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Carbon Nanotubes

Transition-Metal-Catalyzed Unzipping of Single-Walled Carbon Nanotubes into Narrow Graphene Nanoribbons at Low Temperature**

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Graphene, which is the thinnest two-dimensional material in nature, has been extensively studied due to its exceptional mechanical, thermal, electronic, and magnetic properties, and because it has the potential to replace silicon in future electronics and spintronics applications.[1,2] Although pristine graphene is a semimetal, a medium-sized band gap can be opened by cutting into narrow graphene nanoribbons (GNRs).[3,4] Recently, great efforts, for example, lithographic techniques,[5,6] chemical synthesis,[3,7,8] or chemical vapor deposition methods,[9,10] have been dedicated to the synthesis of GNRs. While most of these GNRs are either very wide (width > 20 nm) or have no well-defined clean edges, the synthesis of long, narrow GNRs with well-defined smooth edges at low temperature remains a great challenge.[11]

In the literature, a single-walled carbon nanotube (SWNT) is viewed as a folded or zipped GNR. It is thus very natural to seek the reverse process, unzipping SWNTs, to synthesize GNRs. Various experimental methods, including chemical attack,[12–20] plasma etching,[21] catalytic cutting under microwave radiation,[22,23] lithium intercalation and subsequent exfoliation,[24] electronic unwrapping,[25] and mechanical cutting,[26] have been developed to unzip carbon nanotubes (CNTs, mostly multiwalled CNTs, MWNTs) into GNRs.[11,27–29] Most recently, transition-metal particles (e.g., Co, Ni, or Cu) have been introduced as chemical scissors to cut both MWNTs[30,31] and graphene in hydrogen gas.[32] In the cutting procedure, the transition-metal particles serve as catalysts to break the H−H and C−C bonds and to solvate etched C atoms. These processes do not involve any aggressive chemical treatment, and thus smooth graphitic edges can be easily achieved. Compared to the extensive experimental studies, there are only few theoretical explorations on the mechanism of unzipping CNTs or graphene.[12,33–37] To our knowledge, there is no atomic-level theoretical investigation on the mechanism of catalytic unzipping of CNTs in H_2 gas. Herein, we present an ab initio study on the role of transition metals in SWNT unzipping. The study shows that appearance of a single metal atom dramatically reduces the barrier of SWNT unzipping by about 70 %, from approximately 3.0 to 1.0 eV. Thus, it opens the door to the synthesis of high-quality GNRs at low temperature.

All calculations were performed using the Vienna Ab initio Simulation Package (VASP).[38] We employed the general gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE)[39] as the exchange-correlation functional and the projected augmented wave (PAW) method[40] to describe the interaction between the valence electrons and the ion cores. A climbing-image nudged elastic band (cNEB) method[41] was employed to locate the transition states between the reactants and the products. Spin-polarized DFT were used in all calculations.

A finite long (5,5) SWNT,[42] with 10 rings of carbon atoms (named (5,5)-10), both ends of which were passivated by H atoms, was chosen as the prototype (Figure 1 a). As a reference, unzipping the SWNT with a pure H_2 molecule was studied first. Although this unzipping process is energetically favorable (the reaction enthalpy is 0.73 eV per H_2 molecule, or 16.8 kcal mol^{-1}), a very high reaction barrier (3.11 eV) makes it very difficult, if not impossible, to achieve (Figure 1 a). This high barrier can be attributed to a symmetry forbidden reaction, which is suggested to create a high activation barrier for a [2+2] reaction according to the Woodward–Hoffman symmetry rule.[43]

It is a common knowledge in chemistry that transition metals serve as catalysts for various chemical reactions

