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Direct transition of potential of water droplets to electric energy using aligned single-walled carbon nanotubes*

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In this paper, we report that an electromotive force (EMF) can be induced in a rope of aligned single-walled carbon nanotubes (SWNTs) when water droplets fall on this rope. The magnitude of this EMF depends sensitively on the slant angle of the SWNTs. Most interestingly, both the magnitude and the direction of the induced EFM can be modulated by applying a current to the SWNTs. The concepts of electrical slip and no-slip are proposed and can be quantitatively described by "electrical slip resistance". This kind of generator does not need any magnet, rotor, etc and shows quite a different operating mechanism and design compared with a conventional large scale hydroelectric power generator.

Keywords: single-walled carbon nanotube, water, energy conversion

PACC: 6148, 8220R, 8610F

1. Introduction

Devices that harvest their operating energy from the environment have attracted much attention recently due to their advantages of an extended lifetime and the ability to be positioned into places difficult to access without cabling.[1−3] Zinc oxide nanowires and microfibre–nanowire hybrid structures are shown to be examples of such devices.[4−6] In these potential self-powering devices, it is still quite challenging to increase the output powers of these nanogenerators because of the high inner resistance. The single-walled carbon nanotube (SWNT) has very good mechanical[7,8] and electrical[9] properties which make it a very good material for the fabrication of electric devices. The interaction between carbon nanotube and water has been studied a lot[10−20] because of the small size and the unique structure of the SWNT. The wall of an SWNT is composed of only one atomic layer of carbon atoms, and the charge carriers of nanotubes will have strong coupling with flowing molecules at the interface between SWNT and the liquid as proposed theoretically.[11,12] Ghosh *et al.* showed experimentally that an electromotive force (EMF) was induced by continuum water and/or other polar/ionic fluids flowing over a film of SWNTs.[13−15] They proposed that the free charge carriers existing in the SWNTs were dragged along the nanotube by the fluctuating Coulomb field that was caused by the liquid flowing through the nanotubes.[14−19] These studies indicate that an open-circuit voltage ($V_{\rm oc}$) can be induced in SWNT in a flowing liquid. However, in addition to the flow of liquid, there exist a lot of flows such as raindrops that are very common and it would be of great help to the self-powering device if these water flows could also be used as an energy source. Previous studies concentrated on the energy generated by water, but it must be noticed that the interactions between charge carriers in SWNTs and flowing liquid molecules are mutual,[20] so it is important to study the possible effect of the current in the circuit on the induced $V_{\rm oc}$, especially when the SWNT is used as an energy converter in a self-powered system.

In this paper, we show that an EMF can be induced in a rope of aligned single-walled carbon nanotubes (SWNTs) when water droplets fall on this rope. The magnitude of this EMF depends sensitively on the slant angle of SWNTs. Most interestingly, both the magnitude and the direction of the induced EMF can be modulated by the current flowing through the SWNTs. The efficiency of the energy conversion is as high as 11.6%. The concepts of electrical slip and no-slip are proposed and can be quantitatively described

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by "electrical slip resistance".

2. Experiment

The SWNTs used in this work are synthesized by floating catalytic chemical vapour deposition[20] and the film of SWNTs can reach a size of 20×10 mm^2. After being treated two or three times by diamond drawing dies,[21] a rope of SWNTs can be obtained while the diameter depends on the diamond dies used. For the device shown in Fig. 1(a) the diameter of the SWNT rope is around 1.0 mm, and in some regions the SWNTs are almost parallel to each other because of the treatment of diamond dies as shown in Fig. 1(b).[21] Although the alignments of SWNTs are similar, a significant difference between our result and the result given in Ref. [21] appears in the case of a low density of SWNTs.

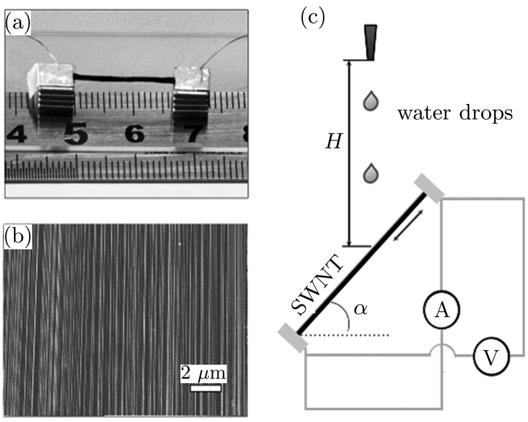

Fig. 1. SWNT device and schematic layout of experimental setup. Panel (a) shows an image of the device where an SWNT rope is ∼1.0 mm in diameter and ∼17.0 mm in length and connected to electrodes, panel (b) exhibits an SEM image of the aligned SWNTs in the device after treatment by diamond wire drawing dies, and panel (c) displays a measurement circuit, where during measuring, the SWNT rope is fixed at a constant distance from the water droplets at an adjustable angle (α) with respect to the horizontal axis. The device is biased with currents, and the voltage is monitored. The arrow indicates the direction of current (upwards: positive; downwards: negative). $H = 200$ mm.

