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Fullerene Peapods

Hydrogen-Driven Collapse of C_{60} Inside Single-Walled Carbon Nanotubes**

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Peapods are hybrid materials with C_{60} molecules encapsulated inside single-walled carbon nanotubes (SWCNTs). Here we provide direct evidence for the surprising ability of hydrogen gas to penetrate into the inner space of SWCNTs in C_{60} peapods and to react with fullerene molecules. Hydrogenation of peapods at 500–550 °C results in a complete collapse of C_{60} molecules encapsulated in the SWCNTs with formation of some large hydrocarbon molecules (fragments of the fullerene cage) similar to a reaction performed under the same conditions with a bulk reference sample of C_{60} powder.

SWCNTs are considered as very promising material for various applications and give many opportunities for new reactions.[1–4] The hollow space inside of SWCNTs can be filled with various molecules, thus providing the opportunity to study reactions in a one-dimensional space.[5]

A large variety of molecules has been encapsulated into SWCNTs.[6,7] One of the best studied examples of encapsulation are peapods, hybrid materials obtained by insertion of fullerenes into nanotubes.[8] Peapods have been prepared with fullerenes of different sizes (C_{60}, C_{70}, C_{82}, etc.), endohedrals, and various fullerene derivatives.[9–19]

Fullerene peapods provided also several examples of chemical reactions performed in one-dimensional spaces inside SWCNTs. For example, the polymerization of C_{60} molecules has been achieved by several methods: electron beam,[20] laser irradiation,[21] and high-pressure high-temperature treatments.[22,23] Fullerene peapods have also been successfully intercalated by alkali metals.[11,24] The formation of double-walled carbon nanotubes (DWCNTs) has been observed as a result of the collapse of fullerenes inside SWCNTs induced by heat treatment.[25,26]

Recently we demonstrated the ability of hydrogen gas to penetrate into the inner space of SWCNTs in C_{60} peapods and to react with fullerene molecules. However, only light hydrogenation of C_{60} inside SWCNTs was achieved in this study (around $C_{60}H_{12-14}$).[27] Our previous studies on bulk samples demonstrated that prolonged hydrogenation of C_{60} using molecular hydrogen at 400–450 °C results first in the formation of fulleranes $C_{60}H_x$ (x up to 52), followed by cage fragmentation (e.g. $C_{59}H_x$ and $C_{58}H_x$) and complete collapse of the cage structure with formation of a complex mixture of hydrocarbon molecules.[28–33] Large fullerene fragments, for example, large polycyclic aromatic hydrocarbons (PAHs) can be formed in the process of fragmentation because of the immediate termination of any dangling bonds formed in the process of C_{60} unzipping under hydrogen reaction conditions.[30,31]

In this study, we increased the temperature of the hydrogenation reaction over the limits of the C–H bond stability in hydrogenated fullerenes (500–550 °C and 50 bar H_2 pressure) to induce a rapid collapse of the C_{60} cage structure with formation of large hydrocarbon molecules (fullerene-cage fragments).

Figure 1 shows Raman spectra from peapod samples hydrogenated at 450, 500, and 550 °C. The only visible change in the Raman spectra after hydrogenation of C_{60} inside SWCNTs at 450 °C is the disappearance of the $A_g(2)$ mode. The same result was observed previously for samples of C_{60} peapods hydrogenated at 400 °C.[27] The C_{60} under these conditions is expected to hydrogenate with formation of a broad distribution of $C_{60}H_x$ compositions with x in the range of tens of atoms.[28–33] The mixture of many compositions results in rather broad and weak spectral features instead of sharp peaks and cannot be observed because of the overlap with SWCNT spectra. Raman spectra from bulk $C_{60}H_x$ powder obtained by reaction with hydrogen gas cannot be recorded using lasers in the visible range of the excitation wavelength because of the high luminescence.

