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Local Young's moduli of as-grown and annealed diphenylalanine nanotubes

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Abstract. Precise measurements of local transversal Young's moduli of as-grown and annealed nanotubes of diphenylalanine have been performed by mechanical nanoindentation. Evaporation of water from the nanochannels leads to pronounced reduction of the values' dispersion, and the characteristic value coincides with previous theoretical estimations. The experimental value of longitudinal Young's modulus measured at polar surface of vertically aligned bundle of nanotubes is reported for the first time.

1. Introduction

Self-assembly of bioorganic molecules into nanotubes is a convenient tool for manufacturing various functional micro- and nanodevices [1]. Recently, nanotubes of the simplest aromatic dipeptide diphenylalanine (D-Phe-D-Phe, FF) have attracted attention of researchers all over the world because of their pronounced piezoelectric [2, 3], ferroelectric [4, 5], and pyroelectric [6] properties. A number of new biosensors, biocompatible microelectronic and micromechanical devices based on FF nanotubes have been suggested [2, 7, 8].

Most of practical applications require the knowledge of FF nanotube mechanical properties, first of all the Young's moduli. However, these values, especially in a polar direction, are still poorly studied. Published values of transversal Young's modulus ranged from 4 up to 27 GPa [9-13]. This is definitely caused by small sizes of the nanotubes and unmanageable fixing conditions at their ends hampering the use of high resolution atomic force microscopy (AFM) [14, 15]. Moreover, water molecules remained in the nanotube's channel after the self-assembling and inhomogeneously distributed along the tube can drastically affect the obtained values [9].

In this work, we performed precise measurements of local transversal Young's modulus of as-grown (water filled) and annealed (empty) FF nanotubes by mechanical nanoindentation, which is devoid of the abovementioned shortcomings of AFM. Moreover, for the first time we measured longitudinal Young's modulus at the polar surface of a vertically aligned bundle of nanotubes.

2. Experimental details

FF microtubes representing bundles of individual nanotubes were grown on the metallized silicon substrate from alcohol-water solution during natural drying under ambient conditions (T=20°C, RH=35%) in accordance with a conventional technique [16]. A muffle furnace was used for thermal annealing of the microtubes. Annealing was performed in air at 80°C for 3 hours.

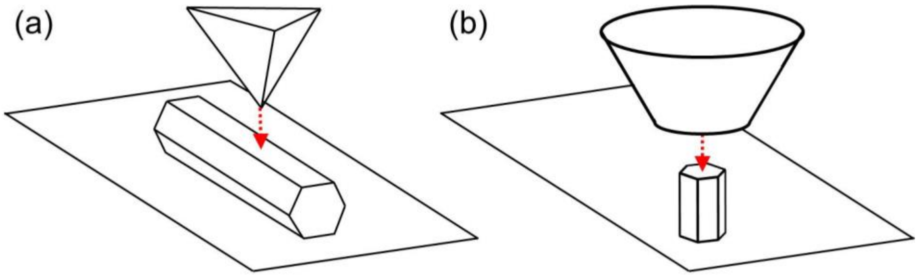

Figure 1. Schemes of the measurements of (a) transversal and (b) longitudinal Young's moduli by mechanical nanoindentation.

Local indentation measurements were performed using nano-hardness tester NanoScan-4D (FSBI TISNCM, Russia). The samples were fixed at a heavy aluminum cylinder. Measurements of transversal Young modulus were performed at nonpolar surface of the microtubes (Fig. 1a) using Berkovich indenter (diamond pyramid) with tip radius below 100 nm. Longitudinal Young modulus was determined by indentation at a polar cut of the microtube fixed vertically by the silver paste (Fig. 1b), using a "flat stamp" indenter with diameter about 100 μm. All measurements were carried out at ambient conditions.

3. Results and discussion

3.1. Transversal Young's modulus

Transversal Young's modulus (E_T) was measured at lateral (nonpolar) surface of the microtubes. As-grown tubes demonstrated pronounced bimodal distribution with two almost equivalent peaks. Characteristic values of these peaks are E_{T1} = 9±3 GPa and E_{T2} = 24±5 GPa (Fig. 2a). The first value, E_{T1}, is close to 8.75 GPa obtained in first-principles calculations [12], whereas the second value, E_{T2}, is close to 27±4 GPa obtained by AFM [10]. Such distribution has been attributed recently to water molecules remained in the tubes' channel and strongly affecting the value of E_T by the formation of radial network of hydrogen bonds [9]. The value E_{T1} was attributed to the Young's modulus of empty nanotubes, value E_{T2} – to Young's modulus of completely filled nanotubes, and intermediate values – to different amounts of water in the nanochannels [9].

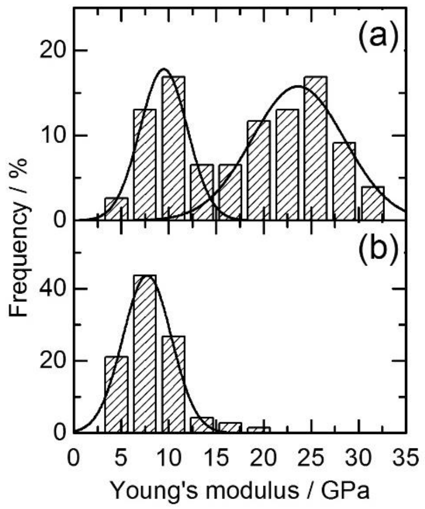

Figure 2. Distribution of transversal Young's modulus values of microtubes FF: (a) as-grown and (b) after annealing during 3 hours. Solid curves demonstrate Gaussian fitting.

