Elastic Response of Carbon Nanotube Bundles to Visible Light

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Distinct macroscopic movements of the filaments consisted of single-wall carbon nanotube bundles were observed under visible light illumination. The movements, sensitive to the intensity of the light, were attributed to the elastic deformations of the bundles of nanotubes. Light-induced electrical currents in the carbon nanotube filaments aligned between two metal electrodes were also observed. The mechanism for the observed phenomena is discussed by considering the physical interlinks of the optical, thermal, electrical, and elastic effects of nanotube bundles. [S0031-9007(99)08979-6]

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The discovery of carbon nanotubes [1] has stimulated extensive research on the properties of these unique structures. Theoretical calculations predicted that carbon nanotubes have extraordinary electronic properties which could be metallic or semiconducting depending on their geometrical structures [2–4]. This has been proved by recent experiments using a scanning tunneling microscope [5,6]. However, these conclusions are applied only to well defined single-wall carbon nanotubes (SWCNTs). In practical high-efficient production, SWCNTs are usually obtained in the form of bundles [7,8]. The direct measurements of electrical conductance [9] and thermoelectric power [10] indicated that the electronic properties are greatly modified when SWCNTs formed bundles. This modification could be explained by considering the effects of intertube or inter-rope contacts, or tubule defects [11]. Recent studies indicated that the structure distortion caused by a surface van der Waals force can also modify the electronic structure of carbon nanotubes [12,13]. These effects may also influence the optical and mechanical properties of SWCNT bundles. Although the theoretical calculation predicted SWCNT bundles having the ideal elastic properties of high tensile stiffness and light weight [14], most of the experimental studies of elastic properties were concentrated on multiwall nanotubes because of the convenience of sample handling and visibility [15–18]. The situation was the same in the optical property investigation [19,20]. For multiwall nanotubes, the intertube interaction has a minimal effect on their properties. In this Letter, we report the newly observed elastic and electric behaviors of SWCNT bundles under the illumination of visible light. We also try to establish physical links among the microscopic mechanism of the optical, thermal, electrical, and elastic effects.

Long and tangled bundles of single-wall carbon nanotubes were produced by laser ablation of a graphite target mixed with 1.2 at.% Ni and Co metal catalysts (for detailed parameters of laser ablation, see Ref. [8]). A flowing argon gas was introduced in the reactor at a rate of 300 SCCM (SCCM denotes cubic centimeter per minute at STP). The as-deposited bundles and other forms of carbon formed weblike filaments of very low density at the downstream side of the quartz tube reactor. We connected to the reactor with a specially designed sample cell with quartz windows, into which two electrodes (Kovar) were introduced. Weblike filaments were collected on the electrodes placed in the way of the argon stream. The sample cell was evacuated to $\sim$0.1 torr after sample collection. The behaviors of the filaments were studied under the illumination of a halogen lamp light source (Olympus LGW, 150 W) and a He-Ne laser (632.8 nm, 10 mW) through the windows. The light-induced movements were recorded by a digital video camera (Sony DCR-TRV9) and an optical microscope (Nikon SMZ-U) with a digital still camera (Fujifilm HC-2000D). The light-induced currents were measured with a high speed current amplifier (Keithley 428) and a digital oscilloscope (Gould 6000).

The optical microscope photograph in Fig. 1(a) shows the weblike filaments collected on the electrodes. They are roughly aligned due to the flowing argon gas. The typical lateral size of an individual filament is of $\sim$20–50 μm. The scanning electron microscope (SEM) photograph in Fig. 1(b) shows the inner structure of a filament. Each filament contains many SWCNT bundles, some of which aligned along the filament and some are tangled. A bundle usually contains several to tens of SWCNTs, as disclosed in Refs. [7,8]. From Fig. 1(b), we can also see small particles of metal catalysts and other forms of carbon attached on SWCNT bundles. It should be noted that these particles were not continuous in the sample, and, hence, are not responsible for the macroscopic light-induced elastic and electric effects described in the following paragraphs. We can thus simply treat the obtained filaments as networks of interconnected SWCNT bundles.

