Hydrogenation, Purification, and Unzipping of Carbon Nanotubes by Reaction with Molecular Hydrogen: Road to Graphane Nanoribbons

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A large variety of materials can be prepared from single-walled carbon nanotubes (SWNTs) by chemical functionalization or filling their inner space with different molecules. However, a number of technological issues need to be solved for practical applications: nanotubes need to be purified from residual catalyst, debundled, and opened for filling. Possibly one of the most unusual and most recent proposed SWNT applications is the synthesis of graphene nanoribbons using various unzipping methods.[1−7] So far, the most common method to open and unzip SWNTs is oxidation.[2,8−10] However, opening by this method results also in partial oxidation of SWNTs, oxygen-terminated nanotube tips, and oxygen-terminated graphene nanoribbons, which could be undesirable for some applications. This stimulates the search for other methods to open and unzip nanotubes.[11] Graphene nanoribbons terminated by hydrogen could be of strong interest for some applications. It would also be extremely interesting to prepare hydrogenated graphene (graphane) nanoribbons. Graphane is an extremely promising material for organic electronics, and a lot of research activity is currently focused on synthesis of this material.[12−16] However, hydrogenation of carbon nanotubes was not yet tested for synthesis of graphene/graphane nanoribbons. Reaction with hydrogen is proposed here as a method for carbon nanotube opening, processing, and unzipping into graphene/graphane nanoribbons.

Hydrogenation of carbon nanotubes has been achieved by several methods, such as

ABSTRACT Reaction of single-walled carbon nanotubes (SWNTs) with hydrogen gas was studied in a temperature interval of 400−550 °C and at hydrogen pressure of 50 bar. Hydrogenation of nanotubes was observed for samples treated at 400−450 °C with about 1/3 of carbon atoms forming covalent C−H bonds, whereas hydrogen treatment at higher temperatures (550 °C) occurs as an etching. Unzipping of some SWNTs into graphene nanoribbons is observed as a result of hydrogenation at 400−550 °C. Annealing in hydrogen gas at elevated conditions for prolonged periods of time (72 h) is demonstrated to result also in nanotube opening, purification of nanotubes from amorphous carbon, and removal of carbon coatings from Fe catalyst particles, which allows their complete elimination by acid treatment.

KEYWORDS: carbon nanotube · SWNT · hydrogen · graphene · graphane

by the action of strong reducing agents.[17,18] A number of studies have also been aimed at direct reaction of SWNTs with hydrogen.[19−25] In most studies, it has been assumed that atomic hydrogen produced, for example, by hydrogen plasma,[22,23] glow discharge,[19] or hot tungsten wire[20,21] methods is required for successful hydrogenation reaction. Strong hydrogen plasma etching has been found to produce pore-like defects in carbon nanotubes and complete collapse at very high hydrogenation temperatures (above 1000 K).[24] Some hydrogenation experiments have also been performed at extremely high pressures in the GPa range.[26,27]

As a result of hydrogenation, dramatic changes of the physical properties of SNWTs have been observed, for example, changes in the conductivity of metallic nanotubes.[28−30] The band gap of nanotubes with a given diameter can be tuned by varying the degree of hydrogenation and metallic tubes converted into semiconducting.[31]
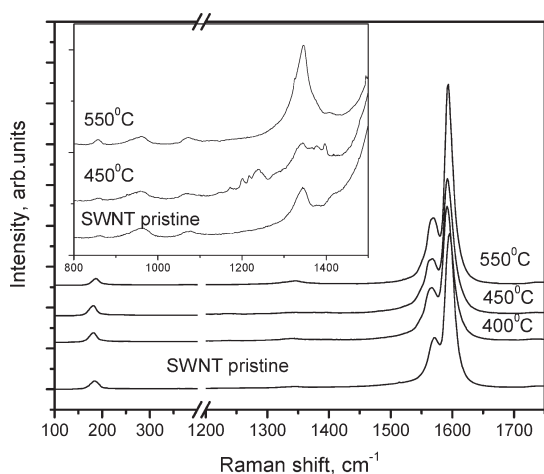
Figure 1. Raman spectra (514 nm laser) recorded from SWNTs hydrogenated at various temperatures compared to the spectrum of a pristine sample. The spectra shown in inset are the same but zoomed to show weak peaks that appear as a result of hydrogenation.

