Single-crystalline polytetrafluoroethylene-like nanotubes prepared from atmospheric plasma discharge

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Atmospheric plasma polymerization of perfluorohexane was investigated in this letter. A large quantity of single-crystalline polytetrafluoroethylene (PTFE)-like nanotubes were formed on a simultaneously deposited film at room temperature without any catalysts or templates. The outer diameter of the nanotubes varied from 60 to 1200 nm with a maximum aspect ratio up to 100:1. Transmission electron microscopy and x-ray diffraction results indicated a single crystal close-packed hexagonal (cph) structure in the nanotubes. Polarization optical micrographs of the nanotubes showed their thermal stability comparable to PTFE. It is suggested that the plasma filament played a key role in the rapid formation of the nanotubes. This atmospheric plasma discharge synthesis can serve as a common method for nanofabrication of many other single-crystalline polymer systems. © *2005 American Institute of Physics.*
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One-dimensional (1D) single-crystalline nanostructured polymers have been sought after as ideal model materials such as single molecules and bulk crystals.[1] They exhibit extremely high specific strength reaching to their theoretical bonding energy due to the periodical and dense packing of atoms which link together by strong covalent bonding along the primary chain. They also display some optical and electronic properties as a result of the high charge densities, high carrier mobilities, and unique quantum confinement effects,[2–4] that are different from those of inorganic and metallic nanocrystals. Therefore, these one-dimensional nanostructured polymers are of great importance in both fundamental studies and engineering applications[5–8] especially in the areas of nanoscale polymeric electronics, optoelectronics, biochemical sensors, solvent-resistant reactors, nonreactive templates, insulating cable shells, and coatings, etc.

Although there have been extensive efforts on the formation of polymer nanostructures with well controlled and specified nanodimensions, it is a great challenge to synthesize them with high crystallinity and purification. In most of the previous studies, the synthesis methods often require confined templates, oriented polymerization catalysts, long and tedious post removing of the templates and catalysts, and special selection for various monomers.[9–21] It is therefore desirable to seek synthesis routes by which one-dimensional single-crystalline polymer nanotubes with high purity can be formed reproducibly and efficiently.

In this letter, we report an atmospheric plasma discharge method by which the single-crystalline polymer nanotubes can be rapidly synthesized at room temperature without any templates or catalysts. Single-crystalline polytetrafluoroethylene (PTFE)-like polymer nanotubes with hexagonal cross sections were rapidly formed on the simultaneously deposition film. Both transmission electron microscopy (TEM) and

x-ray diffraction (XRD) experiments were carried out to study the structural characteristics of the nanotubes. The thermal stability of the nanotubes was investigated by using the polarized photomicroscopy at different temperatures. Growth mechanisms and related structural behaviors of the nanotubes are discussed.

The apparatus used for the fast formation of single crystalline polymer nanotubes was a homemade atmospheric plasma discharge reactor. In this reactor, a gradient electric field with a high voltage of 10–50 kV and a frequency of 10–100 kHz was applied to deposit the single crystalline nanotubes on ordinary glass slides, silicon wafers, and polyester films, etc. Filament plasma was generated between a high voltage strip electrode and a grounded plane electrode. At least one of them was covered with a dielectric barrier. Perfluorohexane (C_6F_{14}) was used as the precursor and fed into the reactor through an argon carrier gas at a flow rate of 1:10. The flow rate of the mixture gas was controlled at 5 SLM through a mass flow controller. No vacuum was needed for the reactor system. After only a few seconds to several minutes, a thin white film was deposited on the entire substrate, onto which a large quantity of nanotubes were identified.

The morphology of as-grown nanotubes was investigated by scanning electron microscopy (SEM) using a JSM-5600LV. Transmission electron microscopy (TEM) images were acquired at an accelerating voltage of 120 kV using a JEOL JEM-200CX. TEM samples of nanotubes were prepared by dispersing them directly on a carbon film supported with Ni grids. The scattering selected area diffraction (SAD) pattern images were taken as soon as possible after focusing, otherwise the polymer nanotubes experienced melting by the electron beam radiation. A Rigaku D/Max 2550 V x-ray diffractometer (XRD) with Cu *K* radiation was used to characterize the synthesized film. The x-ray wavelength was 1.54 Å with a beam size of 3 mm. Polarized optical micrographs were continuously taken by an Olympus B 51 with a hot

