

Synthesis of Carbon Nanotubes by Rolling up Patterned Graphene Nanoribbons Using Selective Atomic Adsorption

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ABSTRACT

We demonstrate a new method (U.S. Patent Appl., serial no. 60/908039) for synthesizing carbon nanotubes (CNTs), using first-principles and classical molecular dynamics simulations. The single-walled nanotubes (SWNTs) are formed by folding graphene nanoribbons patterned on graphite films through adsorption of atoms of varying coverage, which introduces an external stress to drive the folding process. The diameter and chirality of SWNTs can be a priori controlled by patterning graphene nanoribbons with predefined width and direction so that the postsynthesis sorting process is eliminated. Our method allows potentially mass production of identical tubes and easy integration into device structures on a substrate.

Much recent effort has been devoted to developing technical and economical viable methods for synthesizing carbon nanotubes (CNTs) that have exhibited a wealth of fascinating electrical, optical, and mechanical properties with a broad range of applications. Currently, there are three major methods for CNT synthesis, arc discharge,² laser ablation,³ and chemical vapor deposition.⁴ However, these existing methods lack still sufficient control over CNT diameter and chirality and postsynthesis sorting process is often required.^{5–7}

Carbon nanotubes (CNTs) are often visualized as seamlessly rolled-up graphene sheets (ribbons). Depending on the width and direction of the rolled-up graphene ribbons, CNTs of different diameter and chirality would be formed. However, such a *deterministic* process of theoretical visualization has never been realized in real practice. Instead, CNTs are made so far by *stochastic* synthetic processes, including arc discharge,² laser ablation,³ and chemical vapor deposition (CVD),⁴ which renders an inherent difficulty in controlling the tube diameter and chirality. Although much progress has been made recently, especially with CVD methods,^{8–11} in producing well aligned and ordered^{12,13} CNTs with better control in diameter^{14,15} and chirality,¹⁶ synthesizing mass quantities of CNTs with uniform diameter and chirality remains a great challenge. Postsynthesis separation, purification, and sorting process are often required^{5–7} before putting CNTs in use, which amounts to additional technical difficulties and production cost. Therefore, developing new and

alternative methods for synthesizing CNTs is of great interest and economic benefit.

Here, we demonstrate a method¹ of synthesizing CNTs by practically realizing the ideally visualized process of rolling up the graphene ribbons, employing the physical principle of bending of thin films driven by surface adsorption induced stress. The method consists of three basic steps:¹ (1) patterning of graphene nanoribbons (GNRs), (2) rolling up of GNRs into single-walled nanotubes (SWNTs) by surface adsorption at low temperature, and (3) removing surface adsorbates by high-temperature desorption. All the existing CNT synthesis methods^{2–4,8–16} are based on the bottom-up self-assembled growth processes, which are *stochastic* in nature. In contrast, our method, employing a top-down process of patterning, is *deterministic* in nature, with the tube diameter and chirality predefined by patterning. Furthermore, patterning is a parallel process allowing mass production of SWNTs with uniform size and chirality.

Figure 1 shows first-principles molecular dynamics (MD) simulations (see method) demonstrating the feasibility of our idea. First, a GNR of 1.7 nm wide is patterned on a graphite film (Figure 1a1). Then, H atoms of 50% coverage are randomly adsorbed onto the ribbon surface (Figure 1a2). The adsorption introduces a surface stress driving the ribbon to fold downward (Figure 1a3) and detach from the underlying film (Figure 1a4), and finally, the two ribbon edges meet and bond together to form a SWNT (Figure 1a5). The details of the whole process can be viewed on-line in the Supporting