There is a common opinion that molecular hydrogen does not react with nanotube walls at H_2 pressure of a few MPa and the moderately high temperatures. In fact, recently, we have been able to hydrogenate fullerene molecules inside SWNTs (C_{60}@SWNT), so-called "peapods", at 400 °C and 50 bar hydrogen pressure, and no hydrogenation of the nanotube walls was observed in these experiments.[32] The initial aim of the present study was to demonstrate the opening of nanotubes and carbon nanobuds by strong hydrogenation, a reaction predicted based on our previous studies of hydrogen gas reactions with fullerenes.[33] Prolonged hydrogenation of C_{60} by reaction with hydrogen gas was shown to result in complete collapse of the fullerene cage structure at certain reaction conditions.[34−38] Therefore, using the same hydrogenation conditions one should expect cutting the fullerene-like SWNT end cups. At higher temperatures, the nanotube walls could become hydrogenated, and at even higher temperatures, nanotube etching associated with the formation of gaseous hydrocarbons should become possible. Theoretical studies suggest a possibility of SWNT unzipping using hydrogenation.[39]

Results presented in this study demonstrate that annealing in molecular hydrogen can be applied for SWNT side wall hydrogenation, nanotube opening and purification from carbon contaminations, and (combined with acid treatment) purification from Fe catalyst. We also propose to use hydrogenation for unzipping of SWNTs and unzipping of hydrogenated SWNTs as a road for graphane nanoribbon synthesis.

RESULTS AND DISCUSSION

Hydrogenation of Carbon Nanotubes as a Road to the Synthesis of Graphene/Graphane Nanoribbons. Unzipping of SWNTs with hydrogenated side walls is proposed in this study as a road to the synthesis of graphane nanoribbons. While graphene is successfully synthesized now

by several different methods, hydrogenation of graphene and synthesis of graphane are still not completely successful.[12−14] Attempts to hydrogenate graphene were previously performed using atomic hydrogen and were only partly successful due to the geometric constraints: graphene supported on the substrate gets hydrogenated only from one side, while the side attached to the substrate is not available for the reaction.[12] Hypothetically, unzipping of hydrogenated SWNTs allows avoiding this problem: one side of a thus-obtained graphene nanoribbon is already hydrogenated, while other side can be hydrogenated by any of the previously proposed methods. This road to synthesis of graphane seems to be very promising. However, SWNTs with a maximal number of hydrogen atoms attached to the side walls need to be obtained, and unzipping methods for hydrogenated nanotubes that allow preservation of hydrogen on the surface of nanoribbons need to be found.

It is quite possible that some purely chemical method for the hydrogen-preserving unzipping of hydrogenated nanotubes at near ambient temperatures could be developed in the future. However, in this study, we focus our experiments on "one-pot" reaction when both hydrogenation and unzipping of hydrogenated SWNTs is attempted by reaction with hydrogen at high pressure (50 bar) and high temperature (400−550 °C) conditions. Prolonged time of the reaction is an important parameter of hydrogenation experiments. As it follows from our previous experience with hydrogenation of fullerenes, the kinetics of hydrogenation is relatively slow and requires 1−3 days for saturation or the beginning of C_{60} cage structure collapse in the temperature interval of 400−450 °C.[34]

Next sections show evidence for successful hydrogenation of SWNTs by reaction with molecular hydrogen. It is also demonstrated that hydrogenation allows one to purify nanotubes and to open them by hydrogenation. Finally, we provide evidence for the possibility of SWNT unzipping using prolonged reaction with hydrogen at elevated conditions.

Two Different Mechanisms of SWNT Hydrogenation at 400−450 °C. Experimental data obtained in this study confirmed successful hydrogenation of SWNT walls by prolonged reaction with molecular hydrogen. Figure 1 shows Raman spectra recorded from samples annealed in hydrogen at various temperatures for 72 h. Raman spectroscopy is widely used for characterization of carbon nanotubes, and the vibrational signatures of functionalization are now well-established and can be applied for qualitative estimation of hydrogenation effects.[40,41] Spectra shown in the Figure 1 demonstrate that reaction with hydrogen proceeds in different ways in the temperature interval of 400−450 °C (typical for formation of C−H bonds) and for temperatures of reaction which exceed the limit of C−H bond stability in fullerenes and carbon nanotubes (550 °C).
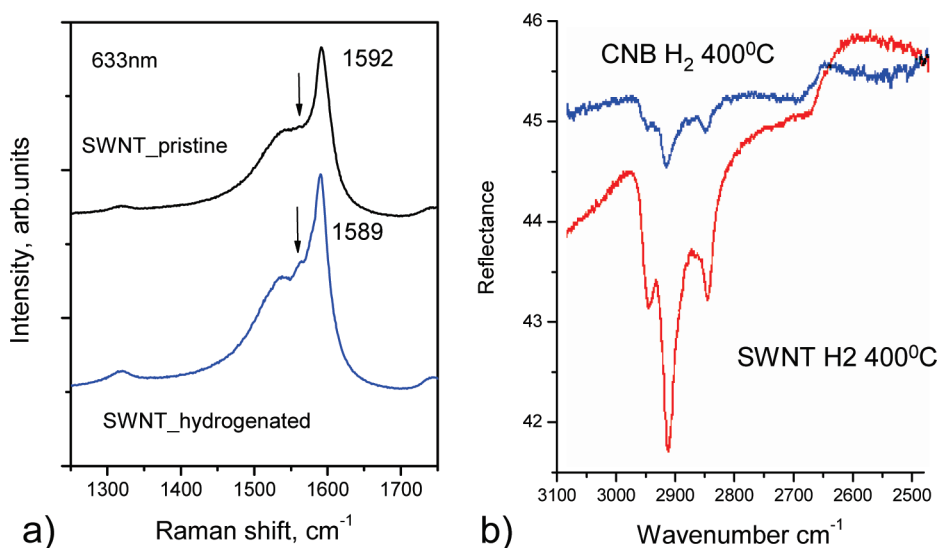
Figure 2. (a) Raman spectra in the region of G and D bands for SWNTs hydrogenated at 550 °C, recorded using a 633 nm laser. Arrows indicate positions of the G band of semiconducting nanotubes. (b) IR spectra of SWNT and CNB samples hydrogenated at 400 °C, region of peaks due to C−H vibrations.

