Electrochemical actuation of carbon nanotube-based actuators

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Abstract

As a carbon material with extremely high mechanical properties, carbon nanotubes (CNTs) are found to also have the electrostatic and electromechanical actuation properties when applied with a potential in the presence of an electrolyte. These actuations happen at only a few volts, while already showing comparable or superior performances than natural muscles. The characteristics of single or nanotube bundles allow us to expect them to function in nano and micro actuator devices based on one or a few hundred nanotubes, their properties can be tuned.

In this paper the basic properties of individual carbon nanotubes are described, as well as the working principles of several actuators that are based on carbon nanotubes. The actuation mechanisms of the actuators based on carbon nanotubes are also explained, by experimental and theoretical works presented in the literature. This paper aims to give a general introduction to the actuation of carbon nanotube-based nanoactuators, and critically confront various viewpoints regarding their mechanisms.

Contents

1. Introduction

1.1 What is an actuator?

ac·tu·ate /ˈaktʃʊeɪt   , -tjʊ-/ verb.
: to make (a machine or electrical device) move or operate

This is the definition of the word "actuate" in the Merriam-Webster dictionary. An actuator is a type of system that will actuate. For example a rotor is an actuator; it actuates by performing a rotational movement. In general, all kinds of systems that can induce motion or operation can be called as actuators. A human can also be called as an actuator by definition.

There are several kinds of macro mechanical actuators, basically divided by the mechanisms or energy source of their actuation: hydraulic, pneumatic, electric, mechanical, etc. However when it comes to actuators with much higher precision, for example those actuators used in nanoelectromechanical systems (NEMS) or microelectromechanical systems (MEMS), there are other new types of actuators working under different driving forces and mechanisms. According to the actuation principles, the commonly seen new-tech actuators used in NEMS and MEMS are divided into two groups. One of them consists of actuators that generate external forces between stationary and moving parts, by thermopneumatic effects, electrochemical effects, electrostatic effects or magnetic fields. The other group consists of actuators that are driven with intrinsic forces, using piezoelectric, thermomechanical, shape memory, electro- and magnetostrictive effects.

1.2 What characterize the actuators?

Actuators of different types used for different applications have their own properties that are the characterization of the performance of the actuators. But in general several aspects of actuators are of interests in most of the applications, including sensitivity, resolution (precision), speed, scale range, hysteresis, frequency response, deadband, reliability, etc. These parameters are usually visually characterized by a so-called transfer function. Transfer function is the relation (response) between the input and output of the actuators. Because of the energy conversion that generally occurs in the actuation, the transfer function is of crucial importance for the characterization of properties. Normally the input is the driven energy source of the actuators, for example force, pressure, heat, electrical signal. The output is the actuation itself, normally characterized by displacement, rotation, deformation, etc. For actuators that involved with the deformations, high strain and modulus is expected for better functioning.

1.3 What is a carbon nanotube?

Carbon nanotubes are first discovered by Sumio Iijima in 1991 [1]. These nanotubes are cylindrical structures that are formed by hexagonally assembled carbon atoms. It can be simply regarded as a result of the rolling of graphite sheets (graphene) into a cylinder. Basically, there are two kinds of carbon nanotubes: single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT). SWNTs have only a single wall of carbon that can be considered as a seamless wrap of a single graphene piece. MWNTs are made of several such nanotubes with different diameters that are concentrically nested. The structure of single-walled carbon nanotubes and multi-walled carbon nanotubes are shown in Fig. 1.
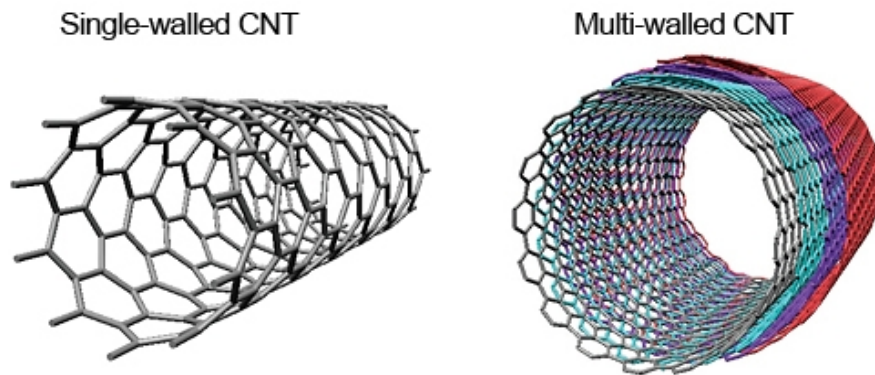

