Nanoassembly of Carbon Nanotubes through Mechanochemical Nanorobotic Manipulations

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Nanoassembly of multi-walled carbon nanotubes (MWNTs) in three-dimensional space is realized by positioning building blocks with nanometer-order accuracy, joining them together through van der Waals forces, and fixing them with chemical bonds through nanorobotic manipulations. Furthermore, MWNT intramolecular junctions are constructed.
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1. Introduction

Nanoassembly is one of the key techniques for molecular nanotechnology. As an extension of scanning probe microscopes (SPMs)[1,2] to three-dimensional space and for relatively large nanometer-scale objects, nanorobotic manipulation systems have shown their effectiveness in nanometer-order positioning, picking and placing, property characterization and simple nanoassembly of nanometer-scale objects.[3–6] In this paper, molecular construction through mechanochemical manipulations for nanoassembly is presented by using carbon nanotubes (CNTs) as objects.

Because of their well-defined geometries,[7] extraordinary mechanical properties,[8–10] various electronic characteristics[11–13] and other extraordinary properties,[14] CNTs have been shown to be one of the most promising materials for nanostructures and functional devices. The potential of engineering application of CNTs to fabricate nanometer-scale electronic devices[15–17] and mechanical systems[18–20] largely depends on the ability to manipulate them in three-dimensional space. Previous works have shown strategies and systems for 3D nanorobotic manipulations of carbon nanotubes,[3,4] and the nanoassembly of multi-walled carbon nanotubes (MWNTs).[6] However, the components were joined through weak van der Waals forces. Assemblies with higher stiffness can be obtained by using electron-beam-induced deposition (EBID),[21–23] however EBID works by adding additional materials to enhance the intermolecular forces between objects.

Although EBID can provide stiffer links between CNTs, it is still too difficult, if not impossible, to control the deposited materials in atomic scale. With a specially designed experiment, we show that it is possible to link CNTs by forming chemical bonds between them through mechanochemical nanorobotic manipulations without adding any additional material.

2. Mechanochemical Nanorobotic Manipulations

Mechanochemical nanorobotic manipulations are defined as mechanosynthesis through nanorobotic manipulations, while mechanosynthesis refers to chemical synthesis controlled by mechanical systems operating with atomic-scale precision, enabling the direct positional selection of reaction sites.[24]

The simplest mechanosynthesis can be realized by bringing two atoms with dangling keys close enough together so that a covalent key is formed, and hence a molecule is assembled. Presently, it is still difficult to form only one

bond with one operation. However, through nanorobotic manipulations, it is possible to form many dangling keys by breaking a nanotube and reforming some bonds by bringing the ends of the tubes with dangling keys close enough together.

