Supporting information for : First principles studies of the effect of nickel carbide catalyst composition on carbon nanotube growth

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It should be realised that the systems studied are model systems which do not aim at mimicking the experimental conditions during a particular instant of CNT growth but rather to pinpoint some crucial situations which are related to CNT growth. The complexity of these model systems, containing amorphous and carbidic clusters as well as different carbon allotropes, puts very high requirements on the transferability of the potential energy surface used during the calculation. One is therefore forced to choose between the accuracy of DFT and the flexibility and speed of less sophisticated potential energy surfaces. As the starting point, the results from DFT calculations are presented with the expectation of future dynamical studies and with the reservation that the models are based on the author's logic and pre-understanding of CNT growth and contacting with electrodes.

Details of the input structures

All atomic configurations in this contribution consist of a CNT attached to either a pure Ni or a Ni-carbide cluster and examples of starting configurations with pure and carbide Ni clusters attached to a $(10, 0)$ CNT are seen in Fig. 1. For most of the systems, several different starting configurations were prepared and the results presented in the paper consequently originate from the most stable structure.

Four different CNT chiralities, $(3, 3)$, $(5, 5)$, $(9, 1)$ and $(10, 0)$, were used in the study. The end of the CNT that is not attached to the catalyst particle was always deactivated, either by a ring of H atoms (for $(3, 3)$) or by a cap (for $(5, 5)$, $(9, 1)$ and $(10, 0)$). The $(3, 3)$ CNT contained either 30 or 36 C atoms while the larger CNTs contained between 60 or 80 C atoms.

The approximate lengths of the CNTs were between 5.4 and 8.5 Å which was expected to be sufficiently long to ensure that the qualitative properties at the end are not affected by the passivated end. To verify this, a few calculations were performed for capped $(5, 5)$ CNTs of lengths 6.4Å, 8.8Å, 11.2Å, i.e., having 2, 3 and 4 armchair rings in addition to the cap, attached to icosahedral Ni_{55} clusters. The adhesion energies between the CNTs and the clusters were approximately 1.63 eV/atom, 1.62 eV/atom and 1.68 eV/atom for the CNTs respectively, when given per C atom at the CNT end. This indicate that even the shortest CNT should be sufficient long to capture qualitative results. This is in agreement with the results presented in Ref. [1], stating that a zig-zag CNT attached to a metal ring should

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have a difference in adhesion energy to the ring of less then 0.1 eV/atom for systems with 2 and 3 zig-zag C rings in addition to the passivation.

The longer CNTs, having either 36 or 80 C atoms, were attached to Ni clusters containing 13 Ni atoms (for $((3,3))$) or 55 Ni atoms (for the other CNTs). The size of the Ni clusters were chosen in order for the cluster to have a slightly larger diameter than the CNTs they were attached to.

The pure Ni clusters had the icosahedral shape with the exception for a reference system containing an amorphous (non-icosahedral) Ni_{55} cluster. This cluster was used to identify possible effects due to the icosahedral geometry of the cluster. Since an amorphous cluster can be created in many ways, the result of the geometry optimisation of systems with amorphous clusters may be sensitive to the starting configuration. To reduce this effect 5 different amorphous clusters were prepared and relaxed. The energy difference between most stable and least stable of these clusters were slightly less than 1.5 eV. The amorphous clusters were created by random positioning of Ni atoms with an appropriate (≈ 2.2Å) interatomic distance. The structures were then relaxed with using an empirical force field, parameterised to reproduce this bonding distance and an optimal bonding distance between C and Ni of 2.0 Å. The bonding energy between C and Ni was chosen to be significantly lower than the Ni-Ni bonding strength in order to favour the formation of a Ni cluster instead of wetting of the C structure. This choice of parameters was motivated by the results presented in Ref. [2] and the use of this relaxation procedure was motivated high potential energies of random structures when used as starting configurations for VASP.

The shorter CNTs, having 30 or 60 C atoms, were attached to Ni-carbides with concentrations $Ni_{13}C_6$ and $Ni_{55}C_{20}$, respectively. The visual appearance of a CNT attached to pure metal and carbide clusters can be seen from Fig. 1 although the structures shown in this figure have been subjected to the more rigorous optimisation process described below.

