

Enhanced π – π Interactions Between a C_{60} Fullerene and a Buckle Bend on a Double-Walled Carbon Nanotube

Sandeep Gorantla¹, Stanislav Avdoshenko², Felix Börrner¹, Alicja Bachmatiuk¹, Maria Dimitrakopoulou¹, Franziska Schäffel¹, Ronny Schönfelder¹, Jürgen Thomas¹, Thomas Gemming¹, Jamie H. Warner³, Gianaurelio Cuniberti², Jürgen Eckert¹, Bernd Büchner¹, and Mark H. Rümmeli¹ (✉)

¹ IFW Dresden, P.O. Box 270116, D-01171 Dresden, Germany

² Institute for Materials Science and Max Bergmann Center of Biomaterials, Dresden University of Technology, Dresden 01062, Germany

³ Department of Materials, University of Oxford, Parks Rd., Oxford OX1 3PH, United Kingdom

Received: 30 October 2009 / Revised: 30 November 2009 / Accepted: 6 December 2009

© The Author(s) 2010. This article is published with open access at Springerlink.com

ABSTRACT

In situ low-voltage aberration corrected transmission electron microscopy (TEM) observations of the dynamic entrapment of a C_{60} molecule in the saddle of a bent double-walled carbon nanotube is presented. The fullerene interaction is non-covalent, suggesting that enhanced π – π interactions (van der Waals forces) are responsible. Classical molecular dynamics calculations confirm that the increased interaction area associated with a buckle is sufficient to trap a fullerene. Moreover, they show hopping behavior in agreement with our experimental observations. Our findings further our understanding of carbon nanostructure interactions, which are important in the rapidly developing field of low-voltage aberration corrected TEM and nano-carbon device fabrication.

KEYWORDS

Carbon nanotubes, fullerenes, low-voltage transmission electron microscopy, molecule trap

Introduction

Hybrid molecular electron donor–acceptor structures comprising a single-walled carbon nanotube (SWNT) with a fullerene (C_{60}) attached externally are attractive for organic photovoltaics [1]. The non-covalent attachment of a guest C_{60} molecule may also be of interest for carbon nanotube-based molecular electronics devices [2–4]. A functional molecule weakly bound to an SWNT is appealing for specialized switching applications. However, despite several interesting side-wall functionalization strategies [5], a route for electronically attractive non-covalent binding

of a C_{60} molecule to a carbon nanotube without any additional organic linkage has not been realized. This is due to insufficient interaction surface area between a fullerene and a straight SWNT since both molecular structures have positive curvatures. A logical solution is to create an area with negative curvature. This should provide the desired surface to weakly bind a molecule through van der Waals (vdW) forces. The buckling formed during the bending of an SWNT offers negative curvature [6]. The SWNT buckling phenomenon has only been investigated theoretically from a mechanical perspective [6, 7]. The mechanical response of buckled SWNTs can strongly influence

Address correspondence to m.ruemmeli@ifw-dresden.de

their conductance [8]. Interactions between encapsulated fullerenes (peapods) and a bent SWNT have also been investigated theoretically [9]. We have not found any theoretical or experimental studies of a fullerene interacting externally with a bent SWNT. Thus, our understanding of the interaction between the outer surface of a bent SWNT and an unbound C_{60} molecule is limited. To realize this idea experimentally a simple and well-established experimental process was revisited, namely, the investigation of double-walled carbon nanotubes (DWNT) formed from SWNT encapsulated with C_{60} , so called peapods. When peapods are annealed at elevated temperatures the fullerenes trapped within the SWNT polymerize forming an inner tube, viz. a DWNT [10]. However, the C_{60} filling process, be it through wet chemistry or via vapor filling, exposes the entire SWNT sample to fullerenes [11, 12]. One can anticipate that a few fullerenes might be “trapped” externally, on an SWNT (or DWNT) via a surface defect, for example, a kink or bend.

In this communication, we present time-sequenced HRTEM *in situ* observations showing the dynamic entrapment of a non-covalently bound C_{60} molecule in the saddle of a bent DWNT. The TEM studies were conducted at 80 kV to minimize knock-on damage due to exposure to the electron beam [13]. Supporting molecular dynamics (MD) simulations were performed to help elucidate the nature of the vdW forces between the buckled region and fullerene.

