of the carbon nanotube. As shown in the
previous studies, the electronic states around the Fermi level are modified by the defects. Thus, the existence of defects may change the chemical reactivity of the nanotube.\textsuperscript{37,38}

Mechanical modification, which can induce defect formation, can also influence the chemical properties of the carbon nanotubes. Mechanical deformation is especially interesting because of the morphological flexibility of the nanotube when subjected to external stresses.\textsuperscript{39,40} Many characteristic mechanical properties are known to originate from special defects formed by non-six-membered rings in a nanotube.

Thus we consider a nanotube with an SWD and a twisted nanotube. Furthermore, we focus on thin tubes, e.g., the (5,0) nanotube, with enhanced reactivity. Enhancement is expected for thinner tubes rather than thicker tubes, as discussed by Seo et al. for NO\textsubscript{2} adsorption.\textsuperscript{41} The (5,0) tube is known to be metallic.\textsuperscript{32} On the (5,0) nanotube wall, we attach metal atoms. We consider the chemical reactivity by determining the chemical trend and then finding a method of enhancing the reactivity.

We prepare an optimized carbon nanotube with 40 C atoms prepared in a supercell of $15 \times 15 \times 8.5\, \text{Å}^3$. To obtain a tube with defects, we use another cell of size $12.3 \times 12.3 \times 12.8\, \text{Å}^3$, which contains 60 C atoms. The value of 12.8 Å is obtained by finding the energy minimum of the pristine (5,0) tube. In this cell, a tube with a Stone–Wales transformation is also prepared and the structure is optimized. Note that there are two possible defect structures with a Stone–Wales transformation per unit cell of the (5,0) tube. We considered a stable structure obtained by rotating a zigzag CC bond to create two 5-membered rings and two 7-membered rings. This structure is energetically lower by 0.25 eV per C atom than the other obtained by rotating the axial CC bond. The optimum value of the cell along the tube axis becomes 12.9 Å, which indicates that the tube with an SWD becomes slightly longer than the pristine tube. The total energy of the nanotube with an SWD is higher than the pristine (5,0) tube by 0.056 eV per C atom. This value is consistent with the known creation energy of a single SWD, which is around 3–5.5 eV.\textsuperscript{33,46}

A twisted (5,0) tube is also prepared using this supercell with 60 C atoms. To determine the twisted structure, an initial configuration of C atoms is given by rotating atomic positions around the tube axis. The rotating angle of each carbon ring around the axis is determined so that a twisted structure is created. By applying structural optimization, a twisted nanotube is obtained. The tube axis again becomes longer and the optimum value of the cell along the tube axis becomes 13.0 Å. The structure obtained has a small flattened section, whose deformation pattern is similar to those found in a former study.\textsuperscript{40} The obtained structure has a total energy of 0.43 eV per C atom, higher than that of the pristine (5,0) tube.

### 4. Single Atom Adsorption on a Pristine (5,0) Nanotube

We considered adsorption sites for various atoms on a pristine (5,0) tube (see Fig. 1). A supercell with 40 C atoms was used. Simulations were initially performed to check the accuracy of the calculation. When our results for adsorption of metal atoms on the (5,0) tube are compared with respect to chemical tendency, stability of adsorption sites and reactivity, there does exist a small difference from those of thicker tubes available in earlier studies. In this work, 25 elements, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Ta, W, Re, Os, Pt, and Au, were tested.

The adsorption sites were almost the same as those found for the (8,0) tube.\textsuperscript{8} Although we performed only spin-unpolarized calculations for each structural optimization for the first test, we concluded that our simulation results preserved reasonable accuracy. Differences in adsorption sites were found for Co, Cu, Ag, and Zn. The stable sites were the H site for Co and the A site for Cu and Ag. However, we could not find any stable site for Zn on the (5,0) tube. The H site is a hollow site just above the center of a hexagon and the A site sits above an axial C–C (CC) bond. In a previous study by Durgun et al.,\textsuperscript{8} Co and Zn preferred the H site and Cu and Ag went to the A site on the (8,0) tube. Although the difference in the stable adsorption site is interesting in itself, we also looked for a better manifestation of qualitative differences in the reactivity among elements.

For 10 selected elements (Ca, Sc, Ti, Fe, Cu, Mo, Ta, W, Pt, and Au), we increased $E_c$ to 30 Ry and performed a convergence check, which resulted in a small shift in atomic positions for most of the calculations. The convergence criterion for the inter-atomic force was $1.0 \times 10^{-4}\, \text{Ry}/\text{a.u.}$, but when a W adsorbed (5,0) tube was optimized carefully, the obtained atomic configuration showed a chemisorbed structure with extraordinary characteristics. In Fig. 2, the obtained (5,0) tube with W is shown. The atomic position of W shifts from the center of the hexagon, four C atoms move towards the W atom, several chemical bonds in the tube wall are significantly modified, and two CC bonds are significantly weakened. Similar rebonding was also seen in a Ta-adsorbed (5,0) tube. The elongated bond length of the CC bond just around the adsorbed metal was 2.57 and 1.63 Å for W and Ta, respectively. A clear shift in the adsorbed metal atom from the symmetric H site to a site surrounded by four C atoms was also seen for Mo and Fe.