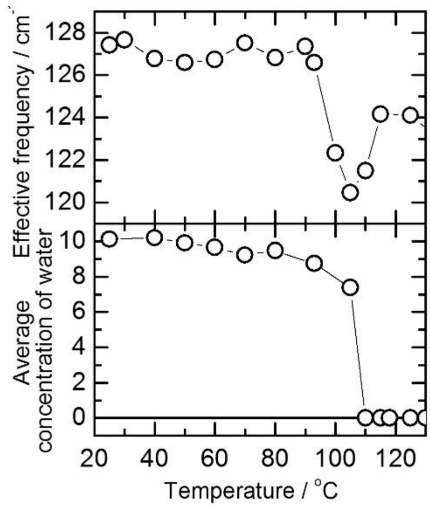

Figure 3. Temperature variation of effective frequency of nanotubes lattice vibration (top) and average concentration of water in the nanochannels (bottom).

To verify this hypothesis, we measured E_T of microtubes subjected to annealing for 3 hours at 80°C. Raman measurements performed earlier at various temperatures [17] showed that the effective frequency of nanotube lattice vibrations (and thus nanotube crystal structure) remained unchanged up to 105-110°C, whereas concentration of water in nanochannels (a number of water molecules per unit cell averaged over the volume about 0.025 μm^3, where Raman spectrum is measured) started to decrease gradually at 70-80°C (Fig. 3). Thus, the chosen annealing regime did not change the structure of the nanotubes, but promoted water evaporation from the nanochannels.

E_T distribution obtained for annealed microtubes demonstrated clear unimodal type with characteristic value 8±3 GPa (Fig. 2b). This value well coincides with that obtained in first-principles calculations for empty nanotubes [12], thus confirming the strong effect of water in the nanochannels on the mechanical properties of FF nanotubes suggested in [9].

3.2. Longitudinal Young's modulus

Measurements of longitudinal Young's modulus (E_L) along the polar axis of the nanotubes represent special interest. Such measurements are hampered by small size of the nanotubes and their preferable horizontal growth at the substrate. In our measurements, the bundle of nanotubes was manually separated from the substrate and fixed vertically by the silver paste (Fig. 1b).

It should be noted that conventional Berkovich-type indenter with tip radius below 100 nm can split the bundle into separate nanotubes during the measurements. Therefore, we used a "flat stamp" indenter with diameter of flat surface about 100 μm, which was much larger than diameter of the tube.

For estimation of the Young's modulus, we used conventional Hooke's law. In a case of uniform rod one can write $F = k{\cdot}\Delta l$, where F is a magnitude of the applied force, and Δl is a change of the rod's length. Spring constant k can be expressed via Young's modulus as $k = E{\cdot}S / l$, where area S of the tube section can be calculated from the optical image, and l is initial length of the tube. Therefore, for longitudinal Young's modulus we obtained $E_L = F{\cdot}l / S{\cdot}\Delta l$.

It is known that Hooke's law is valid for elastic deformations of the solids only. The value of elastic deformation, Δl, can be roughly estimated from the loading-unloading curves as a width of the unloading curve (Fig. 4). Mismatch between the widths of loading and unloading curves corresponds to plastic deformations. Since the plastic deformations always follow the regime of elastic ones, the value of the force F can be found from the loading curve as a value corresponding to Δl (Fig. 4).

The value of E_L obtained using the proposed method is 14±3 GPa. This is very close to 15.85 GPa obtained from first-principles calculations [12]. Theoretical estimations show that E_L weakly depends on the amount of water in the tube nanochannels, probably, because of high mobility of the molecules along the channels [9]. Therefore, the observed discrepancy is mainly due to overestimation of the value of elastic deformation, variation of the cross section area along the tube, and, thus, inexact determination of the force value. Nevertheless, for our best knowledge this experimentally obtained value is reported for the first time.

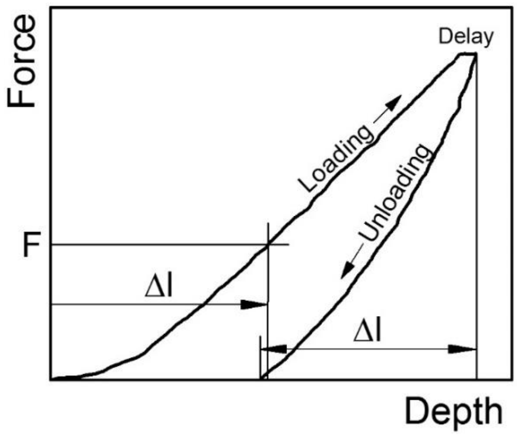

Figure 4. Scheme of elastic deformation and force value determination from loading-unloading curves for estimation of longitudinal Young's modulus.

4. Conclusion

The values of transversal Young's modulus in as-grown and annealed diphenylalanine nanotubes have been measured by mechanical nanoindentation. Systematic analysis of the results revealed the change of values distribution after annealing from bimodal to unimodal type with characteristic value 8 GPa. This confirms the earlier proposed hypotheses about the water effect on the Young's modulus of the nanotubes. For the first time, a value of longitudinal Young's modulus of about 14 GPa has been obtained experimentally. This value coincides with earlier reported first-principles calculations. Obtained results expand the understanding of mechanical properties of diphenylalanine nanotubes and will promote developing new functional devices on their base.

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