Carbon Nanotubes: From Nano Test Tube to Nano-Reactor

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At a glance, the quest of chemical nanoscience is very similar to that of traditional chemistry and includes (i) studying structure, (ii) harnessing functional physical properties, and (iii) controlling the chemical reactions of molecules. Chemical nanoscience is set to achieve all this at the nanoscale and, ultimately, at the single-molecule level.

One of the most powerful methodologies for manipulation of individual molecules and atoms is based on entrapment and confinement and utilizes the principles of supramolecular host−guest chemistry. Over the past three decades, a wide range of hollow nano-containers have been developed including calixarenes, cyclodextrins, cucurbiturils, supramolecular/coordination cages, and bilayer vesicles.[1] Even though carbon nanotubes (CNTs) have made their entrance as nano-containers much more recently[2] their potential advantages over these established systems are already clear. Being built of sp[2]-carbon atoms held together by strong covalent bonds, CNTs are significantly more thermally stable (*ca.* 700 °C in air and up to 2800 °C in vacuum) and mechanically more robust (with tensile strength much higher than that of steel) than any other molecular or supramolecular nano-containers. The concave side of the nanotube has very low chemical reactivity, so that some aggressive chemical process can be contained within the CNT. Furthermore, single-walled carbon nanotubes (SWNTs) are atomically thin, which means that guest molecules can be studied directly, in real space and at the atomic level, by high-resolution transmission electron microscopy (HRTEM)—an imaging tool that can "see" through the nanotube wall.

Carbon Nanotubes as Containers for Molecules. The nanotube diameter is the most important parameter in determining whether or not a molecule can be trapped inside a CNT. As a general rule for successful encapsulation,

ABSTRACT Confinement of molecules and atoms inside carbon nanotubes provides a powerful strategy for studying structures and chemical properties of individual molecules at the nanoscale. In this issue of *ACS Nano*, Allen *et al.* explore the nanotube as a template leading to the formation of unusual supramolecular and covalent structures. The potential of carbon nanotubes as reactors for synthesis on the nano- and macroscales is discussed in light of recent studies.
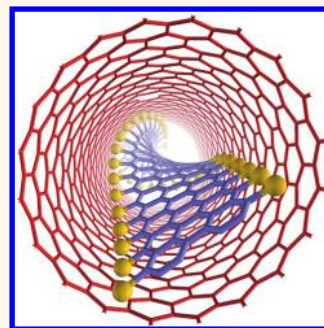
the internal diameter of a nanotube has to be at least 0.6 nm wider than the diameter of the guest molecule. Once encapsulated, the behavior of the guest molecule is greatly affected by confinement. For example, fullerene C_{60} forms molecular arrays inside nanotubes[3−5] that are dramatically different from the face-centered cubic structure of the bulk fullerene. The exact structure of the array is dependent on the nanotube diameter, as simple linear chains of C_{60}, typically observed in a SWNT with diameter of 1.3−1.5 nm, are replaced by more complex packing patterns in wider host CNTs. Inorganic atomic and ionic lattices can be similarly controlled by confinement in nanotubes.[6] Cobalt iodide, for instance, forms a helically twisted structure inside nanotubes that is fundamentally different from bulk CoI_2 crystals,[7] while atoms of iodine assemble into single chains or double and triple helices depending on the SWNT diameter.[8] These and other examples illustrate that the nanotube is not just a passive container: In many cases, it acts as an effective template to control the structures of molecular and atomic arrays.

In this issue of *ACS Nano*, Allen *et al.*[9] explore the behavior of fullerene molecules inside an atypically wide SWNT (*d* = 2.1 nm), where the guest molecules spontaneously arrange themselves into a zigzag array. Each molecule has four nearest neighbors—twice

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as many as compared to a single-file chain formed in SWNTs of typical diameters. The enhanced surface area of the intermolecular contacts significantly stabilizes the molecular array, so that the entire zigzag superstructure turns around its axis without breaking up. In response to the corkscrew motion of the guest molecules, the host nanotube becomes elliptically distorted. The observed diameter of the SWNT fluctuates by as much as 30% over time, which is substantially greater than in previous reports.[7,10,11] The observation that the SWNT can deviate so significantly from the idealized cylindrical shape has important implications for further development of nanotubes as templates since the elastic distortions of nanotubes (particularly wider SWNTs) must be taken into consideration when predicting the structure or rationalizing the dynamic behavior of the encapsulated guest molecules.

