Novel transmission electron microscope imaging of single-walled carbon nanotube systems

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Abstract. A method for analyzing systems of isolated single-walled carbon nanotubes is of paramount importance if their structural characteristics are to be fully understood and utilized. Here we offer an innovative technique for analyzing such systems, with unprecedented contrast, using transmission electron microscope imaging of carbon nanotubes suspended over large holes in a silicon nitride grid. The nanotubes are grown directly on the viewing grids, using the chemical vapor deposition process, thus avoiding the use of chemicals or aggressive treatments. This method is simultaneously noninvasive, re-usable, allows the analysis of multiple structures based on carbon nanotubes and is quickly implemented.

1. Introduction

Carbon nanotubes (CNTs) have become the benchmark form of nanostructure due to their unique atomic structure [1], and a wide range of extraordinary physical properties. A CNTs structural strength is unprecedented [2] and their applications abundant [3, 4], therefore, the analysis of these nano-building blocks is of fundamental importance. CNTs are usually demarcated into two types, single-walled CNTs (SWNTs), and multi-walled CNTs (MWNTs), defined by the number of nested layers of graphene comprising the tubular walls of the nanotube. A SWNTs unique, simple, structure make them prime candidates for nanofabrication materials, yet,
their nanometer-sized dimensions renders the analysis of their structure difficult. The analysis of the structural
makeup of carbon nanotubes is based upon various characterization techniques with the ability to resolve their
structure at the nano-scale. Chief amongst these are the transmission electron microscope (TEM) and atomic
force microscope (AFM), each having their unique applications. This study focuses on the particular aspects of a
unique form of the TEM method.

TEM imaging allows both the imaging of relatively large areas and the precise measuring of nanotube
diameters. Nevertheless, the major limitations of TEM imaging lie in the sample preparation technique, and in
the type of grid used for the sample. The first problem is in the preparation of the tubes: CNTs can be produced
in a multitude of ways, including arc-discharge, laser ablation, and chemical vapor deposition (CVD) [5]. In the
first two aforementioned methods, the CNTs are collected and purified in a solution, which can then be
deposited on a TEM grid. In the last method, the CNTs must be forcibly removed from the surface to which they
are grown, usually by sonication or scraping, and then placed in a solution from which they are then dispensed.
The problems inherent in these techniques are multifold: they induce external force on the CNTs; disallow the
capability of viewing isolated CNTs, as the nanotubes usually adhere into bundles in the solution; and allow the
adhesion of solute molecules to the nanotubes, to name a few [6]. The second problem lies in the TEM grids
themselves. Since the solution of CNTs must be deposited on a surface, the mainstay of TEM grids contain a
layer of carbon in a matrix of copper wires, or holey carbon layers, known as lacey carbon grids. The intrinsic
complication in these grids is that the contrast between the CNT walls and the underlying layer is minimal, as
they are both carbon based.

This study is based on a type of TEM grid that renders the aforesaid obstacles immaterial. Using a specific type
of grid comprising of a thin silicon nitride membrane, with large holes in it, and growing the CNTs directly
on the grids using the CVD process, we have managed to achieve an adept platform for viewing a multitude of
varying structures consisting solely of CNTs. This form of growth allows us to take a “snapshot” of the types of
interactions between isolated, suspended, nanotubes, as well as in individual nanotubes, without any external
manipulation (e.g. AFM). The technique also enables us to actively affect individual suspended nanotubes, with
some limitations, without the fear of destroying the underlying carbon layer by irradiating segments of the tube
with the TEM electron beam.

The technique described in this study allows the unparalleled imaging of a slew of structures based on CNTs,
and we present here only a fraction of some of the different systems researchable using this method. The bulk of
our study concerns SWNTs, due to the particulars of the growth mechanism, but the method is not limited to
these.
2. Experimental

2.1 CVD nanotube growth

Carbon nanotubes are produced in our lab using a CVD procedure. CNTs are produced using nanoparticles of iron catalysts created by placing granules of iron salt, Fe₂(NO)₃, in a solution of 2-propanol, which is then placed in an ultrasound bath for 40 min, followed by centrifugation for 10 min. The catalyst particles are then dispensed onto a clean sample, in liquid form, using a pipette, after which the sample is rinsed in hexane, and dried with nitrogen gas.

The sample is then placed in a 1” tube-furnace, which is heated to 900°C, from room temperature, accompanied by a flow of hydrogen gas (1000 sccm). At the target growth temperature, ethylene (C₂H₄) gas is introduced (20 sccm), for 9 min, which undergoes pyrolysis, and provides the feedstock gas necessary for CNT growth. The system is then cooled-down to room temperature with a constant flow of hydrogen (500 sccm). The entire process, including flow-meters and temperature control, is computer-controlled.