Hydrogenation in the temperature interval of 400−450 °C resulted in weak effects both in the shift of the RBM mode (below the resolution limit) and in the G/D mode intensity ratio. However, clear signs of a hydrogenation reaction are shown by the appearance of many additional weak peaks in the 1100−1400 cm^{-1} region (see inset in Figure 1). These additional modes were not observed for samples hydrogenated at 550 °C, indicating a different reaction mechanism at this temperature. SWNTs hydrogenated at 550 °C showed very clear difference compared to pristine samples. The RBM mode is upshifted to 187 cm^{-1} (from 181 cm^{-1} in pristine SWNTs), and the ratio of the amplitudes of G/D modes decreased, especially strong (by ∼20 times) in spectra of hydrogenated Carbon Nanobuds (CNB) (see Figure 1 and Figures 1S and 2S in Supporting Information). Strong increase in the intensity of the D mode is a sign for an increased number of SWNT defects, which is expected if hydrogen reaction at this temperature occurs by taking away some carbon atoms from nanotube walls (etching).

Clear evidence of SWNT and CNB hydrogenation can also be found from strong changes of the G mode shape, which can be attributed to transformation of metallic nanotubes into semiconducting ones. Raman spectra allow distinguishing metallic nanotubes from semiconducting nanotubes because they exhibit G modes at different positions. A change in the relative intensities of G$^-$ and G$^+$ modes, which corresponds to transformation from metallic to semiconducting nanotubes,[41] was observed starting already in the samples reacted with hydrogen at 400−450 °C. Raman spectra recorded from samples hydrogenated at 550 °C using a 633 nm laser demonstrated the conversion especially clearly due to resonance effects which enhance the intensity of G mode peaks (Figure 2a). Pristine SWNTs showed G$^-$ modes from metallic SWNTs as a broad feature centered at about 1550 cm^{-1}, while after hydrogenation, a distinct new mode appears at 1570 cm^{-1}, which is identified as the G$^-$ mode from semiconducting nanotubes.[24] The observed upshift of the G$^+$ mode (by 3 cm^{-1} in SWNTs and by 6 cm^{-1} in CNBs) is also a typical sign of conversion into semiconducting nanotubes.[41]

Direct evidence of SWNT conductivity change was also obtained using valence band (VB) spectra recorded from samples hydrogenated at 450 °C. The energy difference between the VB edge and the Fermi level of pristine SWNTs (∼0.04 eV) was doubled after treatment (∼0.08 eV), which proves that metallic nanotubes in the pristine mixture were converted into semiconducting tubes by hydrogenation (see Figure 7aS in Supporting Information). The XPS valence band (VB) spectra obtained in a wide energy range (Figure 7bS, Supporting Information) also provided additional evidence of efficient nanotube hydrogenation at 450 °C. The spectra showed significant decrease of the π-derived state intensities and correlated increase of the σ-derived state intensity as a result of transformation of the sp^2 atomic orbital hybridization into sp^3 due to hydrogenation.

Evidence of efficient hydrogenation can also be found from an analysis of IR and UV−vis spectra (Figure 2b and Figures 12S and 13S in Supporting Information). The hydrogenation reaction at 400−450 °C resulted in the appearance of strong peaks from C−H vibrations in the IR spectra, at about 2851, 2920, and 2955 cm^{-1} (Figure 2b). Similar peak positions have been reported previously for hydrogenated carbon nanotubes and for hydrogenated fullerenes.[34]

