Formation of off-centered double-walled carbon nanotubes exhibiting wide interlayer spacing from bi-cables

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Abstract

Novel off-centered coaxial carbon nanotubes have been fabricated by coalescing adjacent double-walled carbon nanotubes (DWNTs) using high temperature heat treatments. The eccentric nanotubes possess wide interlayer spacing, and arise by the merge of two narrow diameter (inner) tubes contained inside a large diameter tubes (also known as bi-cables). We propose a complete description of the coalescence process including the merge of two DWNTs, followed by the formation of bi-cables and the creation of off-centered DWNTs. We also performed molecular dynamics calculations that are in agreement with the experimental observations.

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1. Introduction

The phenomena of interconnecting and coalescing single- or double-walled carbon nanotubes at high temperature thermal treatment and a high-energy electron beam have attracted much attention of various researchers in recent years [1-10], because it is now possible to fabricate complex architectures such as nanotube junction and networks that could exhibit unusual electronic and mechanical properties [11-15].

In particular, DWNTs reveal fascinating physicochemical properties such as thermal stability and structural stability that are superior to SWNTs [9]. Therefore, DWNTs become excellent candidates for fabricating superior field emission devices (FED) [16, 17] and robust nanocomposites. Recently, it has been demonstrated that the outer shells of two adjacent DWNTs could coalesce via a zipping process, leaving the two inner diameter tubes stabilized in the interior of the coalesced tubule (also termed bi-cable) [11]. These structures are unusual and

could be seen as two parallel nanotube transistors that coexist within a single tube, and therefore might have important implications in developing nanoelectronic devices.
A striking result in these bi-cable structures is that the inner diameter tubes (which are encapsulated and exhibit high curvature and reactivity) are able to stand extremely high temperatures (e.g. 1600 - 2000 °C) without coalescing. Therefore, it may be possible to fabricate electronic and mechanical devices using these tubes that are able to stand extreme temperature conditions. However, further studies on the stability of these bi-cables are required.

In this paper, we present the formation of novel off-centered DWNTs exhibiting unusually wide interlayer spacings, which result from the coalescence of two inner SWNTs embedded inside a wide tubule (bi-cables). The off-centered structures can only be produced at annealing temperatures higher than 2000 °C. Therefore, it might be possible to control the formation of different and novel nanotube structures from different annealing processes involving bundles of pristine DWNTs: a) at annealing temperatures between 1500 and 2000 °C, bi-clables can be formed, and b) at temperatures above 2000 °C, off-centered nanotubes can be created. These results lead to the understanding of carbon nanotube behavior at high annealing temperature and therefore, other applications of the reported structures could be proposed in electronics and materials science.

2. Experimental

High purity DWNTs were obtained by combining DWNTs optimized catalytic chemical vapor deposition method and suitable purification process described in the previous studies [18-20]. The DWNTs agglomerate in bundles and do not include visible impurities such as SWNTs or iron catalysts. In order to merge DWNTs, heat treatments at 2100^{o}C under an argon atmosphere were carried out for 30 minutes using a graphite-resistance furnace. Transmission electron microscope (TEM JEM2010FEF) equipped with an Omega-type energy filter operated at 200kV was used to investigate the structure of coalesced DWNTs. Raman spectroscopy measurements were carried out using a Kaiser Holo Lab 5000 system with laser energies of 2.33 eV (532 nm). Molecular dynamics calculations were carried out using the Tersoff potential [21] on two adjacent DWNTs [(4,4)@(10,10)] using time steps of 0.5 fs, and simulation time was 5000 ps. In these calculations, initial temperature of the systems was set to 2000 K.