The temperature used in this growth produces predominantly SWNTs, as these are the form of CNT preferred in this study, and as controlled by the particle size of the catalysts, as well as the growth temperature [7].

2.2 TEM samples

The TEM grids used consist of a 200nm thick membrane of silicon nitride deposited on a silicon substrate using the low-pressure CVD (LP-CVD) process (DuraSiN meshes, Protochips Inc.). The LP-CVD nitride renders the membranes extremely robust in terms of temperature sustainability. This is a critical issue, as the meshes are placed directly in the tube furnace, and must be able to withstand the temperatures described above. The silicon substrate contains a large, etched hole, creating a viewing area in the membrane of 500µm×500µm. Two types of meshes were used in this study, one contained an array of 2µm diameter holes, with a 12µm pitch, and the other, large 40µm×40µm holes, with a 40µm pitch, in the nitride membrane (see figure 1).

The grids are used as the growth substrate for the CVD process, with the catalysts dispensed directly on the nitride membrane. Due to the geometry of the holes, all the suspended CNTs grown over the holes are in the same imaging plane, since they form taut networks across the holes [8], simplifying the focusing of the TEM
beam upon them. Special caution must be taken when handling these grids, as the membranes are prone to breaking upon hard contact.

![TEM nitride grids used in this study. (a) Scanning electron microscope image of a grid containing 2μm holes [scale bar: 10μm] (b) Low-magnification (×390) TEM image of carbon nanotubes growing over the holes in the sample grid. The case illustrated in (b) is an extreme case of nanotube tension [scale bar: (b) 5μm]. The non-trivial imaging of the nanometer-scaled nanotubes, at such low magnification, is described in the text.](image)
2.2 TEM imaging technique

The novel method presented in this study concerns the locating and imaging of nanotubes, which are suspended over holes in a nitride film. Due to the lack of underlying material, the nanotubes are easily located at low magnifications of ×300 in the TEM. Using a slight modification of both the intensity of the beam, as well as the focus (figure 1(b)), tubes can easily be observed. This effect is due to Fresnel fringes under the extreme under-focused conditions created by the electron-waves impinging upon the few nanometer thick nanotubes, as well as the fact that they are suspended over a hole, allowing unimpaired electron beam transmittance.

The combined effect of both the low magnification sampling, as well as the type of grid utilized, make locating the nanotubes for analysis extremely rapid. This sampling can usually be done within minutes of operating the TEM.

TEM images presented in this study were taken with a Philips Tecnai F20 TEM operated at 200keV, and the image analysis was facilitated by Motic Images Plus software.

3. Imaging results

3.1 SWNT binding and buckling

The first system analyzed in this study is that of an individual SWNT buckling. A CNT, especially a SWNT, will buckle under a critical load [8, 9]. Figure 2 displays some exemplifying images of the range of diverse forms of buckling we are able to analyze. Figure 2(a) shows a close up of a wide SWNT adhering to a SWNT bundle. The darkening of the SWNT walls near the buckling points in the image illustrates the flattening of the nanotube due to its binding to the bundle, as well as the deformation caused by the buckle itself, creating a thicker column of atoms for the electron beam to interact with, as simulated by Ruoff et al [10, 11]. The exact structural composition of the buckling can be seen here. Figure 2(b) presents a single walled tube buckling near its junction point to a bundle of SWNTs. Here too, the inner and outer walls of the buckle itself are darker, as there are more atoms packed together in a straight column. Further confirmation of this model is provided by figure 2(c): by tilting the sample in the TEM holder by 20 degrees, the SWNT becomes barely visible at the buckle point due to the lack of carbon atoms of which the electrons diffract.

The image in figure 2(d) illustrates an extreme case of nanotube buckling, with a suspended SWNT binding to the edge of the nitride grid. The SWNT is seen to buckle at four discrete points, with the leftmost buckle being a
buckle-pair, near the surface. The contrast between imaging the suspended segment of tube and the segment over the nitride is also distinctly observable, with the advantage of imaging over the hole quite apparent.