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Carbon Nanotubes as Nano-Reactors. It is logical to extend applications of carbon nanotubes one step further, beyond simple nanocontainers, and toward nanoscale reaction vessels. Shortly after the discovery that molecules can be inserted into SWNTs,[2] it was demonstrated that under irradiation by the electron beam (e-beam)[12,13] or at high temperatures[13,14] the fullerene guest molecules can oligomerize, coalesce, and merge into corrugated tubular structures nested inside the host SWNT. At elevated temperatures, structures formed in this way can anneal further into perfect double-walled nanotubes

(Figure 1a). If fullerenes are treated under similar conditions outside nanotubes (*i.e.*, in the bulk crystal), they form no such linear oligomeric or tubular structures, thus emphasizing that confinement inside the host nanotube has the potential to change the pathway of a chemical process significantly. Recently, a detailed mechanism of fullerene oligomerization was systematically investigated by Koshino *et al.*, who completed a comprehensive aberration-corrected HRTEM (AC-HRTEM) study of the effects of the energy and dose of electrons and temperature of the specimen on the oligomerization process.[15] The transformation processes induced by the e-beam were shown to be complex, starting with the formation of two covalent bonds between neighboring fullerenes, followed by the formation of more bonds and the gradual coalescence of two or more adjacent fullerene "peas" into a "peanut"-like structure (Figure 1e−g).

Regardless of the exact conditions, the fullerene dimers, oligomers, and polymers formed inside SWNTs of typical diameter (*e.g.*, 1.3−1.5 nm) are always linear. However, in their latest study, Allen *et al.* demonstrate that molecules packed in a zigzag array can yield a qualitatively different product.[9] Instead of forming a typical "peanut", three neighboring fullerene cages merge into a "trefoil" structure (Figure 1d). Formation of such an elaborate molecular structure consisting of a complex combination of carbon rings *via* standard synthetic chemistry routes would be a long and tortuous task, yet in the confines of the SWNT, this product is formed spontaneously.

It appears that other carbon-containing molecules, such as functionalized azafullerene $C_{59}N$,[16] polyaromatic hydrocarbons,[17] or ferrocene,[18] also readily turn into internal nanotubes upon heat treatment, thus indicating that this transformation is a general, thermodynamically driven process. However, it was only after a first well-defined and controlled chemical reaction

was demonstrated inside a SWNT (Figure 1b,c)[19] that carbon nanotubes received recognition as viable nanoscale reactors and were celebrated as the world's tiniest test tubes.[20] Under moderate heating, fullerene epoxide $C_{60}O$ undergoes ring-opening oligomerization and polymerization forming irregular, angular-shaped, and convoluted $(C_{60}O)_n$ structures in bulk. In contrast, when the epoxy ring of $C_{60}O$ is opened within a SWNT, the reactive intermediates are able to form only linear structures, such as perfectly straight unbranched polymeric chains (Figure 1b,c), which would be almost impossible to synthesize by other means. More recent examples illustrating that confinement in nanotubes leads to the formation of qualitatively different products include linear polymers of $(C_{59}N)_n$ (Figure 1h),[21] graphene nanoribbons (Figure 1i),[22,23] and direct transformation of $Fe−C_{60}$ and $Ru−C_{60}$ complexes into C_{70}.[24]

Activation of Reactions by the Electron Beam. The methodology of HRTEM has been instrumental in the discovery and investigation of chemical reactions in nanotubes. Although electron microscopy provides images of molecules with nearly atomic resolution in real time, it has a serious drawback related to the electron beam. The guest molecules are constantly bombarded by electrons during HRTEM imaging, so that some of the kinetic energy of the e-beam transferred to the molecules can trigger chemical transformations, as illustrated in the study by Allen *et al.*[9] These e-beam-induced reactions are undesirable if the objective is to obtain images of intact molecules. However, if the energy and dose of the electrons are carefully controlled,[15,24,25] the *in situ* transformations can provide valuable information about the chemical properties of the molecules and shed light on their reactivity in the confined environment. When interpreting the chemical reactivity observed under the e-beam, it is important to remember that carbon nanotubes are
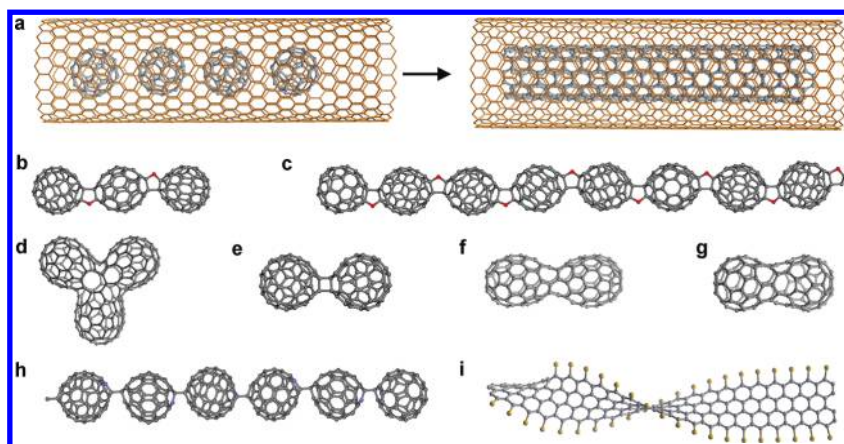
Figure 1. A variety of unusual molecular nanostructures can be synthesized inside single-walled carbon nanotubes. (a) Fullerenes C_{60} transform into an internal nanotube; (b) oligomers and (c) polymers $(C_{60}O)_n$; (d) "trefoil", and (e–g) variety of dimer molecules formed from three or two fullerene cages, respectively; (h) polymer $(C_{59}N)_n$; (i) sulfur-terminated graphene nanoribbon. (Molecular models for (d) were provided by Dr. C. S. Allen and for (f,g) by Dr. M. Koshino.)