It should be stressed that the above mentioned dissolution of either 6 or 20 C atoms corresponds to the removal of an integer number rings form the CNT end, i.e., the pure metal clusters and carbide clusters are attached to CNT ends with the same geometry, although the lengths of the CNTs differ. For each CNT chirality the total number of C and Ni atoms were held constant independently of whether the CNTs were attached to pure metal or carbide clusters. Furthermore, the number of C and Ni atoms were held constant, to 80 C and 55 Ni, for the chiralities $(5,5)$, $(9,1)$ and $(10,0)$. This allows for a direct

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comparison of total energies obtained for CNTs of these chiralities attached to both pure metal and carbide clusters.

For the systems with $(5,5)$, $(9,1)$ and $(10,0)$ CNTs attached to $Ni_{55}C_{20}$ clusters four different carbide clusters were created. These clusters were created by two different procedures. In the first procedure, the C atoms were positioned below the first Ni layer of an icosahedral Ni cluster as the subsurface position has been suggested as the lowest energy position for C atoms on Ni slabs and clusters[3–5]. In the second procedure, a cluster was created by random positioning of 75 atoms. By random, 55 of these were chosen to be Ni atoms and 20 were chosen to be C atoms.

For both preparation procedures, care was taken when placing C atoms in order to ensure that the C atoms were evenly distributed and that the interatomic distances, both Ni-C and C-C, were not unreasonably small.

The CNT was placed "by hand" on the cluster surface. Once again the relaxation procedure described above was employed order to avoid unreasonably high potential energies.

Despite the efforts made to reduce the stress (high potential energies) in the initial carbide and amorphous structures, they are not likely to be in a minimum energy structure. These structures were therefore quickly relaxed using either a tight-binding Monte Carlo method, previously used in Refs. [2, 4, 5], or VASP. The final structures obtained from these relaxation procedures were used as starting structures for a $\approx$ 1-2 ps long molecular dynamics (MD) simulation using VASP with low accuracy (spin restricted, low PW energy cutoff, etc.). The aim of these MD simulations were to allow the atomic system to leave the highlands of the energy landscape in favour for lower energy regions. This preparation process is expected to allow the system to relax to geometries which are more relevant to the experimental situations of CNT growth and docking of Ni (carbides) onto open CNT ends.

The final configurations from the MD simulations were used as the starting configurations for the high accuracy structural optimisations using the parameters discussed in the Paper.

The data presented in the Paper originate from the most stable system obtained for each CNT chirality, with the only constraint was that no new C polygons were formed in association with the CNT. This was avoided since this can be expected to introduce energetical effects that are not included in the study.

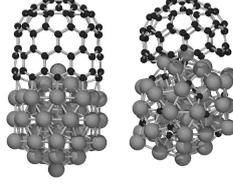The adhesion energies between the CNT and Ni(carbide) were calculated as the energy

FIG. 1: Typical starting configurations with a Ni_{55} cluster attached to a $(10,0)$ CNT (left) and a $Ni_{55}Ni_{20}$ cluster attached to a $(10,0)$ CNT (right).

difference between the CNT-cluster system and the individual components, i.e. the CNT and the cluster particle. For the data presented, the energies of the CNT and the cluster particle were calculated independently of the CNT-cluster system, i.e. the CNT had never been attached to the cluster particle. Some tests were done by first relaxing the $CNT_{80-X}Ni_{55}C_X$ and then detaching the structure and relaxing the individual parts again in order to obtain energies $E_{CNT_{80-X}}$ and $E_{Ni_{55}C_X}$. Typically, both the CNTs and metal clusters were more prone to end up in lower energy structures when relaxed independently of each other. For this reason, independent relaxation was chosen for all calculations despite the substantial increase in the time required for the calculations.

Finally, it should be noted that these structures, and especially the systems containing a Ni carbide, have a very complicated geometry and are associated with an equally complicated energy landscape. This means that the calculated energies of the relaxed structures may be very sensitive to the starting conditions. What can be concluded is that neither the $CNT_{80-X}Ni_{55}C_X$ nor the $Ni_{55}C_X$ system is more likely to end up in a better minimum energy structure than the other, i.e., sometimes $CNT_{80-X}Ni_{55}C_X$ is in the lowest position and sometimes $Ni_{55}C_X$ is in the lowest state. This means that one has to be very careful when drawing conclusions based only one set of calculations, e.g., for only one chirality, and conclusions based on small energy differences. However, conclusions can be drawn from the general trends exhibited by the many calculated systems. The results reported in this contribution should hence be understood and treated as trends rather than exact numbers and in no case has the ambition been to present any exact quantitative results.

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