Do Nickel and Iron catalyst nanoparticles affect the mechanical strength of carbon nanotubes?

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ABSTRACT

The growth of carbon nanotubes (CNTs) is strongly mediated by the interaction between Carbon atoms and catalyst nanoparticles, in particular in processes like chemical vapor deposition or floating method. However, the effects these nanoparticles on the mechanical strength of the grown CNTs have remained elusive. Using molecular dynamics dynamic simulations via ReaxFF force fields, the interactions between defect-free single wall CNTs and a series of Nickel (Ni) and Iron (Fe) nanoparticles (NPs) are studied. Pure metal NPs significantly reduce the strength of the CNTs whereas oxidized NPs have more limited detrimental effects. For the same Oxygen content, we also observe that the Fe oxide NPs weaken C–C bonds, i.e. CNTs grown in the presence of Ni particles have higher mechanical strength comparing to those obtained from Fe-based nanoparticles. An analysis of the formation and dissociation of chemical bonds between the C, O, Ni and Fe atoms together with the stress analysis during tensile tests also enable us to elucidate the role of the NPs on the failure mechanisms. The C–C bonds interacting directly with Ni atoms are weakened and therefore control the failure of the CNTs. Surprisingly, the failure of the same CNTs in contact with Fe nanoparticles is driven by the weakening of C–C bonds not directly bonded to Fe atoms.

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1. Introduction

Nowadays, carbon nanotubes (CNTs) are embedded in materials in various forms including individual nanofilaments [1–4], aerogels [5], fibers [6,7], grafted [8] or deposited [9] on solid substrates with the objective to improve properties of the matrix and/or fibrous reinforcements they are combined with. Organic polymers [10–13] are probably the family of materials which mostly benefited from the intensive use of these nanoparticles with significant improvements of thermal, electrical, and mechanical properties [11,14,15]. This trend is, however, less obvious when fiber reinforced polymer composites are targeted. Lab scale experiments incorporating CNTs dispersed in the matrix, deposited around the fibers, or directly grown on the fibers did outline the positive effects of the nano-reinforcements. Upscaling these processes remains, however, challenging [16–18]. From this perspective, the continuous fabrication of CNT aerogels based on the "Cambridge process" [5] which can afterward be transformed into fibers (or veils) is one of the most promising approaches to a production of 10–30 m/min [19].

The most extensively used method to synthesize CNTs is the chemical vapor deposition (CVD) process [20,21] where the catalytic chemical activity of transition metal nanoparticles (NPs) (mostly) deposited on a support promotes the dissociation–diffusion–precipitation mechanism [22,23]. In this mechanism, the carbon source, mostly in the vapor phase, is first dissociated by metal NPs and the produced carbon atoms dissolve in NPs and finally precipitate to form CNTs. The floating method applied by the Cambridge group relies on the same basic principle except that the CNTs are grown from Fe NPs injected in a solution and "float" in the reactor chamber [5]. The solvent acts as the carbon feedstock.

Regardless of their final form, CVD grown CNTs are mostly obtained from a catalyst metal particle acting as a seed [24]. The most commonly used NPs are composed of transition metals usually Ni , Fe, or Co as well as their oxides and alloys. A low and high adhesion between the substrate and the NP leads respectively to a top-growth mode, i.e. the particle is at the top of the CNTs, and to a bottom-growth mode with a particle positioned on the substrate Depending on the precise growth conditions, intermediate configurations are also possible with (part of) particles located in the tube. The oxidation state of these particles is not exactly known for their active participation in the CNT growth, especially because the highly reducing environment of the CVD reactor promotes the transformation of metal oxide NPs into pure metal NPs [25]. This

transformation strongly depends on the substrate used [26] as well as the size and the initial oxidation state of NPs.

Generally, NPs are used at a high concentration to favor high yield. Therefore, concentrations of these residual particles in the final CNT material is non-negligible and can amount as high as 30 wt.% for the wide-spread HiPco single-wall CNTs [25] or 12 wt% for the floating method [13]. These particles are considered as impurities as they impede the intrinsic electrical and thermal properties of the CNTs. Multiple procedures based on oxidative chemical or physical treatments like ultra-sonication or centrifugation have then been proposed to purify these CNTs, but they remain complicated, un-scalable and can even be detrimental to the CNTs [27–30]. However, to the authors' knowledge, there is very little known about the effects of these particles on the mechanical properties of the CNTs. This work aims to address this issue.

Numerous experimental [31–33] and modeling [34–46] works have been conducted so far almost exclusively without the presence of NPs. A few experimental [47,48] and theoretical investigations [49–59] confirm that Ni and Fe catalyst NPs strongly interact with the structure of CNTs especially when walls are weakened by the presence of vacancies. Increasing the distance between covalently bonded C atoms is an alternative way to weaken them, for example, by imposing a strain along the main direction of the tube. In other words, loading defect-free CNTs in the presence of catalyst NPs would indirectly quantify the detrimental effects of the NPs on their mechanical properties.