Analysis of near-edge X-ray adsorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS) spectra recorded from samples hydrogenated at
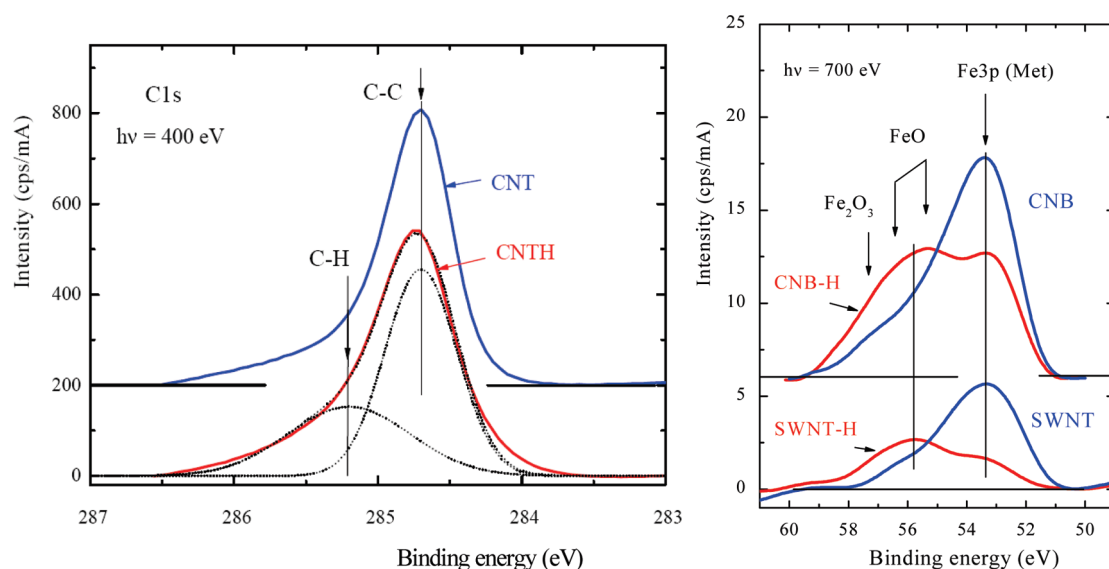
Figure 3. (Left) C1s XPS spectra of SWNTs and SWNTs-H (hydrogenated at 450 °C) recorded with photon energy of $h\nu$ = 400 eV. The spectrum of SWNTs-H is decomposed into contributions from C—C and C—H couplings. (Right) Fe3p XPS spectra of SWNTs/SWNTs-H and CNBs/CNBs-H recorded with photon energy of $h\nu$ = 700 eV.

450 and 550 °C provided not only direct evidence for hydrogenation of nanotube walls but also an estimate for the degree of hydrogenation. Once again, hydrogenation is significantly different for temperatures of 450 and 550 °C. The C1s line from pristine nanotubes (E_B = 284.70 eV, in excellent agreement with literature data that report it in the range of 284.75 eV[21,42] to 284.65 eV[43]) showed a decrease in intensity after hydrogenation at 450 °C, while a new line with higher binding energy (E_B = 285.2 eV) had emerged (see Figure 3).

The new state was attributed to C—H coupling with the sp^3 state of carbon. The precise fitting of the C1s spectrum of hydrogenated SWNTs (SWNTs-H) with two components allows quantification of the fraction of hydrogenated carbon atoms from the ratio of integrated intensities and gives 36 ± 9 atom % hydrogenation. The degree of hydrogenation is only about a factor of 2 smaller compared to the value of 65 ± 15 atom % achieved for SWNTs treated with atomic hydrogen by Nikitin et al.[21] The high efficiency of nanotube hydrogenation is confirmed also by the drop in intensity of the π plasmon observed in C1s XPS shakeup spectra (see Figure 6S, Supporting Information). Transformation of C=C double bonds to C—H bonds due to hydrogenation was also identified in our samples from NEXAFS spectra of pristine SWNTs and hydrogenated nanotubes near the carbon K-edge (see Figure 5S, Supporting Information). A comparison of the intensities of the π^* peaks for SWNTs and SWNTs-H allowed another evaluation of the extent of SWNT hydrogenation by molecular hydrogen. The fraction of hydrogenated carbon atoms in SWNTs-H obtained from NEXAFS is 25 ± 7 atom %, which is somewhat lower than the value obtained from XPS data. It should be noted that XPS gives information

mainly about individual nanotubes on the surface of the sample, while NEXAFS probes whole bundles of tubes, and a similar discrepancy was observed, for example, in ref 21.

Similar analysis was also performed for a SWNT sample annealed in hydrogen at 550 °C. As noted above, this temperature exceeds a limit of C—H bond stability, and reaction of hydrogen with carbon nanotubes should proceed mostly by formation of light hydrocarbons (e.g., methane) and SWNT etching. Indeed, the fraction of hydrogenated carbon atoms in SWNTs-H obtained by NEXAFS does not exceed 6 ± 3 atom %. C1s XPS spectra of SWNTs and SWNTs-H were found to be practically identical, which confirms the chemical similarity of carbon atoms before and after nanotube hydrogenation and NEXAFS data concerning a low extent of carbon atom hydrogenation (see Figures 8S—11S in Supporting Information for more details). At the same time, physical properties of the hydrogenated SWNTs changed drastically.