excellent thermal and electronic conductors. Considering the fact that the e-beam irradiates only a tiny segment of a very thin (one to several nanometers in diameter) and extremely long (tens of micrometers in length) carbon nanotube, the heat and charge generated by the e-beam in the encapsulated molecules should be expected to dissipate quickly through the nanotube sidewalls, so that the nano test tube acts as an effective sink for heat and charge. The thicker, and hence more conducting, walls of the nanotube as well as close contact between the guest molecules and the inner surface of nanotube[26] were shown to enhance the stability of encapsulated molecules under the e-beam. Even though it is not possible to measure the temperature inside the nano test tube directly, *in situ* observations of transformations in carbon nanostructures indicate that the temperatures of carbon nanotubes and their contents are unlikely to rise significantly above the ambient temperature of the specimen (*i.e.*, room temperature in most cases), so that the observed reactions are mainly caused by the direct impact of the incident electrons of HRTEM.[27]

As demonstrated by Allen *et al.*[9] and by other groups, the e-beam of HRTEM provides an "energy bath" for the molecules in the form of the kinetic energy of electrons. Because

the e-beam is an unusual source of energy as compared to heat, light, or electrochemical potential sources typically employed to promote chemical reactions, the relevance of *in situ* HRTEM observations to the preparative synthesis is often questioned. Despite the scepticism, if the mechanisms of e-beam interactions with molecules[15] and carbon nanocontainers[28] are thoroughly analyzed and understood, the time-resolved HRTEM imaging of chemical reactions can guide the further development of carbon nanotubes toward nano-reactor applications. Most of the knowledge about reactivity in the confines of CNTs observed at the nanoscale can, in principle, be transferred to and harnessed for practical preparative synthesis. Indeed, some of the reactions discovered by HRTEM, such as C_{60}@SWNT to double-walled nanotube (DWNT) transformation[13,14] or the formation of sulfur-terminated graphene nanoribbons,[22] can be successfully replicated on the macroscale.

Toward Preparative Synthesis in Carbon Nano-Reactors. In parallel with the investigation of chemical reactions at the nanoscale driven by HRTEM, some significant progress has been achieved in catalytic reactions inside carbon nanotubes aimed at preparative synthesis.[29,30] The general strategy adopted in this field appears to be a reverse of that described above, as products and rates of chemical reactions measured at

the macroscale are related to the local nanoscale structure of the nanotube reactor. In contrast to the HRTEM *in situ* experiments that typically utilize SWNTs, most of the studies using macroscale approaches are performed in multiwalled carbon nanotubes (MWNTs) or in hollow carbon nanofibers (CNFs, consisting of stacked graphitic cones rather than concentric nanotubes as in MWNTs) whose internal diameters are considerably larger than the size of the guest molecules (Figure 2). The difference between the energies of surface adsorption (E_a) and encapsulation energy (E_e) is significantly lower for wider nanocontainers (Figure 2b) in comparison to SWNTs (Figure 2a). As a result, it is much more difficult to ensure that the reactant molecules are encapsulated in the MWNTs/CNFs rather than adsorbed on their outer surfaces, and that the reactions indeed take place inside these nano-reactors.

