STRETCHABLE AND WEARABLE STRAIN SENSORS USING SUPER-ALIGNED CARBON NANOTUBE (SACNT) FILMS

RESEARCH REPORT

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1. INTRODUCTION

Due to an increasing need for devices that are able to be stretched or bended while maintaining functionality, stretchable electronics have attracted much attention in recent years. The stretchable electronic devices facilitate human interaction and biofeedback, such as interactive electronics, implantable medical devices and robotic systems with human-like sensing capabilities [1]. The ability to integrate the properties of flexibility and stretchability into electronic devices could lead to the development of skin-like sensors that stretch reversibly, sense strain, sense pressure, bend into hairpin turns, integrate with collapsible, stretchable and mechanically robust displays and solar cells, and also wrap around non-planar and biological surfaces such as skin and organs, without wrinkling. Stretchability – the ability to conform to and cover movable and arbitrarily shaped objects – could be exploited in the development of wearable devices that can be embedded into clothes and garments or even attached directly to the skin. Possible applications of this include the detection of human motion, monitoring personal health and therapeutics.

Conventional rigid metallic films cannot provide such stretchability. Yet, owing to the difficulties to develop stretchable electric materials, the current mainstream strategy in attempting to achieve stretchability is not to develop new materials, but instead to engineer new structural constructs from established materials [2]. Khang et al., reported in the Science journal that ultrathin silicon structures formed into buckled ("wave" like) geometries offered stretchability, and the strain applied to the device was absorbed by deformation of the silicon structures. Consequently, the functional materials are then exposed to a minimal amount of strain limited by the stretch of the silicon structures. In this case, the metallic film itself is still not stretchable. The stretchability is achieved through silicon structures, which limit the stretchability of the whole system.

A different approach is to assemble a device from stretchable materials. Examples of stretchable materials include polymer composites with conductive fillers [3-4] and extremely thin metal films on stretchable polymer substrates [5]. The Troster's group reported that the strain sensor measured large strain up to 80% in textiles with limited durability.

All the existing techniques mentioned above are still unable to meet the increasing demand for better stretchability performance of sensors that can accurately sense a variety of forms of motion of the subjects, particularly human body.

To my knowledge, I am the first to propose to use a new type of stretchable electric nanomaterial consisting of super-aligned carbon nanotube (SACNT) films. The carbon nanotubes (CNTs) are an extremely interesting type of material due to their unique 1-D structure, along with their excellent mechanical, thermal, and electrical properties [6]. Many promising applications have been demonstrated. SACNT [7-9] arrays represent high quality and highly ordered CNT structures, in which CNTs are almost perfectly parallel aligned with each other and perpendicular to the substrate. With these super arrayed structures, SACNT is able to, ideally, fully utilize the CNT’s excellent anisotropic properties.

The purpose of this project is to use a new type of material - super-aligned carbon nanotube (SACNT) films to make stretchable and wearable strain sensors and demonstrate the potential applications for developing human-friendly devices.

2. INTRODUCTION TO CARBON

Carbon is a chemical element with symbol C, atomic number of 6, and electron configuration of [He] 2s22p2. Carbon is the fourth most abundant chemical element in the universe by mass. It is also the second abundant element by mass in human body.

The well-known allotropes of carbon are diamond, graphite, amorphous carbon, and fullerenes. Figure 1.1 shows crystallographic structures of these allotropes.