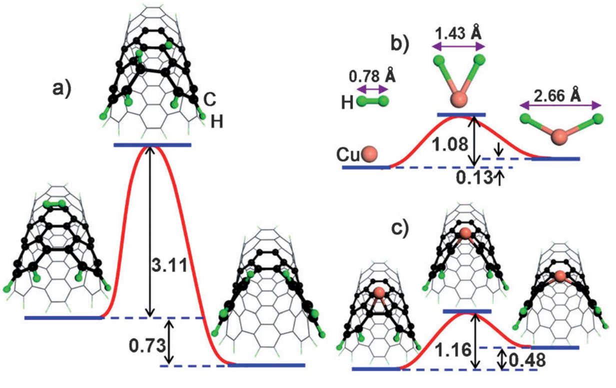

Figure 1. a) Unzipping of a SWNT with a hydrogen molecule, b) Cu-atom-catalyzed H−H bond breaking, and c) Cu-atom-catalyzed C−C bond breaking on the edge of a short (5,5) SWNT.

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because of their abundance of both free electrons and d orbitals, which have the property of providing and withdrawing electrons from the transition state of a reaction. Here, the appearance of a transition metal is expected to change the symmetry-forbidden concerted reaction into a stepwise symmetry-allowed reaction. Figure 1 b,c confirms this expectation. As is clearly shown in Figure 1 b, a copper atom catalyzes the break of the H–H bond with a small energy barrier of 1.08 eV. More importantly, with the assistance of a Cu atom, the energy barrier for breaking the C–C bond in a SWNT drops to 1.16 eV, which is notably smaller than the 3.11 eV in H_2 cutting. We thus expect that the presence of a transition metal will significantly reduce the energy barrier of SWNT unzipping in H_2 gas.

We now consider the process of unzipping a (5,5) SWNT with the assistance of a Cu atom in H_2 gas. We first calculated the possible Cu adsorption sites on the tube and found that the Cu atom prefers to stay between the carbon atoms of a C–C bond near the tube end, which has a formation energy advantage of 0.11 eV over the middle of the tube. We thus unzipped the tube from one end rather than from the middle. The Cu-catalyzed SWNT cutting process is as follows:

1) The Cu atom adsorbs on the edge of the SWNT wall and breaks the C–C bond to form a bridged C-Cu-C intermediate (Figure 1 c and 2 a).
2) A H_2 molecule adsorbs to the Cu atom with a weak binding energy of 0.3–0.4 eV. The dissociation of the H_2 molecule into two H atoms does not occur as it does with a free Cu atom, although the H–H bond is significantly weakened, as indicated by the elongated H–H bond length (from 0.72 Å in H_2 to 0.83 Å in C-H_2@Cu-C; see C-M-C and TS1–1 in Figure 2 a).
3) The H–H bond is broken and one H atom diffuses to one of the bridged C atoms by the simultaneous breaking of the C–Cu bond. An intermediate with one C atom passivated by H and another C atom passivated by a Cu–H group is formed (see H-C···C-M-H in Figure 2 b).
4) The remaining H atom in the Cu–H group further diffuses to another C atom to create a terminal C–H bond. The saturation of the two C atoms with the two H atoms releases the catalyst atom and results in a partially unzipped SWNT (see F1(I2) in Figure 2 b).
5) The released Cu atom is ready to move ahead to catalyze the unzipping of another C–C bond of the SWNT (see F1(I2) in Figure 2 b).