3. Results and Discussion

Using TEM, we confirmed that pristine DWNTs included almost no impurities such as iron

catalysts, and formed hexagonally packed structure (Figs. 1(a-b)). We also determined that pristine DWNTs were of high purity by Raman spectroscopy (Fig. 1(e)). Although Raman spectroscopy is very sensitive to defects and impurities within nanotubes [22], our pristine DWNTs showed almost no defect-induced band (D-band). When using the following equation $\omega_{RBM} = 218.3/dt + 15.9$ [22], we were able to estimate the tube diameters [dt is the tube diameter (nm) and ω_{RBM} is the RBM frequency in wave number (cm^{-1})]. After heat treatment, we observed a decreased intensity of 315 cm^{-1} bands, corresponding to the inner tube (0.73 nm), and we also noted an enhancement of a shoulder peak at 158 cm^{-1} and 190 cm^{-1} (related to 1.29 nm to 1.54 nm outer tubes; see Fig. 1e).

Using TEM, we determined the inner tube diameters of DWNTs to be 0.6-0.9 nm; values that are consistent with diameter determinations using the Raman spectroscopy. It is also known that at heat treatment temperatures between 1500 and 2000°C, a special Raman active mode called coalescence induced (CIM) mode, is observed at ~1850 cm^{-1}[23,24], but when the heat treatment temperature is over 2000 °C, the signal disappears as in the present case (Fig. 1e). The CIM mode is associated with linear carbon chains that trigger the coalescence of DWNTs.

High temperature heat treatments are useful for interconnecting and coalescing DWNTs. Figs. 1(b-c) depict TEM images of the heat treated DWNTs at 2100°C. From the low magnification TEM image (Fig. 1c), we could observe that the bundles become straighter when compared to the pristine material (more curved and curled bundles appear). In the heat treated sample (Fig. 1d), we could also observe intriguing cross sections of DWNT bundle exhibiting novel off-centered tubular structure (see arrow in Fig. 1d) together with numerous bi-cable structures (at least 4) [11]. A higher magnification TEM image of two adjacent DWNTs and the off-centered DWNT are depicted Fig. 2a & Fig. 2b, respectively. The interlayer distances of pristine DWNTs were measured to be about 0.36nm, which is slightly wider than the *ABAB…* graphite layer spacing (0.335 nm). In addition, for the off-centered DWNT (Fig. 2b), we found that the outer and inner diameters are ca. 3.25 nm ($d1_{out}$) and 1.68 nm ($d1_{in}$), respectively. From these TEM measurements, we have found that the following equation could be related between the circumferences of the off-centered coalesced DWNT and standard DWNTs within the same bundle (outer diameter; d_{out}, inner diameter; d_{in}).

$$d1_{out} = 2d_{out}, \quad d1_{in} = 2d_{in} \quad \text{..... (1)}$$

This result suggests that two DWNTs have merged `neatly' without any considerable loss of carbon atoms during the heat treatment process.

When taking into account the previous findings on bicables [11], we now propose the full path of the coalescence process of two adjacent DWNTs. We can now confirm that the bicable structure is a metastable state (transition state), and if thermal disturbances and/or defects occur within the inner tubes, these tubes could coalesce further so as to generate an unusual off-centered DWNT. When assuming that two DWNTs with the same chirality (inner tube diameter: 0.8 nm, outer tube diameter: 1.52 nm, and interlayer distance: 0.36 nm; see Fig. 3a) merge into a single coaxial tube via zipping process, the outer tube becomes enlarges to 3.04 nm, whereas the inner tube increases to 1.6 nm; interlayer spacing between two tubes in the DWNT increases to 0.72nm (see Fig. 3b). Therefore, the inner tube could become round and off-centered with an interlayer spacing of 0.36 nm (on one side) and 1.08 nm on the other side (see Fig. 3c). Furthermore, if we consider van der Waals interactions between two concentric tubes [25, 26], the DWNT needs to be deformed and could then result in a structure like the one shown in Fig. 2b & Fig. 3d. Although, we do not observe the CIM mode in our experiments (performed at annealing temperatures >2000°C), linear carbon chains could also play an important role in the coalescence of the inner SWNTs (embedded in a wider tubule), so as to form off-centered concentric tubes (see interlinked chains in the calculations shown below). Note that if the population of these linear chains is not high, the observation for the CIM mode seems unlikely.