Fig. 1. The structure of single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). (Adapted from [2].)

Although a single graphene layer is a semiconductor with a zero band gap, the single-walled nanotube can be either a conductor or semiconductor. They have different properties depending on their allotropes. The sheet direction about which the graphene is rolled to form a cylinder can be described with the chiral vector (n, m) where n and m are integers from the vector equation $C_h = na_1 + ma_2$ [3]. A schematic drawing of the vector component and direction is shown in Fig. 2. The direction of rolling and the diameter thus only depend on this vector. When $m = n$ the nanotube is called an armchair tube and when $m = 0$ or $n = 0$ the nanotube is called a zigzag tube, elsewise the nanotube is called a chiral tube. If the value $n - m$ is dividable by three, the nanotube is considered to be conductive, else it is considered to be semiconductive with a band gap that inversely depends on the nanotube diameter.
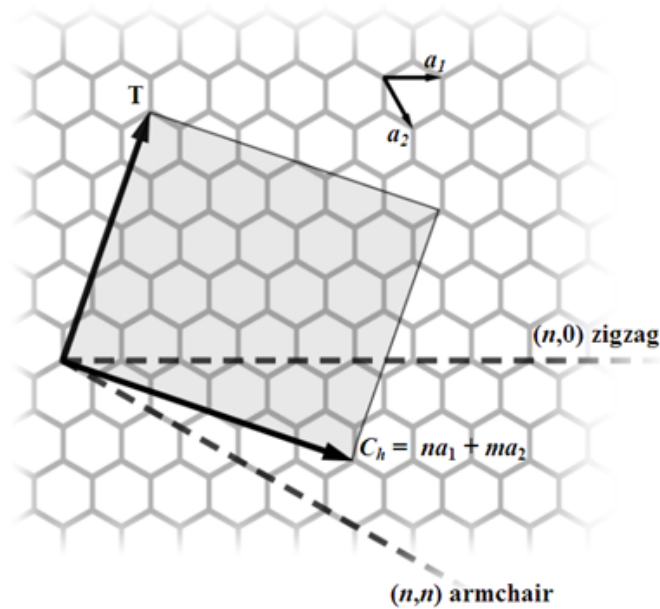
Fig. 2. The nanotube can be constructed by "rolling up" a graphene sheet. Different types of carbon nanotubes are rolled up with different chiral vectors $C_h = na_1 + ma_2$. (Adapted from Wikipedia. [4])

Nanotubes have good mechanical properties. Young's modulus ranging from 270 GPa to 1 TPa and tensile strength ranging from 11 to 200 GPa are found for variety kinds of nanotubes [5]. Thermal stability of SWNTs can reach up to 2800 °C in vacuum; thermal conductivity of an individual MWNT (> 3000 W/mK) is greater than that of natural diamond and the basal plane of graphite (both around 2000 W/mK) [6]. The electric-current-carrying capacity is about 1000 times higher than copper wires [7]. Superconductivity has also been observed, but only at low temperatures, with transition temperatures of ~0.55 K for 1.4-nm-diameter SWNTs [8] and ~5 K for 0.5-nm-diameter SWNTs grown in zeolites [9]. Their mechanical strength enables their application in nanocomposite materials.

SWNTs with diameters ranging from ~0.4 to > 3 nm and MWNTs with diameters ranging from ~1.4 nm to > 100 nm are made usually by carbon-arc discharge, laser ablation, or chemical vapor deposition (CVD) [10].