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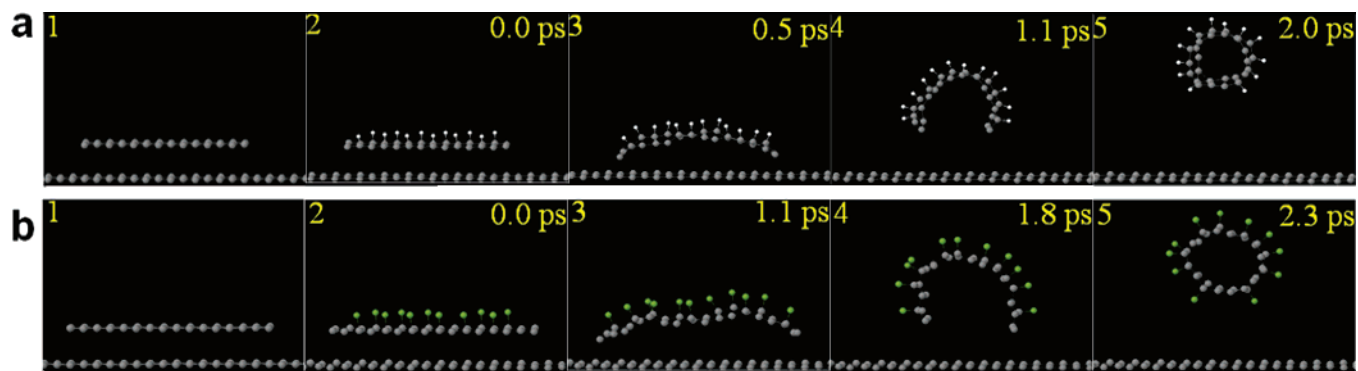


Figure 1. First-principles MD simulation of (a) H and (b) F adsorption induced CNT formation. White, green, and gray balls are hydrogen, fluorine, and carbon atoms, respectively. Notice that CNTs moving away from the substrate surface is an artifact of our simulation because the substrate layer of graphite was artificially fixed to save computation time.