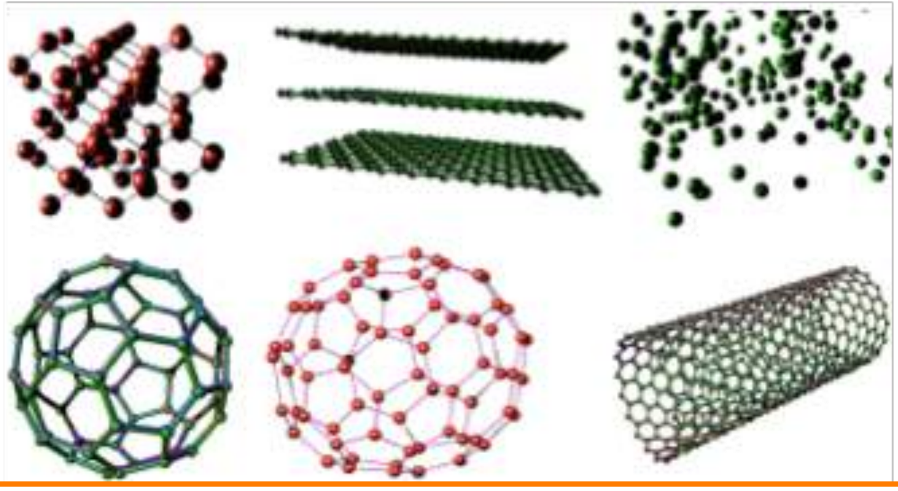


Fig. 1. Allotropes of carbon. a Diamond. b Graphite. The carbon atoms are bonded together in sheets of a hexagonal lattice. Van der Waals force bonds the sheets together. c Amorphous carbon. The carbon atoms are randomly arranged. d Spherical fullerence, C60. The carbon atoms of fullerenes are bonded together in pentagons and hexagons. e Ellipsoidal fullerence, C70. The arbon atoms are bonded together in an ellipsoidal formation. f Tubular fullerene, SWCNT. The carbon atoms are in a tubular formation. (See ref[8])

Diamond consists of pure sp3 hybridized carbon atoms. It is renowned for its extreme hardness. Diamond is mainly applied in industrial cutting and polishing tools besides being the most popular gemstone in our life.

Graphite has a layered and planar structure (Fig.1b). Amorphous, as its name says, does not have any crystalline structure (Fig.1c). Amorphous carbon can be used as inks, paints, and industrial rubber fillers.

The fourth allotrope of carbon is fullerene, which is located at a nanometer level. Fig.1d-f illustrates the structures of fullerene members. With the development of nanotechnology and nanometer engineering, fullerence plays an important role in the nanometer applications.

Carbon nanotubes (CNTs) are elongated cylindrical fullerenes with diameters of nanometers and lengths of microns even millimeters.

3. CARBON NANOTUBES

3.1 Introduction to carbon nanotubes

The carbon atoms in a carbon nanotube (CNT) are bonded in a curved sheet that forms a hollow cylinder in the nanometer scale, similar to that in other fullerenes. The length of CNTs may range from less than a micron to several millimeters or even centimeters, while the width is measured in nanometers. Their unique nanostructures result in many extraordinary properties such as high tensile strength, high electrical and thermal conductivities, high ductility, and high thermal and chemical stability.

CNTs are typically categorized as single-walled CNT (SWCNTs), double-walled, (DWCNTs), and multi-walled (MWCNTs) with respect to the number of graphite layers. The aspect ratios of individual CNTs can reach 10^7 (length/width), further enhancing the degree of anisotropy of CNTs.

With the unique structures of CNTs, CNTs possess:

1) Anisotropic mechanical properties: CNTs are much softer in the radial direction than along the tube axis.
2) Anisotropic electrical properties: the electrical resistivity in the CNT axis direction is much lower than that in the radial direction.
3) Anisotropic thermal conductivity: All CNTs are expected to be very good thermal conductors along the axis direction.
4) Anisotropic thermal diffusivity: the structure of aligned CNT arrays is expected to induce a large anisotropy of the thermal diffusivity along the directions parallel and perpendicular to the CNT alignment.

3.2 Super-aligned Carbon Nanotubes (SACNT)

Super-aligned carbon nanotube (CNT) arrays are distinguished from ordinary vertically aligned CNT arrays by their “super-aligned” nature, that is, the CNTs in super-aligned arrays have a much better alignment than those in ordinary arrays, which is a consequence of the narrower diameter distribution and higher nucleation density. The super alignment can make the anisotropic properties on CNTs even more pronounced, i.e., the SACNT enhanced the anisotropic mechanical property, electrical, and thermal conductivities. I used a scanning electron microscope (SEM) to see the structures of SACNT and ordinary CNT. Fig. 2 shows the SEM images of the SACNT made in our research center and the ordinary CNT made from other research group.