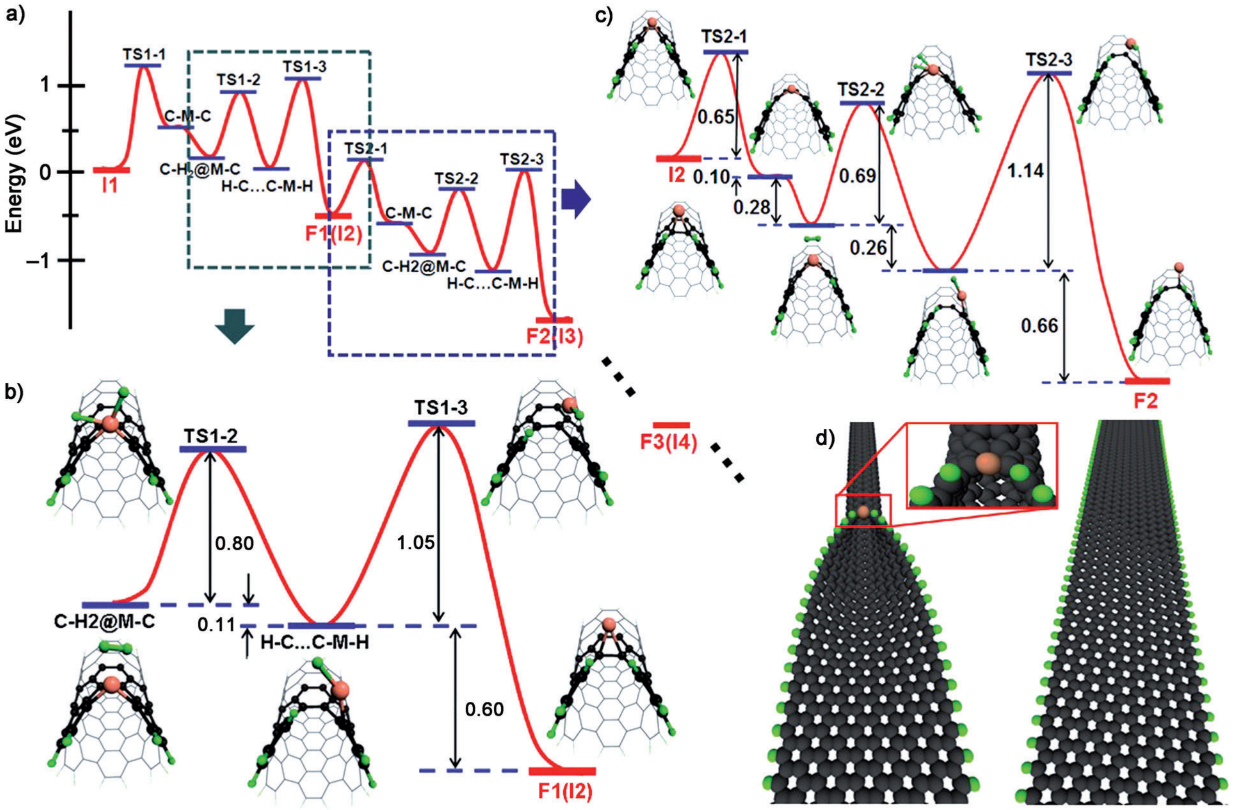

Figure 2. Cu-atom-catalyzed unzipping of a (5,5) SWNT into a narrow zigzag GNR in H_2 gas. I1 to F1 and I2 to F2 (a) show the four substeps of cutting the first and the second C–C bonds, respectively, on an open end of a (5,5) SWNT: 1) I1→C-M-C, the Cu atom breaks the C–C bond (details shown Figure 1 c). 2) C-M-C→C-H_2@M-C, one H_2 molecule adsorbs to the Cu atom from gas phase. 3) C-H_2@M-C→H-C···C-M-H, the H_2 molecule dissociates into two H atoms, one of which simultaneously passivates a C atom and releases the H@M to bind to another C only (details shown in the first step of Figure 2 b); 4) H-C···C-M-H→F1, the remaining H atom passivates another C atom and then releases the free Cu atom to a nearby C–C bond (details shown in the second step of Figure 2 b). c) Details of the second C–C bond cutting, which almost repeats the first C–C bond-cutting procedure. Repeating the above process eventually unzips a (5,5) SWNT into a long narrow GNR (d).

6) Steps (1)–(5) are repeated to cut the next nearby C–C bond. Repeating the above process many times will eventually unzip the whole tube into a long and narrow zigzag GNR (Figure 2).