Figure 2c depicts a typical TEM image of a bi-cable found in the bundle; the shape of the outer tube is clearly dumbbell-like, and encapsulates two inner tubes. This dumbbell shape is clearly stabilized within the hexagonally packed DWNT bundle. Note that Figure 1d, shows numerous bi-cables and dumbbell-like structures within the hexagonally packed bundle. It is also noteworthy that in the bi-cable structure, the distance between the two inner tubes is ca. 1.4 nm, which is larger than that of the theoretical and perfect coalesced tube (see Figs. 3b-c). The distance between the inner tubes is much larger than the van der Waals interaction distance, and we would expect no interactions between the inner tubules.

During coalescence occurring inside a DWNT bundle, one could expect that a dumbbell-like configuration be rapidly transformed into an oval shape, which has lower surface energy. If two encapsulated shells or tubules exhibit the same chirality, coalescence between them is expected to occur rapidly, ending up with the unusual DWNT with an off-centered configuration (Fig. 2b & Fig. 3d).

In order to carefully track the coalescence process of DWNTs with less environmental

constraint, we have performed a classical molecular dynamics simulation using Tersoff potential on two adjacent DWNTs [(4,4)@(10,10)] (see movie in a supporting material). The initial temperature was set to 2000K. As shown in Fig. 4b, after 20ps, we first observed the quick coalescence of the outer tubes, leaving intact the inner tubes (Fig. 4b). As time passes by, the inner tubes start to interact and coalesce into a larger tube, thus leading to the formation of an off-centered DWNT (see Fig. 4c). It is important to note that during the coalescence of the inner tubes, linear carbon chains are established (Fig, 4b), and we believe that these chains catalyze significantly the coalescence process. We have found that the bi-cable structure is metastable (but still stable within bundles below ~2000 K), and off-centered tubes are more stable but need to be formed above ~2000 K when the inner tubes of the bi-cables merge.

4. Conclusions

New stable off-centered DWNTs exhibiting wide interlayer spacing were formed using high temperature heat treatments above 2000 °C. This phenomenon is understood by the coalescence of two encapsulated tubes inside a bi-cable structure. We expect that the off-centered DWNT exhibiting wide interlayer spacing possess unusual electronic and mechanical properties derived from wide interlayer spacing. We also noted that the formation of off-centered DWNTs is strongly dependent on the surrounding environment with in the bundle structure. We believe that in order to merge efficiently, two inner tubes in the bi-cables, these should have the same chirality. Our results indicate the possibility to control the structure of DWNTs by changing the heating temperature. We envisage that interconnections of these novel co-axial tubes will exhibit different electronic properties when compared to perfect and concentric DWNTs.

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Figure Captions

Fig.1 (a-b) TEM images of pristine DWNTs, and (c-d) heat treated DWNTs; note that in (d), the cross sections of DWNT bundle exhibit a novel off-centered tubular structure (indicated by an arrow) together with numerous bi-cable structures and pristine (unreacted) DWNTs, and (e) Raman spectra for the pristine and annealed samples at 2100 °C, and note the absence of the CIM mode (usually located at 1850 cm-1).

Fig.2 High magnification TEM images of: (a) two adjacent and pristine DWNTs; (b) and off-centered DWNT, and (c) a typical bi-cable structure.

Fig. 3 Schematics of cross sections showing: (a) two adjacent DWNTs exhibiting inner diameters of 0.8 nm and outer of 1.52 nm; interlayer spacing 0.36 nm; (b) a coalesced DWNTs that results by merging the two inner and outer tubes shown in (a), where the inner tube has a diameter of 1.6nm and the outer of 3.04 nm (note that the gap between the tubes is 1.44nm); (c) a coalesced DWNT showing that the inner tube (1.6 nm) is off-centered and the outer tube cross section is perfectly round, and (d) a DWNT showing an off-centered inner of 1.6nm inside an oval-like tube.