The remarkable mechanical, electrical and thermal properties of carbon nanotubes can be translated to a macroscopic scale by making SACNT sheets. The key feature of a super-aligned CNT array is that continuous unidirectional sheets, composed of a thin layer of parallel-aligned pure CNTs, can be directly drawn from it in solid state. The prerequisite for these vertically aligned CNTs to transform into horizontally aligned thin films is that the CNTs in super-aligned arrays have very clean surfaces and thus very strong van der Waals interactions with neighboring CNTs.

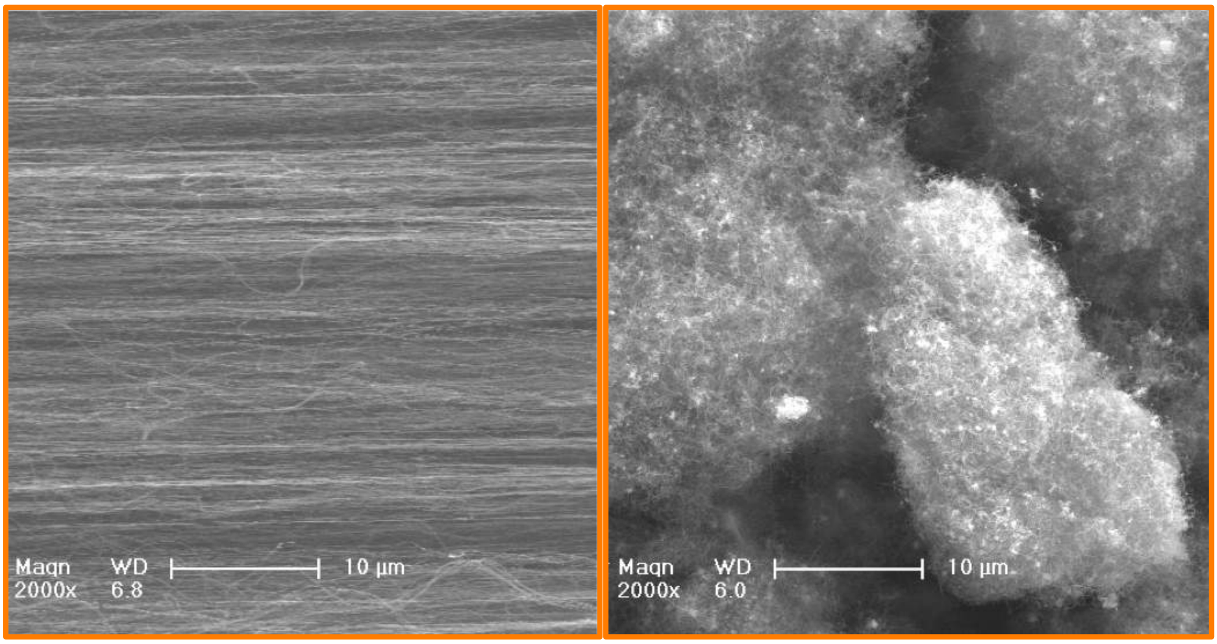


Fig.2. SEM images of SACNT and ordinary CNT. a. SACNT, b. ordinary CNT.

The as-produced sheets are transparent and highly conductive, which is also distinguished from random CNT films by their “unidirectional” nature, that is CNTs in it are parallel-aligned in the draw direction and end-to-end jointed forming continuous thin films. Another very important property of the SACNT is that the CNTs are super aligned so that along the direction that is perpendicular to the drawing axis, called radial direction, the flexibility and stretchability are the best in comparison with the random CNT films or even with the other direction. On the other hand, if the CNTs are bundled together in a twisted manner, the CNTs along the perpendicular direction are more easily broken, and therefore its stretchability is less relaible. This fascinating property is the foundation of using SACNT to make strain sensors, which can have better performance. Fig. 3 demonstrates the stretchability of SACNT and random CNT. Our experimental results will verify the assumption.

Fig.3 Comparison of stretchability of SACNT and random CNT

Typically, an SACNT array with an area of 0.01 m^2 can be totally converted to a SACNT film of about 6-10m^2, depending on the height of the SACNT array. The SACNTs are very straight and few defects. The SACNT approach is advantageous due to the simple fabrication process and low cost, which are favorable for industrial scalability. SWCNTs, on the other hand, are expensive, and they usually become tangled during industrial CVD growth, resulting in abundant conglomerations of SWCNTs in the dispersion step. The removal of such conglomerations also means that only a very small fraction of SWCNTs can be utilized to fabricate strain sensors.