The SWNT rope is connected to electrodes and forms a suspended structure as shown in Fig. 1(a). This device is fixed at a position where droplets of water (diameter ∼3 mm) from a bottle of deionized water (Millipore, 18 M$\Omega \cdot$cm^{-1}) can fall on the rope of SWNT. Then it is connected to a Keithley 4200-SCS system (voltage resolution 1 μV) to carry out the measurement.

3. Results and discussion

The resistance of the device usually ranges from several ohms to tens of ohms. The dynamic characteristics of voltage with a certain current bias are monitored over the entire falling process of the water droplets at a certain angle between the SWNT rope and the horizontal axis (Fig. 1(c)).

At an angle of 75°, when the water droplet begins to contact it, a sharp voltage ($V_{\rm oc}$) jump from zero to 70 μV is found and the voltage returns to its original value in about 6 s (Fig. 2(a), upper curve, no electrical current in the SWNT rope). Meanwhile, we can see with the naked eye that water flows along the SWNT rope. These processes can be repeated quite well (Fig. 2(a)). The magnitude of the voltage ($V_{\rm oc}$) jump is closely related to the slant angle of the SWNT rope (Fig. 2(a)). When the slant angle is reduced, the voltage jump becomes small and finally no obvious voltage change can be found at an angle of zero. It is interesting to note that the restoring time for the voltage ($V_{\rm oc}$) to jump back to its original value becomes longer for smaller slant angles of SWNT rope.

To investigate the mechanism of these interesting observations, we carry out the following experiments. At an angle of 75° (Fig. 2(b)), a series of positive current biases are applied during the experiment (current direction: from bottom to top electrode). It can be found that similar voltage jumps appear when water droplets fall on the SWNT rope. The magnitude of the voltage jump increases when the current bias becomes larger. Interesting phenomena happen when a series of negative current biases are applied (Fig. 2(c)). At small negative currents (absolute value), the voltage jumps are still upward but the magnitude decreases gradually (Fig. 2(c), upper curves). At a critical value of current (−5.00 mA), the voltage jumps disappear (Fig. 2(c), middle curve). When the current is larger than this critical value, the voltage jumps appear again but become downward, which is in sharp contrast to the upward jumps at positive and smaller negative currents. The relationship between average voltage jump and current is plotted in Fig. 2(d), which shows a linear behaviour. In Fig. 2(d) the other two curves correspond to the cases at slant angles of 45° and 10°, separately, which also show linear dependence of the voltage jump on current.

We should point out here that the voltage jumps in Fig. 2 are not due to the possible elastic deformation and the change of resistance of SWNT rope when water droplets collide with the rope, owing to the following reasons: firstly, in the case of open circuit in Fig. 2(a), the V_{oc} has a maximum value of 70 μV at an angle of 75° and another maximum value of nearly zero at an angle of 0° while the possible elastic deformation should be largest at angle 0°; secondly when the direction of current switches over, the voltage jumps should increase for positive current and decrease for negative current if they are caused by elastic deformation and change in resistance of SWNT rope. However, as seen clearly from smaller values of currents in the lower part of Fig. 2(b) and upper parts of Fig. 2(c), the voltage jumps both increase when water droplets collide with the SWNT rope. Therefore, this voltage jump is an induced electromotive force (EMF).