Fig. 4 Frames obtained from the molecular dynamics simulation of two DWNTs [(4,4)@(10,10)] and t=0 (a), after 20 ps (b) and after 30 ps (c). The result indicates that the bi-cables are formed before the off-centered tubes are created during thermal annealing. We believe that the hexagonal packing with the DWNT bundle is responsible for stabilizing the bi-cable structures at high temperatures.

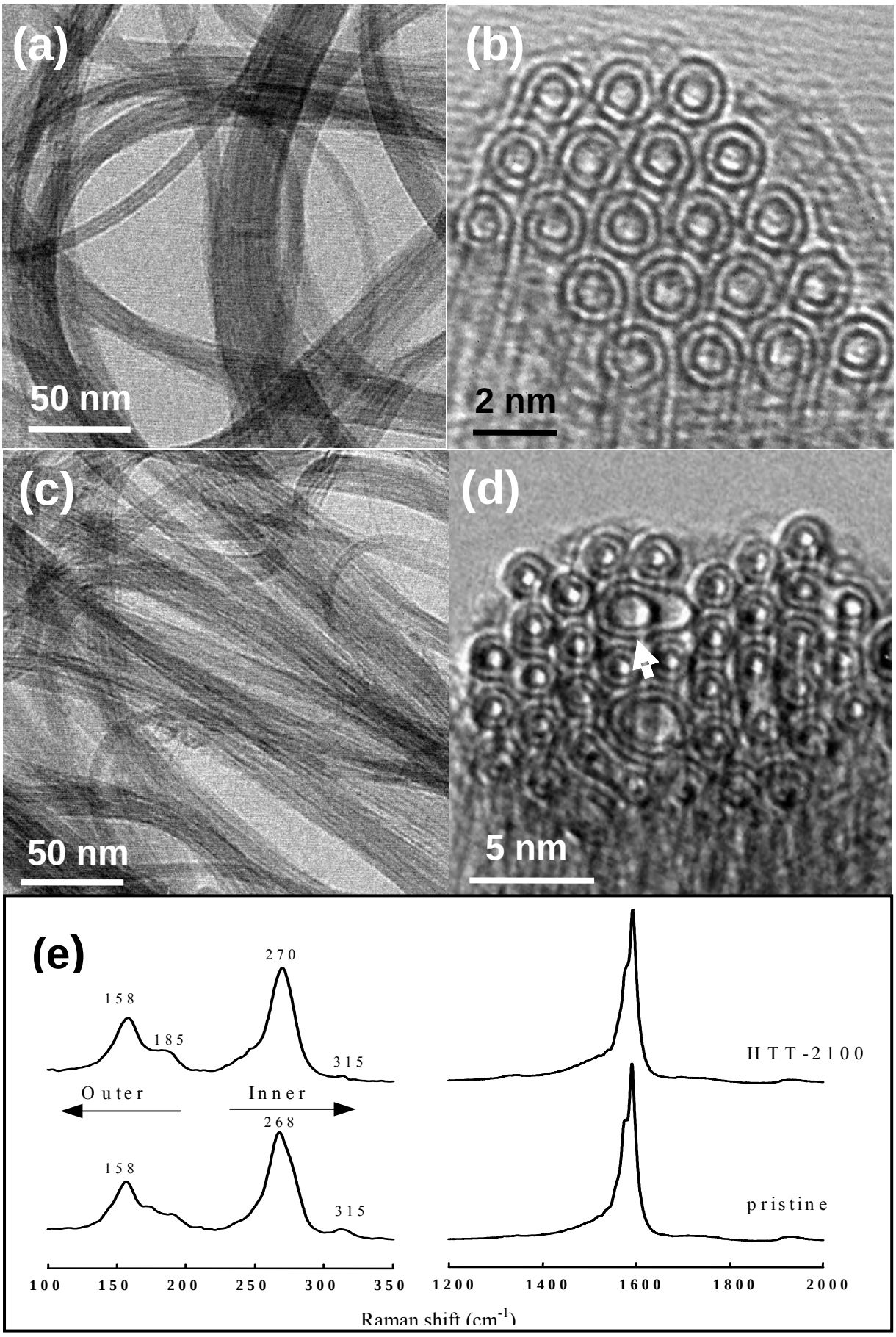
(a)
50 nm
(b)
2 nm
(c)
50 nm
(d)
5 nm
(e)
158
185
270
315
Outer
Inner
268
158
315
100
150
200
250
300
350
HTT-2100
pristine
1200
1400
1600
1800
2000
Raman shift (cm-1)