In summary, the properties of SACNTs are that they have higher surface density and better alignment than ordinary CNTs. The super properties make them ideal candidates for stretchable strain sensors, with the stretchable direction being perpendicular to the drawing axis. In addition, the SACNTs are easily made at a low cost because of simple fabrication. Therefore, SACNTs are favorable for industrial scalability.

4. METHODS/EXPERIMENTS

4.1 Synthesis of SACNT

Many groups have reported that they are able to synthesize CNT arrays. However, very few groups have successfully synthesized super aligned arrays, which was patented by Tsinghua-Foxconn Nanotechnology Research Center, where I conducted all of my experiments.

The method we used to synthesize SACNT is chemical vapor deposition (CVD) [6]. Chemical Vapor Deposition (CVD) is a chemical process used to produce high-purity, high-performance solid materials [8]. The process is often used in semiconductors to produce thin films. The advantages of CVD are its simple setup and operation and its easy scale-up at low cost. Therefore, the CVD method has been widely used. During a standard CVD, a substrate is coated with a layer of metal catalytic nanoparticles, most commonly nickel, cobalt, iron, or a combination of elements. The size of the catalytic particles can be controlled by patterned deposition of the metal. To initiate the growth of nanotubes, two gases are blended into the reactor: a process gas (such as ammonia, nitrogen or hydrogen), and a carbon-containing gas (such as acetylene, ethylene, ethanol or methane). Nanotubes grow at the sites of the metal catalyst; the carbon-containing gas is broken apart first at the surface of the catalytic nanoparticles, and the obtained carbon fragments are transported to the edges of the catalytic nanoparticles, where the carbon fragments form into the carbon nanotubes. The catalytic nanoparticles can stay at the tips of the growing nanotubes during the growth process, or remain at the nanotube bases, depending on the adhesion between the catalytic nanoparticles and the substrate. The diameters of the nanotubes that are to be grown are related to the size of the metal particles. Fig. 4 shows a schematic diagram of the growth mechanism in general.

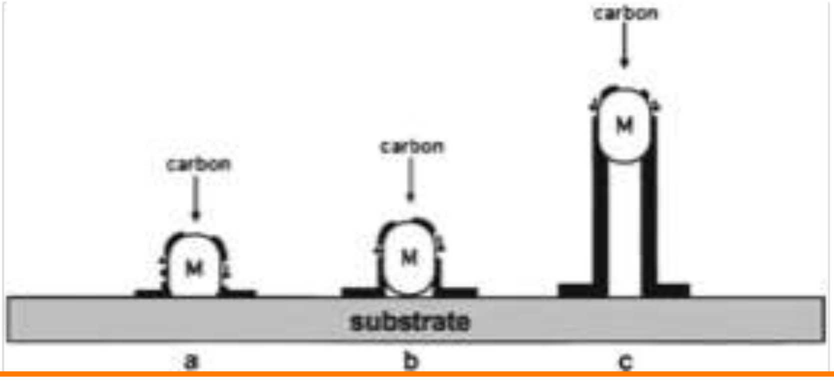


Fig.4 Schematic illustration of the growth mechanism.

As is known, for CNT growth by a CVD method, hydrocarbon precursors are first cracked by a catalyst heterogeneously and then carbon atoms are incorporated into the CNTs after transportation through the catalyst [6]. This is the normal axial growth process of CNTs. However, there are other processes involved in the CVD growth of CNTs. The first one is that hydrocarbon molecules decompose over the surface of the CNTs, another one is that pyrolysed carbon atoms can directly be deposited on the surface. Both processes result in the formation of amorphous carbon (AC) over newly grown surfaces, which will substantially decrease the van der Waals force between the CNTs. Therefore, to achieve the synthesis of super-aligned arrays, one has to control some of the parameters, such as partial pressure and temperature, to guarantee a much higher axial growth rate than AC deposition rate. The following precautions turn out to be important in the synthesis of super-aligned CNT arrays. 1) According to the results, the optimal temperature range for low pressure (LP) (2 Torr) CVD is from 680 to 720C. 2) The main requirement for the substrates is a polished flat surface. 3) Another key step is preparing densely packed catalyst particles with a narrow size distribution, which will result in CNTs with nearly the same diameter. Consequently the CNTs will have the same axial growth rate, which results in perfect van der Waals bondings from top to bottom.