1.4 What is a carbon nanotube-based actuator?

Carbon nanotube-based actuators are actuators that are constructed with carbon nanotubes. These actuators can be created with single-walled nanotubes (SWNT) or multi-walled nanotubes (MWNT). They can be made of individual nanotubes or a collective of nanotubes that forming bundles or networks. For example, the nanotube sheets called "buckypaper" are conventionally obtained by peeling the filtered SWNTs

dispersed in a liquid after washing and drying [11]. These sheets can act as artificial muscles when a potential is applied in an electrolyte, and a cantilever-based actuator is realized as a result of the bending of the electrodes when a potential is applied [12].

2. Carbon nanotube-based actuators

2.1 Buckypaper

Baughman et al. [12] first demonstrated the electrochemical actuator properties of carbon nanotubes in 1999. They use SWNT sheets as electrolyte-filled electrodes of a supercapacitor, and inject electronic charge into the electrode by applying voltage. A so-called double layer is formed at the interface between the SWNT sheet and the electrolyte by the surface charge of the sheet and the electrolyte ions. The injected charge will cause the dimension change because of the change in covalent bonds in the SWNTs. This kind of SWNT sheet was first termed as "buckypaper" by Dr. Smalley and his research group [13]. SWNTs were made by the pulsed-laser vaporization method and purified by washing, centrifugation, and cross-flow filtration. A suspension of bundles consisting hexagonally packed SWNTs are formed. Buckypaper were then produced by vacuum filtration of the nanotube suspension on a poly(tetrafluorethylene) filter, and the dried nanotube sheets were peeled from the filter without further treatment.

Baughman and coworkers used two simple experiments for the demonstration of the electrochemical actuation of the buckypaper. In the first demonstration a Scotch double-stick tape is adhesively sandwiched by two pieces of buckypaper to form so-called bimorph cantilever actuator, which is then vertically suspended in a NaCl electrolyte. When a dc voltage of few volts is applied on the two pieces of the buckypaper, a bend of around one centimeter is observed for the tip of the cantilever. A reverse effect is found when a reversal potential is applied. Fig. 3 shows the schematic drawing of the side view of the demonstration.
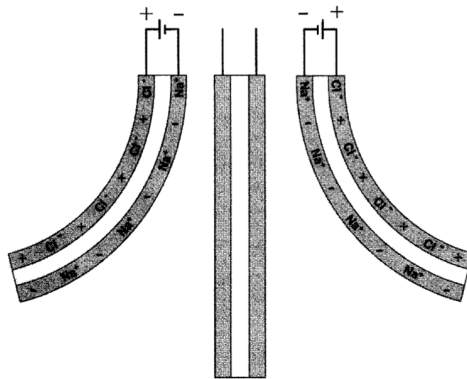

Fig. 3. Schematic side view of a cantilever-based actuator operated in aqueous NaCl as electrolyte. Two stripes of buckypaper (shaded) are stick to a layer of Scotch double-stick tape (white). Charges of either sign are injected into either side of the buckypaper, which are balanced by the Na^+ and Cl^- ions at the interfaces between the buckypaper and the electrolyte. When a voltage is applied, the cantilever will bend because of the expansion or contraction of the buckypaper because of the induced charges. [12]

