Pressure-driven opening of carbon nanotubes

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The closing and opening of carbon nanotubes (CNTs) is essential for their applications in nanoscale chemistry and biology. We report reactive molecular dynamics simulations of CNT opening triggered by internal pressure of encapsulated gas molecules. Confined argon generates 4000 bars of pressure inside capped CNT and lowers the opening temperature by 200 K. Chemical interactions greatly enhance the efficiency of CNT opening: fluorine-filled CNTs open by fluorination of carbon bonds at temperature and pressure that are 700 K and 1000 bar lower than for argon-filled CNTs. Moreover, pressure induced CNT opening by confined gases leaves the CNT cylinders intact and removes only the fullerene caps, while the empty CNT decomposes completely. In practice, the increase in pressure can be achieved by near-infrared light, which penetrates through water and biological tissues and is absorbed by CNTs, resulting in rapid local heating. Spanning over a thousand of bars and Kelvin, the reactive and non-reactive scenarios of CNT opening represent extreme cases and allow for a broad experimental control over properties of the CNT interior and release conditions of the confined species. The detailed insights into the thermodynamic conditions and chemical mechanisms of the pressure-induced CNT opening provide practical guidelines for the development of novel nanoreactors, catalysts, photo-catalysts, imaging labels and drug delivery vehicles.

Introduction

Carbon nanotubes (CNTs) are tubular cylinders of carbon atoms exhibiting unusual strength, elasticity, electrical conductivity, thermal conductivity and other unique properties.1–5 CNTs find applications in electronics, optics, catalysis, energy storage, imaging, sensing, medicine, etc.5–16 The number of research papers dedicated to CNTs, their derivatives, and CNT containing composite materials continues to grow exponentially, despite 24 years since the first publication.

CNTs are employed in medical treatments and drug delivery, owing to their ability to penetrate lipid bilayers, reach cellular nucleus, and encapsulate drug molecules, DNA fragments and other biologically relevant guest species.14,17–26 In addition, CNTs absorb near-infrared light that penetrates through water and biological tissues, allowing one to activate tissue imbedded CNTs remotely and locally by a laser, forming the basis for cancer treatments. Chemical reactions performed inside CNT nanoreactors exhibit different thermodynamics, kinetics and product yields, compared to unconfined systems.27–29 The CNT inner space creates a possibility for asymmetric catalysis and production of different isomers starting from the same reactants and depending on the CNT diameter. This feature opens a wide avenue to tune selectivity and adjust catalytic conditions.30,31 Similarly, photo-catalysts exhibit different and often enhanced performance inside CNTs.32 In the course of the above processes, a cargo or reactant molecule has to be sealed inside a CNT and then released from the CNT, when required. It is particularly important in this context to establish and understand the features and trends associated with the sealing and opening of carbon nanoscale pores.

Recent chemical literature contains multiple success stories of delivering biologically relevant molecules to target cells. Even though the toxicity issues of CNTs are not fully resolved yet, rapid development of different CNT containing drug delivery systems is continuously reported. Rusling and coworkers17 developed the first targeted killing of cancer cells in vivo using a drug–CNT bioconjugate. The first line anticancer agent cisplatin and an epidermal growth factor were attached to single-walled CNTs to deliberately target squamous cancer cells. According to the authors, the efficacy of their drug delivery system is better than that of the non-targeted bioconjugates. Fan and coworkers18 prepared a CNT–graphene nanosheet–iron oxide nanoparticle hybrid to perform efficient loading and delivery of anticancer drugs. This hybrid exhibits superparamagnetic properties and strongly binds 5-fluorouracil with an unexpectedly high load capacity. The authors conclude that the prepared system will find interesting applications in drug delivery.

Recently, Giri and coworkers19 contributed a system for a sustained release of hydrophobic drugs, such as diclofenac...
sodium. The new system uses acrylic acid grafted guar gum-carboxy functionalized multi-walled CNTs in in situ composite membranes. The CNTs increased hydrophobicity of all acrylic acid grafted membranes through an interaction with the matrix. Transdermal drug delivery was achieved by Gharib and coworkers\textsuperscript{23} using a CNT-polymide composite material. This material was used to fabricate hollow microneedles. Patterned bundles of CNTs were used as a porous scaffold to define the geometry of the microneedle. CNT–dendrimer hybrid nanomaterials were utilized by Rashidian and coworkers.\textsuperscript{33} The resulting drug delivery systems readily penetrate cell membranes, allow high drug loading and target tumor cells by means of a magnetic field assigned to α-F\textsubscript{2}O\textsubscript{3} nanoparticles. Chaban and Prezhdo\textsuperscript{34} combined CNT efficacy in photo-induced cancer treatment and drug delivery, proposing a unified protocol for focused delivery and release of drug molecules.