Figure 1

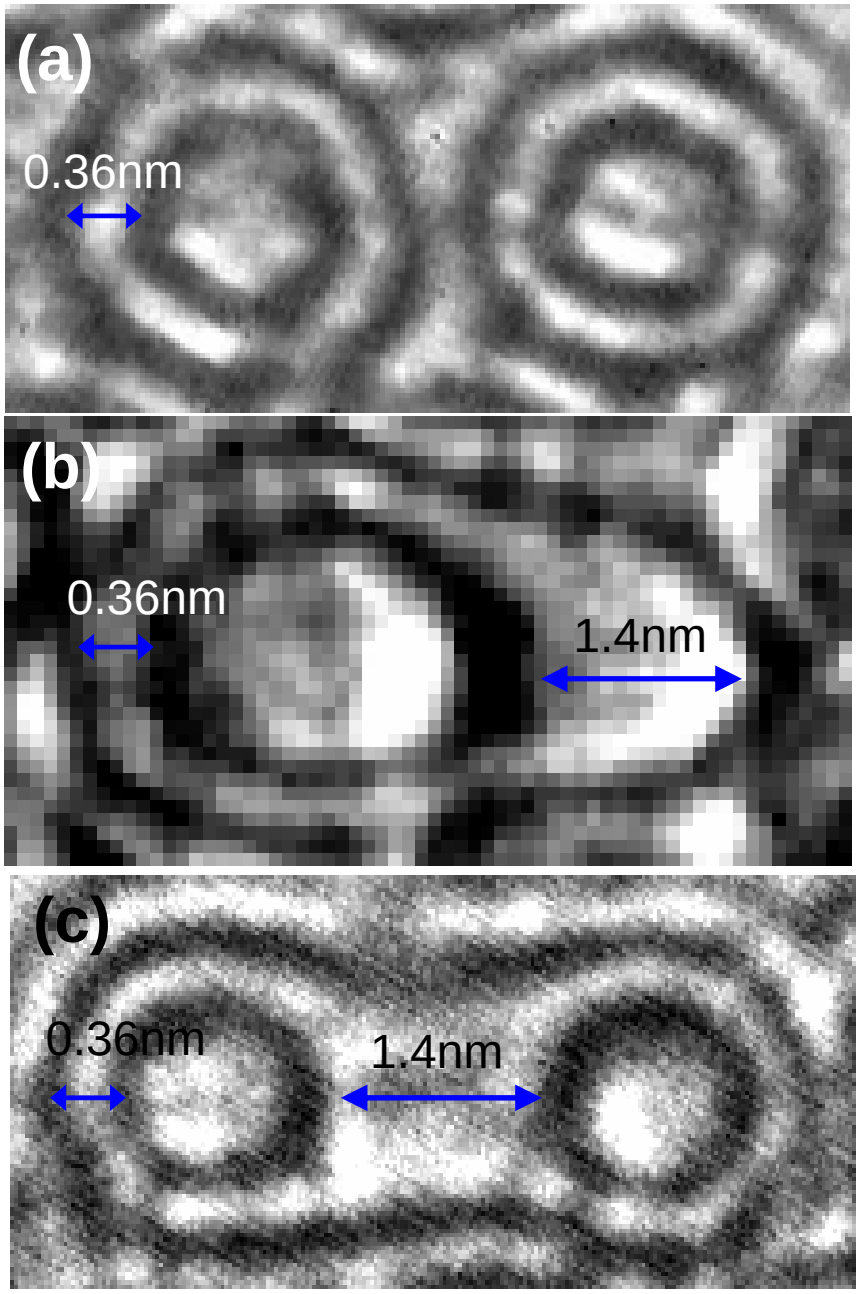

Figure 2

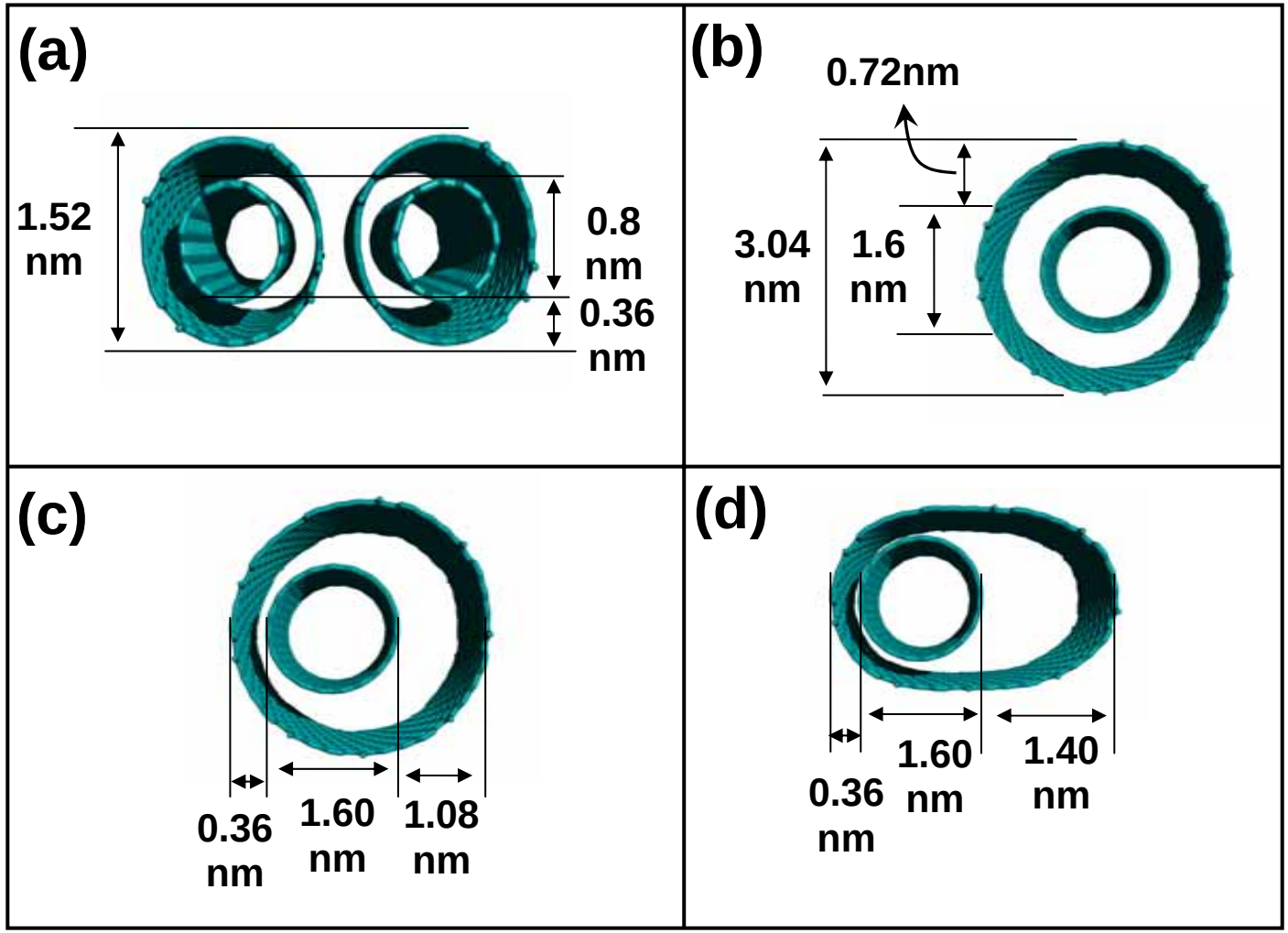
(a)
1.52 nm
0.8 nm
0.36 nm
(b)
0.72nm
3.04 nm
1.6 nm
(c)
0.36 nm
1.60 nm
1.08 nm
(d)
0.36 nm
1.60 nm
1.40 nm