Figure 4 represents the VB spectra of SWNTs and SWNTs-H. The VB edge of pristine SWNTs practically merges with the Fermi level, indicating the metallic conductivity of the essential part of tubes. The VB edge shifts by 0.7 eV after hydrogenation, pointing to transformation of the metallic and narrow band gap tubes into semiconductors with a rather wide band gap.

This trend is confirmed by the work function enhancement from 4.6 eV for SWNTs to 5.3 eV for SWNTs-H, which was estimated by measurement of secondary electron threshold. These data are in good agreement with Raman spectroscopy results presented above. However, the nature of transformation is not clear. Hydrogenation itself cannot provide the strong effect in conversion of metallic tubes into semiconducting
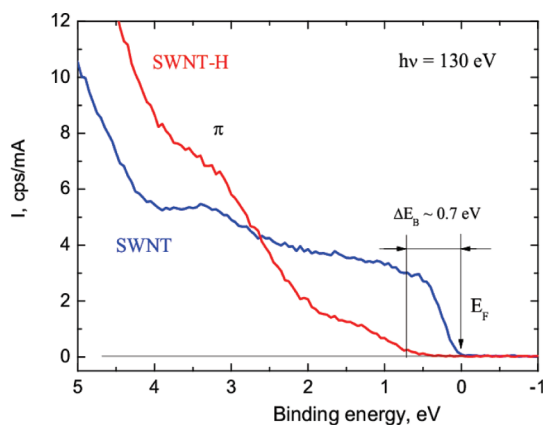
Figure 4. Valence band XPS spectra of SWNTs and SWNTs-H hydrogenated at 550 °C recorded with photon energy of $h\nu$ = 130 eV.

tubes for these samples. The data presented above prove that at 550 °C the amount of hydrogen attached to carbon atoms is about 6-fold lower compared to samples treated at 450 °C, while conversion into the semiconducting state is more pronounced. Therefore, the increased amount of semiconducting nanotubes could be related to defects created in metallic nanotubes either by hydrogen etching or by coalescence of some nanotubes within bundles due to etching effects of hydrogenation.

It is interesting that the total weight of nanotube powder samples annealed in hydrogen at 550 °C was found to decrease by almost 30% after 3 days, which confirms the etching mechanism of the reaction. One should note that influence of nanotube diameter, chirality, metallic/semiconducting properties, *etc.* on the hydrogenation of carbon nanotubes by molecular hydrogen is unknown at the moment.

In summary of this section, hydrogenation of SWNT side walls by reaction with molecular hydrogen (25−36% carbon atoms in hydrogenated state) occurs starting from temperatures of 400−450°. The hydrogenation degree can possibly be increased by prolonging the reaction, but already at this level, it is sufficient for using SWNTs-H as a precursor for possible preparation of graphane nanoribbons by chemical unzipping. Hydrogenation at 550 °C demonstrated rather different results: relatively low hydrogen content (~6% of carbon atoms hydrogenated) and more pronounced transformation of metallic nanotubes into semiconducting nanotubes. Hydrogenation reaction also helps to purify SWNTs from metallic catalysts and other forms of contamination carbon as discussed below.

Catalytic Effect of Fe Nanoparticles: Hydrogenation and Removal of Carbon Shells. Hydrogenation of the nanotube walls observed in this study is seemingly in contradiction with our previous experiments, which showed no hydrogenation of nanotubes at the same conditions while only fullerenes inside SWNTs were hydrogenated.[32] However, this difference can be explained taking into account the effect of the metallic catalyst. The samples of peapods

studied earlier were cleaned from all traces of metal catalysts, while the samples hydrogenated in this study contained large numbers of Fe nanoparticles embedded into graphitic carbon onions. We suggest that Fe nanoparticles act as catalysts to promote hydrogenation of SWNTs and CNBs. Hydrogen is known to dissociate from molecular into atomic form on the surface of metallic particles at moderately high temperatures. It can also migrate from nanoparticles to the carbon support according to the "spillover" mechanism known to occur in many catalytic reactions.[44] This suggestion is confirmed by a change in the chemical state of Fe nanoparticles, which become oxidized after hydrogenation and exposure of sample to air (see Figure 3). Iron catalyst nanoparticles in our samples of pristine or vacuum-annealed SWNTs are preserved in a non-oxidized state for months when exposed to air due to protection by the carbon overlayers. The fullerene-like surfaces of the carbon coating that surrounds Fe nanoparticles in pristine SWNTs are expected to react with hydrogen at 400−450 °C.[33−38] Prolonged hydrogenation of fullerenes at these conditions was earlier demonstrated to result in cage structure collapse and formation of light hydrocarbons.[34−37] The XPS data proved that the carbon coatings were removed from the Fe particles by prolonged hydrogenation, which resulted in rapid air oxidation of catalyst particles evident from an increase of the oxide contribution to Fe3p XPS spectra (Figure 3). Therefore, iron particles were exposed to hydrogen in the process of reaction and available for spillover. The hydrogenation of nanotubes most likely starts at the points where Fe particles attach to nanotubes and proceeds by migration of hydrogen atoms. At 400−450 °C, hydrogenation results in partial removal of the fullerene-like onions which enclose Fe catalyst particles, which is evidenced by their partial oxidation when exposed to air. Experiments performed with samples hydrogenated at 550 °C demonstrated that all carbon coatings enclosing Fe particles in pristine samples were successfully removed by annealing in hydrogen. That was proved by acidic treatment of hydrogen-annealed SWNTs, which resulted in almost complete removal of the Fe contamination while the same acid treatment of pristine samples leaves Fe nanoparticles intact due to carbon coating (Figure 5). Chemical analysis showed that the amount of Fe had decreased after hydrogen annealing/acid treatment from 16−17 to 0.4−0.5 mol % or by a factor of 40−45 on average. Reference sample heated in vacuum at 550 °C and subjected to acid treatment did not show change of the iron content, which excludes a possibility of temperature-induced Fe elimination and confirms that carbon shells were removed by hydrogenation in the experiments described above. It can be concluded that hydrogen treatment at 550 °C is rather efficient for purification of SWNTs and production of catalyst-free CNT samples.