1. Experimental

1.1 SWNT synthesis

The starting SWNTs were synthesized via a laser evaporation route. Prior to the filling process they were purified and opened by annealing in air at 653 K for 60 min [14]. The peapods were prepared by the hot vapor filling method [12]; high purity fullerenes (MER Corp.) mixed with the opened SWNTs were heated in a sealed quartz tube under high vacuum (10^{-7} hPa) at 723 K for 5 days. After the filling step, the peapods were annealed under dynamic high vacuum (10^{-6} hPa) at 1598 K for 90 min. This annealing process converts the peapods into a DWNT.

1.2 HRTEM imaging

Time-sequence high-resolution (HRTEM) imaging was performed using an FEI Titan³ transmission electron microscope, equipped with an objective lens spherical aberration corrector. The instrument was operated at 80 kV. The electron beam current densities ranged between 0.01 and 0.1 pA/nm².

1.3 Classical MD simulations

The classical MD trajectory integration for an isolated fullerene–SWNT system was carried out using the noscale molecular dynamics (NAMD) 2.7 package with a number of particles, volume and temperature (NVT) Langevin thermostat and 2.0 femtosecond (fs) time steps [15]. The assisted model building with energy refinement (AMBER) 99 force field was used for the sp² carbon atoms of the C_{60} and the SWNT [16]. All atoms were assumed to be uncharged. The MD simulation time for each trajectory was around 20 picoseconds (ps). The visualization and trajectory analyses were performed with the aid of the visual MD (VMD) package [17]. For more details of the initial conditions of the classical MD simulations see the electronic supplementary material (ESM).

2. Results and discussion

In Fig. 1 (panels (a) to (d)) a DWNT with a buckled region around which a fullerene interacts is presented. During the HRTEM study the fullerene oscillates between various positions within the saddle of the buckled region. Panels *a* and *d* show the two extreme positions at the right and left of the DWNT that the fullerene can adopt. Panels *b* and *c* show two intermediate positions. These two intermediate positions are close to the center of the buckled region and during the continuous time-sequence HRTEM imaging (5 min), the C_{60} molecule showed a strong preference for these locations. To better visualize the physical structure of the system, we generated visualization simulations of the hybrid molecular structure and corresponding locations of the fullerene. These are presented in panels i–iv of Fig. 1. It should be borne in mind that in actuality the bend lies



mostly into (or out of) the back plane and varies from frame to frame because the free standing DWNT was oscillating slightly during the HRTEM study. Faint lines visible across the host tube around the buckle (left and right of the inner tube) are just visible. They arise from an increased density of C atoms forming in the plane of view due to the buckle. The complete series of time-sequence image frames and their compilation into a movie are given in the ESM. The dynamic movement of the fullerene around the buckle region is striking for a variety of reasons. The movement of the fullerene clearly shows the presence of weak non-covalent binding forces. Interactions between π electron systems result in weak bonding as, for example, between graphene layers in graphite. In the case of a straight carbon nanotube and a fullerene, the mutual positive curvature of the structures leads to a minimal contact/interaction point and is insufficient to trap a fullerene. However, a buckle in a nanotube, as in this instance, provides a complementary curved surface to that of the fullerene, in essence, increasing the interaction area of the vdW forces.

To check this assumption, various theoretical calculations using classical MD were conducted for

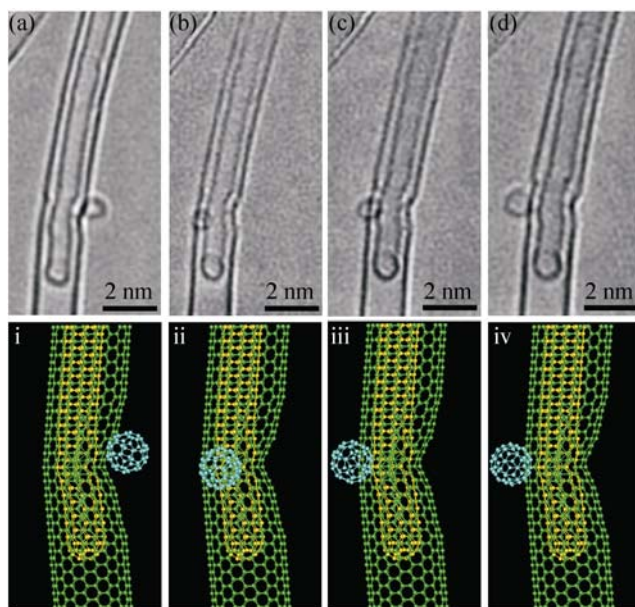


Figure 1 (a–d) Time-sequence HRTEM images capturing the motion of a C₆₀ molecule around a buckle bend on the surface of a DWNT. (i–iv) Schematic representation of the observed hybrid molecular structure dynamics