Figure 1 shows a typical result of specially designed experiments to show the mechanosynthesis of nanotubes. All the experiments are performed with a nanorobotic manipulation system[6] installed in the ultrahigh vacuum (UHV) chamber of a field-emission scanning electron microscope. As shown in Fig. 1(a), an MWNT (length $L_1 = 1329$ nm, diameter $D_1 = 42$ nm) is fixed between a substrate and an AFM cantilever with a CNT tip using electron-beam-induced deposition,[22] and the substrate and the AFM cantilever can be respectively actuated in three-dimensional space with two units of the above-mentioned nanorobotic manipulation system. The MWNT samples were synthesized by a standard arc discharge process without any purification, which ensures that the nanotubes are of the highest possible quality. By pulling the two ends of the MWNT, it is broken into two parts as shown in Fig. 1(b). The fact that the total length of the two broken parts $L_2 = l_{21} + l_{22} = 2369$ nm ($l_{21} = 1565$ nm and $l_{22} = 804$ nm) is greater than L_1 can be explained through the so-called "sword-in-sheath" failure,[10] i.e., one or several shells of the nanotube has been broken when pulling the inner tubes out from the outer layers. The difference of diameters/radii ($R_1 = 14$ nm and $R_2 = 21$ nm) also shows that the left tube passed inside the right one before being broken. By pushing two nanotubes close enough together so that they are head-to-head, a new one is formed as shown in Fig. 1(c). Note that the length of this nanotube is $L_3 = 2343$ nm, which is slightly shorter than before they were joined together, and the difference in length is $L_2 - L_3 = 26$ nm, which can be explained by the deformation of the nanotubes [refer to inset of Fig. 1(c)] and/or measurement errors. To test the strength of this nanotube, it was pulled again by moving the substrate (left of the nanotube) downward as shown in Fig. 1(d). The maximum axial connection force can be determined by measuring the deformation of the AFM cantilever which has a stiffness constant of 0.03 N/m at the moment of breaking, and the result is $F = 790.1$ nN. The direction of the force is along the tube as shown in the inset of Fig. 1(d). Figure 1(e) shows the cantilever and substrate after the nanotube is re-broken, and the inset shows that the nanotube breaks at a different site which is evident by comparing the lengths of the two nanotubes with that in Fig. 1(b), which suggests that the tensile strength of the connected nanotubes shown in Fig.
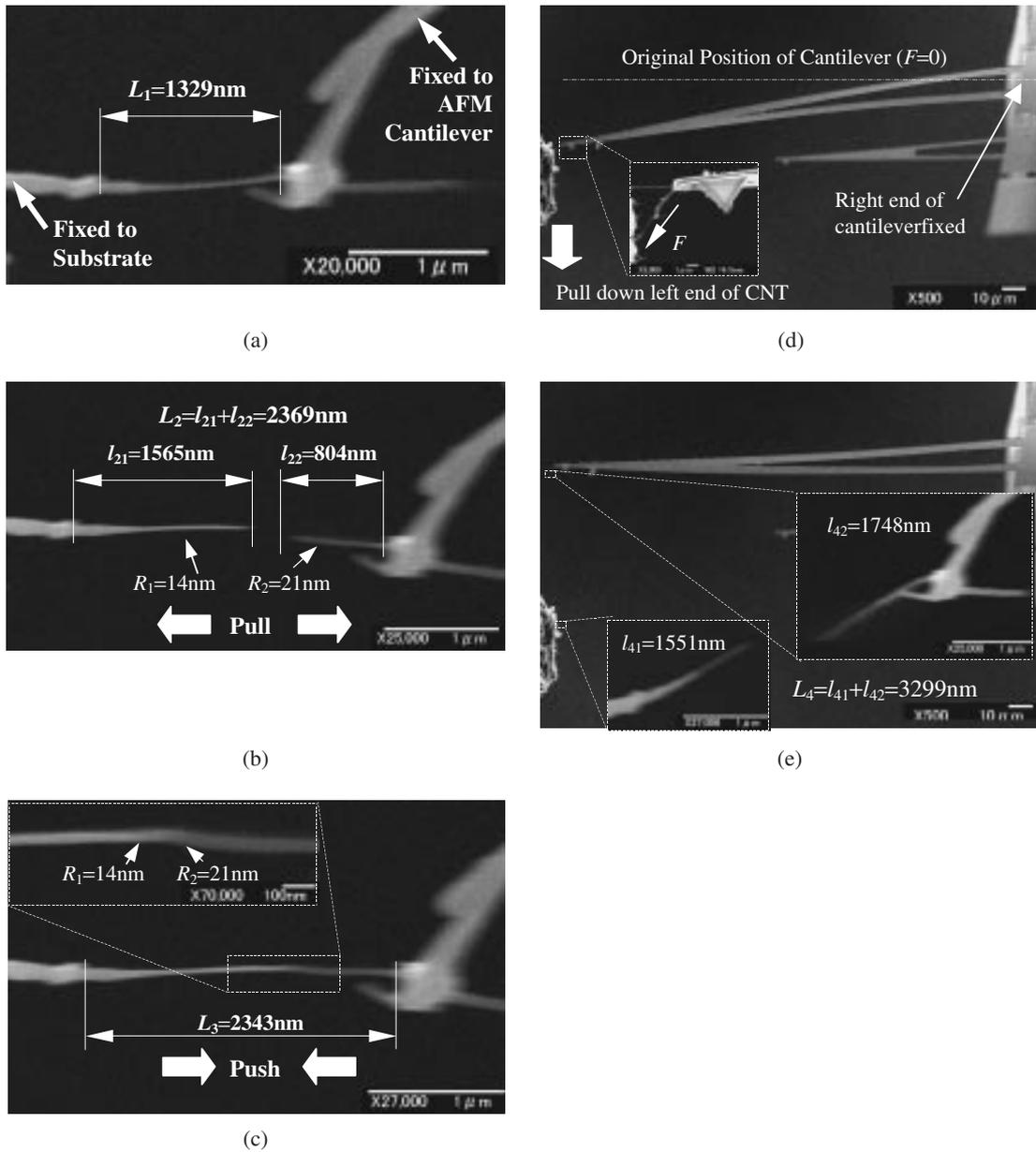
(a)