The other demonstration is more straightforward. A single piece of buckypaper is fixed at one end and the other end is attached to a horizontal poly(vinyl chloride) (PVC) cantilever. When a alternating potential is applied with respect to the saturated calomel electrode (SCE), the length of the buckypaper will expand or contract depending on the sign of the injected charge. The change in the length of the buckypaper will cause the deflection of the cantilever, whose displacement is then measured with a reflecting mirror and an optical sensor. The schematic drawing of the setup is shown in Fig. 4. Quantitative analysis of the results reveals that a stress (as high as 0.75 MPa) significantly higher than the peak capacity of human skeletal muscle ($\sim$0.3 MPa) and a maximum strain of $\sim$0.2% is generated during the isometric contraction of the nanotube sheet.
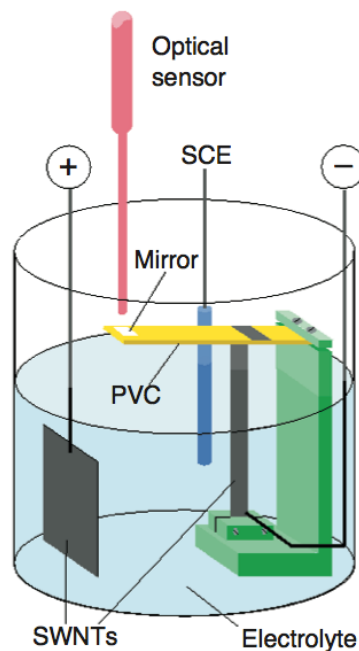

Fig. 4. The schematic drawing of the setup used for the measurement of the length change of the SWNT sheet when a potential is applied (versus a SCE). Changes in the length of the nanotube strip bend the PVC cantilever that carries an attached mirror, whose displacement is measured with the optical sensor. [12]

2.2 Actuation of single SWNTs

The electrochemical actuation properties of the buckypaper does not seem to be comparable to that of the experimentally derived for individual nanotube bundles [14]. Baughman and coworkers suggest that the buckypaper still needs to be optimized. Additionally, it is important to experimentally investigate the actuation properties of individual SWNTs.
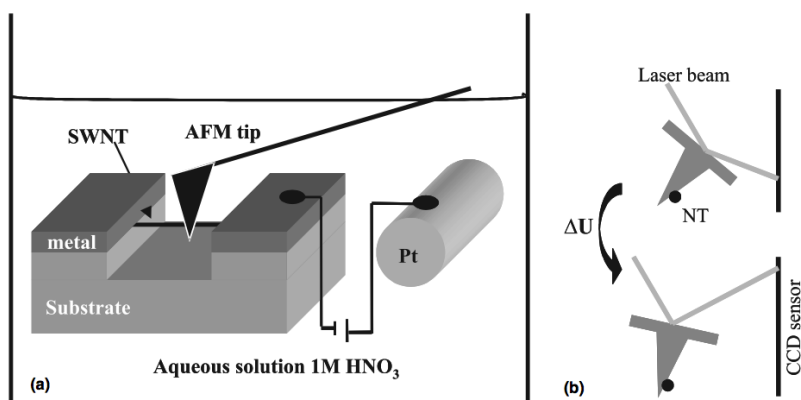
Fig. 5. (a) A schematic drawing of the setup used to demonstrate and characterize the electrochemical properties of an individual SWNT. (b) The lateral deformation of the SWNT is measured by an AFM. [15]

A novel approach is developed by Baughman et al. to study the actuation of an individual nanotube [15, 16]. The schematic drawing of the principle for demonstration and characterization of the electro-mechanical properties of an individual freestanding SWNT is shown in Fig. 5. The freestanding SWNT is prepared by etching a trench into a silicon chip, and then place a nanotube across this trench with its edges fixed by metal layers. The system is then placed into the electrolyte and a voltage is applied. An atomic force microscope (AFM) tip is placed on top of the SWNT and it causes a deformation of the SWNT. When changing the applied voltage, the length of the SWNT is expected to change and the displacement of the tip is recorded. The nanotube expanded in a similar way as a buckypaper in an electrolyte, and the relative nanotube length change is less than 1%. A stress up to 26 MPa is observed in further attempts for isometric SWNT actuators [17].

However, the above-mentioned approach generally suffers from the reproducibility problems and they find it hard to locate the individual nanotubes on the surface. Another approach was developed using pre-patterned markings on the silicon wafers before the deposition of sacrificial layers of poly(methyl methacrylate) and the nanotube [18]. A suspended SWNT is also produced after using the electron beam lithography (EBL). Young's modulus of around 0.6 TPa was determined using the force determination with the relationship between the deformation of the cantilever and the perpendicular direction height.