different temperatures between a straight and buckled SWNT with a chiral index [10, 10] and a C₆₀ fullerene. The maximum allowable depth of the buckled region was determined assuming an inner SWNT with a [5, 5] chiral index (as this was the best match from our experimental observations). In our model the vdW forces are approximated by the Lennard–Jones potential and the depth of the energy minimum will depend on the curvature of the buckle. A first approximation of the energy of interaction can be defined as an ensemble average of the total energy inside and outside the “buckle”: $E_{\text{att}} = \langle E_{\text{in}} \rangle - \langle E_{\text{out}} \rangle \sim 30$ kJ/mol, which translates into a characteristic temperature of $T_{\text{esc}} \sim E_{\text{att}} / (3/2 N_{\text{mol}} k_{\text{B}}) \sim 1200$ K. We analyzed 20 ps trajectories for several temperature points between 300 and 1400 K (with 200 K intervals). In the case of a *straight* tube, above 1100 K, the fullerene molecule escaped the surface irreversibly within 2 ps. Similar studies on a *buckled* tube show a different behavior. Figure 2 shows a multiple-frame representation covering a 20 ps time interval for the buckled tube/fullerene configuration. The individual frames show the dynamic motion of a trapped fullerene within the buckled region at different temperatures of 300 and 1200 K. In our simulation, an artificial deformation—due to displacement within two symmetrically independent sites—is mimicked. The arbitrarily chosen sites are an appropriate description for selected deformations. Hence, our theoretical model can only provide an approximation to the experimental environment in which the arbitrarily defined sites could, in reality, move. The system used allowed several scenarios (different bending degrees and temperatures) in the tube to be investigated. As shown in Fig. 2(a), at 300 K the fullerene remains localized around one of the fixed carbon atom sites during the entire 20 ps simulation time (see ESM). When the temperature is increased to 1200 K the fullerene is observed to hop within the confinement of the saddle. Multiple-frames from our calculations show the motion of the fullerene to localize between the two fixed carbon atom sites, as shown in Fig. 2(b) and the ESM. This hopping or oscillating behavior shows remarkable similarities to our *in situ* observations. The two fixed localized deformation sites are separated by a benzene-like ring (Fig. 2(c)). The fullerene is able

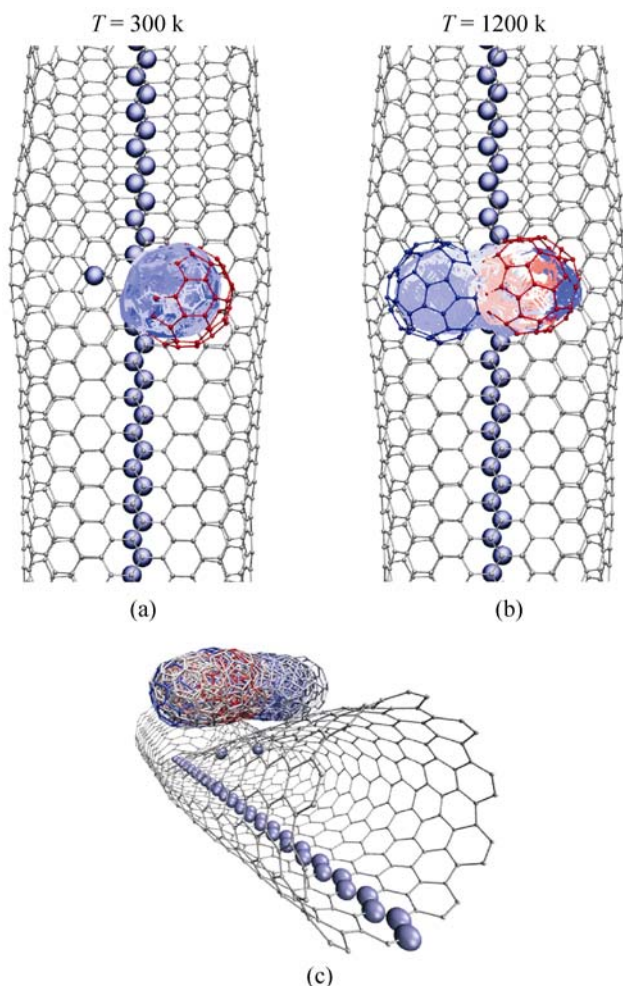


Figure 2 Twenty picoseconds of classical MD trajectory of the buckled SWNT, and multiple-frames representation of the fullerene dynamics are shown: (a) at 300 K, the fullerene remains localized around one of the fixed carbon atom sites during the entire 20 ps simulation time; (b) at 1200 K the fullerene is observed to hop within the confinement of the saddle and localize between the two fixed carbon atom sites; (c) the two fixed localized deformation sites are separated by a benzene-like ring