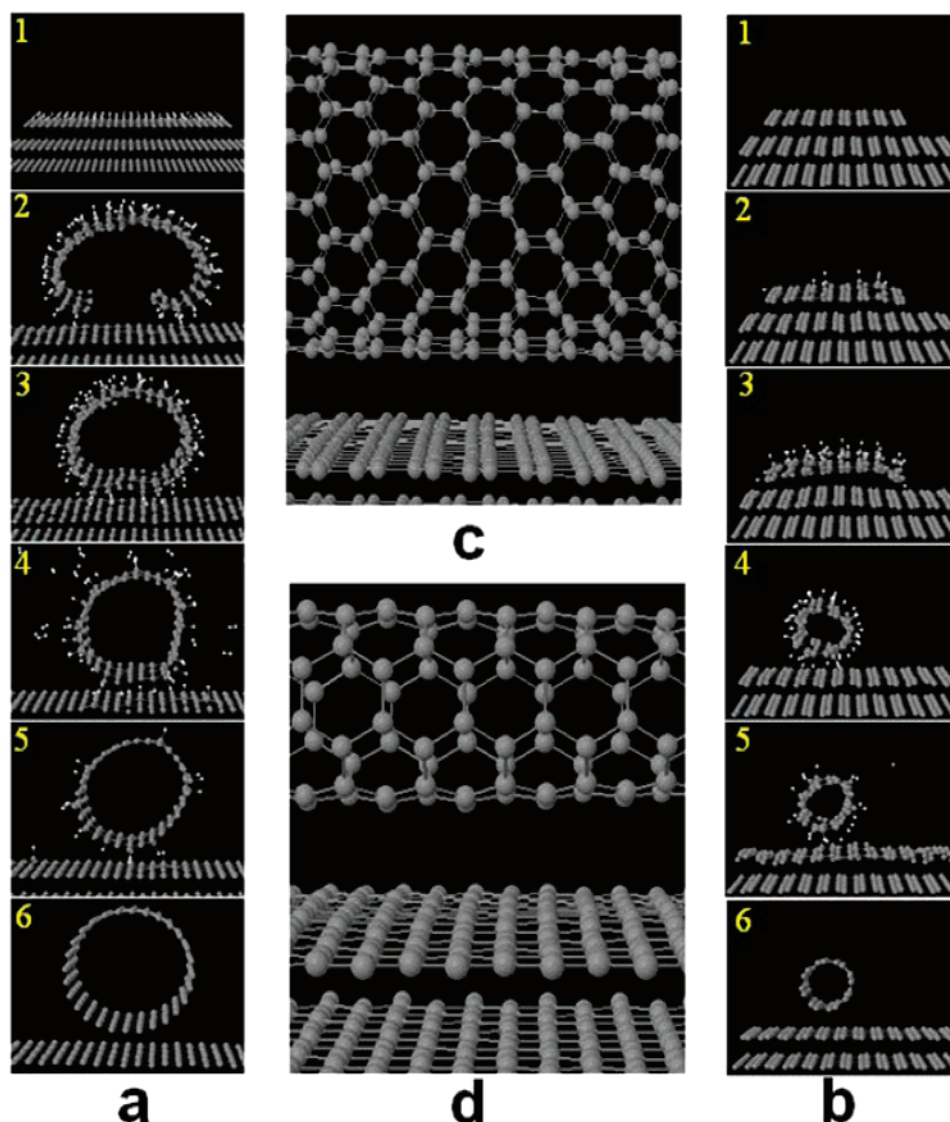


Figure 2. Classical MD simulation of CNT formation. (a) and (b) demonstrate the formation of 0.9 nm (diameter) zigzag and 0.5 nm (diameter) armchair SWNTs, respectively. (a1–a3) and (b1–b4) show the tube formation at room temperature after (a) and with (b) adsorption of H atoms, respectively. (a3–a6) and (b4–b6) show the desorption of H atoms at 1800 K. (c) and (d) show the perspective side view of zigzag and armchair SWNTs resulting from process (a) and (b), respectively. Atom label is the same as Figure 1.

Information Video 1. Similarly, Figure 1b shows the same process using a wider ribbon of 2.0 nm and adsorption of F atoms of 45% coverage (Supporting Information Video 2).

The process is applicable to GNRs of different width and direction, which leads to formation of SWNTs of different diameter and chirality. To explore such a possibility, we have