2.3 Nanotweezers

The actuation of the single nanotubes reveals the possibilities of producing nanodevices such as nanotweezers. Kim et al. [19] and Akita et al. [20] have made nanotweezers

using MWNTs and SWNTs, respectively. In the nanotweezers made of SWNTs, silicon cantilevers for AFM were used as the substratum of the nanotweezers. Two SWNTs were fixed to the sides of the tip by carbon deposition. When a potential is applied between the two arms of the nanotweezers, charges of different sign will be injected and the two tips of the arms will be closed because of the electrostatic attraction force. Applying different potentials can effectively open and close the tips of the nanotweezers. The nanotweezers made of MWNTs that works with similar principles. The differences are that the SWNTs as the two arms of the nanotweezers are attached to independent substrates. The closing of the nanotweezers is accomplished by the electrostatic force introduced by the applied voltage; the opening of the nanotweezers is achieved by macroactuators attached to the substrates. Fig. 6 shows the images of the actuation of the nanotweezers made of MWNTs (left) and SWNTs (right).
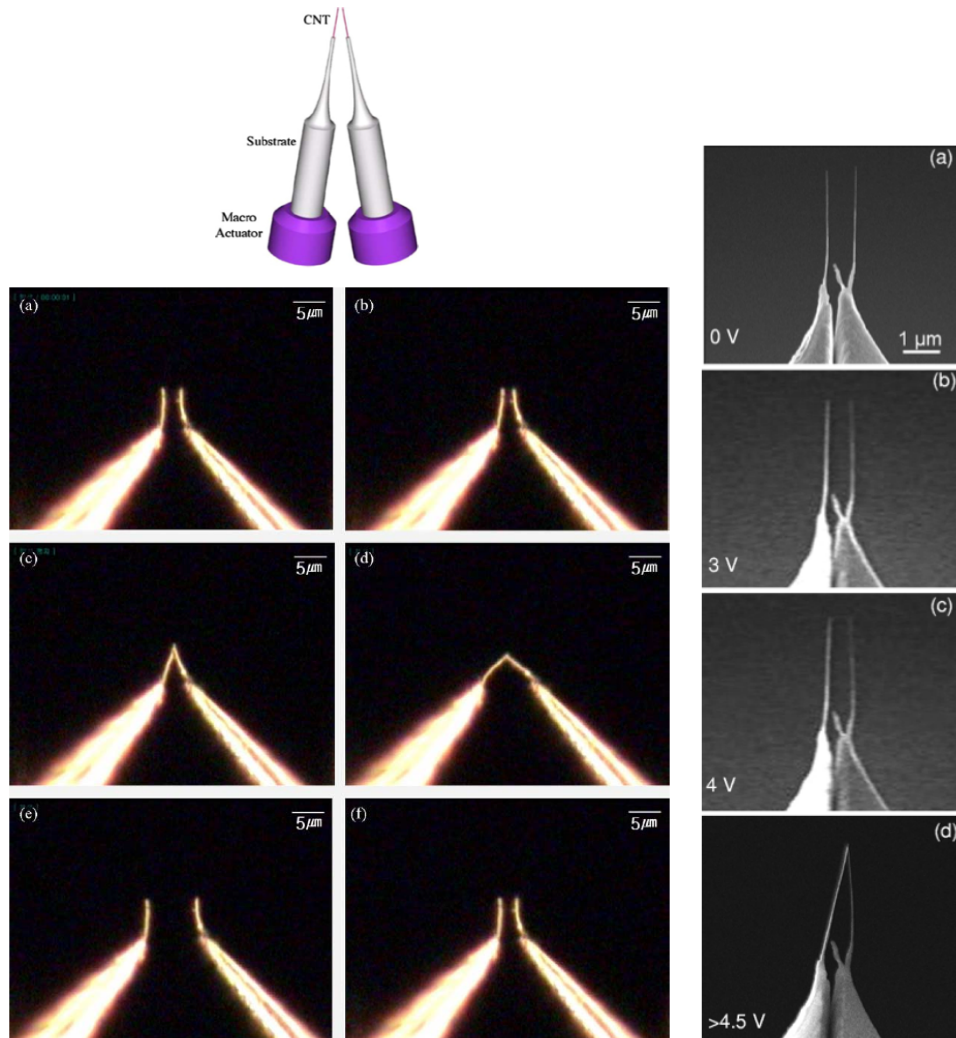