Typically, reactions are chosen such that they take place only in the presence of a metal catalyst (*i.e.*, the molecules cannot react in the bulk phase or upon contact with the nanotube). The catalyst is inserted into nanotubes in the form of metal-containing molecules or metal nanoparticles, and MWNT− or CNF− catalyst composites formed in this manner are thoroughly analyzed by TEM to ensure that most of the catalytic species are inside the
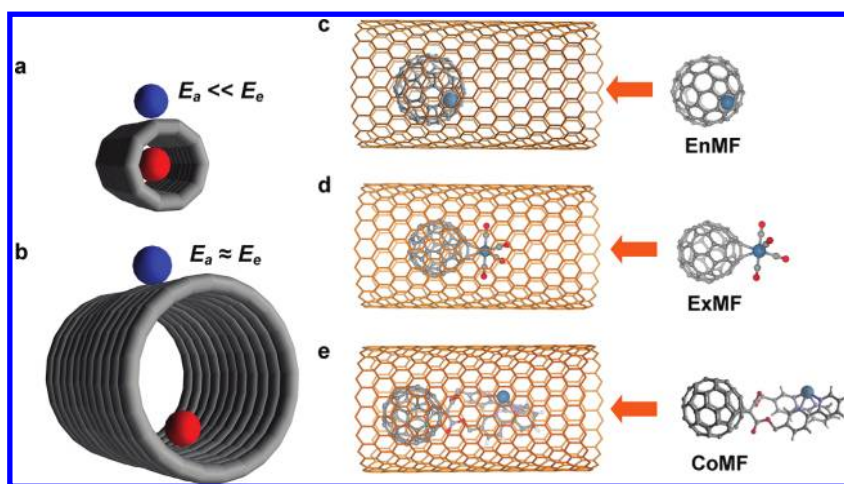
Figure 2. Confinement effects are more pronounced in narrower nano-reactors (a) where the energy of encapsulation of a reactant (E_e, red molecule) is significantly greater than the energy of surface adsorption (E_a, blue molecule), as compared to (b) wider nano-reactors, where E_a and E_e are almost identical. Three different strategies for the delivery of catalytic metal atoms into narrow nanotubes utilizing (c) endohedral, (d) exohedral, and (e) coordination metallofullerenes.

nano-reactors. Because the success of the catalyst encapsulation fully determines whether reactions will take place in nanotubes or outside of them, substantial effort has been invested into the optimization of this process. In general, metal can be delivered into CNFs or MWNTs as preformed nanoparticles ready for catalysis[31−33] or inserted in the form of a metal compound, which then decomposes into metal nanoparticles inside the nanotube.[34,35] Even though the efficiency of these methods can be high, which ensures that the majority of catalytic centers are encapsulated inside nanoreactors, a minor but significant proportion of nanoparticles (typically 10−20%) can still be located on the surface. To account for these, all reactions are meticulously compared with control samples where the catalyst is adsorbed on the MWNT/CNF outer surface, which allows the genuine effects of nano-reactors on chemical reactions to be pinned down.[29,30]

Allen et al.[9] insert metal centers into nanotubes as discrete atoms, using a different method. They utilize endohedral metallofullerenes (EnMFs), in which individual metal atoms of lanthanum are "packaged" within fullerene carbon cages. The encapsulation of EnMFs is driven by strong and highly specific van der Waals interactions of the convex sur-face of the fullerene and the concave surface of the SWNT, which can reach up to 290 kJ/mol, thus ensuring that all metal atoms are securely entrapped inside nanotubes (Figure 2c). The fullerene cages can be broken down by the e-beam or by heating, so that the metal atoms are released into the internal cavity of nanotubes, making them available for catalysis. Although the usage of EnMFs is an efficient and reliable technique for encapsulating metals, it is limited mostly to the metals of group III of the periodic table (Sc, Y, and lanthanides). Furthermore, the scarcity of endohedral fullerenes severely limits this method to small scales (typically, one to a few milligrams of material). To address this problem, exohedral metallofullerenes (ExMFs) have been successfully introduced as vehicles for the transport and encapsulation of Os and Re (Figure 2d)[36,37] and, most recently, Fe and Ru atoms in SWNTs,[24] thus providing an alternative to EnMFs. The metal atoms in ExMFs are attached to the surfaces of fullerenes and are hence readily available for catalysis, as demonstrated by in situ HRTEM experiments.[24,36,37] Importantly, the introduction of ExMFs broadens the range of the metals that can be reliably inserted into SWNTs to a large group of transition elements, including the platinum group metals that are instrumental for catalysis. The significantly wider availability of ExMFs over EnMFs makes them more suitable for practical applications. However, a fullerene cage functionalized with a ligand group capable of binding to any of the transition metal ions, such as the chelating 2,2′-bipyridine (Figure 2e),[38] may prove to be even more versatile for delivering transition metals into SWNTs than ExMFs or EnMFs. Despite their surface being modified, such coordination metallofullerenes (CoMFs) retain their high affinity for the nanotube interior and, potentially, can transport virtually any metal in the periodic table into a SWNT. Even though the catalytic activity of fullerene complexes inside nanotubes has not yet been explored on the preparative scale, the HRTEM observations of Allen et al.[9] and other recent studies[24,37] indicate that discrete metal atoms can play an important catalytic role within the confines of the nano-reactor, often dramatically changing the pathways of reactions and leading to the formation of unexpected products.