However, the luminescence disappeared in the powder C_{60} samples hydrogenated at temperatures above 500 °C (Figure 1 b). The C_{60} after annealing in hydrogen at 500–550 °C transforms into a black powder (highly hydrogenated fullerenes are yellow in color) which is amorphous on XRD, shows no signatures of fullerenes in the Raman spectra, mostly not soluble in organic solvents, and showed only a broad range of hydrocarbons (around 250–450 amu) in the MALDI MS spectra recorded from toluene extracts. The fact of a complete collapse of C_{60} in hydrogen-annealed bulk samples is behind any doubts while the final product is a rather complicated mixture of hydrocarbons.

Peapod samples hydrogenated at 500 and 550 °C also showed a number of new peaks in the Raman spectra after the collapse of C_{60} inside the SWCNTs. Most clearly recognizable

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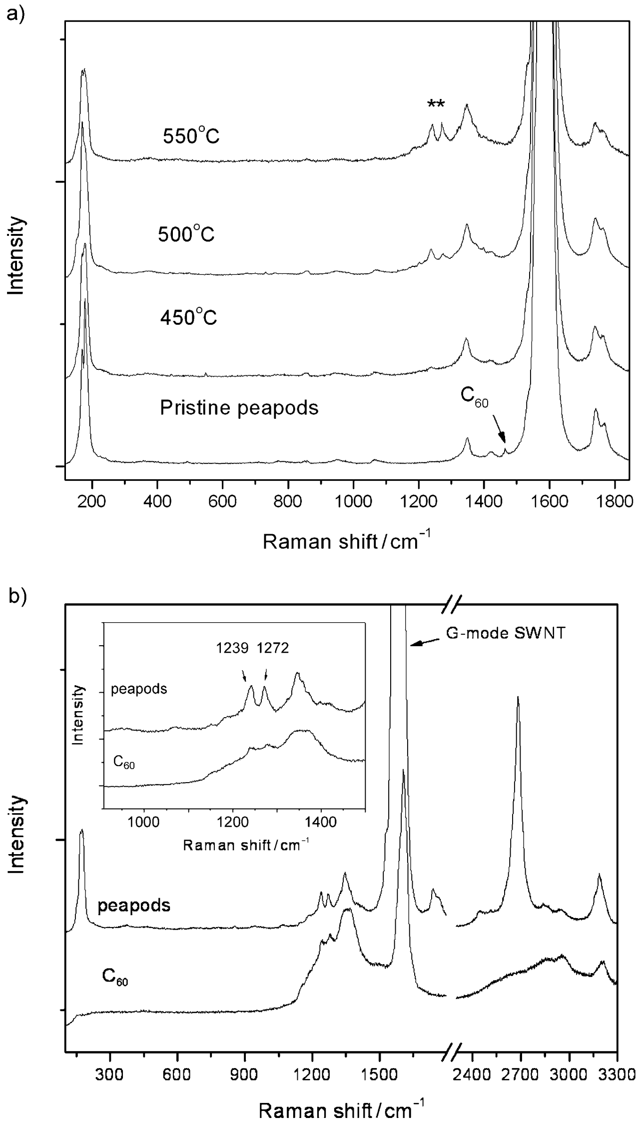

Figure 1. a) Raman spectra recorded from samples of pristine peapods and peapods after hydrogenation at elevated temperatures (450, 500, and 550 °C). b) Raman spectra from a peapod sample hydrogenated at 550 °C compared to the spectrum of a reference powder sample of C_{60} hydrogenated at the same pressure/temperature conditions. The spectra were recorded using a 514 nm laser.

new peaks are found at 1239 and 1272 cm^{-1} (marked by stars in Figure 1 a), some smaller peaks are also observed at 1183, 1322, and 1368 cm^{-1}. Two small peaks are also found in the spectral region of C–H vibrations at 2843 and 2870 cm^{-1}. It is also interesting that an increasing laser power from 1 to 100 % did not result in significant changes in the Raman spectra from "collapsed peapods" (see the Supporting Information).