(b)

(c)

(d)

(e)

Fig. 1.   Mechanochemical manipulations: (a) original state, (b) formation of dangling keys, (c) formation of covalent bonds, (d) force measurement, and (e) re-broken nanotube.

1(c) is not weaker than that of the nanotube itself.

3.   Discussion

It has been known that between atoms in solids there are only four possible types of bonds, i.e., three primary bonds including covalent bonds, metallic bonds and ion bonds, and a secondary bond, namely, the van der Waals (vdW) bond. In this experiment, bonding occurs between pure carbon atoms, so metallic or ion bonds cannot be formed. Also, note that static electric force cannot occur because the MWNTs were connected and grounded. So, the remaining possible bonds are only van der Waals and covalent bonds. Because it is very difficult to obtain an atomic resolution of the connection site *in situ* for the nanotubes shown in Fig. 1(c), it is more practical to give a reasonable justification by analyzing the tensile strength and/or connection forces. For example, the van der Waals force between a pair of carbon atoms changes along with the distance between them as
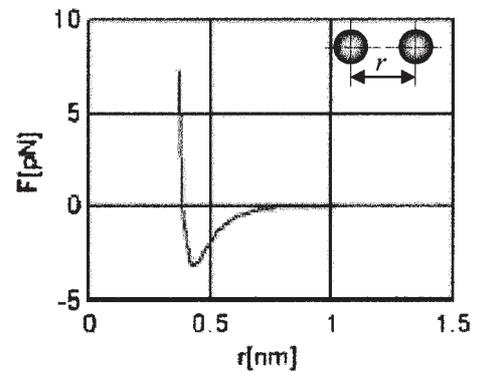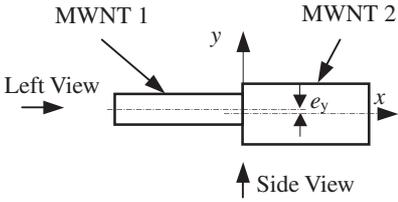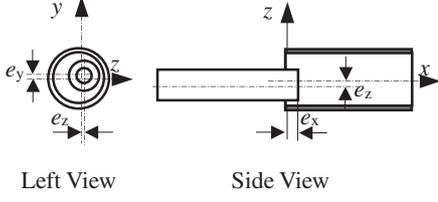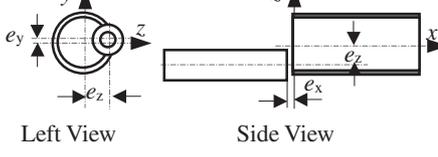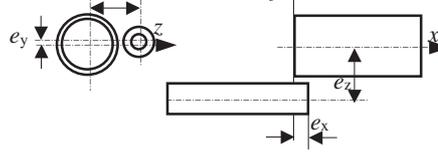

Fig. 2.   Van der Waals forces between carbon atoms.

shown in Fig. 2, and the maximum attraction is 3.17 pN as $r = 0.43$ nm. If the carbon atoms were bonded with a sp^2 bond (bond length $r = 0.144$ nm) as in nanotubes, the

Table I. Possible Configuration of Connections through van der Waals Forces.