Despite the fact that the assembly of the nanotube−catalyst systems currently used for studying reactions in solution or gas phase require further optimization, there is strong evidence that the macroscopic parameters of chemical reactions

TABLE 1. Effects of Carbon Nano-Reactors on Chemical Reactions

interactions between CNT and catalyst	interactions between CNT and reactants	interactions between CNT and products
enhanced stability of catalyst inside nanotube	attractive interactions between nanotube interior and reactant molecules leading to higher local concentration and effective pressure inside nano-reactors	restriction of reaction space inside nanotube favoring formation of one product (*e.g.*, linear isomer) over another (*e.g.*, branched isomer)
electron transfer between catalyst and interior surface of nanotube altering catalytic activity	alignment of reactant molecules within nanotube facilitating reaction	efficient transport of product molecules from nano-reactor to bulk phase
chemical reactions between metal catalyst and nanotube interior leading to transformations of CNT sidewall	van der Waals or electron transfer interactions between reactants and nanotube interior lowering activation energy	

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(*e.g.*, reaction rate, yield, or selectivity) are affected by confinement in MWNTs and CNFs. A wide range of reactions experimentally studied in carbon nano-reactors, including hydrogenation, hydroformylation, syngas conversion, ammonia decomposition, metal oxide reduction, and epoxidation,[29,30] reveal some measurable effects of the confinement. The observed effects can be divided into three main categories related to the interactions of the nano-reactor with the catalyst, reactant molecules, or product molecules, respectively (Table 1).

The confinement of catalytic nanoparticles within carbon nano-reactors appears to enhance their stability against sintering and coalescence, which in turn prolongs their activity. Electronic interactions between a metallic nanoparticle and the nanotube interior surface can further tune the electronic state and hence the activity of the catalyst.[39] It should be noted, however, that the nanotube interior is not as inert toward metal catalysts as was initially believed. HRTEM observations clearly show that small clusters of La[15] or Dy[26] can catalyze a rupture of the nanotube container, while individual metal atoms of Re trigger a series of structural transformations in the nanotube sidewall.[37]

The high affinity of reactant molecules for the nanotube cavity can create a higher local concentration of reactants inside the nano-reactor than in the surrounding liquid or gas phase, which in turn can potentially increase the reaction rate, improve the yield, or alter the ratio of the products. It is expected that in some cases the effective pressure within the nanotube will be higher than in the bulk,[40] which will have further implications for the reaction pathway. On the molecular level, the collisions between reactant molecules within the confines of a nanotube may differ significantly from those in the bulk. For example, confinement in a nanotube may align reactant molecules in orientations particularly favorable for a specific reaction mechanism. Furthermore, physicochemical interactions between guest molecules and the nanotube sidewall, such as van der Waals or electron-transfer interactions, are expected to have tangible effects on the activation energies of the reactions. Intuitively, nanotubes with smaller internal diameters are expected to have greater effects on the positions, orientations, and dynamic behavior of reactant molecules and therefore may be more suitable for nano-reactor applications. However, a channel of a one-dimensional nano-reactor that is too narrow is prone to blockages and restricted diffusion rates of reactants/products to and from the nanotube, thus slowing down reactions. Therefore, it is unlikely that one type of nanotube will be used as a universal nano-reactor, as different reactions have different steric and electronic requirements that must be satisfied by confinement.