Figure 1 b shows that new peaks in the Raman spectra recorded from peapods hydrogenated at 550 °C are remarkably similar to spectra from reference C_{60} powder sample hydrogenated at the same temperature. However, the spectra of "collapsed peapods" showed much sharper peaks (e.g. 1239 and 1272 cm^{-1}) reflecting less complex compositions. C_{60} molecules in peapods are confined in a 1D space and cannot react with each other as easily as in the bulk powder. The spectra shown in Figure 1 b prove that the collapse of C_{60} inside peapods occurs under hydrogenation conditions similar to bulk C_{60} powder.

Hydrogenation of C_{60} at 450 °C and complete collapse in the samples hydrogenated at 500 and 550 °C is also confirmed by experiment with heat treatment of these samples (and reference peapod sample) in argon at 950 °C, Figure 2.

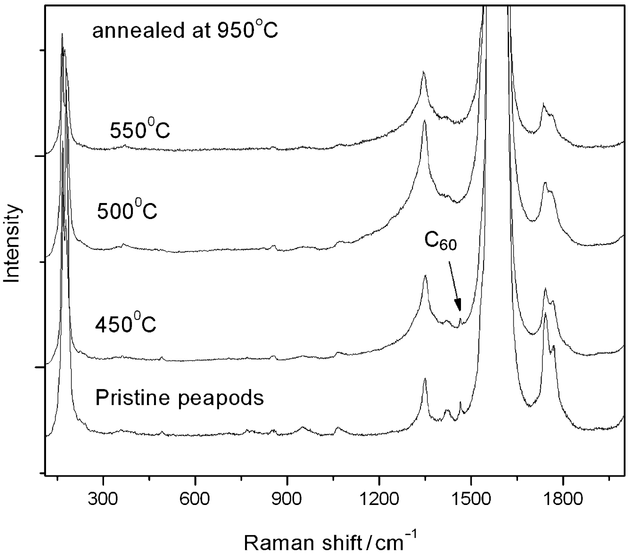

Figure 2. The same samples as in Figure 1 after annealing in argon at 950 °C. The spectra are zoomed to the spectral region below 2000 cm^{-1} which shows fullerene peaks. The G-mode of the SWCNT has a much higher relative intensity compared to the peaks from C_{60} and is over-scaled. The spectra were recorded using a 514 nm laser.

The temperature of annealing is well above the point of C–H breaking in $C_{60}H_x$ (500–550 °C[29,34]) and just below the known temperature point of formation of double-walled carbon nanotubes because of thermally induced coalescence of C_{60} molecules inside SWCNTs.[22,35] Indeed, the Raman spectrum recorded from the reference (not hydrogenated) sample of annealed peapods showed peaks from C_{60} and no traces of a collapse of fullerene molecules or formation of inner tubes. According to previously published data most of the pristine C_{60} can be recovered after annealing of $C_{60}H_x$.[29,34] The peapod sample hydrogenated at 450 °C showed the same transformation: the $A_g(2)$ mode of pristine C_{60} is recovered after annealing at 950 °C with a somewhat smaller intensity relative to pristine peapods.

In contrast, Raman spectra recorded from peapod samples hydrogenated at 500 and 550 °C and annealed at 950 °C showed only peaks from SWCNTs.

All additional peaks observed after hydrogenation of peapods disappeared after annealing but C_{60} was not recovered. These data confirm that the hydrogenation above 500 °C results in a collapse of the C_{60} cage with formation of some hydrocarbon molecules. Light hydrocarbons are likely to evaporate from tubes while larger PAHs are known to

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transform into amorphous carbon deposits above 700 °C (temperature of the C–H bond break).

Analysis of the TEM images recorded from C_{60} samples annealed in hydrogen at 500 and 550 °C confirms that most of the fullerenes disappeared from the samples because of the collapse of the cage structure (Figure 3). Most of the tubes also remain single-walled, but filled with some carbon "debris".