In order to realize large-scale applications of unidirectional CNT sheets, there are two challenges in this field [7]. The first challenge is how to scale up the synthesis, including enlarging the area of arrays and achieving batch growth. The second challenge is how to achieve controlled syntheses of super-aligned CNT arrays with the desired tube-diameter, number of walls, and length to meet a variety of industrial demands.

Basically, we synthesized SACNT in a control way. The first issue is how to control tube-diameter and length of super-aligned CNT arrays. By controlling the thickness of catalyst films, i.e., the size of the iron Fe, the tube-diameter of super-aligned CNTs can be tuned. The length of super-aligned CNT arrays can be easily altered by the growth time with the longest arrays reaching 900 um.

Our super-aligned CNT arrays were synthesized in an atmospheric-pressure chemical vapor deposition (AP-CVD) tube furnace. Fig.5 shows the experimental setup.

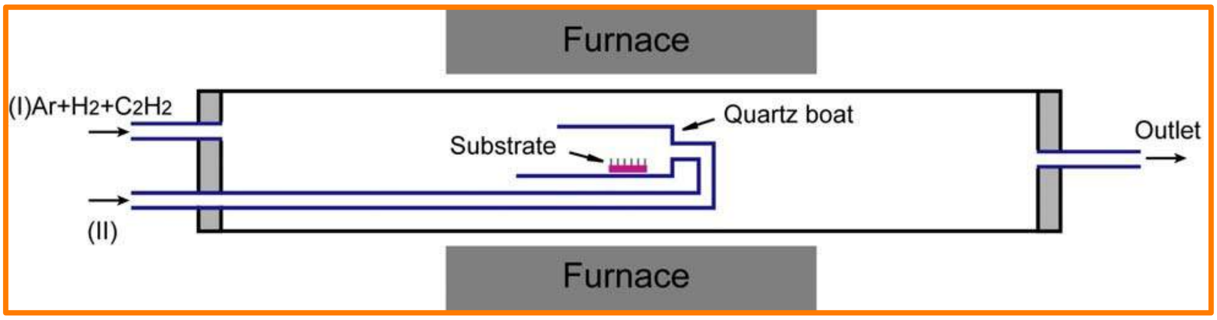


Fig.5 The experimental setup.

The furnace (reactor) consists of a 2.7 cm diameter quartz tube and a semi-opened quartz boat with an inlet that was convenient for controlled operations. The experimental steps to synthesize SACNT are:

1) The substrates were SiO2/Si wafers coated with thin Fe films deposited by electron beam (e-beam) evaporation.
2) The substrate was first placed inside the semi-opened quartz boat
3) The substrate was heated up in the flowing argon gas through inlet II to the growth temperature of 660~680C for 15 minutes.
4) H_2 and C_2H_2 were added to the Argon gas to start the growth of super-aligned CNT arrays
5) Choose $Ar/H_2/C_2H_2$ =200/100/30 sccm at 680C for Fe =0.2nm to get a mean tube diameter of 6.2nm. A/H2/C2H2=200/100/30 sccm at 680C for Fe=3.2nm to get a mean tube diameter of 6.8nm.

We found that the as-grown arrays could not make sheets well if the Argon gas was not flowing into the furnace first. This indicates that the ambient gas has influenced the nucleation process of super-aligned CNT arrays dramatically.

We also found it much easier to synthesize super-aligned CNT arrays with a wide range of thickness of Fe films and growth conditions in our semi-opened quartz boat, compared with the synthesis in a totally opened one. The main difference between these two cases is likely to be the local flow rate and flow pattern of the reaction gases caused by different geometry around the substrates.