Figure 2. TEM images of nanotube buckling. (a) A single-walled nanotube adhering to a nanotube bundle, with two distinct buckles. The darker fringes near both buckles are due to the higher concentration of carbon atoms caused by the flattening of the tube walls. (b) A single-walled tube buckling at the junction point with a nanotube bundle. The distinct form of the buckle, as well as the darker fringe of the deformed wall is visible. (c) The same buckle as in (b), tilted at a 20 degree angle (in the direction shown in the inset), making the buckle and
tube less visible. [Scale bar (both): 5nm] (d) A nanotube buckling at various points, due to its interaction with the surface. The numbers in this image are referred to in the text of section 4. [Scale bar: 20nm]

3.2 SWNT twisting

A SWNT can also undergo twisting, resulting in a radial distortion of the tube’s walls. This has been shown in the past using AFM [12] and TEM [13] on MWNTs only, yet the images here show a near perfect demonstration of this effect in a SWNT, including the crossover point in the center of the twist. It should be noted however, that tube twisting is a rarity in our TEM growth samples.

Figure 3(a) shows a SWNT twisting with two visible twisting points, along its axis (a third point over the membrane is barely visible). The image is a combination of two closely spaced images, superimposed. At the center of each twisting point, the walls of the SWNT are seen to crossover (see inset in figure 3(a)). In this particular example, the crossover angle, taken in reference to the axis of the tube, was 8-9°, with a distance between crossover nodes of 50nm (including the barely visible node over the nitride grid). Simulations of nanotube twisting [6] have predicted the radial deformation of a twisted tube. Figure 3(b) is taken from measurements done on this image (see inset in figure 3(b)), along a common interval length of 2.5nm. As can be unmistakably seen, the nanotube’s diameter goes from its rest diameter of 4.3nm (measured far from the twisting point), down to 2nm at the crossover, and up to 6nm at the midpoint between the two buckles. The radial deformation in such a tube is thus quite large. This measurement is the first of its kind for a SWNT, and is preferable to those done with AFM, as nanotubes lying on a surface are already slightly deformed, due to their interaction with the surface [11, 12, 14].
Figure 3. Nanotube twisting. (a) Combination of two images showing the distinct twists in a single-walled nanotube, including the crossover point and the widening of the tube [scale bar: 20nm]. Inset: close up of one of the crossover segments [scale bar: 2nm] (b) Graph illustrating the amount of radial deformation occurring to the twisted tube. The diameter at the right side of the graph is near that of the rest diameter of the suspended tube (~4.3nm). Lower inset: image of the twisting points including the measuring bars from the commercial imaging software.

3.3 Radial deformation and binding-particle imaging

The method employed here gives extremely accurate experimental measurements of the amount of deformation an individual SWNT can receive due to their interaction with either the surface or to other nanotubes [11]. Figure 4(a) shows an example of an elongation of the SWNT’s diameter, due to the van der Waals interaction between it and the tubes (bundles) to which it is adhering. As in the case of twisting, the method here achieves the only known way of measuring a tube’s deformation due to another tube’s influence. A detailed discussion of which is found in ref. [11].

Yet another effect observable using the presented method is illustrated in figure 4(b), which shows two segments of tubes with material adhering to them. This material is commonly associated with carbon. Chemical investigation (EDX) of this type of material is inconclusive, as only trace elements of carbon and oxygen, (as
well as silicon, and sometimes copper, which is due to the scattering of the electrons from the grid's silicon substrate, and the TEM sample holder, respectively) are detected. Nevertheless, the lack of a carbon underlying area, in addition to their being grown directly on the grid, without the need for a dispersing solution, provide an ideal platform for measuring the adhesive properties of materials to nanotubes. As carbon nanotubes are being investigated as possible medicinal carriers [15], or as filtration membranes [16], these properties are best tested in a suspended state, without the complications of the carbon grid interacting with the material in question.

![Image](image_url)

**Figure 4.** (a) Radial deformation in a nanotube. The diameter of the tube is stretched upon contact with another tube bundle [scale bar 20nm]. (b) Two suspended nanotubes crossing over the hole show material clinging to the nanotube walls. The composition of this material is uncertain [scale bar: 20nm].
4. Active analysis

The TEM can be used as an active source of dynamic measurements, in analogy to the way the AFM tip can be used to drag CNTs along a surface [17]. By increasing the intensity of the electron beam, by means of the condenser systems of the microscope, at 200keV, a powerful beam of energy can be produced on a miniscule segment of tube. Such a large amount of energy can destroy the carbon bonds in the nanotube [18]. This problem can be multiplied due to the lack of heat dissipation: The heat created by the electrons is usually dissipated into the underlying grid, whereas in the case of suspended tubes, the heat must be dissipated along the tube itself, until reaching the anchor points at the membrane edge. Directing the beam intensity onto a single point of a suspended CNT can cause one of three effects: The first is that the CNT can break at some point along the crystalline structure. Second, is that the structure of the CNT is slowly destroyed due to carbon-bond breaking caused by the irradiating beam. This leads to amorphous-type strings, with the tubular structure destroyed. Third, when near the hole’s edge, a suspended CNT will adsorb material onto it from the surface. Imaging the first type of effect is difficult, as a broken, tensely-suspended nanotube tends to snap sharply (similar to a rubber band) upon breaking. A combination of the second two effects can also occur in tandem.