Figure 2a–d shows the full process of the Cu-catalyzed unzipping of the (5, 5)-10 SWNT. Each bond unzipping includes four reactions, three of which have barriers (marked as TS*i*–1, TS*i*–2, and TS*i*–3, where *i* indicates the order of the unzipped bonds); the adsorption of the H_2 molecule is barrierless. A detailed description of the unzipping of the first and the second C–C bonds is shown in Figure 1c and Figure 2b,c. The breaking of the first C–C bond with Cu has a lower barrier of 1.16 eV. Although the separation of the C–C bond is energetically unfavorable (the energy rises to 0.48 eV, see Figure 1c), the separated C–C bond formation can be stabilized by H termination in the following step. As shown in Figure 2b, the adsorption of H_2 releases 0.35 eV. The breaking of the H_2 molecule and the passivation of one C atom occur simultaneously, with a corresponding energy barrier of 0.80 eV and an energy drop of 0.11 eV. In the next step, the passivation of another C atom needs to overcome a barrier of 1.05 eV with an energy drop of 0.60 eV. The consumption of one H_2 molecule and the surmounting of three consecutive energy barriers (1.16, 0.80, and 1.05 eV) are required to fully unzip a C–C bond. All three barriers are significantly lower than that involved in breaking a C–C bond with an H_2 molecule directly, which is 3.11 eV. Using the energy of the H_2 molecule as a reference, the barrier of the full process is 1.16 eV. Thus, with a Cu atom as catalyst, a C–C bond can be easily unzipped in H_2 gas in one second at a moderate temperature of approximately 487 K or (estimated by transition-state theory, $10^{12}\exp(-E_b/kT)\approx 1$, where $E_b = 1.16$ eV).

As stated, the cutting of every C–C bond occurs in a very similar manner, and we thus expect no dramatic differences in the energy barriers and energy changes at each step. In the unzipping of the second bond (Figure 2c), the breaking of the C–C bond with a Cu atom is energetically favorable (the product is 0.10 eV lower in energy than the reactant). More importantly, the corresponding energy barrier drops to 0.65 eV, which is significantly lower than the barrier to the breaking of the first C–C bond of 1.16 eV. The other two barriers to unzipping the second C–C bond are 0.69 and 1.14 eV, respectively, and the corresponding formation energies are reduced by 0.26 and 0.66 eV, respectively, which are comparable to those in the unzipping of the first C–C bond. By repeating the unzipping process, the whole SWNT is eventually well cut into a smooth zigzag nanoribbon, as shown in Figure 2d.

As can be clearly seen in Figure 2a, the unzipping of each C–C bond is exothermic, and the barriers become continuously lower. For example, the total energy drop during the unzipping of the first C–C bond is 0.59 eV (see Figure 1c and Figure 2b), whereas the energy drop during the unzipping of the second and the third bonds rises to 1.30 and 1.92 eV (see Figure 2a), respectively. This result indicates that the unzipping of a SWNT is experimentally feasible.

It is clear that the SWNT curvature energy, which is approximately $10.0\,l/D$ eV, where l is the tube length and D is the tube diameter,[44] released during the unzipping is the main driving force. Certainly, unzipping along the tube axial direction is energetically more favorable, as the energy released at each step along this direction is greater than that along other directions. Specifically, the metal atom moves 0.213 and 0.246 nm each step for unzipping along the armchair (AM) and zigzag (ZZ) directions, respectively. Thus, unzipping along the ZZ direction would release more curvature energy than that along the AM direction. Therefore, we conclude that the most favorable unzipping direction is a zigzag direction which is closest to the tube axis.

To verify the proposed mechanism, we further systematically investigated the unzipping of several SWNTs with different diameters and chiralities. As shown in Table 1 and Figure S3–S5 in the Supporting Information, a Cu atom can efficiently unzip most SWNTs with a small barrier of approximately 1.0 eV, and thus the general picture that a TM catalyst atom can be used to unzip a SWNT efficiently remains valid. Moreover, a general trend, that the larger the SWNT's diameter, the greater the barrier of breaking a C–C bond, is shown (Table 1). This finding is as anticipated, because unzipping of small SWNTs releases large curvature energy. The trend indicates that small SWNTs can be easily unzipped, and thus it is expected that narrow GNRs may be synthesized by well-controlled experimental conditions. Meanwhile, the barrier also weakly depends on the SWNT's chirality, and it seems that the barrier of unzipping an armchair SWNT is smaller than that of unzipping a chiral one with equal diameter.