Fig. 6. Optical and SEM images of the actuation of the nanotweezers made of MWNTs (left) and SWNTs (right) when different voltages are applied. [19, 20]

2.4 Rotational actuator based on carbon nanotubes

Fennimore et al. [21] has demonstrated a carbon nanotube-based rotational actuator. Fig. 7(a) shows the conceptual drawing of the rotational actuator. The suspended MWNT as both the rotor plate support and the electrical feedthrough is embedded in the conducting anchors of two blocks (A1, A2). A metal plate rotor (R) is attached to middle of the MWNT. Between the two blocks three stators are placed around the rotor, including two in-plane stators (S1, S2) and a "gate" stator (S3). The entire actuator assembly is integrated on a silicon chip. Fig. 7(b) shows the scanning electron microscope (SEM) image of the nanoactuator. When a potential is applied between the rotor and the stators, electrostatic charges of different sign are injected into the stators and the rotor. The attraction between them will rotate the rotor thus twist the MWNT that attached to it. A torsion up to 20° is observed via the rotation of the rotor plate, when applying up to 50 V between the rotor plate and the gate stator. A torsional spring constant of 10-15 to 10-12 Nm was found, from which a shear modulus of 100 to 300 GPa was calculated for a MWNT having a diameter of 10 nm and an effective length of 2 μm.
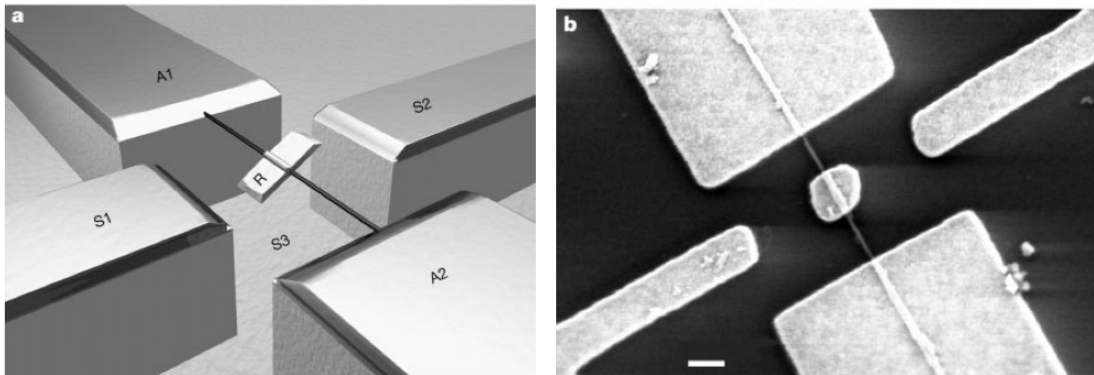

Fig. 7. (a) Schematic drawing of rotational nanoactuator. The nanoactuator is an analogue of a 3-stator electromagnetic motor but with electrostatic force as the driving mechanism. (b) Scanning electron microscope (SEM) image of real nanoactuator as proposed in (a). Scale bar, 300 nm. [21]