to easily transfer across that barrier above a critical temperature, when the amplitude of the motion of the trapped fullerenes is sufficient. This critical temperature is close to the escape temperature found with an undistorted (straight) SWNT. A 2-D representation of the vdW interaction energy (kJ/mol) map as a function of the position of the center of mass of the fullerene with respect to the SWNT is shown in Fig. 3. This clearly shows the enhanced localization of vdW forces between the fullerene and buckled SWNT and provides a good explanation for the entrapment of the fullerene. It is interesting to note that these

experiments were conducted at room temperature. Under these conditions one can transform peapods to a DWNT via electron beam irradiation. One can also reproduce this transformation of peapods to a DWNT by annealing at temperatures around 1100–1300 K [18]. This indicates that although the actual tube temperatures may be well below 1100 K [19], fullerenes trapped within an SWNT under the electron beam emulate circumstances in which the energy is provided through heating at temperatures around 1000–1300 K. The theoretical findings obtained in this study show a critical temperature for the escape of a fullerene from a straight tube of around 1100 K and in the case of a bent tube the fullerene begins to hop at around 1200 K. This hints that a fullerene on the surface of an SWNT in HRTEM, albeit at room temperature, approximates conventional annealing conditions with temperatures around 1000–1300 K, similar to the peapod to DWNT transformation discussed above. This is further supported by there being no previous reports (to the best of our knowledge) of non-covalently bound fullerenes lingering on the surface of a defect-free and straight SWNT.

Towards the end of HRTEM study, the bend in the host SWNT relaxed slightly and the inner tube then moved further down, as is clearly apparent by comparing frames (a) and (b) in Fig. 4. This highlights how bends can restrict the movement of species residing within a host SWNT, essentially acting as a nano-valve. More importantly, the fullerene remained attached despite the curvature relaxation. This demonstrates the efficiency of vdW forces, even when the structural distortion is minor.

3. Conclusions

In situ HRTEM allows the dynamic interactions between a single C_{60} molecule and the buckled region of a bent DWNT to be observed. The fullerene interaction is clearly non-covalent and can be attributed to enhanced π - π interactions (vdW forces). Classical MD calculations confirm vdW forces can indeed be sufficient to trap a fullerene in a buckle region of a nanotube. Moreover, they show hopping behavior in agreement with our experimental observations. Our findings further our understanding of carbon