The internal diameter is similarly important for the diffusion of reaction products out of the nano-reactor, which should proceed without dislodging the catalyst or hindering the entrance of reactants. Owing to the atomically smooth internal surface of carbon nanotubes, the diffusion of atoms and small molecules within the nanotube channel is efficient[29] and can be significantly higher than in other porous materials.[30]

CONCLUSIONS AND OUTLOOK

The properties of carbon nanotubes as nanoscale containers and chemical reaction vessels are currently being explored by two orthogonal strategies. The study by Allen *et al.*[9] in this issue of *ACS Nano* is a perfect example of the first strategy, relying on *in situ* monitoring of chemical transformations in nanotubes at the single-molecule level. The electron beam serves simultaneously as an imaging tool and as a source of energy promoting reactions in nanotubes. The rich and diverse range of

reactions demonstrated in nanotubes by HRTEM shows that confinement at the nanoscale can dramatically change the pathways of chemical reactions, in many cases leading to unexpected products. The discovery of reactions by direct space imaging in real time offers a fundamentally new way of studying the chemical properties of molecules. As the power of the e-beam is being tamed *via* the development of low-voltage aberration-corrected HRTEM techniques and by careful control of the electron dose, chemical transformations observed inside nanotubes become increasingly relevant to preparative synthetic chemistry. There is still much to be done to improve our understanding of the exact mechanisms of the interactions between the e-beam and molecules, which should enable nanoscale observations to guide the development of synthetic chemistry in the future. Carbon nano-containers offer an excellent platform for this strategy.

The second strategy is macroscopic in its methodology and builds on the concepts of heterogeneous catalysis. It transfers the extensive knowledge of catalysis in nanoporous structures to carbon nanotubes. The effects of molecular confinement are studied by careful analysis of the reaction products formed inside hollow carbon nanostructures (MWNTs or CNFs). Even though it is not always possible to state with confidence whether the reactions take place on the interior or exterior surface of the nanotube, or indeed in the bulk phase (*e.g.*, due to the catalyst leaching), the latest studies provide compelling evidence that it is possible to control preparative chemical reactions by confinement in nanotubes. One of the key challenges for this strategy is the fact that, in most systems studied to date, the internal diameters of the nano-reactors greatly exceed the van der Waals diameters of the guest molecules. Although wider diameters of nanotubes are useful for maintaining the efficient diffusion of reactants/products to and from the nano-reactor, they prohibit the exploration of the fundamental effects of confinement at the nanoscale, which, as shown by the first strategy, are essential for controlling reactions.

Both strategies demonstrate that carbon nanotubes are much more than just passive containers. They act as highly efficient templates for complex molecular arrays, possess a wealth of functional physicochemical properties that could be harnessed to control encapsulated guest molecules, and provide excellent platforms for imaging molecules and studying chemical reactions. Carbon nano test tubes are becoming nano-reactors and may change the way we study and make molecules in the near future.