Liu and coworkers\textsuperscript{35} contributed a detailed and insightful study of the thermal decomposition of nitromethane on functionalized graphene sheets, which were obtained by introducing oxygen containing groups. The research was accomplished by ab initio molecular dynamics. It was shown that carbon vacancy defects within the plane of the functionalized graphene greatly accelerate thermal decomposition of nitromethane and its derivatives. The graphene sheets remained intact during the simulated reactions. Zhu and coworkers\textsuperscript{36} explored the microscopic dynamic response and decomposition mechanism of β-octahydro-1,3,5,7-tetranitro-1,3,5,7-tetracocin (an important explosive) under shock conditions using tight-binding density functional theory. The reaction of the explosive was initiated by fission of the molecular ring at the carbon–nitrogen bond located in the vicinity of the major axis. Subsequently, the carbon–hydrogen bonds and nitrogen–nitrogen bonds were destroyed. The authors underlined that the simulated dynamic response behavior depended on the angle between the chemical bond and the shock direction.

Chemical reactions inside CNTs were exemplified by Eliseev and coworkers,\textsuperscript{28} who proposed a simple two-step approach for an assured filling of CNT channels with A\textsubscript{18}B\textsubscript{17} and A\textsubscript{14}B\textsubscript{16} one-dimensional chalcogenide nanocrystals. The proposed method is based on an intermediate metal iodide and a molten medium technique, with a subsequent chalcogenation inside CNT. Khlobystov and coworkers\textsuperscript{27} studied reactions of the inner surface of CNTs and nanoprotrusion processes. Importantly, in contrast to the original belief, they proved that the inner surface of CNT is reactive in the presence of catalytically active rhenium atoms. According to Smith and coworkers,\textsuperscript{29} CNTs can dictate stereo- and regio-selectivity of Diels–Alder reactions. Molecular dynamics simulations demonstrated that the 1,4-\textit{exo} adduct is produced instead of the expected 9,10-adduct. It was noted that the reactant size and the CNT radius play major roles in the determination of the final product structure. A comprehensive review of the effects of confinement inside CNTs on chemical catalysis can be found in ref. 37.

Motivated by the broad interest to obtain efficient and robust CNT opening on demand, this work reports a theoretical investigation of pressure- and chemistry-driven CNT decomposition as initiated, for instance, by laser-induced heating. We simulate CNT opening in real-time using a reactive atomistically-precise interaction model and varying the nature of the filler. The considered scenarios cover a broad range of local temperature and pressure, demonstrating the possibility of extensive experimental control over CNT interior properties and conditions for the release of confined species.

**Methodology**

The simulations were performed using reactive molecular dynamics (RMD) with the force field obtained from van Duin and coworkers.\textsuperscript{38,39} RMD differs from classical MD, since it employs much more sophisticated intra- and inter-molecular potentials, which aim to reproduce a realistic potential energy surface for a given system. In particular, RMD allows chemical bonds to be broken and formed, while classical MD typically does not. RMD is different from quantum chemical methods, since it does not employ time-consuming iterative procedures and is generally much less computationally demanding. A linear scaling of performance can be theoretically achieved in RMD much easier than with any quantum chemical method. The RMD simulations were carried out in ADF2013.

CNT (10,10) with a length of ca. 13.5 Å was considered as a model of a single-walled nanotube with an ideal geometry. Three primary RMD systems involving CNT (10,10) were studied, including an empty CNT, and argon(Ar)-filled CNT, and a fluorine(F\textsubscript{2})-filled CNT. The RMD simulations were repeated at a number of temperatures ranging from 2000 to 4800 K, for 2000 ps each. An integration time-step of 0.1 fs was selected to suitably reproduce high-frequency bond vibrations upon decomposition at high temperatures. The Andersen thermostat was employed to control constant temperature with a relaxation time constant of 0.1 ps.

**Results and discussion**

Fig. 1 depicts empty and gas-filled CNT (10,10). The CNT structure in all RMD systems is stable, although it is somewhat deformed due to thermal motion under room conditions. Note that argon and molecular fluorine are gases at room temperature. Visual examination of the CNTs indicates that deviations from the ideal CNT geometry are more significant in the filled CNTs. This observation originates from local pressures generated by the gases inside the filled CNTs, whereas the internal and external pressures are equal in the case of the empty CNT. In the following, we will demonstrate that the internal pressure undermines CNT stability and that this effect can be quantified from the reactive simulations.