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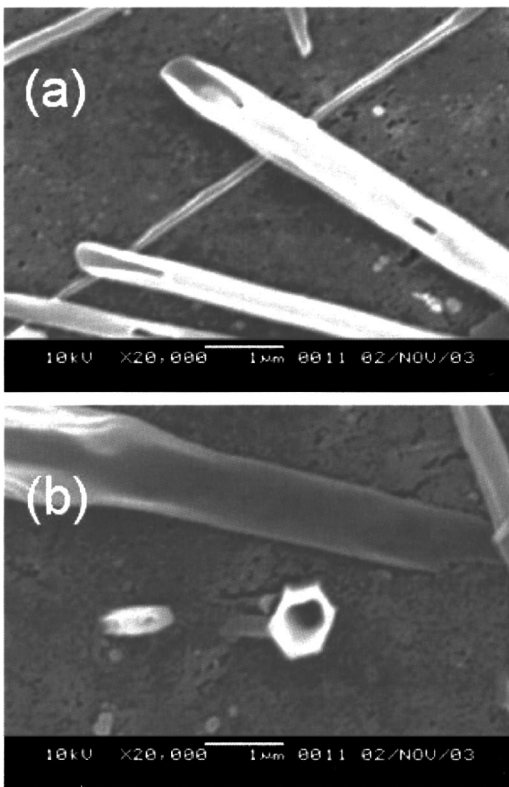
FIG. 1. SEM images of PTFE-like nanotubes: (a) PTFE-like nanotubes lying on the surface of a loosely packed nanoparticulate layer; (b) cross section of the broken PTFE-like nonotubes, clearly showing hexagonal shape.
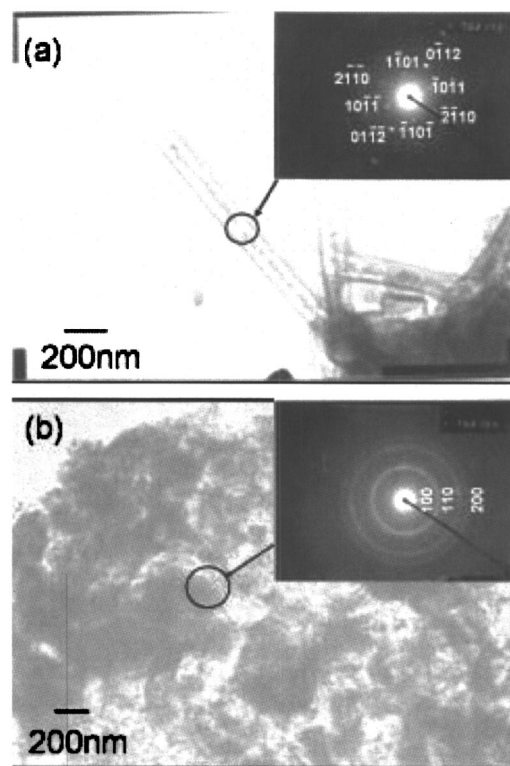

FIG. 2. Crystal structure characterization of PTFE-like nanotubes through TEM: (a) TEM image of PTFE-like single crystalline nanotubes and the SAD pattern (inset); (b) TEM image of PTFE-like polycrystalline nanoparticulates and the SAD pattern (inset); (a) displays possible single crystal closed packed hexagonal phase of structure in nanotubes. Inset in (b) shows hexagonal phase of structure in the polycrystalline nanoparticulate layer.

stage at a constant heating rate. For comparing the thermal stability of the nanotubes with PTFE, small pieces of PTFE were cut off from PTFE polymer from 3F Co. (melting point 310 °C) and also observed with a polarized optical microscope. The heating rate was the same as in observing the deposition films.

Figure 1 shows the SEM images of the as-grown single crystalline nanotubes on a glass substrate. The synthesis time needed for growing these nanotubes was only 3 min. As can be seen in Figs. 1(a) and 1(b), the nanotubes are formed on the surface of a nanoparticular film which is deposited simultaneously with the nanotubes. These nanotubes exhibit a hexagonal outer geometry with an open end. The outer diameter of these tubes is between 60 and 700 nm with a wall thickness of 50–120 nm. The maximum aspect ratio observed is on the order of 100:1. The nanotubes on the substrate also appear massive in quantity. Some of the nanotubes tend to lie parallel to the background particulate layer. Portions of the nanotubes grow vertically from the layer and protrude directly upward from the background film, indicating their close structural and compositional relationship with the background. Also observed in Figs. 1(a) and 1(b) is that the background nanoparticulate film is composed of loosely packed nanoparticles on the glass substrate. These loosely packed nanoparticles have a mean particle size of 50 nm.

Figure 2 shows the TEM image of the nanotubes [Fig. 2(a)] and the selected area diffraction pattern (SAD) within the nanotube [inset of Fig. 2(a)]. Based on the sharp electron diffraction spots in SAD, it is clear that the nanotube has a single crystal phase, which is indexed to a close-packed hexagonal (cph) structure. In sharp contrast, however, the diffraction pattern on the background nanoparticulates exhibits

an entirely different behavior. As shown in Fig. 2(b), the ring patterns from these nanoparticulates on the substrate suggest a polycrystalline structure of a hexagonal phase.