Finally, hydrogenation was tested on Fe-free SWNT sample purified from catalyst by combination
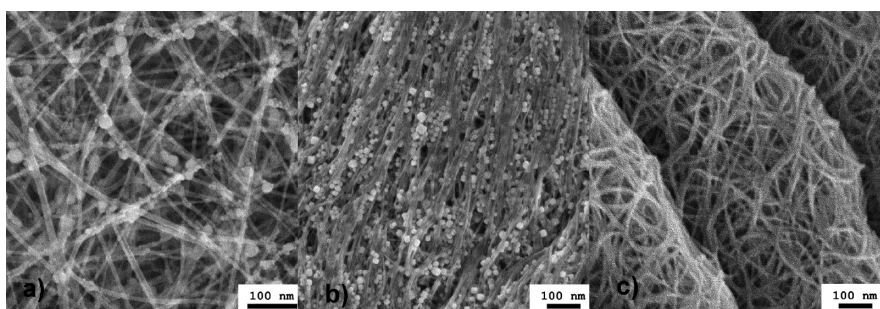
Figure 5. SEM images taken from (a) pristine CNT sample, (b) hydrogen-treated sample, and (c) hydrogen-treated sample after removal of Fe particles using HCl treatment.
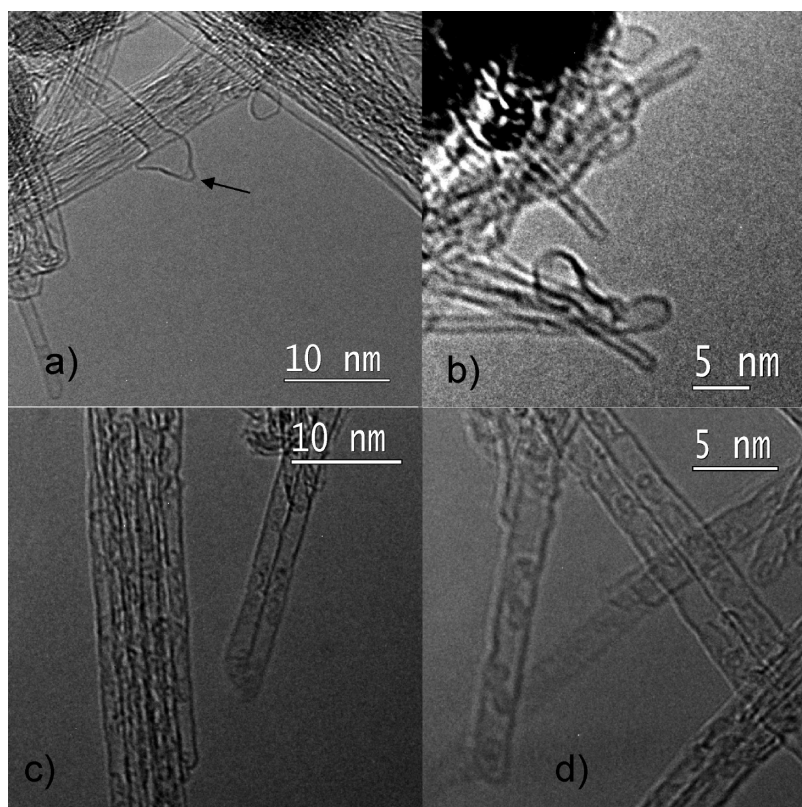

Figure 6. TEM images taken from hydrogen reacted (550 °C) samples of SWCNTs and CNBs: (a) graphene nanoribbon from unzipped nanotube (marked by arrow), (b) CNT with cone-like end produced by unzipping of nanotube tip; (c,d) CNBs with significantly reduced number of fullerenes attached to the outer walls and some fullerenes inside tubes.

of oxidation/HCl treatment. After 3 days of hydrogenation at 450 °C and 50 bar H_2 pressure, only very slight changes were observed for this sample. In particular, no additional peaks in the spectral region of 1200−1500 cm^{-1} typical for a hydrogenated sample (inset in Figure 1) were observed in the Raman spectra of the Fe-free sample.