To realize larger degree of rotational displacement, the outer shell of the MWNT is compromised by applying a voltage high enough between the gate stator and the rotor plate. When the outer shells of the MWNT are broken, it is expected to act as a low-friction bearing system. The inner remains of the MWNT are given with a dramatic increase in rotational freedom. Using appropriate combinations of stator signals, the rotor can be positioned to arbitrary angles between 0° − 360°. Fig. 8 shows a set of SEM images recorded of the nanoactuator in the 'free' state (applied voltage is canceled), being rotated using quasi-static dc stator voltages.
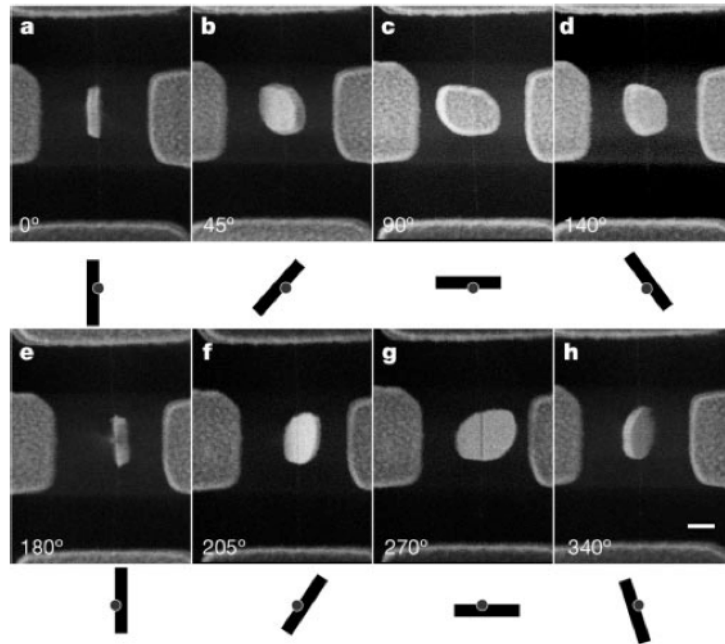
Fig. 8. A set of SEM images show that after been rotated by applying different voltages between the rotor and the stators, the actuator rotor plate can be placed at different angles when no potential is applied. Scale bar, 300 nm. [21]

3. Working mechanisms of carbon nanotube-based actuators

Comparing the structure of carbon nanotubes with that of graphene, they are similar in most aspects. The differences are results of the differences of their dimensions. The graphene is a two-dimensional material. The force that between the graphene layers of the graphite is van der Waals force. As for carbon nanotubes the dimension of the 2D hexagonal carbon atoms arrangements are greatly reduced, thus more interfaces are produced for carbon nanotubes.

For the nanotweezers and the rotational nanoactuator previously demonstrated in Section 2.3 and 2.4, the electrostatic force is the only driven force that is involved. It is easily explained by the attractive or repulsive force induced by the injected charges when a potential is applied. Nevertheless, the actuations of buckypaper and that of single nanotubes are electrochemical. Electrolytes play an important role in injecting the charge and balance the charge by ions.

However, there are two major mechanisms that induce the electrochemical actuation of carbon nanotubes. The first mechanism is the quantum mechanical effect that involves the band state of carbon nanotubes. For both carbon nanotubes and graphene, the carbon atoms within the structure are covalently bonded from sp^2 hybridization. When adding electrons to the structure, the added electrons populate the band state with anti-bonding character. Thus it weakens the bond and increases the bond length. When removing electrons from the structure, the bonding states are depopulated. But the depopulation is less efficient. Guo et al. [22] used Hartree-Fock (HF) and density functional theory (DFT) simulations to demonstrate electrostrictive deformation of a SWNT. The charge-induced axial strains for both armchair and zigzag nanotubes were predicted to be greater than 10% for electric field strength within 10 V/nm. This calculated strain is exceptionally high comparing to those get from experimental results (~0.2%) [12]. Axial deformation of a nanotube is attributed to two aspects of geometrical changes: (1) elongation of the C-C bonds, and (2) the distortion of the carbon hexagonal rings.
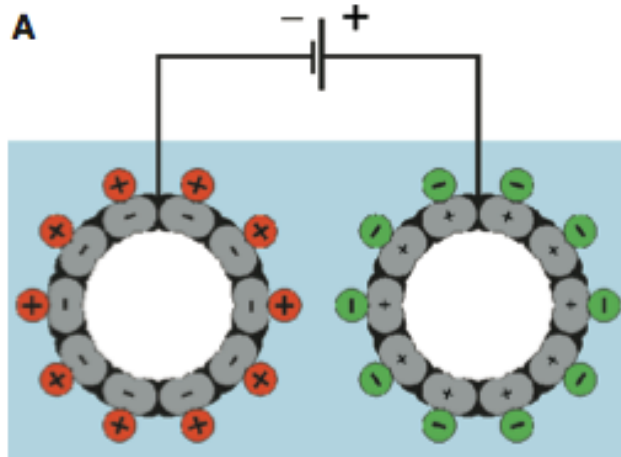
Fig. 9. Schematic drawing of the forming of electrostatic double layer at the interface between the nanotubes and electrolyte when a potential is applied. [12]