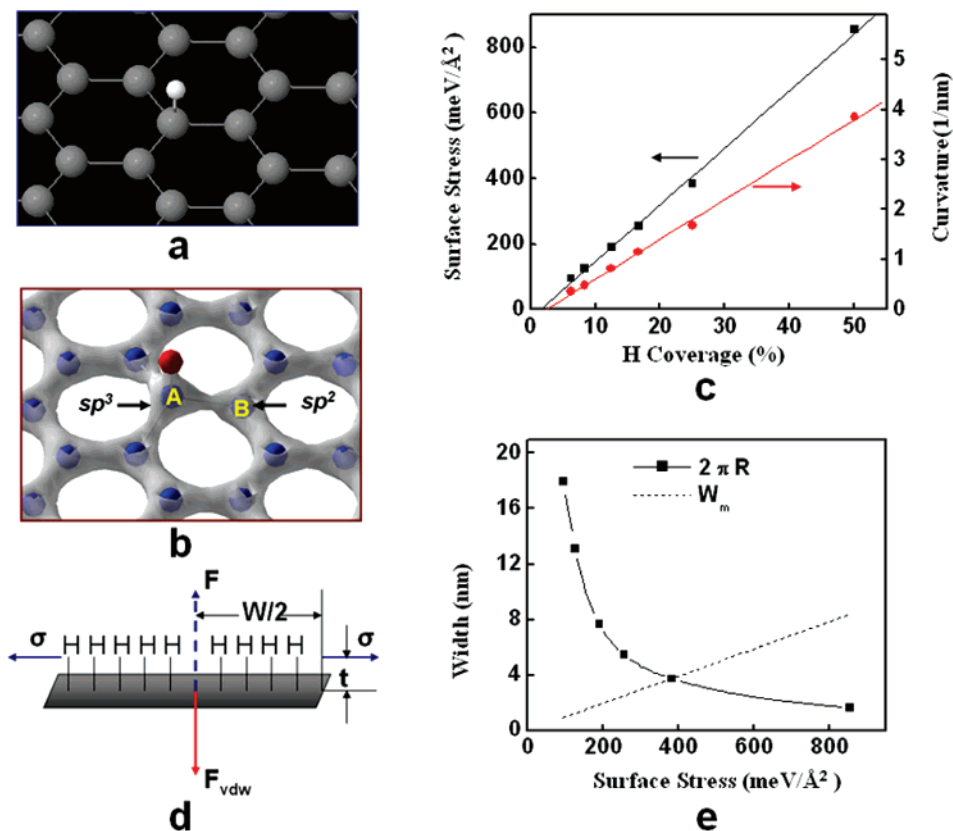


Figure 3. Stress generation and force balance analysis. (a) Ball-stick and (b) charge density plot of graphene lattice with one H atom adsorbed on surface. Small white and red spheres are H atoms, and big gray and blue spheres are C atoms. (c) The surface stress and bending curvature as a function of H coverage. Solid line is a guide to the eye. (d) Schematics illustrating the force balance in the GNR layer upon adsorption of H atoms. (e) Comparison of tube perimeter and the maximum lift-off GNR width as a function of surface stress.

carried out extensive classical MD simulations (see method) to form many different SWNTs because it is computationally too demanding to do so using first-principles MD method. Figure 2a shows snapshots of classical MD simulations, illustrating formation of a (14,0) zigzag SWNT (Figure 2c), using 45% H coverage adsorbed on a (13,0) GNR¹⁷ of ~3.3 nm wide. The initial adsorption and rolling-up process are carried out by MD simulations at room temperature (Figure 2a1–3). After the tubes are formed, they are heated to a high temperature of 1800 K to desorb the surface H atoms to make clean tubes (Figure 2a4–6). The details of the process in Figure 2a can be viewed online in the Supporting Information Video 3.

In the above examples, all the H atoms are put on the GNR surface at once before MD simulations. In real experiments, we expect that H atom flux increases the coverage gradually, so the GNR relaxes and bends as the H atoms being continually adsorbed onto its surface. To simulate this deposition process, we couple the MD with a Monte Carlo (MC) algorithm, allowing H atoms to be deposited at a rate of ~40 mol/(cm² s) up to the desired coverage. One example of the MD/MC simulations is shown in Figure 2b and also in Supporting Information Video 4. The H atoms land randomly onto the GNR surfaces as well as along the edges. We found that GNR starts to fold well before the final coverage is reached (Figure 2b2–3). Because folding and tube formation take a short time (a few ns or

less at room temperature), we did not observe the H migration on the surface. A small number of H atoms occupying the edge sites do not prevent the bonding of the two ribbon edges, although they slow down slightly the bonding process. In addition, bonding of one part of the ribbon edge has a “zipping effect” on the remaining edges.

The driving force for the SWNT formation is the *stress* induced by surface adsorption such as H atoms. The surface adsorption induced bending of thin films is a well-known phenomenon, as being exploited in mechanochemical sensors.¹⁸ For given molecular coverage, the thinner the film is, the larger the bending curvature will be. Our approach represents the extreme case of bending of the thinnest possible C film of one-atomic-layer thick to achieve the largest bending magnitude, i.e., the smallest radius of bending curvature in the range of nanometers to form nanotubes. The diameter of SWNTs can be controlled by tuning the coverage of adsorbates to change the adsorption induced stress. For H adsorption on GNR (or graphite film in general), our first-principles calculations show that the preferred H adsorption site is on top of a C atom (Figure 3a) with a binding energy of 0.9 eV. This leads to a transition of the bonding configuration of the C atom underneath H from *sp*² to *sp*³ (Figure 3b). As a result, this C atom is pulled up by ~0.3 Å while its three neighboring C atoms are pushed out and down, inducing a tensile stress in the GNR. Our calculations further show that the induced stress increases linearly as H coverage

increases and so does the bending curvature (Figure 3c) following the Stoney formula. The maximum H coverage used on GNR is 50%, corresponding to upper limit of H adsorption on graphite surface found in experiments.¹⁹