In conclusion, even though catalyst NPs are indispensable to grow CNTs, only a few atomistic scale observations and quantum chemical calculations have indicated potential modifications of the graphitic structure due to the strong interactions between metal and C atoms. A logical follow-up question concerns the effect of these particles, especially Ni- and Fe-based, on the mechanical performances of the CNTs. Therefore, as a first step, reactive MD simulations predicting the behaviors of 5,5 SWCNTs loaded along the tube direction while in contact with Ni and Fe NPs with different oxidation states have been performed. It was observed that the strength of the CNTs is significantly reduced compared to pristine tubes when pure metal NPs are considered. This detrimental effect was reduced by increasing the oxidation level of the NPs. A detailed analysis of the bond strength between the C, O, Ni and Fe atoms and a stress analysis shed lights on the failure mechanisms and demonstrated that the two types of metal atoms do not weaken the C–C bonds prematurely in the same way even though the stress–strain curves look similar.

2. Simulations and methods

The ReaxFF parameter sets used hereafter combines the latest version of the ReaxFFC-2013 parameter set by Srinivasan et al. [60] and the ones developed by Zou et al. [61] to model the interactions between Ni and O atoms. This potential is an extension of the previously published parameters by Mueller et al. [62] for Ni/C/H/O interaction which was trained based on the quantum dataset comprising equation of states (EOS), the heat of formation for Ni and NiC, the binding energies of hydrocarbons on various Ni crystal surfaces, and the binding characteristics of Ni to hydrocarbon fragments. The Ni/O parameters were derived from EOS for Ni and NiO and vacancy formation energy in Ni crystals. This force field has been widely used for modeling of CNT/Graphene and metal/metal oxide nanoparticle interactions [63,64]. Additionally, C/Fe/O ReaxFF description was acquired by updating the C parameters in the previously developed potential parameters by Shin et al. [65–67].

The model systems are composed of an NP positioned in between 2 CNTs (145 Å in length). The distance between the NP and the tubes was fixed to 2 Åto make sure the NP interacts right

from the beginning of the simulation with the tubes (Fig. 1). A larger distance does not guarantee that the NP stays close to the tubes. It is different from the top, and bottom growth modes as the NP is outside the tube and not inside. This configuration was however chosen as the curvatures of the tubes, and the NP do not match, i.e., it is more difficult for the metal atoms to bond to C atoms. Following the same idea, defect-free 5,5 CNTs were considered, lowering the interactions between the two elements. Such geometry should, therefore, limit the effect of the NP, i.e., all other configurations (presence of vacancies, zig-zag CNT, NP inside the CNT) should show a more pronounced effect. These systems are simplistic, but they contain all the basic ingredients to describe the details of the interactions between the NPs and the CNTs.

To construct the initial structures of both Fe- and Ni-oxide NPs, a hybrid Grand Canonical-Monte Carlo (GC-MC) and MD simulation were utilized. Before the oxidation steps, the pure NPs were equilibrated at room temperature ($\sim$300 K). Then, the O atoms were inserted into the NPs under $\mu VTN_{Ni/Fe}$ ensemble, with the constant chemical potential of oxygen (μ_{O2}), volume (V), Temperature (T) and some iron or nickel atoms ($N_{Ni/Fe}$). The chemical potential of O atoms was determined based on the free energy of fictitious reservoir of O_2 with 300 K temperature and $P_{O2} = 10^{-4}$ atm. During the MC trials, O atoms can be randomly inserted into, extracted from or moved into the NPs structure. The potential energy of the system after each MC trial moves is minimized using conjugate gradient (CG) method with a convergence criterion of 0.5 kcal/mol. After every 20 successful GC-MC iterations, subsequent MD runs with 10 ps under isobaric–isothermal condition (NPT) at 300 K temperature and 0.1 MPa pressure were performed to well equilibrate the oxidized NPs. Four Fe-based and three Ni-based particles, namely Fe, Fe_2O, FeO, and Fe_2O_3 and Ni, Ni_2O, and NiO were respectively constructed. The particles were made large enough (between 4.3 Å and 7.7 Å in radius for respectively the Ni and Fe_2O_3 NPs) to avoid the interactions between the tubes and include Ni or Fe atoms not bonded to C atoms. It makes it possible to quantify, during the simulations, the effect of the formation of Fe–C or Ni–C bonds on the Fe–Fe and Fe–O (or on Ni–Ni and Ni–O) bonds.

The tubes were loaded by imposing a constant velocity on the C atoms positioned at the extreme ends of the tubes. A strain rate of 0.2 ns^{-1} was selected based on the criteria defined by Jensen et al. [68] and Mortazavi et al. [69–71]. The first series of simulations were performed with a time step of 1 fs. Each of these simulations was then restarted at three moderate strains (0.08, 0.10, 0.12) with a time step of 0.5 fs [68] slightly changing the distribution of the initial atom velocities. It is important to repeat the simulations, mimicking an experimental procedure, as failures of the tubes occur catastrophically when a few initial C–C bonds are stretched beyond their maximum length. Small numerical fluctuations might, however, lead to a premature cleavage of the bonds and consequently to bias estimations of the stress and strain at failure. With a minimum of 6 tested tubes per NP, the consistency of the results could be checked and standard errors calculated. The LAMMPS [72] software was used to predict positions, velocities, stresses, and strains in the NVT ensemble using a Nose–Hoover thermostat at 300 K. The stresses were obtained via the stress/atom LAMMPS keyword, and the nanotube wall thickness was fixed to 0.34 nm.

3. Results and discussions

The results focus first on the prediction of strain–stress curves from which stress and strain at failure can be extracted and the effect of the NPs quantified (Section 3.1). The failure mechanisms are then unraveled by scrutinizing how NP interacts with the nanotubes via a detailed analysis of the bonds formed (bond orders,