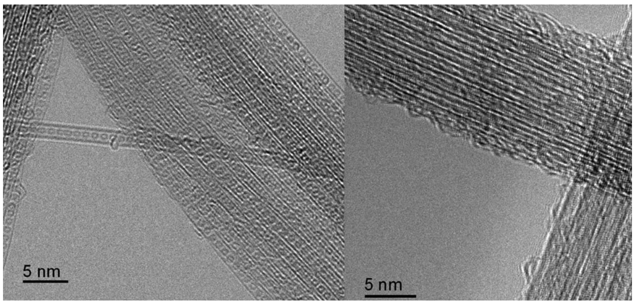

Figure 3. TEM images of pristine peapods and peapods annealed in hydrogen at 550 °C.

Figure 4 a shows fast Fourier transforms (FFTs) taken from the images collected from a large pristine peapod bundle. Figure 4 a clearly shows the periodicity typical for C_{60} molecules packed inside SWCNTs. After treatment at 450 °C some periodicity (Figure 4 b) is still visible. Figure 4 c shows FFT from a similar SWCNT bundle after annealing in hydrogen and no trace of periodicity typical for C_{60} is found.

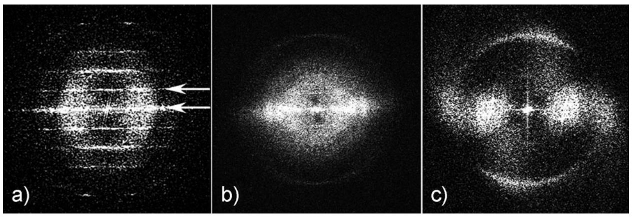

Figure 4. The Fourier-transformed HRTEM images taken from bundles of: a) pristine peapods, hydrogenated at b) 450 °C, and c) 550 °C, respectively. The arrows in (a) demonstrate a 9.8 Å periodicity because of the fullerenes packed inside the SWCNTs. The same periodicity but with much weaker lines is found in (b) and absent in (c) confirming the reaction and collapse of the fullerene molecules after annealing at 450 and 550 °C, respectively.

The TEM characterization also allows to find relatively rare objects and to get insight on reaction process on various stages (possibly some nanotubes are less accessible for hydrogen penetration).

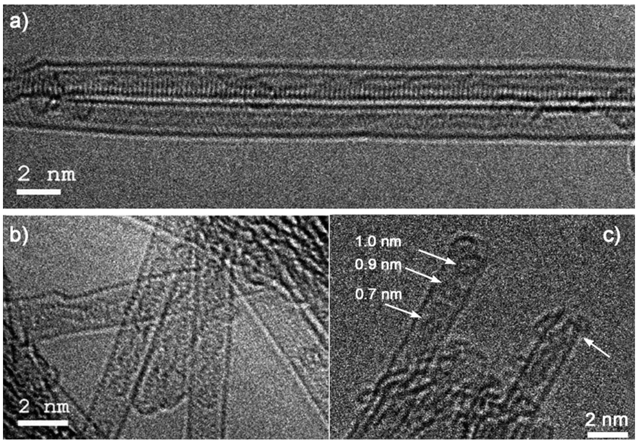

Figure 5. The HRTEM images recorded from peapod samples hydrogenated at 450–500 °C: a) inner nanotube inside a SWCNT formed as a result of the C_{60} fusion. In the upper tube some helical structure is observed (500 °C). b) Different stages of the coalescence of C_{60} molecules (500 °C). c) Hydrogenation at 450 °C: fullerene molecules with increasing size towards the opening at the nanotube tip. The molecule closest to the opening is too large to be a fullerene as noted by the diameters of the molecules. The nanotube on the right side shows a polymeric chain consisting of five to six fullerene molecules near the region of the nanotube opening.

Several TEM images collected from peapod samples annealed at 500–550 °C (Figure 5 a) exhibit some helical inner objects similar to graphene nanoribbons observed in our previous study[38] and nonhelical objects more similar to inner nanotubes. Figure 5 b shows the polymerization and fusion of C_{60} molecules into inner tubules of irregular shape. Different stages of the tubule formation can be observed, starting from chainlike connected spherical molecules. It should be emphasized that the coalescence of fullerenes is not caused by the electron beam from transmission electron microscope. Several unmodified peapods were observed in the same sample and they were not affected by the electron beam under the imaging conditions (see the Supporting Information).