Figure 3

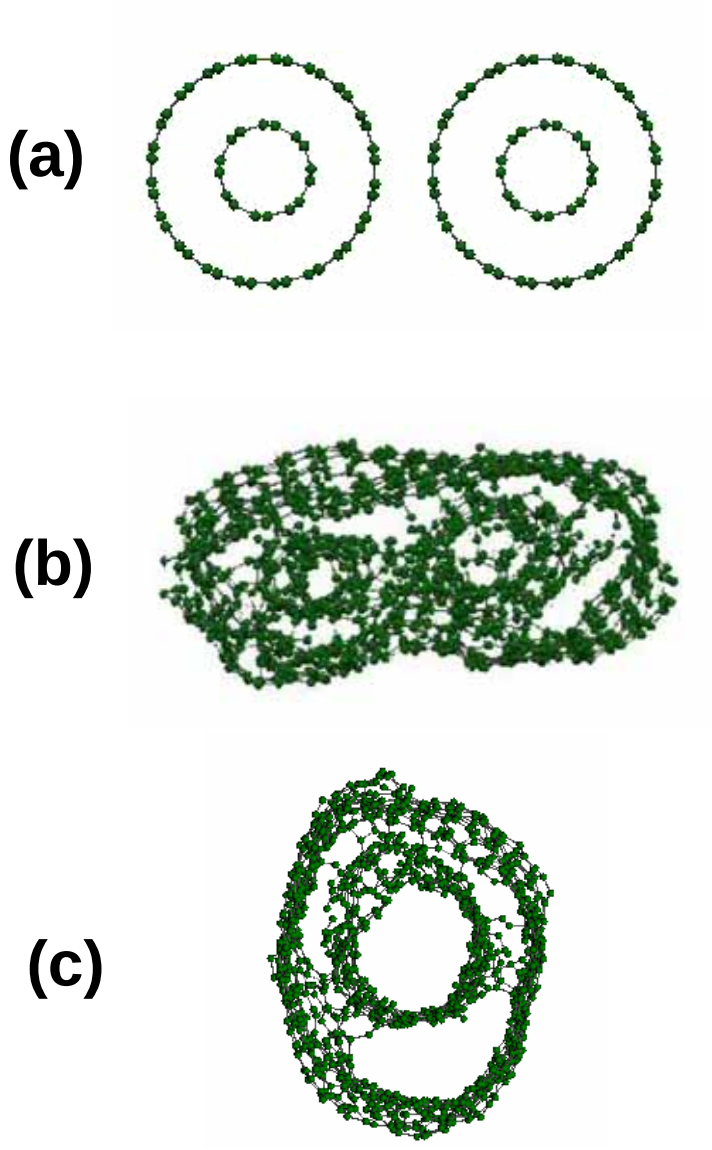

Figure 4