When the collected filaments were exposed to a visible light, they showed distinct movements such as stretching, bending, and repulsion. When the light illumination was removed, the filaments restored to their original position and morphology. Thus the movements are elastic. The

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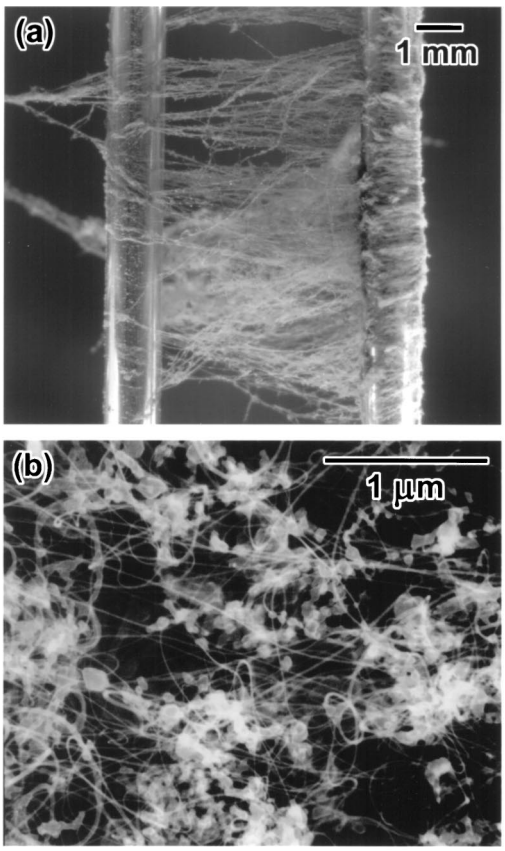

FIG. 1. (a) The weblike filaments collected on two electrodes. They are roughly aligned due to the flowing argon gas. (b) The SEM photograph showing the inner structure of a filament. The white stringlike contrasts are SWCNT bundles. Small particles are consisted of metal catalysts and other forms of carbon.

direction and amplitude of the movement of a filament strongly depends on its morphology and its environment. Usually, a thinner and shorter one moves in a fixed direction independent of the light illumination while a thicker and longer filament moves in the same direction with light illumination. Figure 2(a) shows a filament of ~ 10 μm in diameter and ~ 1 mm in length with one end attached on the electrode and the other end free. Figure 2(b) shows its movement under the illumination of the halogen lamp (~ 20 mW/cm^2). The free end displaced about 0.17 mm in the direction (indicated by a solid arrow) opposite to that of light illumination (indicated by a hollow arrow). In addition to the displacement in the figure plane, the dangling filament was also tilted upward, which causes the image of the free end out of focus in Fig. 2(b). We should notice that the dangling filament under the light illumination is nearly perpendicular to the edge of the matrix it attached to. This is a general tendency for thin dangling filaments we observed. Another feature in Fig. 2(b) is that the light-induced elastic deformation happened only in a very limited region near the contact of the filament with the matrix, while the general shape of the filament is not changed. These features are quite different from the cases shown in Figs. 2(c) to 2(f), where two thick and

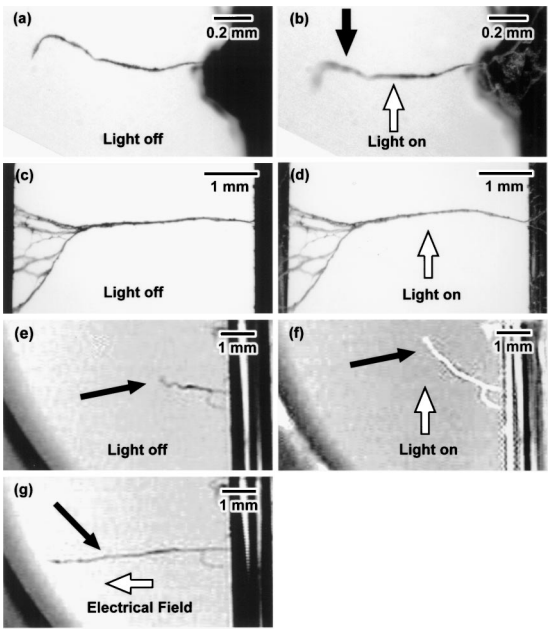

FIG. 2. (a) A thin filament with one end attached on the electrode and the other end free. (b) The movement of the filament in (a) under the illumination of a halogen lamp (~ 20 mW/cm^2). The free end displaced about 0.17 mm in the direction (indicated by a solid arrow) opposite to that of light illumination (indicated by a hollow arrow). The image of the free end in (b) is out of focus because of the upward tilting. (c) A thick filament with two ends fixed to electrodes. (d) Bending of the filament in (c) under the illumination of the halogen lamp. The middle part of the filament displaced about 0.16 mm in the direction of light (indicated by a hollow arrow). (e) A thick filament with one free end. (f) Bending of the filament in (e) under the illumination of the halogen lamp. The free end displaced as much as 1.3 mm in the direction of light (indicated by a hollow arrow). (g) The fully stretched filament in an electrical field [17]. The hollow arrow in (g) indicates the direction of the electrical field. The solid arrows in (e), (f), and (g) indicate the same filament.