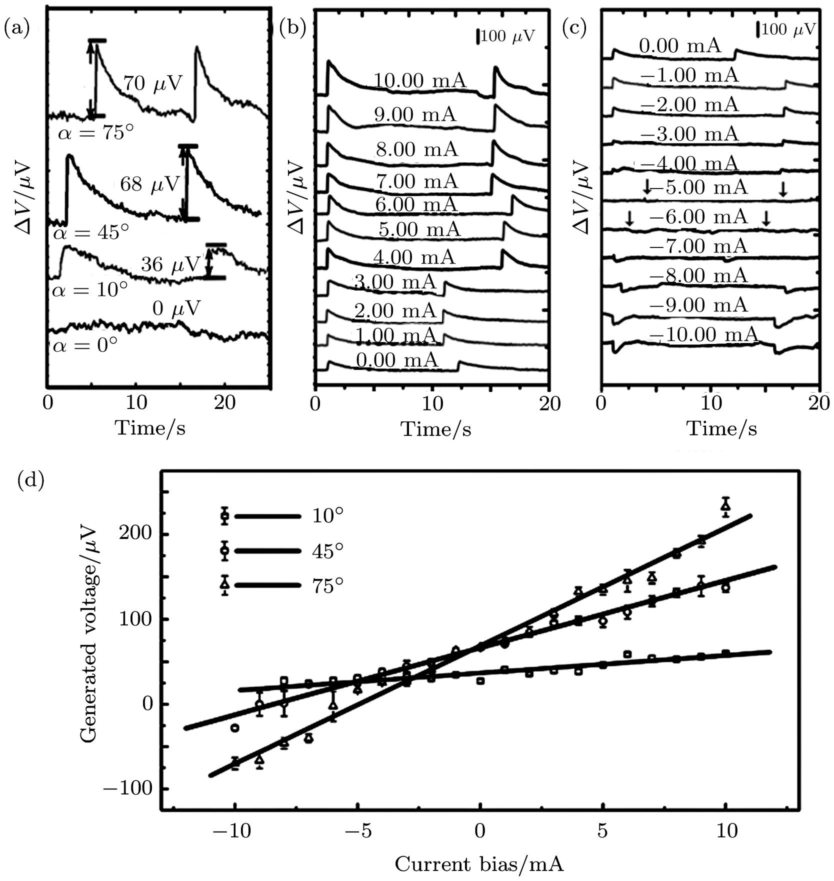

Fig. 2. Dynamic response and recovery characteristics of the device when water droplets fall on the SWNT rope at different slant angles and current biases. Panel (a) shows the dynamic V_{oc} (open-circuit voltage) characteristics with slant angles of 75°, 45°, 10° and 0° from top to bottom. Panel (b) displays the dynamic voltage characteristics at a slant angle of 75° with positive current biases and increasing voltage jumps induced by water droplets with current rising. Panel (c) indicates the dynamic voltage characteristics at a slant angle of 75° with negative current biases. The magnitudes of voltage jumps decrease gradually to zero, and then increase downwards under larger currents. The arrows indicate the time when water droplets fall on the SWNT rope. All curves in panels (a), (b) and (c) are vertically offset for clarity. Panel (d) exhibits linear dependences of the voltage jumps induced by water droplets on current bias and slant angle; the error bars of data points represent the average absolute deviations of the generated voltage.

It should be noted that the alignment of SWNT is critical for inducing an EMF in the gathering of energy from water drops. As shown in Fig. 3, a film of SWNT with a size of 22×5 mm^2 is connected to electrodes. The SWNTs in the film are usually entangled together and poorly aligned as shown in Fig. 3(b). When water droplets fall on the film of SWNTs, no obvious voltage jumps are found under a current bias of 0.00 mA or ±1.00 mA, indicating the importance of SWNT alignment for the EMF generation (Fig. 3(c)).

The SWNT rope has a very small inner resistance (∼ several ohms), so the short-circuit current can be as high as several or tens of microamperes,[6,13] and the electrical power induced by an individual device can be estimated from the following equation:

$$P = VI = V^2/R, \tag{1}$$

where P is the electrical power, V the open-circuit voltage, I the short-circuit current, and R the inner resistance. A maximum value of 680 pW can be obtained in the case of Fig. 2(a) (upper curve).[6]

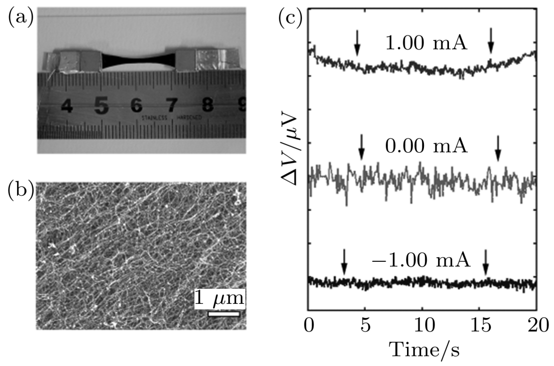

Fig. 3. Experimental results with SWNT film device. Panel (a) shows an optical image of the device, where the SWNT film is about 22×5 mm^2 and connected to electrodes. Panel (b) exhibits a typical SEM image of the SWNT film, where there is no alignment of SWNT before the treatment by diamond wire drawing dies. Panel (c) displays dynamic voltage characteristics of the device when water droplets fall on the SWNT film. The current bias corresponds to 0.00, ±1.00 mA, respectively. Each curve is offset for clarity. The arrows indicate the moment in time when water droplets fall on the SWNT rope.