We may consider the curious chemisorption as a specific feature of the (5,0) tube. The calculation condition of the spin-unpolarized approximation might lead to a difference from the spin-polarized solution. The spin-polarized GGA recalculation of the (5,0) tube with a W atom did not show similar strong bond cuttings, although a shift of the adsorption site from the H site was seen. In the case of W
adsorption on a (5,5) tube, the W atom went to the H site and we found no clear sign of bond breaking. However, the above strong chemical rebonding found in the simulation of a thin (5,0) tube with W is the first evidence of possible strong chemical reactivity of metal atoms on active nanotube walls. Subsequently, we considered enhancing the reactivity of the tube wall by inserting defects and by mechanical modification.

5. Adsorption on a Tube with a Stone–Wales Defect

We can see further evidence that some transition metal elements react strongly with a tube wall. The adsorption of W atoms was thereafter investigated using a nanotube with an SWD. The W atom was initially placed 3 Å above the tube around a seven-membered ring. The optimized structure again showed the formation of a tungsten–carbon complex. The inter-atomic distances are summarized in Table I. The CC bonds lengthened around the adsorbed site. The same tendency is found for Nb and Ta. The mean distance from an adsorbed metal atom to C atoms is denoted by CM. The adsorbed atom is located around this seven-membered ring. The mean distance from an adsorbed metal atom to C atoms is denoted by CM.

To confirm the difference in the electronic structure between W-adsorption and Pt-adsorption, we obtained the Kohn-Sham band structure of metal-adsorbed (5,0) nanotubes with SWDs. In Fig. 3, we show the three band structures. Compared with the SWD. In Fig. 3, we show the three band structures. In (b), the isosurface of the charge distribution is overlaid. In (c), the isosurface of the charge distribution is overlaid.

| Metal | CC1 | CC2 | CM  |
|-------|-----|-----|-----|
| None  | 1.465 | 1.458 | —   |
| Nb    | 2.638 | 3.013 | 2.171 |
| Mo    | 1.564 | 1.603 | 2.211 |
| Ta    | 2.663 | 3.091 | 2.148 |
| W     | 2.619 | 3.020 | 2.108 |
| Pt    | 1.487 | 1.520 | 2.159 |
| Au    | 1.505 | 1.453 | 2.139 |

6. Adsorption on a Twisted Nanotube

The enhancement of the reactivity of a tube wall is more clearly seen if we consider a twisted nanotube. In Fig. 4(b), we show an optimized structure obtained by adsorption of a W atom on a twisted (5,0) nanotube. We also show the initial twisted tube in Fig. 4(a), which was obtained by the method explained in §3. A large shift of the C atoms is evident, as well as a breakage in the tube wall. In this process, the valence charge density is completely redistributed. As clearly seen in Fig. 4, several CC bonds are broken.

In Table II, we summarize the adsorption energy of a metal on various nanotubes considered in this study. Considering the adsorption energy on the twisted nanotube,
In this study, the effects of single-metal adsorption on deformed nanotubes were investigated. The reactivity of the tube wall was shown to be high for W, Ta, and Nb. These late transition-metal elements with 5d or 4d electrons have rather high electron affinity, but when Pt or Au, which have comparable high affinity, are adsorbed, a similar reaction was not observed, even when deformed tube walls were considered. The origin of the chemical trend is thus the formation of metal–carbon complexes found for transition-metal elements.

We have shown clear differences between the examined transition-metal elements and noble metals, and hence,
global chemical trends on the reactivity have been concluded. Our simulations show that when W, Ta, or Nb atoms are adsorbed on a deformed tube, the adsorbed atoms go to defect sites where a metal–carbon complex is easily created. We have also considered a twisted nanotube. The reaction with these transition-metal atoms is greatly enhanced when a deformed tube is used. The opening of a big breakage is observed in simulation results. Again, the creation of a local metal–carbon complex is a trigger for this remarkable reaction. This enhancement by mechanical modification is expected even for thicker nanotubes. The interesting phenomena observed in our simulations demonstrate that we can expect enhanced reactions in the following applications.

**Identifier of SWD**

The position of an SWD can be detected by stable adsorbrates, i.e., W, Nb, or Ta atoms, at the defect sites. Direct observation is possible by electron microscopy or STM, as well as measurements using local probes.

**Nanotube cutter**

In a solution, W, Nb, or Ta ions can be easily prepared by, for example, Suzuki–Miyaura cross-coupling catalysts. 47 When torsion is applied to a nanotube, the tube wall can be broken. Thus, the catalytic molecule can be used as a nanotube cutter. We can use nanotubes in a bundle. It would be much easier to twist a bundle than to create torsion in a tube.

**Creation of nanographene**

After the breakage of a tube wall occurs, a solution can be changed into a stronger reducing environment by the addition of hydrogen. The complex structure in the metal-adsorbed nanotube might be hydrogenated. At the same time, the adsorbed metal atom may be reduced and released from the carbon structure. We will then have an opened nanocarbon structure, produced from the closed nanotube. The broken wall of the tube will produce graphene flakes. A possible advantage of this method is the mass production of selected nanographene structures. 48,49 if nanotubes with a single chirality could be obtained.

**Test of mechanical strength of a tube**

The above redox process could be an experimental method of testing the mechanical stability of a nanotube by finding products and measuring the rate of reactions.

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