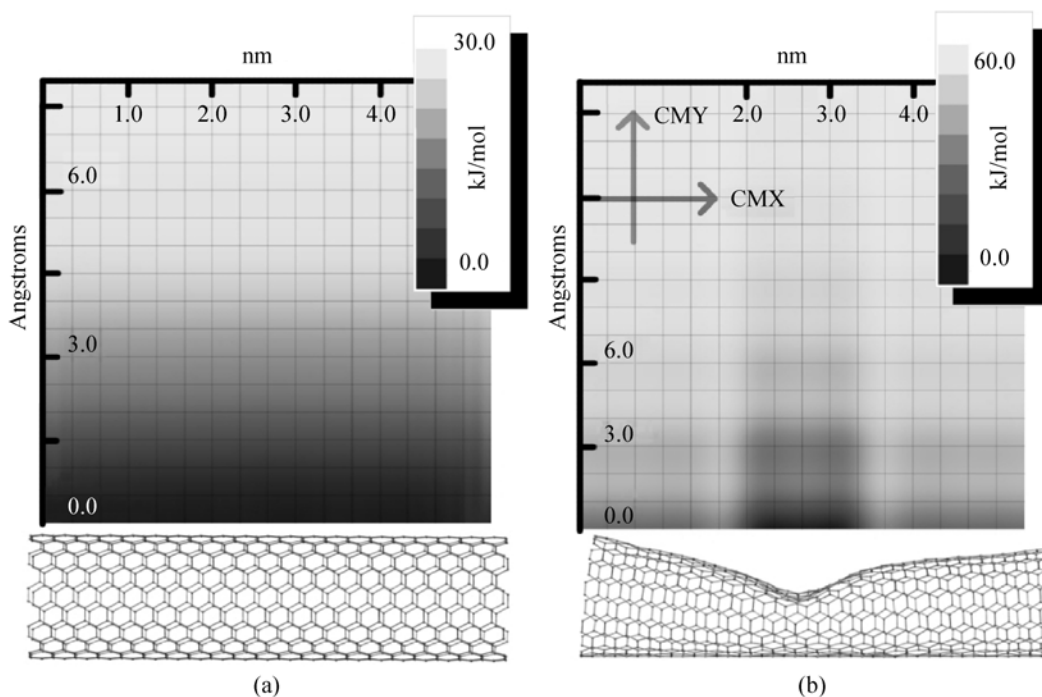


Figure 3 2-D vdW energy (kJ/mol) map represented as a function of the distance of the fullerene center of mass (CM) from the outer surface for a (a) straight and (b) buckled SWNT. The energy calculated from the equilibrium value, and the position of CM in the Y direction are given

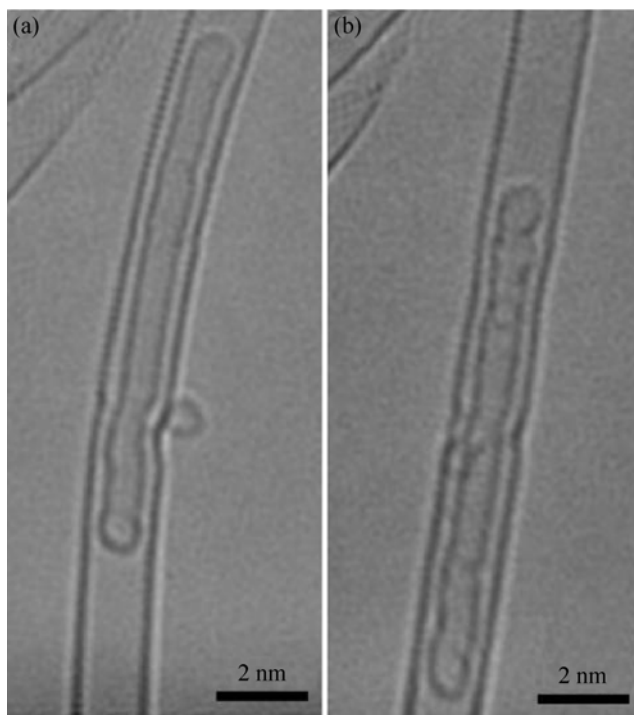


Figure 4 Two TEM micrographs highlighting the relaxation of the buckle. (a) The initial frame (unrelaxed form) and (b) the final frame (some relaxation has occurred). The tube behaves as a nano-valve

nanostructure interactions, which are important in the rapidly developing field of low voltage aberration corrected TEM and nano-carbon device fabrication.

Acknowledgements

SG acknowledges the “Pakt für Forschung und Innovation”, and FS the Cusanuswerk for financial support. AB thanks the European Union (EU) for a Marie Curie (MC) fellowship (multifunctional carbon nanotubes for biomedical applications (CARBIO)). MD thanks the Deutscher Akademischer Austausch Dienst (DAAD). SA and GC thanks the EU project carbon nanotube devices at the quantum limit (CARDEQ) and the Korea Science and Engineering Foundation World Class University (WCU) Project No. R31-2008-000-10100-0.

Electronic Supplementary Material: Details of the TEM image capture, image processing and molecular dynamics calculations and a movie for better visualization of the interaction dynamics between the attached C_{60} molecule around the buckle bend on the

outer surface of the SWNT are available in the online version of this article at <http://dx.doi.org/10.1007/s12274-010-1012-6> and are accessible free of charge.