Figure 5 displays some of the effects of short term “burning” of the CNT using the electron beam of the TEM as a gun. In these images, the beam was focused (intensity) for 1 min, and then subsequently imaged. Figure 5(a) shows a typical buckle point in a bundle of CNTs near the nitride edge. After a minute of high intensity irradiation, the CNT segment is seen to be enveloped by carbon layers (Figure 5(b) and (c)). Figure 5(c) shows a high resolution close up of what was the buckling point. The subtle lines appear to be graphite-like fringes in the encapsulation layers, which probably encompass a partially denatured tube. Figure 5(d) shows the result of e-beam burning of the twisted SWNT of Figure 3. As is evident, the twist in the SWNT is no longer visible due to the apparent denaturing of the CNT structure.
Figure 5. Active electron beam burning of the samples using the TEM. (a) A typical buckle of a nanotube (bundle) near the nitride grid edge [scale bar: 10nm]. (b) Image of the same segment, after focusing the intensity of the beam, for 1 min [scale bar: 10nm]. (c) High resolution close up of (b), showing the layers of carbon encapsulating the tube [scale bar: 5nm]. (d) An image of the twisted tube of figure 3(a), after 1 min of high intensity beam. The twists in the tube are seen to have blurred due to the tube's denaturing [scale bar: 20nm].

An additional case of invasive TEM radiation is seen in figure 2(b). The original positioning of the tube consisted of only 3 buckles (points 1, 2 and 3 in figure 2(b)). While the buckled system is energetically stable, by irradiating the system for a number of minutes, one of the original buckles (point 3) popped off the surface, creating the fourth buckle (point 4) midway between them. Note how the SWNT does not revert back to its original, tubular, shape. This is most probably a result of either structural damage to the SWNT, or due to its having been bound to the carbon-covered edge of the nitride grid. In any event, the resulting structure presented in figure 2(b) remained stable.

5. Discussion and summary

This study has described an innovative method of imaging and analyzing a few of the forms of interactions and defects occurring in CNT systems. It describes a unique platform of TEM grids containing suspended CNTs which can be used as a tool for verifying the numerous simulations of CNT structural effects and defects existing. These systems form spontaneously, allowing dissection of a system in terms of energy-stability possible, without the need for ascribing external forces to the structures analyzed [6].
The technique employed here has many advantages over existing experimental methods, including AFM techniques [17, 19]. Foremost amongst these is the lack of background noise, usually caused by a carbon grid, enabling the highest resolution achievable with the TEM, as well as rendering insignificant the effects of the substrate on the tubes themselves (in the form of radial deformation, and chemical bonding). The robustness of the grids employed allows their recycled use: The grids can be plasma-cleaned and then reused in the CVD process, as opposed to most carbon grids, which are practically disposable. In addition, the technique is relatively non-invasive (unless desired to be), in contrast to most AFM techniques. Finally, while the resulting systems are unique in the sense that one cannot control exactly what type of structure will be grown, the suspended growth dynamics ensure that nearly all the effects mentioned above (with the exception of SWNT twisting) occur on each sample per CVD growth. Thus, the method employed here is advantageous in terms of representative sampling, enabling the user to quickly ascertain the location and type of system to be analyzed, over the entire span of the sample.

The possible drawbacks of this technique are in the thermal instability of suspended nanotubes [20]. All the nanotubes are tautly stretched across the holes [8], yet, due to the heat dissipation in the tube, as mentioned above, long sections of SWNTs tend to oscillate when viewed for long periods of time, with a chance of them breaking, or denaturing [18].

The TEM-CNT technique used here has other conceivable uses beyond those mentioned above. The newly devised field of TEM holography [21] requires the use of holey-grids for imaging. By growing the CNTs directly onto the grid, it ensures the existence of suspended CNTs over the holes. Finally, by tilting the specimen holder, 3-D modeling of CNTs can be achieved by taking multiple 2-D images of the sample, at various angles.

By using this simple technique for viewing isolated nanotube structures, a reliable platform for verification of simulated CNT statics results can be achieved. This can be of particular advantage to studies trying to verify the physical modeling veracity of their simulations. In addition, the technique described can be useful in the study of other forms of nanowires, and is not limited to CNT analysis.

Acknowledgements

The authors thank Protochips Inc. for their information regarding the TEM nitride meshes. This research was funded by an ISF grant.
References