Observed Fact	Geometrical Model of Inset of Fig.1 (c) Top View (Observed in vertical to electron beam)	MWNT 1: External radius: $R_1=14$ [nm], internal radius: r_1 (unknown) MWNT 2: External radius: $R_2=21$ [nm], internal radius: r_2 (unknown) Measured connection force: F=790.1 [nN] Hamaker constant between nanotubes: $$A = \pi^2 C \rho^2 = 2.842 \times 10^{-20} \ [J]$$ (where, $C = 32.00 \times 10^{-79} \ [J \cdot m^6]$ is carbon atom-atom pair potential constant, and $\rho = 3 \times 10^{28} \ [m^{-3}]$ is the number of carbon atoms in unit volume). Layer separation of carbon atoms in MWNTs: D=0.34 [nm]
Case	**Layout**	**Maximum Axial Connection Force**
(a)	Left View Side View Geometric constraints: $\sqrt{e_y^2 + e_z^2} \le r_2 - R_1 - D$	The strongest connection [20] can be obtained as $e_x = L_2 - L_3 = 26$[nm] , $r_1 = 0$ and $r_2 - R_1 = D$ (i.e., $\sqrt{e_y^2 + e_z^2} = 0$), $$F_a = 0.32\pi R_1 = 14.07 [\text{nN}] << F$$
(b)	Left View Side View Geometric constraints: $r_2 - R_1 - D \sqrt{e_y^2 + e_z^2} < R_1 + R_2 + D$	The strongest connection can be obtained as $e_x = 0.34$ [nm], $r_1 = r_2 = 0$, and $\sqrt{e_y^2 + e_z^2} = 0$, $$F_b = \frac{A R_1^2}{6 e_x^3} = 23.62 [\text{nN}] << F$$
(c)	Left View Side View Geometric constraints: $\sqrt{e_y^2 + e_z^2} \ge R_1 + R_2 + D$	The strongest connection force can be obtained as $e_x = 0.34$ [nm], $r_1 = 0$, $r_2 = 0$ and $\sqrt{e_y^2 + e_z^2} = R_1 + R_2 + D$, $$F_c = s w e_x = 0.20 [\text{nN}] << F$$ where, s=2 [MPa] is the interfacial shear stress of nanotubes, and w=3 nm is the contact width of the MWNTs[25].

connection force will be 7.28 nN, i.e., 2328 times stronger than the maximum van der Waals attractive force. It is clear that the measurement of the connection force is much easier than that of the separation measurement which requires sub-nm resolution. (Parameters are adopted from ref. 24.)

For Fig. 1(c), all of the possible van der Waals connections are summarized in Table I. We can see that cases (a), (b) and (c) are all impossible because the maximal connection forces are all much smaller than the measured force.

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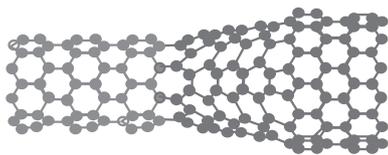
Fig. 3.   sp² bonding of MWNTs.

The only option remaining is the case shown in Fig. 3, i.e., covalent bonds are formed between the nanotubes, which must be the joining mechanism shown in Fig. 1(c). Furthermore, it can be concluded that dangling keys form in both ends of MWNTs as the nanotubes shown in Fig. 1(a) break into two parts [Fig. 1(b)]. Most importantly, the nominal tensile strength of the connected nanotube:

$$T = \frac{F}{\pi R_1^2} = 1.3 \, \text{GPa} \qquad (1)$$

agrees with the measured values of the tensile strength of nanotubes ($\sim$1.4 to $\sim$2.9 GPa[10]) well, which means the connected site is not weaker than the original one, and therefore they should have the same type of bond—sp² bonds, as shown in Fig. 3. This finding also shows the impossibility of other connections caused by other intermolecular and surface forces. For example, according to Allinger's MM2 bond-stretching parameters (C–H: 460 N/m, C–O: 536 N/m, and C=C: 960 N/m),[24] C–H and C–O bonds are much weaker than C=C (sp²), so the meniscus force caused by condensed water—even if these bonds existed in our UHV chamber—cannot provide a connection as strong as that of the nanotube itself.

4.   Conclusions

In summary, mechanochemical nanorobotic manipulations have been presented and demonstrated with a specially designed experiment. Because they do not require additional molecules for the connection of building blocks, they provide better defined geometries than EBID. Because they link atoms through strong covalent bonds, they provide a much stronger connection strength than that of van der Waals bonds. The method has strong potential in nanotechnology since it can be used to construct atoms with dangling keys, and to assemble them in desired places to construct new structures.

Acknowledgement

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