There needs to be a correspondence between the adsorbate coverage and the ribbon width for the method to work. The optimal choice is to use a ribbon width, W equal to the tube perimeter length, $2\pi R$, where R is the radius of bending curvature defined by the adsorbate coverage. If the ribbon width is too large, much larger than $2\pi R$, then two open nanotubes will form at the two ends instead of one closed nanotube (see online Supporting Information Figure 1). On the other hand, if the ribbon width is smaller than $2\pi R$, then the ribbon will fold into an incomplete tube.

Another important factor is that the patterned GNR is in fact not a freestanding film but bonds weakly to the underlying layer via van der Waals attraction. Consequently, the stress induced by H adsorption must be large enough to overcome such attraction so that the GNR can detach from the underlying film through the bending process. Suppose that H adsorption induces a surface stress of σ , it will apply a bending moment of $M = \sigma t/2$, where t is the “effective” film thickness including the adsorbate layer (Figure 3d). Equivalently, this moment can be thought of as created by an upward force F at the midpoint of the ribbon (Figure 3d), which gives rise to $F = 2\sigma t/W$, where W is the ribbon width. To lift off the ribbon, F has to be larger than or equal to F_{vdw} , the van der Waals force of attraction. Thus, we can estimate the maximum ribbon width for a given stress σ (i.e., H coverage), is $W_m = 2\sigma t/F_{\text{vdw}}$.

The existence of the maximum ribbon width for the detachment sets an upper limit on the nanotube radius (R) that can be made, with $2\pi R \leq W_m$. One may try to decrease coverage and hence σ to increase R ($R \propto 1/\sigma$, Figure 3e), making a larger tube, but this will decrease W_m ($W_m \propto \sigma$, Figure 3e). So, there is a minimum coverage (smallest σ) one has to use that corresponds to the largest tube, as defined by the crossing point of $R(\sigma)$ and $W_m(\sigma)$ curves in Figure 3e. For H adsorption, theoretical calculation gives the minimum stress of $\sim 380 \text{ meV}/\text{\AA}^2$ for lift-off, which corresponds to a maximum tube radius of $\sim 0.7 \text{ nm}$. This is confirmed by direct MD simulations, showing that a lower H coverage cannot induce large enough bending to detach the GNR from the graphite film.

Because using a single layer of patterned GNR can only produce SWNTs with a limited size, e.g., $R \leq \sim 0.7 \text{ nm}$ for H adsorption, we have also designed a process based on the same bending principle to overcome this limitation by using two layers of patterned GNRs (Figure 4) instead of a single layer. The top layer GNR needs to have a width equal to or slightly larger than the bottom layer (Figure 4). As H atoms are introduced, they adsorb on the top GNR only, causing it to bend downward. As it bends down, its two edges will meet and then bond with the two edges of the bottom GNR, as if the two layers of ribbon are “stitched” together, forming a SWNT (Figure 4a2,b2). Once the tube is formed, H atoms on the top half of the tube are desorbed at high temperature (Figure 4a3–5,b3–5). The details of this process are