REFERENCES AND NOTES

1. *Molecular Encapsulation: Organic Reactions in Constrained Systems*; Brinker, U. H., Mieusset, J.-L., Eds.; Wiley: New York, 2010.
2. Smith, B. W.; Monthioux, M.; Luzzi, D. E. Encapsulated C_{60} in Carbon Nanotubes. *Nature* **1998**, *396*, 323–324.
3. Warner, J. H.; Ito, Y.; 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.
4. Khlobystov, A. N.; Britz, D. A.; Ardavan, A.; Briggs, G. A. D. Observation of Ordered Phases of Buckminsterfullerene in Carbon Nanotubes. *Phys. Rev. Lett.* **2004**, *92*, 245507.
5. Troche, K. S.; Coluci, V. R.; Braga, S. F.; Chinellato, D. D.; Sato, F.; Legoas, S. B.; Rurali, R.; Galvao, D. S. Prediction of Ordered Phases of Encapsulated C_{60}, C_{70}, and C_{78} Inside Carbon Nanotubes. *Nano Lett.* **2005**, *5*, 349–355.
6. Sloan, J.; Kirkland, A. I.; Hutchison, J. L.; Green, M. L. H. Structural Characterization of Atomically Regulated Nanocrystals Formed within Single-Walled Carbon Nanotubes Using Electron Microscopy. *Acc. Chem. Res.* **2002**, *35*, 1054–1062.
7. Philp, E.; Sloan, J.; Kirkland, A. I.; Meyer, R. R.; Friedrichs, S.; Hutchison, J. L.; Green, M. L. H. An Encapsulated Helical One-Dimensional Cobalt Iodide Nanostructure. *Nat. Mater.* **2003**, *2*, 788–791.
8. Guan, L.; Suenaga, K.; Shi, Z.; Gu, Z.; Iijima, S. Polymorphic Structures of Iodine and Their Phase Transition in Confined Nanospace. *Nano Lett.* **2007** *7*, 1532–1535.
9. Allen, C. S.; Ito, Y.; Robertson, A. W.; Shinohara, H.; Warner, J. H. Two-Dimensional Coalescence Dynamics of Encapsulated Metallofullerenes in Carbon Nanotubes. *ACS Nano* **2011**, DOI: 10.1021/nn204003h.
10. Ran, K.; Zuo, J. M.; Chen, Q.; Shi, Z. J. Electron Beam Stimulated Molecular Motions. *ACS Nano* **2011**, *5*, 3367–3372.
11. Warner, J. H.; Wilson, M. Elastic Distortions of Carbon Nanotubes Induced by Chiral Fullerene Chains. *ACS Nano* **2010**, *4*, 4011–4016.
12. Hernandez, E.; Meunier, V.; Smith, B. W.; Rurali, R.; Terrones, H.; Buongiorno Nardelli, M.; Terrones, M.; Luzzi, D. E.; Charlier, J.-C. Fullerene Coalescence in Nanopeapods: A Path to Novel Tubular Carbon. *Nano Lett.* **2003**, *3*, 1037–1042.
13. Luzzi, D. E.; Smith, B. W. Formation Mechanism of Fullerene Peapods and Coaxial Tubes: A Path to Large Scale Synthesis. *Chem. Phys. Lett.* **2000**, *321*, 169–174.
14. Bandow, S.; Takizawa, M.; Hirahara, K.; 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.
15. Koshino, M.; Niimi, Y.; Nakamura, E.; Kataura, H.; Okazaki, T.; Suenaga, K; Iijima, S. Analysis of the Reactivity and Selectivity of Fullerene Dimerization Reactions at the Atomic Level. *Nat. Chem.* **2010**, *2*, 117–124.
16. Simon, F.; Kuzmany, H.; Bernardi, J.; Hauke, F.; Hirsch, A. Encapsulating $C_{59}N$ Azafullerene Derivatives Inside Single-Walled Carbon Nanotubes. *Carbon* **2006**, *44*, 1958–1962.
17. Fujita, Y.; Bandow, S.; Iijima, S. Formation of Small-Diameter Carbon Nanotubes from PTCDA Arranged Inside the Single-Wall Carbon Nanotubes. *Chem. Phys. Lett.* **2005**, *413*, 410–414.
18. Shiozawa, H.; Pichler, T.; Grüneis, A.; Pfeiffer, R.; Kuzmany, H.; Liu, Z.; Suenaga, K.; Kataura, H. A Catalytic Reaction Inside a Single-Walled Carbon Nanotube. *Adv. Mater.* **2008**, *20*, 1443–1449.
19. Britz, D. A.; Khlobystov, A. N.; Porfyrakis, K.; Ardavan, A.; Briggs, G. A. D. Chemical Reactions Inside Single-Walled Nano Test-Tube. *Chem. Commun.* **2005**, 37–39.
20. *Guinness World Records 2006*. Guinness Media, 2005.
21. Pagona, G.; Rotas, G.; Khlobystov, A. N.; Chamberlain, T. W.; Porfyrakis, K.; Tagmatarchis, N. Azafullerenes Encapsulated within Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc.* **2008**, *130*, 6062–6063.
22. Chuvilin, A.; Bichoutskaia, E.; Gimenez-Lopez, M. C.; Chamberlain, T. W.; Rance, G. A.; Kuganathan, N.; Biskupek, J.; Kaiser, U.; Khlobystov, A. N.

Self-Assembly of a Sulphur-Terminated Graphene Nanoribbon within a Single-Walled Carbon Nanotube. *Nat. Mater.* **2011**, *10*, 687–692.

23. Talyzin, A. V.; Anoshkin, I. V.; Krasheninnikov, A. V.; Nieminen, R. M.; Nasibulin, A. G.; Jiang, H.; Kauppinen, E. I. Synthesis of Graphene Nanoribbons Encapsulated in Single-Walled Carbon Nanotubes. *Nano Lett.* **2011**, *11*, 4352–4356.

24. Nakamura, E.; Koshino, M.; Saito, T.; Niimi, Y.; Suenaga, K.; Matsuo, Y. Electron Microscopic Imaging of a Single Group 8 Metal Atom Catalyzing C—C Bond Reorganization of Fullerenes. *J. Am. Chem. Soc.* **2011**, *133*, 14151–14153.

25. Kaiser, U.; Biskupek, J.; Meyer, J. C.; Leschner, J.; Lechner, L.; Rose, H.; Stoger-Pollach, M.; Khlobystov, A. N.; Hartel, P.; Muller, H.; *et al.* Transmission Electron Microscopy at 20 kV for Imaging and Spectroscopy. *Ultramicroscopy* **2011**, *111*, 1239–1246.