The fusion of fullerene molecules observed in Figure 5 is the result of their reaction with hydrogen, which removes some carbon atoms from the cage. Formation of hydrogenated fullerene dimers was observed in our previous studies on hydrogenation of a bulk C_{60} powder and confirmed by independent studies.[28,36] On the other hand, experiments presented here were performed at higher temperatures and "etching" effects of hydrogen reactions (and coalescence) had to be much stronger.

It can be concluded that hydrogenation at extreme conditions induces dimerization and polymerization of C_{60} molecules inside peapods followed by their fusion and disintegration in smaller fragments while only a few inner tubes formed, consistently with results obtained from Raman spectroscopy which showed no vibrational signatures of double-walled carbon nanotubes.

Finally, it is interesting to discuss the possibility to use hydrogenation of C_{60} for the synthesis of hydrogen-terminated graphene nanoribbons encapsulated in SWCNTs.[37] It could be anticipated that hydrogen termination of dangling bonds prevents the formation of inner nanotubes upon the collapse of the fullerene cage structure. Indeed, very few nanoribbon-like objects with helical twisting were found in our samples. However, results demonstrate that high temperatures of reaction (above 500 °C) and a 50 bar H_2 pressure favor the etching mechanism of reaction with formation of

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hydrocarbon molecules and do not provide conditions required for nanoribbon formation.

In summary, direct evidence of the reaction between C_{60} molecules encapsulated in SWCNTs and hydrogen gas is provided. Hydrogen is able to penetrate into SWCNTs even when they are filled with fullerene molecules which results in hydrogenation at moderate temperature ($C_{60}H_x$ forms at 400–450 °C). The fullerene cage completely collapses inside SWCNTs by reaction with hydrogen gas at higher temperatures (500–550 °C) and formation of various hydrocarbon molecules. Hydrogenation at extreme temperature conditions also facilitates the formation of a large variety of products: fullerene dimers, polymers, fused chains of fullerene molecules, encapsulated nanotubules of irregular shape and, possibly, some hydrogen-terminated graphene nanoribbons with typical helical structures. It can be expected that our study will open new fields of gas reactions with molecules encapsulated in one-dimensional spaces inside carbon nanotubes.

Experimental Section

The C_{60} peapods were prepared using methods described elsewhere.[38] Samples of C_{60} peapods were hydrogenated at various temperatures and a hydrogen pressure of 50 bar for three days (70–72 h). An additional experiment with hydrogenation at 550 °C showed that the collapse of C_{60} was achieved already after 18 h of reaction. Four samples were annealed in argon at 950 °C in one single experiment (three hydrogenated peapod samples and one sample of pristine peapods) in sealed stainless-steel containers.

Reference samples of bulk C_{60} powder were hydrogenated at 500 and 550 °C for 24 h. Selecting the duration of the reaction for bulk powder was based on our recent in situ monitoring experiments of C_{60} hydrogenation.[33] The weight of the samples after annealing in hydrogen decreased by about 50 % after the experiment because of the formation of gaseous hydrocarbons. The shorter experiment duration for bulk C_{60} powder was selected because of a much faster reaction rate relative to C_{60} encapsulated in peapods.[29] The Raman spectra were recorded with a Renishaw inVia spectrometer using lasers operating at 514 and 633 nm. The high-resolution TEM images were collected on a JEOL JEM-2200FS with a corrector of spherical aberrations ($Cs \leq 0.005$ mm). To minimize the destructive influence of electron irradiation all samples were analyzed at 80 kV acceleration voltage and the minimal possible electron illumination time.

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[1] G. B. Blanchet, M. Kanungo, H. Lu, G. G. Malliaras, *Science* **2009**, *323*, 234.

[2] *Chemistry of carbon nanotubes*, *3-volume set*, 1st ed., American Scientific Publishers, Los Angeles, California, CA, **2007**.