To estimate the energy transfer efficiency of the SWNT device, we assume that each hexagon on the wall of the SWNT can adsorb one water dipole, and the total number of water molecules involved in the double layer model can be obtained as

$$N = \frac{N_l \times S_t}{S_0}, \tag{2}$$

where S_0 is the area of one hexagon (5.23×10^{-20} m^2), S_t is the surface area of an individual SWNT and N_l is the number of SWNTs in the SWNT rope, which can be expressed as follows:

$$S_t = \pi d_t l_0, \tag{3}$$

$$N_l = (D/d)^2 \times (l/l_0), \tag{4}$$

where d_t is the average diameter of the SWNTs (1.5 nm), l_0 is their average length, D is the diameter of SWNT rope (∼1 mm), l is the length of SWNT rope (17.0 mm), and d is the average spacing between individual SWNTs (∼100 nm). The potential energy of these water molecules is

$$E_p = \frac{N}{N_{\mathrm{A}}} \times M \times g \times h, \tag{5}$$

where N_{A} is Avogadro's number (6.02×10^{23}), $M = 18 \times 10^{-3}$ kg$\cdot$mol^{-1}, $g = 9.8$ m$\cdot$s^{-2}, and $h = 0.2$ m. Then we can obtain the potential energy of the water molecules involved in the energy transfer process E_p (8.97 nJ). The electrical energy generated by the SWNT rope with a water drop can be calculated from the following formula:

$$E_{\mathrm{e}} = \int_0^T \frac{U^2(t)}{R}\,\mathrm{d}t, \tag{6}$$

where U is the voltage generated, T is the restoration time and R is the inner resistance. A typical value of E_{e} at zero current bias and a slant angle of 75° is calculated to be around 1.04 nJ. According to the calculation, the efficiency of the energy conversion is 11.6%, correspondingly

The interface between SWNT and water is unique because the wall of SWNT is composed of only one atomic layer of carbon atoms. In this interface, the traditional and simplest boundary condition is the no-slip condition, which implies that water molecules adjacent to the wall of SWNT are assumed to have the velocity of the wall.[22] However, it is demonstrated that this no-slip condition for the interface between SWNT and water molecules is inapplicable.[23,24] In the present work, we refer to the traditional boundary conditions as atomic no-slip or slip because they are determined by relative movement of atoms or molecules in the interface between the liquid element and the surface of a solid. Meanwhile, we propose concepts of electrical slip and no-slip whether an electrical-related phenomenon happens or not in the solid part of the interface (such as SWNT in this work).

The interface between the SWNT and water dipoles is schematically shown in a double layer structure (Fig. 4(a)). The electric field, which prevents electrons from escaping (work function),[25] is quite nonuniform and perpendicular to the wall of the SWNT. Under this electric field, the dipoles of water are attracted and point toward the SWNT. At a zero current bias, when the water droplets begin to contact the SWNT, the water dipoles nearest to the SWNT wall form a double layer structure with the SWNT wall, and flow downwards along the SWNT after collision (Fig. 4(a)). Through the double layer structure, the carriers of the SWNT are dragged by water dipoles.[12,13,17] From the direction of the EMF, the carriers in the SWNT being dragged by flowing water dipoles have positive charges, which is consistent with the result of an SWNT rope field emission transistor.[26] Therefore, a positive voltage jump

(EMF) can be measured while water droplets are falling on the SWNT rope. The characteristics (magnitude and its duration) of this EMF are closely related to the slant angle of SWNT rope as shown in Fig. 2(a). A larger slant angle of SWNT corresponds to a larger velocity of water along the SWNT and a small duration in the double layer. This is in good accordance with the characteristics of the induced EMF for different slant angles of SWNT (Fig. 2(a)). In this situation, we refer to the boundary condition of the interface as positive electrical slip (Fig. 4(a)). When a positive current bias is applied, the current flows upwards as shown in Fig. 4(a). When the water droplets flow on