Annealing of Nanotubes in Hydrogen: Etching and Unzipping. The temperature of 550 °C exceeds known temperatures of C−H bond breaking in fullerenes[38] and is close to the stability limit of carbon nanotubes in hydrogen. It is obvious that high temperature favors the reaction of hydrogen with carbon to form light hydrocarbons, such as methane. As a result, the hydrogen treatment of SWNTs and nanobuds at 550 °C leads to formation of

gaseous light hydrocarbons rather than to hydrogenation of the nanotube walls. Therefore, it is possible to consider the reaction of SWNTs with hydrogen at these conditions as an etching.

Hydrogen etching affects first of all other kinds of carbon rather than nanotube walls: amorphous carbon, fullerene-like particles, and carbon onions. This effect was especially clearly demonstrated in experiments with hydrogenation of carbon nanobuds. In this case, carbon nanobuds can be considered as extremely "dirty" nanotubes contaminated with various other forms of carbon. A detailed TEM study of CNB samples subjected to prolonged hydrogen treatment at 550 °C proved that, even for that kind of extremely complex
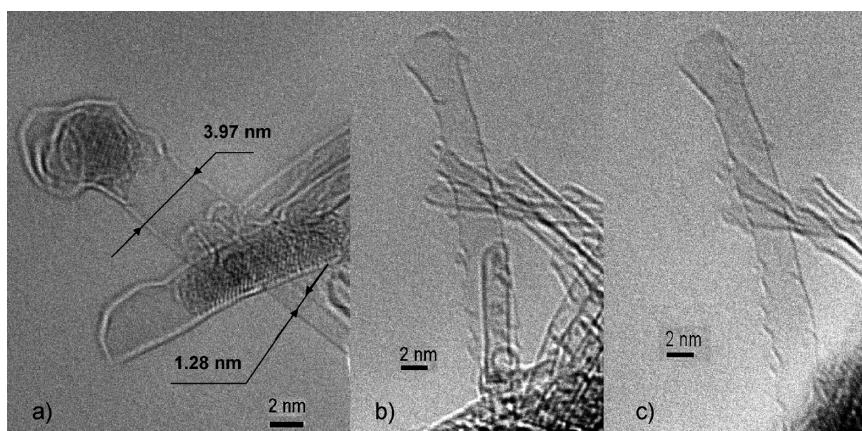
Figure 7. TEM images of sample subjected to hydrogenation of (a) SWNTs and graphene nanoribbons, (b) another graphene nanoribbon, (c) the same nanoribbon as in the (b) tilted 20°.

carbon material, the nanotubes were purified to a large extent. As shown in Figure 6, hydrogen treatment at 550 °C removed most of the fullerene-like "bubbles" from the surface of carbon nanotubes, while some of the fullerene molecules migrated inside the nanotube inner space (which proves that nanotube caps were removed from pristine closed tip nanotubes). Purification of carbon nanotubes in the CNB can also be confirmed by detailed analysis of Raman spectra, for example, by an upshift of the G mode to a position more typical for SWNT samples (see Figures 1S and 4S in Supporting Information for more details).

Etching reaction of hydrogen on the edges of nanotubes is preferable compared to direct etching of the nanotube wall and starts at lower temperatures (400−450 °C). Careful examination of TEM images obtained from samples hydrogen treated at 400−550 °C (Figure 6) revealed numerous examples of partial unzipping of nanotube walls in the region of tips. Many images showed an unusual geometrical configuration of SWNT ends with balloon-like or cone-like features. These features can be explained by partial unzipping of the nanotube, which starts on the edge and goes along the length of the tube. The unzipping could also possibly start on the Fe particles which later dropped out due to removal of carbon material around them.

Some images recorded from hydrogenated samples also revealed nanotube unzipping into nanoribbons (see Figures 6 and 7). It is not easy to distinguish graphene nanoribbon from nanotubes using TEM images; however, the diameter of the graphene nanoribbon unzipped from the nanotube should be about 3 times larger compared to the diameter of the parent nanotubes. Figure 6a demonstrates one of the graphene nanoribbons with a balloon-like end. Some parent nanotubes with nanoribbons obtained by unzipping are shown in Figure 7. The dimensions of nanoribbons correlate well to the width of unzipped nanotubes (Figure 7a). The nanoribbon shown in Figure 7a,b (images taken with tilt of 20°) also

demonstrates very specific wave-like shape of edges, which is expected if it was formed as a result of nanotube unzipping. It is very likely that unzipping of nanotubes starts on Fe nanoparticles and goes further along the tube. Figure 7a shows unzipped part of the nanotube close to the Fe nanoparticles. It is important to emphasize that nanoribbons produced by reaction with hydrogen should be hydrogen-terminated. As soon as carbon−carbon bond breaks occur due to unzipping, all dangling bonds will be terminated by hydrogen at the conditions of the reaction.