[3] A. G. Nasibulin, A. Kaskela, K. Mustonen, A. S. Anisimov, V. Ruiz, S. Kivisto, S. Rackauskas, M. Y. Timmermans, M. Pudas, B. Aitchison, M. Kauppinen, D. P. Brown, O. G. Okhotnikov, E. I. Kauppinen, *ACS Nano* **2011**, *5*, 3214.

[4] A. Kaskela, A. G. Nasibulin, M. Y. Timmermans, B. Aitchison, A. Papadimitratos, Y. Tian, Z. Zhu, H. Jiang, D. P. Brown, A. Zakhidov, E. I. Kauppinen, *Nano Lett.* **2010**, *10*, 4349.

[5] T. Takenobu, T. Takano, M. Shiraishi, Y. Murakami, M. Ata, H. Kataura, Y. Achiba, Y. Iwasa, *Nat. Mater.* **2003**, *2*, 683.

[6] T. Okazaki, Y. Iizumi, S. Okubo, H. Kataura, Z. Liu, K. Suenaga, Y. Tahara, M. Yudasaka, S. Okada, S. Iijima, *Angew. Chem.* **2011**, *123*, 4955; *Angew. Chem. Int. Ed.* **2011**, *50*, 4853.

[7] A. N. Khlobystov, D. A. Britz, G. A. D. Briggs, *Acc. Chem. Res.* **2005**, *38*, 901.

[8] B. W. Smith, M. Monthioux, D. E. Luzzi, *Nature* **1998**, *396*, 323.

[9] L. H. Guan, K. Suenaga, Z. J. Shi, Z. N. Gu, S. Iijima, *Phys. Rev. Lett.* **2005**, *94*, 045502.

[10] D. J. Hornbaker, S. J. Kahng, S. Misra, B. W. Smith, A. T. Johnson, E. J. Mele, D. E. Luzzi, A. Yazdani, *Science* **2002**, *295*, 828.

[11] D. E. Luzzi, B. W. Smith, *Chem. Phys. Lett.* **2000**, *321*, 169.

[12] M. Terrones, E. Hernandez, V. Meunier, B. W. Smith, R. Rurali, H. Terrones, M. B. Nardelli, D. E. Luzzi, J. C. Charlier, *Nano Lett.* **2003**, *3*, 1037.

[13] M. Kalbac, L. Kavan, M. Zukalova, L. Dunsch, *J. Phys. Chem. C* **2007**, *111*, 1079.

[14] G. Pagona, G. Rotas, A. N. Khlobystov, T. W. Chamberlain, K. Porfyrakis, N. Tagmatarchis, *J. Am. Chem. Soc.* **2008**, *130*, 6062.

[15] Z. Liu, M. Koshino, K. Suenaga, A. Mrzel, H. Kataura, S. Iijima, *Phys. Rev. Lett.* **2006**, *96*, 0.

[16] E. Nakamura, M. Koshino, T. Saito, Y. Niimi, K. Suenaga, Y. Matsuo, *J. Am. Chem. Soc.* **2011**, *133*, 14151.

[17] A. N. Khlobystov, K. Porfyrakis, M. Kanai, D. A. Britz, A. Ardavan, H. Shinohara, T. J. S. Dennis, G. A. D. Briggs, *Angew. Chem.* **2004**, *116*, 1410; *Angew. Chem. Int. Ed.* **2004**, *43*, 1386.

[18] J. H. Warner, A. A. R. Watt, L. Ge, K. Porfyrakis, T. Akachi, H. Okimoto, Y. Ito, A. Ardavan, B. Montanari, J. H. Jefferson, N. M. Harrison, H. Shinohara, G. A. D. Briggs, *Nano Lett.* **2008**, *8*, 1005.

[19] A. Debarre, R. Jaffiol, C. Julien, D. Nutarelli, A. Richard, P. Tchenio, *Phys. Rev. Lett.* **2003**, *91*, 085501.

[20] E. Hernández, V. Meunier, B. W. Smith, R. Rurali, H. Terrones, M. B. Nardelli, M. Terrones, D. E. Luzzi, J. C. Charlier, *Nano Lett.* **2003**, *3*, 1037.