Figure 3 shows the x-ray diffraction 2θ-scan of the same sample shown in Fig. 1 on the glass substrate. The diffracted area also includes the background nanoparticulates on the substrate, therefore a mixture of both nanotubes and background material. After a careful XRD analysis we find that these diffraction peaks belong to two different structures. The peaks at $2\theta=15.5°$ ($d=5.705$ Å), $2\theta=26.9°$ ($d=3.317$ Å), $2\theta=31.3°$ ($d=2.855$ Å), and $2\theta=39.5°$ (d
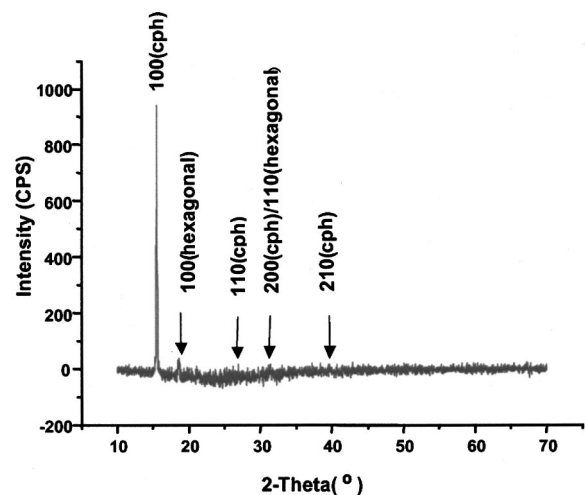

FIG. 3. XRD spectrum from the as-deposited sample containing nanotubes and nanoparticulates on the glass substrate.
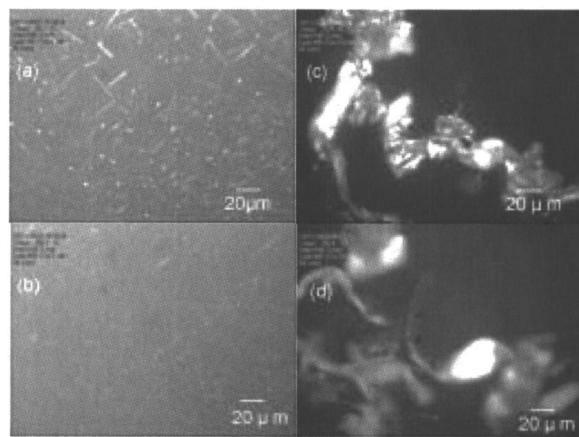
FIG. 4. Comparison of thermal stability of observable nanotubes and PTFE polymer slices through polarization micrographs at different testing temperatures: (a) nanotubes at 36.7 °C; (b) nanotubes at 350.1 °C; (c) PTFE polymer slices at 25.5 °C; and (d) PTFE polymer slices at 350.4 °C. The birefringence of the nanotubes and PTFE polymer slices is not so obvious when heating up to 350 °C, showing similar melting evidence and high thermal stability of PTFE polymer.

=2.281 Å) can be well indexed to a closed packed hexagonal structure with (h,k,l) Miller indices of (100), (110), (200), and (210), respectively. The other set of diffraction peaks includes $2\theta=18.6°$ ($d=4.761$ Å) and $2\theta=31.3°$ ($d=2.866$ Å). As polycrystalline PTFE usually shows the same specific diffraction peaks which belong to a hexagonal phase above 19 °C with $a=0.566$ nm and $c=1.95$ nm in the hexagonal unit cell,[22] these two peaks are assigned to a hexagonal structure of [100] and [110] in the most possibility. These results are consistent with the SAD results shown in Figs. 2(a) and 2(b). Therefore, it is confirmed that there are two types of structures among the sample materials studied, namely, the cph structure for the nanotubes and the hexagonal structure for the nanoparticulates, respectively. It should also be noted that both phases are well crystallized on the substrate. The lattice constant of the closely packed hexagonal structure of the nanotubes is indexed to be $a=6.348$ Å and $c=10.231$ Å according to the SAD pattern and the XRD calculations.

The thermal stability of the as-obtained nanotubes was observed through the hot-stage polarized optical microscopy. As shown in Fig. 4, the observable nanotubes with large size retain a needle-like morphology at 36.7 °C [Fig. 4(a)] and exhibit high birefringence in the crystal edge region. Upon heating up to 350 °C [Fig. 4(b)], the nanoparticulate layer appears melted and mobile in the vision field but the nanotubes still display clear birefringence although not as strong as at 36.7 °C. Small slices of PTFE exhibit high birefringence of polycrystalline at room temperature [Fig. 4(c)]. Upon heating up to 350 °C, they also melt as the film [Fig. 4(d)]. They completely melt when heating up to 370 °C. This implies significant thermal stability of the single crystal polymer nanotubes comparable to PTFE bulk polymer. The FTIR spectrum and XPS experiment data also display a PTFE-like polymer structure of the film (data not shown here).[23]

This atmospheric plasma discharge method opens an approach in the one-step fast formation of single crystal PTFE-like polymer nanotubes with high thermal stability. The rapid formation process of nanotubes is independent of monomer type and only associated with plasma conditions and the electric field gradient. Therefore, the novel plasma polymerization process can also be applied to the nanofabrication of other single-crystalline polymers with potentially excellent properties and wide range of applications.

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