It is interesting to note that nanoribbons exhibited well-ordered graphene carbon packing in some regions, while in other parts, no order is observed (Figure 7). The disorder could be due to random attachment of hydrogen atoms to some of the carbons. In principle, the unzipping of hydrogenated nanotubes could lead to formation of not only graphene but also graphane nanoribbons. It should be noted that some nanoribbons were observed in the samples heat treated in the whole range of studied temperatures, 400−550 °C, not only for highest temperatures as could possibly be expected. Therefore, unzipping at 400−450 °C occurs on carbon nanotubes with hydrogenated side walls, and it is very likely that at least part of the hydrogen remains attached to the so-produced graphene nanoribbons. However, in this study, we are unable to distinguish graphene and graphane nanoribbons. Bulk characterization methods cannot be used for this purpose due to a relatively small amount of unzipped nanoribbons in our samples, while TEM images do not provide information about the presence or absence of hydrogen in the nanoribbons. It is also an open question why some nanotubes got unzipped at the conditions of certain experiment while other nanotubes were preserved. Unzipping could be related, for example, to certain properties of nanotubes themselves or to catalytic effects of Fe nanoparticles and specific features of particle attachment to the nanotube. The latter suggestion is confirmed by

numerous observations of balloon-like and cone-like nanotube tips. Catalyst nanoparticles are often attached in the nanotube end parts and are likely to act as starting points for nanotube unzipping.

Further experimental work is required to produce more pure nanoribbon samples, either graphene or graphane ones. It is expected that isolated nanotubes will be more easily unzipped by hydrogen than our samples, which consisted mostly of bundles. Higher temperatures of hydrogenation, higher hydrogen pressures, and longer periods of hydrogenation and the use of samples with isolated nanotubes will possibly allow complete unzipping of all nanotubes into nanoribbons terminated by hydrogen on the edges. It should be noted that unzipping of SWNTs using chemisorption of hydrogen was theoretically predicted in 2003 by Lu et al.[39] but never previously observed experimentally to our knowledge.

CONCLUSIONS

Summarizing the results presented above, the reaction of hydrogen gas with carbon nanotubes and carbon nanobuds in the temperature range of 400−550 °C occurs efficiently, most likely due to the effect of Fe nanoparticles acting as a catalyst for hydrogen dissociation. Reaction performed at 400−450 °C results in hydrogenation of the side walls of SWNTs with formation of covalent C−H bonds for approximately one-third of all carbon atoms. Hydrogen treatment at higher temperatures (550 °C) results in etching nanotubes with formation of hydrocarbons. The hydrogen etching removes carbon coatings from Fe particles which are otherwise inaccessible for acid treatments and allows their removal by acid treatment. Hydrogenation helps to open SWNTs by removing fullerene-like nanotube tips with partial unzipping of edges into cone-like or balloon-like features. Complete unzipping of some nanotubes into hydrogen-terminated graphene nanoribbons was demonstrated, confirming previously published theoretical predictions.[39] Unzipping of hydrogenated carbon nanotubes is proposed as a possible road to preparation of graphane nanoribbons.

METHODS

Single-walled carbon nanotubes and carbon nanobuds (CNBs) were synthesized by aerosol CVD method based on CO decomposition on iron particles produced by pyrolysis of ferrocene vapor as described elsewhere.[45−47] Iron catalyst nanoparticles embedded in carbon coatings were present in our samples, thus making it a composite carbon/Fe material. Pristine nanotubes were around 300 nm long with an average diameter about 1.5 nm, while CNBs were around 2.2 nm in diameter, as determined by statistical measurements from TEM images. Detailed characterization of the pristine SWNTs and CNBs used for hydrogenation in our experiments is available in our previous publications.[31−33]

The hydrogenation reaction was performed in the temperature interval of 400−550 °C and at a H_2 pressure of 50 bar. Typical duration of annealing in hydrogen gas was ∼78 h to ensure complete hydrogenation. The heating and cooling took about 30 min and was also done under 50 bar. After being cooled, the sample pressure was released to ambient. Hydrogenated samples were characterized by Raman and IR spectroscopy, EXS, NEXAFS, XPS, and UV−vis spectroscopy. NEXAFS and XPS spectra were recorded from samples of pristine SWNTs and SWNTs hydrogenated at 450 and 550 °C using synchrotron radiation of BESSY II (Helmholtz-Zentrum, Berlin). Raman spectra were recorded using Renishaw spectrometer equipped with 514 and 633 nm lasers.

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