The constructed systems (Table 1) were equilibrated at 298 K using 50 ps long MD runs. The used equilibration times...
are sufficient, since the fillers retain gas-like structures under confinement, whereas the CNT structure is relaxed based on the intra-molecular potentials, whose corresponding frequencies are below 1.0 fs. Thus, the RMD systems obtain their global free energy configurations quickly. Afterwards, the MD systems were heated up to 2000–4800 K and their stabilities were investigated at a number of temperatures.

It should be noted that the decomposition temperatures of ideal CNTs exceed the experimentally observed values, ca. 1000 K, significantly. Ideal CNTs are extremely strong and elastic, as is known from the respective mechanical properties. However, structural defects, which are omnipresent in commercial CNTs and are a direct consequence of the chosen production method, decrease their thermal stability. Furthermore, the armchair CNT (10,10) is narrow with a diameter of ca. 1 nm, while experimentally identified CNTs reach up to 50 nm in diameter. Wide single-walled CNTs are typically less stable than narrow CNTs. Oxidants in the atmosphere favor low-temperature oxidation reactions, impacting stability of the entire nanostructure.

Fig. 2 depicts the evolution of the selected energy terms in the case of the argon-filled CNT (10,10) at 4200 K. Other RMD systems exhibit qualitatively similar trends. All intra-molecular energy components increase in the course of the RMD simulation, since the systems lose their structures (increase entropy) at high temperatures. Decrease of the van der Waals energy is due to the formation of multiple separate particles,

![Fig. 1](image1.png)

**Fig. 1** Atomic configurations of the simulated systems at room temperature: (a) empty CNT (10,10); (b) CNT filled by argon atoms; (c) CNT filled by molecular fluorine, F₂.

<table>
<thead>
<tr>
<th>System</th>
<th>Start of decomposition, #iterations per 10³</th>
<th>End of decomposition, #iterations per 10³</th>
<th>Simulated temperature, K</th>
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<td>Empty CNT (10,10)</td>
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<td>—</td>
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<tr>
<td></td>
<td>—</td>
<td>1800</td>
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<td>4600</td>
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<td>—</td>
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<tr>
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<td>400</td>
<td>2200</td>
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<td>CNT (10,10) + 50 F₂</td>
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</table>

![Fig. 2](image2.png)

**Fig. 2** Evolution of energy terms upon explosion of CNT (10,10) filled with 50 argon atoms: (a) conjugation energy between carbon atoms; (b) carbon–carbon covalent energy; (c) van der Waals energy for bonded and non-bonded C–C, Ar–Ar, and C–Ar interactions; (d) carbon–carbon–carbon valence angle energy.
which can approach one another more efficiently, as compared to the static CNT structure. The decomposition of CNT, as well as any other thermal decomposition, is entropically favorable.

Destruction of the argon-filled CNT occurs at 200 K lower than the destruction of the empty CNT, which occurs at 4400 K. This is an effect of the local internal pressure. Argon is an example of a gas that does not interact chemically with CNTs. Thus, the pressure effect can be separated. We believe that the observed 200 K decrease in the decomposition temperature of the ideal CNT is a practically interesting phenomenon. Being corrected with respect to CNT natural defects, it offers a mechanism to release encapsulated agents from CNTs.

Chemical interactions greatly enhance the efficiency of the CNT opening; see the fluorine-filled CNT case (Table 1). Here, the temperature is decreased by 900 K compared to the empty CNT. Molecular fluorine is a strong oxidant, especially at high temperatures. Thus, in addition to the internal pressure, the decomposition is fostered by fluorination and, consequently, partial destruction of aromaticity. This CNT opening mechanism is another option to remove CNT caps. Opening from inside is different from the conventional opening solutions, which involve various oxidation agents. Our results are in qualitative agreement with those of Khlobystov and co-workers. For certain applications, e.g. in vivo, aggressive oxidants cannot be safely supplied. In those cases, decomposition from inside is particularly promising. The oxidants can be encapsulated inside the CNT. When needed, the reaction is initiated and the tube loses its integrity. The products of this reaction are carbon fragments functionalized with the reactants, e.g. fluorinated carbon. These products exhibit lower toxicity than the original reactants. The simplest initiation pathway, as exemplified in the present work, is a temperature increase, which can be achieved by laser heating.

The remainder of the work characterizes decomposition pathways and provides certain quantitative descriptors. Fig. 3 shows the local internal pressures inside CNT (10,10). The pressure vs. temperature is systematically higher in the case of

![Fig. 3](image1.png)

**Fig. 3** Pressure generated inside CNT (10,10) by confined fluorine molecules (red solid line) and by confined argon atoms (green dashed line) at elevated temperatures.