26. Chuvilin, A.; Khlobystov, A. N.; Obergfell, D.; Haluska, M.; Yang, S; Roth, S.; Kaiser, U. Observations of Chemical Reactions at the Atomic Scale: Dynamics of Metal-Mediated Fullerene Coalescence and Nanotube Rupture. *Angew. Chem., Int. Ed.* **2010**, *49*, 193–196.

27. Banhart, F. Irradiation Effects in Carbon Nanostructures. *Rep. Prog. Phys.* **1999**, *62*, 1181–1221.

28. Krasheninnikov, A. V.; Nordlund, K. Ion and Electron Irradiation-Induced Effects in Nanostructured Materials. *J. Appl. Phys.* **2010**, *107*, 071301.

29. Serp, P.; Castillejos, E. Catalysis in Carbon Nanotubes. *ChemCatChem* **2010**, *2*, 41–47.

30. Pan, X.; Bao, X. The Effects of Confinement Inside Carbon Nanotubes on Catalysis. *Acc. Chem. Res.* **2011**, *44*, 553–562.

31. Castillejos, E.; Debouttiere, P.-J.; Roiban, L.; Solhy, A.; Martinez, V.; Kihn, Y.; Ersen, O.; Philippot, K.; Chaudret, B.; Serp, P. An Efficient Strategy To Drive Nanoparticles into Carbon Nanotubes and the Remarkable Effect of Confinement on Their Catalytic Performance. *Angew. Chem., Int. Ed.* **2009**, *48*, 2529–2533.

32. La Torre, A.; Rance, G. A.; El Harfi, J.; Li, J.; Irvine, D. J.; Brown, P. D.; Khlobystov, A. N. Transport and Encapsulation of Gold Nanoparticles in Carbon Nanotubes. *Nanoscale* **2010**, *2*, 1006–1010.

33. Tessonnier, J.-P.; Ersen, O.; Weinberg, G.; Pham-Huu, C.; Su, D. S.; Schlögl, R. Selective Deposition of Metal Nanoparticles Inside or Outside Multiwalled Carbon Nanotubes. *ACS Nano* **2009**, *3*, 2081–2089.

34. Costa, P. M. F. J.; Sloan, J.; Rutherford, T.; Green, M. L. H. Encapsulation of Re_xO_y Clusters within Single-Walled Carbon Nanotubes and Their *In Tubulo* Reduction and Sintering to Re Metal. *Chem. Mater.* **2005**, *17*, 6579–6582.

35. Endo, M.; Kim, Y. A.; Ezaka, M.; Osada, K.; Yanagisawa, T.; Hayashi, T.; Terrones, M.; Dresselhaus, M. S. Selective and Efficient Impregnation of Metal Nanoparticles on Cup-Stacked-Type Carbon Nanofibers. *Nano Lett.* **2003**, *3*, 723–726.

36. Chamberlain, T. W.; Champness, N. R.; Schroder, M.; Khlobystov, A. N. Piggyback Ride for Transition Metals: Encapsulation of Exohedral Metallofullerenes in Carbon Nanotubes. *Chem.—Eur. J.* **2011**, *17*, 668–674.

37. Chamberlain, T. W.; Meyer, J. C.; Biskupek, J.; Leschner, J.; Santana, A.; Besley, N. A.; Bichoutskaia, E.; Kaiser, U.; Khlobystov, A. N. Reactions of the Inner Surface of Carbon Nanotubes and Nanoprotrusion Processes Imaged at the Atomic Scale. *Nat. Chem.* **2011**, *3*, 732–737.

38. Fan, J.; Chamberlain, T. W.; Wang, Y.; Yang, S. H.; Blake, A. J.; Schroder, M.; Khlobystov, A. N. Encapsulation of Transition Metal Atoms into Carbon Nanotubes: A Supramolecular Approach. *Chem. Commun.* **2011**, *47*, 5696–5698.

39. Guo, S.; Pan, X.; Gao, H.; Yang, Z.; Zhao, J.; Bao, X. Probing the Electronic Effect of Carbon Nanotubes in Catalysis: NH_3 Synthesis with Ru Nanoparticles. *Chem.—Eur. J.* **2010**, *16*, 5379–5384.

40. Ledoux, M. J.; Vieira, R.; Pham-Huu, C.; Keller, N. New Catalytic Phenomena on Nanostructured (Fibers and Tubes) Catalysts. *J. Catal.* **2003**, *216*, 333–342.

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