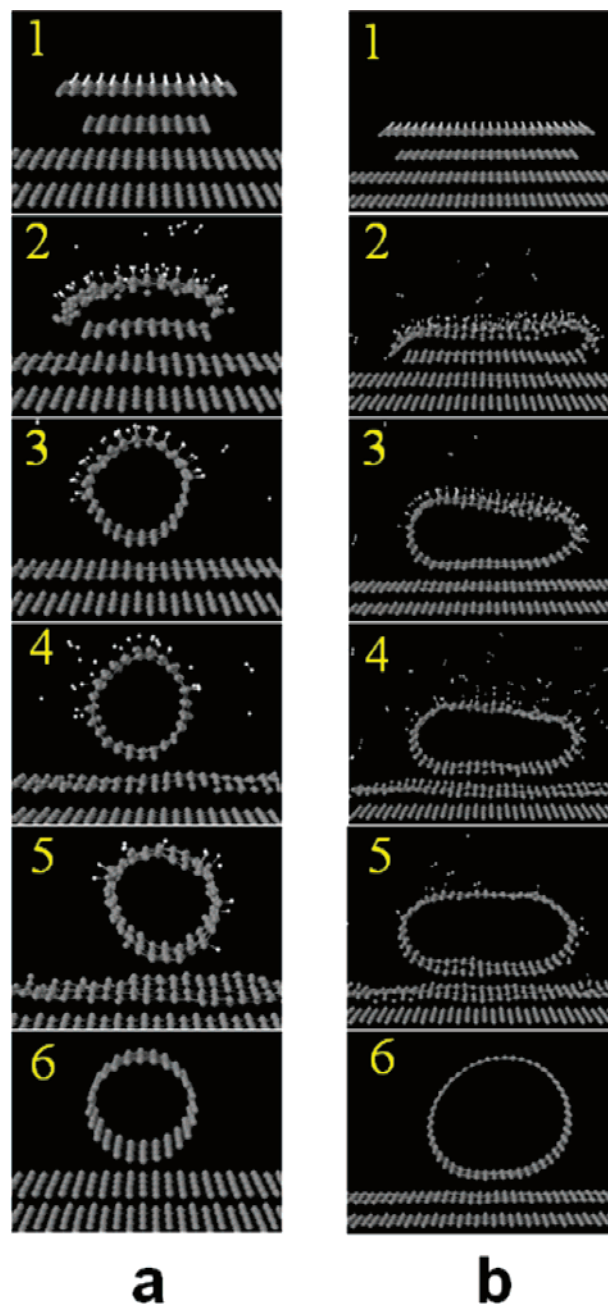


Figure 4. Double-layer method for CNT synthesis. (a) and (b) show the formation of 1.0 and 2.2 nm (diameter) SWNTs, respectively. (a1–a3) and (b1–b3) show the formation of CNTs at room temperature after adsorption of H atoms; (a3–a6) and (b3–b6) show the desorption of H atoms at 1800 K. Atom labels are the same as in Figure 1.

animated in online Supporting Information Video 5. Using this double-layer method, we can in principle produce SWNTs of any size. However, due to van der Waals interaction, the tube may become flat when its diameter is too big (Figure 4b), and it has been shown that the ground-state structure of a very large SWNT may adopt a dog-bone shape.²⁰

Our proposed approach represents a unique application of GNRs, which has attracted intensive recent interest as a new class of nanomaterials.^{17,21} The experimental realization of our approach depends on the ability of patterning GNRs with

controlled width and edge quality, a challenge that will be met in order to realize the potential of GNRs for all possible applications. Currently, GNRs as small as 10–15 nm wide has been fabricated,²² which is already sufficiently small for the two-layer process (Figure 4) but larger than the maximum width (3–4 nm) required for the single-layer process (Figure 2) using H adsorption. The maximum width might be increased by using adsorption of different atoms. Also, we anticipate that the principle underlying our approach for making CNTs can be generally applied to make other forms of nanostructures from different materials. For example, nanotubes and nanocoils have been made from bilayer thin films employing the bending induced by misfit strain,^{23–27} as the nanomechanical architecture of strained bilayer films.²⁵ It is possible to make these nanostructures using only one-layer film of a single material by applying our approach via surface adsorption followed by desorption.

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Supporting Information Available: Details of first-principles molecular dynamics, classical molecular dynamics and Monte Carlo algorithm, supporting figure for double tube formation, supporting videos (MPG) for CNTs formation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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