![Fig. 4](image2.png)

**Fig. 4** Mechanisms of CNT (10,10) opening: (a) empty CNT at \( T = 4400 \) K; (b) argon-filled CNT at \( T = 4200 \) K; (c) fluorine-filled CNT at \( T = 3500 \) K. Opening of CNT (10,10) system starts from the region of fullerene cap in all systems, although the mechanism depends on the system. Empty CNT decomposes when the energy of thermal vibrations, \( kT \), exceeds the potential energy of carbon–carbon covalent bonds. When bonds break, carbon atoms form long unsaturated chains. The argon-filled CNT opens at 200 K lower than the empty CNT due to additional internal pressure of the gas (Fig. 3). The fullerene cap is removed and argon atoms leave the tube. After argon atoms escape and the pressure difference vanishes, the CNT decomposition stops. Opening of fluorine-filled CNT (10,10) takes place at a significantly lower temperature (3500 K). Fluorine atoms attach to the CNT sidewalls and cap, and promote chemical decomposition.
argon. This is in accordance with our expectations, since argon atoms interact weakly with one another, deviate less from the ideal gas behavior, and therefore, are more mobile. Additionally, a certain number of fluorine molecules are involved in the reaction with CNT, which decreases pressure further. The observed pressures range from 3400 to 4600 bar. The pressure vs. temperature dependence is linear.

The CNT opening reactions exhibit some similarities and some differences (Fig. 4). All CNTs start decomposition from the CNT cap. This is in line with general knowledge suggesting that the cap is less stable than the CNT body. A high temperature, 4400 K, is required to initiate breakage of the first carbon–carbon bonds. Afterwards, the nanotube unknits relatively quickly.

Selected geometrical features of the CNTs near the decomposition temperature are given in Fig. 5 and 6. At 298 K, the C–C bond length in the cap amounts to 1.44 Å with the standard deviation of 0.02 Å. These values correspond to a good thermal stability of the capped CNT (10,10). Thermal expansion occurs at 4000 K. The C–C lengths in the sidewall become 1.46 Å, whereas the C–C lengths in the cap become 1.45 Å. In turn, the C–C bonds in the five-membered rings of the cap are 1.48 Å. These distances constitute a good illustration that pressure-driven CNT decomposition initially starts from the five-membered rings of the CNT cap, whose bond lengths fluctuate by ±0.08 Å. The C–C–C angle in the pentagon is 107° before breakage.

Somewhat unexpectedly, the diameter of the empty CNT decreases upon heating, compare 13.70 Å at 298 K to 13.58 Å at 4200 K (Fig. 6). These diameters were defined as distances between the opposite carbon atoms, averaged over time. In turn, the diameter of the argon-filled CNT at 4200 K is 13.78 Å. That is, the CNT expands only when it contains an encapsulated gas. Furthermore, the gaseous filler quenches the magnitude of radial fluctuations by a factor of two: 0.5 Å vs. 0.9 Å (T = 4200 K). Nevertheless, the reduced fluctuation does not make the argon-filled CNTs more stable than the empty CNT (Table 1).

Conclusions

To recapitulate, we demonstrated an extensive control over the mechanism, temperature, pressure and products of CNT opening for applications as nanoreactors, catalysts, imaging and drug delivery vehicles. Reactive simulations of empty and filled CNTs showed that pressure of a confined gas can be utilized to remove CNT caps in a predictable manner. The
decomposition temperature of the argon-filled CNT (10,10) is ca. 200 K smaller than that of the empty CNT (10,10). Chemical interactions greatly facilitate CNT opening. When CNT (10,10) was filled with an oxidant gas, i.e., molecular fluorine, the CNT decomposition temperature decreased by ca. 900 K due to the fluorination of the CNT caps, ultimately leading to fluorinated hydrocarbon products. In certain applications, e.g. in vivo, aggressive oxidants cannot be supplied from the outside, and decomposition from inside becomes particularly promising. Importantly, pressure induced CNT opening removed only CNT caps, leaving the CNT cylinders intact. In contrast, thermal decomposition of the empty CNT destroyed the entire tube. The uncovered details of the CNT decomposition mechanisms create a broad range of possibilities for tuning of CNT thermal stability, internal pressure, temperature and opening protocol.

We employed perfect CNT models. Commercially available CNTs are known to be less stable due to defects, dopants, surfactants and other species. In such cases, decomposition starts from the defects, and the reported decomposition temperatures will have to be corrected for each practical application in mind. The pressure and temperature control over the CNT opening should be possible in realistic systems as well.

The reported results are important for a broad range of applications, in which CNT opening on demand is necessary. Such applications include reactions within a nanoscale confinement and targeted drug delivery. Local heating by a laser can be employed to generate the correct temperature. Laser heating is particularly facile with CNTs, since they absorb near-infrared light that penetrates through water and biological tissues.

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