Table 1: Reaction barriers and formation energies ΔE (products relative to reactants) of the Cu-catalyzed first C–C bond breaking. SWNTs with different diameters, chiralities, and segment lengths are considered.

System	Tube diameter [Å]	Barrier [eV]	ΔE [eV]
(6,6)	8.14	1.38	1.02
(5,5)-10[a]	6.78	1.16	0.48
(5,5)-9[b]	6.78	1.06	0.49
(5,4)	6.11	1.08	0.62
(5,3)	5.48	1.06	0.39
(4,4)	5.42	0.80	−0.05
(3,3)	4.07	0.60	−0.41

[a] A (5,5) SWNT segments with ten rings of carbon atoms. [b] A (5,5) SWNT segments with nine rings of carbon atoms.

The only exception is the zigzag SWNT, whose first bond unzipping procedure is different from that of others. As shown in Figure S5 in the Supporting Information, the barrier of unzipping the first bond of a (7,0) SWNT is 1.79 eV, and the formation energy increases 0.05 eV after unzipping, while the unzipping of the second C–C bond of same SWNT occurs in exactly the same manner as for an AM tube and the corresponding barrier and formation energy are significantly reduced to 1.04 and −0.94 eV, respectively. It is well known that the populations of zigzag SWNTs in most SWNT samples are very small,[45] and thus the relatively high barrier of unzipping zigzag SWNTs does not change the main conclusion of the study.

Finally, we point out that although we chose Cu as catalyst to unzip SWNT herein, this recipe is general and workable for most other transition metals. As shown in Table 2, the barriers to break an H–H bond and a C–C bond with iron, cobalt, nickel, palladium, or platinum are even lower than that of the Cu-catalyzed system. (Their reaction paths are presented in Figure S6 in the Supporting Information.)

Table 2: Reaction barriers and ΔE (products relative to reactants) in breaking the H–H bond in H_2 and a C–C bond in a SWNT with transition metals.

Metal	H–H break in H_2		C–C break in CNT	
	barrier [eV]	ΔE [eV]	barrier [eV]	ΔE [eV]
Mn	0.86	−0.50	0.49	0.14
Fe	0.27	−0.50	0.10	−0.33
Co	0.14	−0.37	0.08	−0.63
Ni	0[a]	N/A	0.03	−0.37
Cu	1.08	0.13	1.16	0.48
Pd	0.11	0.10	0.39	0.16
Pt	0[a]	N/A	0.11	−1.03

[a] The reaction is barrierless.

In summary, we propose an efficient process to unzip single-walled carbon nanotubes into narrow graphene nanoribbons in H_2. With the help of a single transition-metal atom, the energy barrier of the entire process is significantly reduced to 1.16 eV, which means that the unzipping process might occur at a slightly elevated temperature (e.g., 200–300 °C). The low-temperature operation is important for electronic and spintronic device fabrication. Furthermore, the theoretical study presented herein achieves a deep insight into the mechanism of the extensively explored transition-metal-particle-catalyzed unzipping of MWNTs and graphene.[29–31] For example, besides the catalytic etching of C atoms, the H termination of edge C atoms along the cutting channel is crucial for driving the catalyst particle moving forward.

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[42] The HOMO–LUMO gaps of finite (5,5) SWNT segments oscillate in a range between 0.11 and 0.39 eV (see Figure S1 in the Supporting Information). The unzipping of a (5,5) tube segment with the smallest HOMO–LUMO gap (labeled as (5,5)-9) is found to be very similar to that of (5,5)-10, which possesses a large gap. NEB calculations (see Table 1 and Figure S2 in the Supporting Information) show that the three energy barriers in the first C–C bond breaking are 1.06, 0.64, 1.22 eV, respectively for (5,5)-9 and the corresponding formation energy drops 0.77 eV, which are very close to those (1.16, 0.8, 1.05, 0.59 eV) of the (5,5)-10.

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