[21] H. Kataura, Y. Maniwa, M. Abe, A. Fujiwara, T. Kodama, K. Kikuchi, H. Imahori, Y. Misaki, S. Suzuki, Y. Achiba, *Appl. Phys. A* **2002**, *74*, 349.

[22] B. B. Liu, Y. G. Zou, M. G. Yao, Y. Y. Hou, L. Wang, S. D. Yu, P. Wang, B. Li, B. Zou, T. Cui, G. Zou, T. Wagberg, B. Sundqvist, *Phys. Rev. B* **2007**, *76*, 195417.

[23] S. Kawasaki, T. Hara, T. Yokomae, F. Okino, H. Touhara, H. Kataura, T. Watanuki, Y. Ohishi, *Chem. Phys. Lett.* **2006**, *418*, 260.

[24] S. Okada, *Phys. Rev. B* **2005**, *72*, 035428.

[25] S. Bandow, T. Hiraoka, T. Yumura, K. Hirahara, H. Shinohara, S. Iijima, *Chem. Phys. Lett.* **2004**, *384*, 320.

[26] F. Ding, Z. W. Xu, B. I. Yakobson, R. J. Young, I. A. Kinloch, S. A. Cui, L. B. Deng, P. Puech, M. Monthioux, *Phys. Rev. B* **2010**, *82*, 041403.

[27] E. Abou-Hamad, Y. Kim, A. V. Talyzin, C. Goze-Bac, D. E. Luzzi, A. Rubio, T. Wagberg, *J. Phys. Chem. C* **2009**, *113*, 8583.

[28] A. V. Talyzin, B. Sundqvist, Y. M. Shulga, A. A. Peera, P. Imus, W. E. Billups, *Chem. Phys. Lett.* **2004**, *400*, 112.

[29] A. V. Talyzin, Y. M. Shulga, A. Jacob, *Appl. Phys. A* **2004**, *78*, 1005.

[30] A. V. Talyzin, Y. O. Tsybin, J. M. Purcell, T. M. Schaub, Y. M. Shulga, D. Noreus, T. Sato, A. Dzwilewski, B. Sundqvist, A. G. Marshall, *J. Phys. Chem. A* **2006**, *110*, 8528.

[31] A. V. Talyzin, Y. O. Tsybin, A. A. Peera, T. M. Schaub, A. G. Marshall, B. Sundqvist, P. Mauron, A. Zuttel, W. E. Billups, *J. Phys. Chem. B* **2005**, *109*, 5403.

[32] A. V. Talyzin, Y. O. Tsybin, T. M. Schaub, P. Mauron, Y. M. Shulga, A. Zuttel, B. Sundqvist, A. G. Marshall, *J. Phys. Chem. B* **2005**, *109*, 12742.

[33] S. M. Luzan, Y. O. Tsybin, A. V. Talyzin, *J. Phys. Chem. C* **2011**, *115*, 11484.
[34] S. M. Luzan, F. Cataldo, Y. O. Tsybin, A. V. Talyzin, *J. Phys. Chem. C* **2009**, *113*, 13133.
[35] R. Pfeiffer, T. Pichler, Y. A. Kim, H. Kuzmany, *Carbon Nanotubes* **2008**, *111*, 495.
[36] Y. V. Vasil'ev, S. G. Kotsiris, I. O. Bashkin, V. E. Antonov, A. P. Moravsky, T. Drewello, *J. Phys. Chem. B* **2005**, *109*, 11875.
[37] A. V. Talyzin, I. V. Anoshkin, A. V. Krasheninnikov, R. M. Nieminen, H. J. Albert, G. Nasibulin, E. I. Kauppinen, *Nano Lett.* **2011**, *11*, 4352.
[38] H. Kataura, Y. Maniwa, T. Kodama, K. Kikuchi, K. Hirahara, S. Iijima, S. Suzuki, W. Kratschmer, Y. Achiba, *Electron. Prop. Mol. Nanostruct.* **2001**, *591*, 251.

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