long filaments ($\sim 50-100$ μm in diameter and ~ 5 mm in length) bent under the light illumination. The bending is the result of the elastic deformation that happened homogeneously in the filaments. The deformation moved both filaments away from the light source. The amplitudes of movements were different because of their different environments. The filament in Figs. 2(c) and 2(d) has two ends fixed to electrodes. The middle part of the filament displaced about 0.16 mm in the direction of light. The free end of the dangling filament in Figs. 2(e) and 2(f), however, displaced as much as 1.3 mm. The full length of the filament in Figs. 2(e) and 2(f) were shown in Fig. 2(g), where it was stretched in an electrical field established by applying a voltage of 10 V between the electrode and the cell wall [21]. The displacement of the filament in Fig. 2(f) is also much larger than that in Fig. 2(b).

The light-induced elastic effect is very sensitive to the intensity but not to the wavelength and polarity of the light source as long as it is in the visible range.

Experiments using the halogen lamp with various color filters or the He-Ne laser with different polarization directions gave the same effect. The degree of the deformation was, however, dependent on the intensity of the illumination. An example of this dependence is given in Fig. 3. Figures 3(a) and 3(b) show the shapes of a filament tip (indicated by a white arrow) under the strong ($\sim$30 mW/cm^2) and weak ($\sim$5 mW/cm^2) illumination of the halogen lamp light source. The strong light induced a repulsion of nanotube bundles and resulted in a small loop at the tip of the filament in Fig. 3(a), but a weak light did not [Fig. 4(b)]. Figures 3(c) and 3(d) show that a similar repulsion happened when the same filament was illuminated by the He-Ne laser ($\sim$800 mW/cm^2) or when an electrical field was applied.

Determination of the physical mechanism for the light-induced movements is difficult because of the complicated structure of the filaments [Figs. 1(b)]. The photon pressure effect can be excluded because the movement direction is not always identical with that of the light. The thermal expansion is also hard to explain the large movement amplitude. Considering the similarity of the filament behavior under the light illumination with that under the electrical field [Figs. 2(g) and 3(d)], we believe the electrostatic interaction played an important role in the observed phenomenon. This argument was supported by the detection of light-induced electrical current in the filaments aligned between two metal electrodes. Figure 4 shows the current measurement results on the sample shown in Fig. 1(a) when the spot of He-Ne laser irradiated on 4(a), one of the electrodes, and 4(b), the middle part of the filaments between the electrodes. The light-induced current in Fig. 4(a) has a long response time ($>$100 sec) and can be attributed to the thermal-couple effect between carbon and metal electrode (Kovar). The one in Fig. 4(b) with a short response time ($<$100 ms) is the contribution from the internal structure of filaments where carbon nanotube bundles are randomly connected. A similar response time of light-induced movement ($<$100 ms) implies that it shares the same

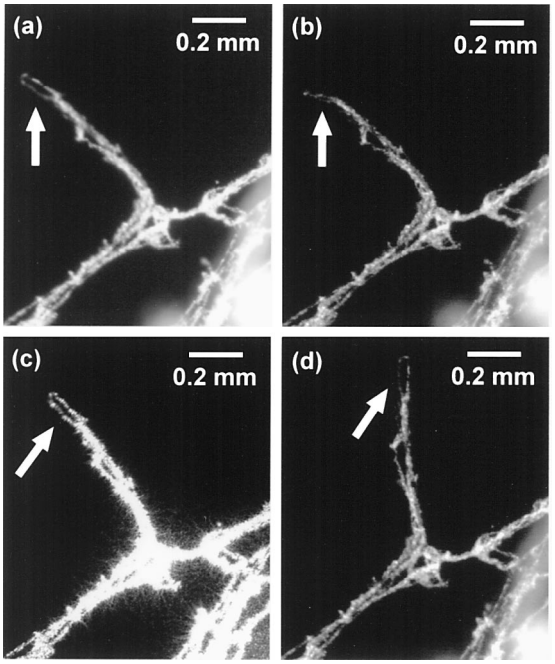

FIG. 3. (a) The strong light ($\sim$30 mW/cm^2) induced a repulsion of nanotube bundles and formed a small loop at the tip of the filament. (b) The same filament tip under the weak ($\sim$5 mW/cm^2) illumination gave an obviously different shape. (a) and (b) are illuminated by a halogen lamp light source. (c) Illumination by a He-Ne laser ($\sim$800 mW/cm^2) gives the same result as (a). (d) The same filament in an electrical field also gave a similar tip shape. The different orientation of the filament in (d) is because the SWCNT bundle tends to align along the electrical field [17]. The white arrows in all photographs indicate the same filament tip.