The second mechanism is electrostatic double layer effect, which is formed at the interfaces between carbon nanotubes and electrolyte. When applying a potential between the two electrodes of the actuator system, opposite charges will be induced by the potential in the two electrodes. As in the case of two electrodes are both nanotubes, the ejected charges will have different signs. As shown in Fig. 9, the charges in the SWNTs are fully balanced by the ions in the electrolyte (solid or liquid or gaseous). These balanced positive and negative charge are the so-called electrostatic double layers (DLs). These DLs will also induce strains in the carbon nanotubes thus deform the bonds within the carbon nanotubes.

The electrochemical actuation of the carbon nanotube-based actuators depends on both mechanisms. Baughman et al. [12] suggest that in the actuation of buckypapers for low charge densities the strain due to quantum mechanical effects from an expansion for electron injection to a contraction for hole injection, and expansion is resulted from both quantum chemical effects and electrostatic DL charging for high-density charge injection of either sign. Also, if electrostatic effects dominate, the electrode dimension would be a minimum at the potential of zero charge (pzc) while it is not the case in their results. The implication is that quantum chemical effects are greater than classical columbic effects for the buckypapers.

Rogers et al. [23] studied the physics behind the actuation of monolayer graphene immersed in an ionic liquid (IL) electrolyte via ab initio density functional methods by incorporating the complete ion-ion, ion-electron, and electron-electron interactions that exist in real electrochemical DLs. By charging the graphene both with and without the IL electrolyte present, they determined the precise contribution made by the DL to the overall actuation. They found that even for moderate graphene charge injection, the contribution of the electrostatic DL to the overall strain equaled or exceeded that of the quantum-mechanical strain resulting from charge injection only. Moreover, the presence

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of the IL DL enabled the monolayer graphene to achieve strains in excess of 1%, which was shown to not be otherwise possible via the quantum mechanical effect alone. They conclude that the electrochemical actuation of covalent carbon materials, such as graphene and carbon nanotubes, in the presence of an electrolyte is mostly due to the existence of an electrostatic DL.

The deviation in the predominant actuation mechanisms between experimental results and theoretical simulations may results from the difference in materials used. The ab initio DFT calculations were done with graphene, which has a lower Young's modulus comparing to SWNTs, according to calculations done by Van Lier et al. [24]. The difference in stiffness may vary the effectiveness of the actuation induced by different mechanisms. Another possible explanation is that the SWNT bundles prepared in the experiments demonstrated by Baughman and coworkers are not ideal. There properties depend not only on the properties of those individual nanotubes, but also on how the bundles are packed and orientated. This may also deviates the experimental results from the theoretical ones.

4. Conclusions

The deformation of carbon nanotubes by an applied potential in the presence of an electrolyte has been observed in different experiments. Carbon nanotubes exhibit great electrical-into-mechanical-energy transduction properties. This leads to the construction of electrochemical actuators based on carbon nanotubes. The mechanisms for the electrochemical actuation of both bundled and individual carbon nanotubes are proposed. However, the results deviate for some reasons, and the mechanisms are still not clear. Future work is needed for a better fundamental knowledge of their structure/property relations before they are brought into applications.

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