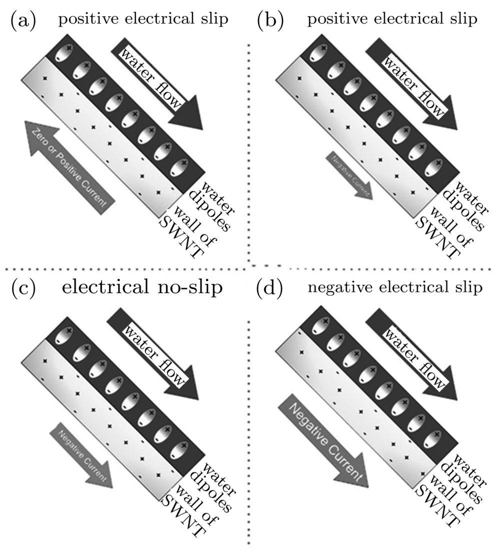

Fig. 4. Comparison of boundary condition among atomic slips with positive electrical slip, electrical no-slip and negative electrical slip. Panel (a) shows that at a zero or positive current, the flowing of water dipoles corresponds to positive electrical slip and an EMF is induced. Positive electrical slip means that the bottom electrode has a higher voltage. Panel (b) exhibits that at a small negative current (value), the flowing of water dipoles still corresponds to positive electrical slip and an EMF with the same direction is induced. Panel (c) displays that at a critical negative current, no EMF is induced, which is called electrical no-slip. Panel (d) indicates that at a larger negative current (value), the direction of the induced EMF is reversed, which is called negative electrical slip. We can see that the electrical slip can be tuned by the current under the same traditional atomic slip conditions (under these conditions, water dipoles still flow downwards).

the SWNTs, the current tends to decrease because of the coupling with water dipoles in the double layer. In this case, a positive voltage jump is observed. A larger current corresponds to a higher tendency of current decreasing when the water droplets fall on the SWNT each time; therefore, a higher EMF is observed, in which case the boundary condition is also named positive electrical slip (Figs. 2(b) and 4(a)).

When a small negative current bias is applied, the current flows downwards (Figs. 2(c) and 4(b)). In this situation, the carriers of SWNT (carrying positive charges) are accelerated when a water droplet falls on the SWNT. This also results in an upward EMF and corresponds to positive electrical slip (upper curves in Fig. 2(c); Fig. 4(b)). As the negative currents increase, the EMF induced becomes smaller. Finally, no EMF is induced when the water falls on SWNT at a critical negative current. In this situation, the interface condition is named electrical no-slip even though the water still flows downwards and atomic slip exists (middle curve in Fig. 2(c); Fig. 4(c)).

For negative currents over the critical value, the carriers of SWNT are decelerated when the water droplet falls on SWNT. This leads to a downward EMF and corresponds to negative electrical slip (lower curves in Fig. 2(c); Fig. 4(d)).

From the above discussion, we can see the important differences between one kind of slip and another kind of no-slip: the same atomic slip condition can correspond to positive electrical slip, negative electrical slip and even electrical no-slip, depending on the current in the solid part of the interface (Fig. 4). Meanwhile, the electrical slip and electrical no-slip can be well understood by the slope of the linear fitting line in Fig. 2(d). The slopes of these lines are in units of Ω. For example, the slopes are 14.0, 7.7 and 2.0 mΩ for slant angles of 75°, 45° and 10°, respectively. It is worthwhile noting that the device shown here has a resistance of 7.2 Ω, which represents its intrinsic electrical property and does not change regardless of the angle between the SWNT and horizontal axis. When the SWNT is used as an energy converter, the "electrical slip resistance" (the slope in units of Ω), which is used to describe the electrical slip or no-slip, depends sensitively on its relative geometry.

Comparing the theoretical and experimental results reported before,[12–16] we demonstrate the following advances in this work. First, the effect of the current in the circuit on the induced EMF is studied, which is important for the application of an SWNT energy harvesting system. Second, the concepts of electrical slip and no-slip are proposed to explain the interesting effect of current on the induced EMF and can be quantitatively described by "electrical slip resistance". Finally, our experiments show that the alignment of SWNTs in the rope is necessary for the results reported here. This indicates that the treatment of diamond wire drawing dies and the alignment of SWNTs in the rope are critical for an SWNT energy harvesting system.

4. Conclusions

We have demonstrated that aligned SWNT rope can transfer the potential of water droplets to electrical energy directly. In contrast to conventional large scale hydroelectric power, the generator we proposed here shows quite a different operating mechanism and design. For example, no huge magnet, rotor, etc is needed, and this system can be a very good complement to a solar power system on rainy days or at night. In the meantime, we proposed concepts of electrical slip and no-slip to describe characteristics of the induced EMF. The efficiency of the energy device is fairly high (∼11.6%), and it is possible to improve the efficiency by optimizing the structure and the design of SWNT devices.

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