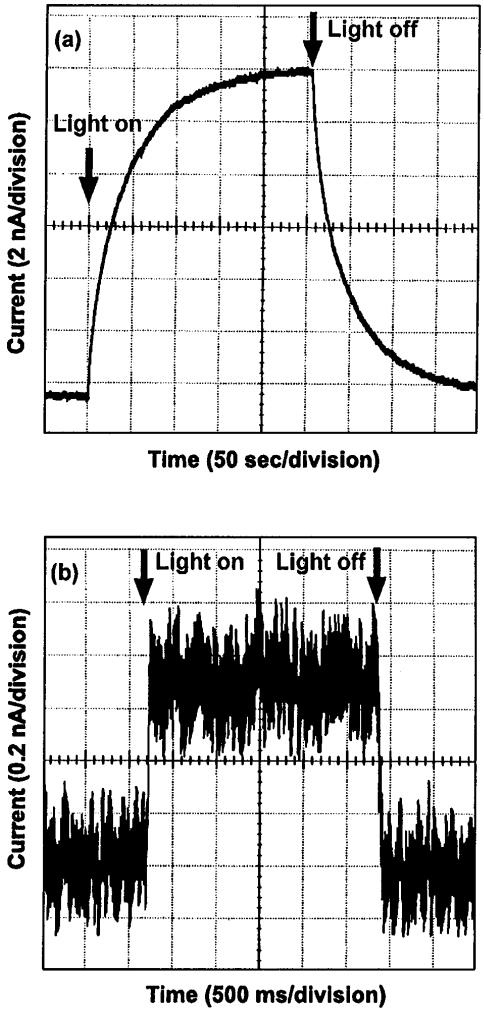

FIG. 4. The measurement results of light-induced currents on the sample shown in Fig. 1(a) when the spot of a He-Ne laser irradiated on (a) one of the electrodes and (b) the middle part of the filaments between the electrodes. The saturated current in (a) is about 13 nA and the rising time is about 200 sec. The saturated current in (b) is about 0.6 nA and the rise time is less than 100 ms.

origin with that of the light-induced electricity in the bundle structure.

A previous study showed that the thermoelectric power of a SWCNT mat is one order higher than that of graphite, which was explained by the break of electron-hole symmetry due to the intertube interaction, the charge transfer from metallic tubes to the semiconductor ones, and interbundle or intertube barriers [10,11]. This argument is also suitable to explain the observed light-induced electricity in the bundle network which can be simplified to be a network of numerous photovoltaic cells or thermoelectric cells. We should also note that the as-produced SWCNT bundles are highly curves as shown in Fig. 1(b) and in Ref. [8]. The inherent deformation may lead to an increase of local density of states (LDOS) near the Fermi level and a shift of the valence band edge due to increased π-σ hybridization in the deformation region [13]. This could also induce carrier separation between tubes or bundles. Because the resistance is very high at the intertube and interbundle contacts [the measured resistance between the two electrodes in Fig. 1(a) was about 12 kΩ, and would be higher if the number of filaments decreased], local charge accumulation could cause electrostatic repulsion between nanotube filaments. Furthermore, the surrounding matrix could establish a relatively strong electrostatic field. Under a randomly oriented electrical field $\mathbf{E}$, a SWCNT acquires dipole moments $\mathbf{P}$ pointing mainly along their axes because of their highly anisotropic characteristics [22]. The resulting torque $\mathbf{P} \times \mathbf{E}$ makes the tube align along the direction of the electric field if the movement is not restricted by its environment [20,21]. For a thin and short filament, the realignment is mainly determined by the field of the nearby matrix and thus makes it perpendicular to the edge of the matrix and independent of the illumination direction. For a thick and long filament, the absorption of light is high enough to make the established electrostatic fields inside the filament decisive, and it tends to move away from the light source in order to decrease its internal energy.

In conclusion, we observed the elastic movement of filaments of SWCNT bundles under the illumination of visible light. The elastic behavior was explained by the electrostatic interaction of the SWCNT bundles as a result of a photovoltaic or light-induced thermoelectric effect that is physically related to the modification of electronic structure during the bundle formation. Apparently, more work should be done to clarify the mechanism and the detail dependence of the elastic and electric behavior with light wavelength in order to apply the new property of the SWCNTs into multifunctional devices.

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