References

- [1] Li, C.; Chen, Y. H.; Wang, Y. B.; Iqbal, Z.; Chhowalla, M.; Mitra, S. A fullerene-single wall carbon nanotube complex for polymer bulk heterojunction photovoltaic cells. *J. Mater. Chem.* **2007**, *17*, 2406–2411.
- [2] Allara, D. L.; Dunbar, T. D.; Weiss, P. S.; Bumm, L. A.; Cygan, M. T.; Tour, J. M.; Reinerth, W. A.; Yao, Y.; Kozaki, M.; Jones, L. Evolution of strategies for self-assembly and hookup of molecule-based devices. *Ann. NY Acad. Sci.* **1998**, *852*, 349–370.
- [3] Jaochim, C.; Gimzewski, J. K.; Aviram, A. Electronics using hybrid-molecular and mono-molecular devices. *Nature* **2000**, *408*, 541–548.
- [4] Moth-Poulsen, K.; Bjornholm, T. Molecular electronics with single molecules in solid-state devices. *Nature Nanotechnol.* **2009**, *4*, 551–556.
- [5] Sun, Y. P.; Fu, K.; Lin, Y.; Huang, W. J. Functionalized carbon nanotubes: Properties and applications. *Acc. Chem. Res.* **2002**, *35*, 1096–1104.
- [6] Yakobson, B. I.; Brabec, C. J.; Bernholc, J. Nanomechanics of carbon tubes: Instabilities beyond linear response. *Phys. Rev. Lett.* **1996**, *76*, 2511–2514.
- [7] Yao, X.; Han, Q.; Xin, H. Bending buckling behaviors of single- and multi-walled carbon nanotubes. *Comput. Mater. Sci.* **2008**, *43*, 579–590.
- [8] Postma, H. W. Ch.; Teepen, T.; Yao, Z.; Grofoni, M.; Dekker, C. Carbon nanotube single-electron transistors at room temperature. *Science* **2001**, *293*, 76–79.
- [9] Zhu, J.; Pan, Z. Y.; Wang, Y. X.; Zhou, L.; Jiang, Q. The effects of encapsulating C₆₀ fullerenes on the bending flexibility of carbon nanotubes. *Nanotechnology* **2007**, *18*, 275702.
- [10] Bandow, S.; Takizawa, M.; Hirahara, L.; Yudasaka, M.; Iijima, S. Raman scattering study of double-wall carbon nanotubes derived from the chains of fullerenes in single-wall carbon nanotubes. *Chem. Phys. Lett.* **2001**, *337*, 48–54.
- [11] Monthieux, M. Filling single-wall carbon nanotubes. *Carbon* **2002**, *40*, 1809–1823.
- [12] Warner, J. H.; Yasuhiro, I.; Zaka, M.; Ge, L.; Akachi, T.; Okimoto, H.; Porfyrakis, K.; Watt, A. A. R.; Shinohara, H.; Briggs, G. A. D. Rotating fullerene chains in carbon nanopeapods. *Nano Lett.* **2008**, *8*, 2328–2335.
- [13] Smith, B. W.; Luzzi, D. E. Electron irradiation effects in single wall carbon nanotubes. *J. Appl. Phys.* **2001**, *90*, 3509–3515.
- [14] Rummeli, M. H.; Loeffler, M.; Kramberger, C.; Simon, F.; Fülöp, F.; Jost, O.; Schöenfelder, R.; Grüeneis, A.; Gemming, T.; Pompe, W.; Büchner, B.; Pichler, T. Isotope-engineered single-wall carbon nanotubes: A key material for magnetic studies. *J. Phys. Chem. C* **2007**, *111*, 4094–4098.
- [15] Kale, L.; Skeel, R.; Bhandarkar, M.; Brunner, R.; Gursoy, A.; Krawetz, N.; Phillips, J.; Shinozaki, A.; Vardarajan, K.; Schulten, K. NAMD2: Greater scalability for parallel molecular dynamics. *J. Comp. Phys.* **1999**, *151*, 283–312.
- [16] Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Gould, I. R.; Merz, K. M.; Ferguson, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. W.; Kollman, P. A. A second generation force field for the simulation of proteins, nucleic acids, and organic molecules. *J. Am. Chem. Soc.* **1995**, *117*, 5179–5197.
- [17] Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Mol Graphics* **1996**, *4*, 33–38.
- [18] Warner, J. H.; Ito, Y.; Rummeli, M. H.; Gemming, T.; Büchner, B.; Shinohara, H.; Briggs, G. A. D. One-dimensional confined motion of single metal atoms inside double-walled carbon nanotubes. *Phys. Rev. Lett.* **2009**, *102*, 195504.
- [19] Bahnhart, F. Irradiation effects in carbon nanostructures. *Rep. Prog. Phys.* **1999**, *62*, 1181–1221.