4.2 Synthesis of SACNT Strain Sensors

To get SACNT strain sensors we need to transform vertically aligned CNTs into horizontally aligned thin sheets. And the radial direction which is perpendicular to drawing axis becomes very flexible since they are super aligned, and not twisted. The process to make sheets is as follows:

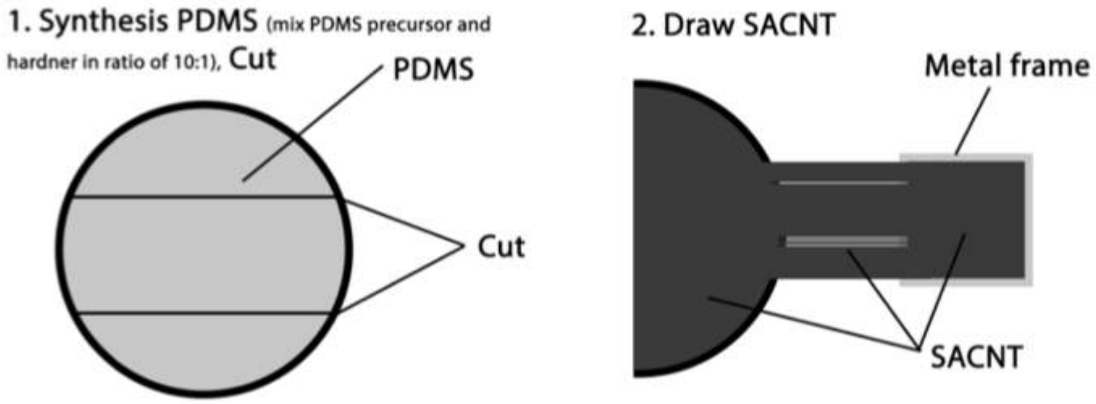
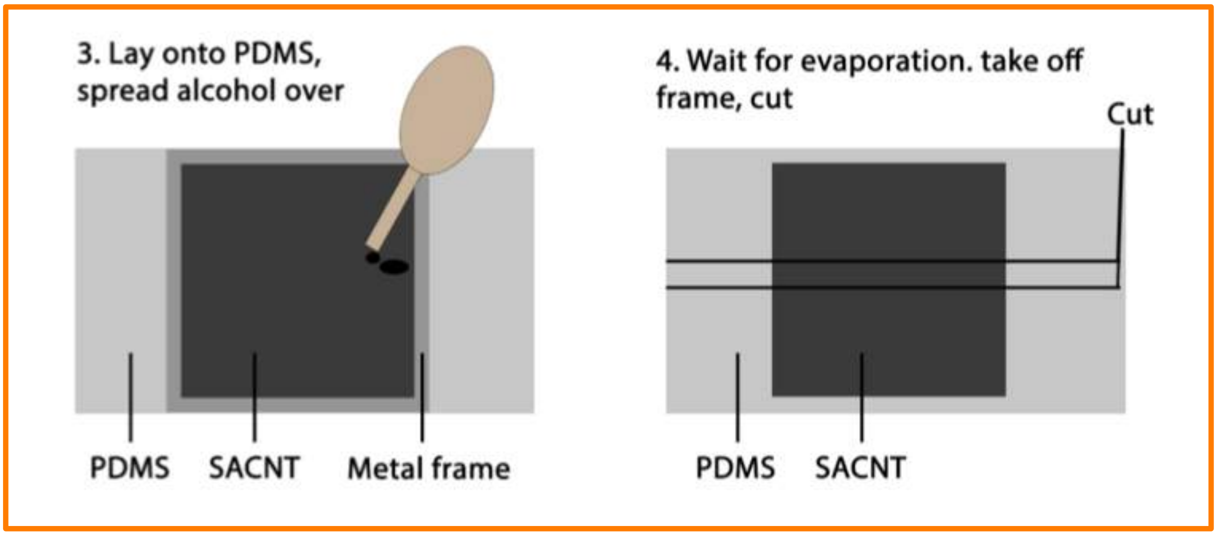


Fig.6 (above and below). Schematic illustration of making SACNT strain sensors.



1) Synthesize PDMS: PDMS precursor and hardener in ratio of 10:1 at 80C for 30 minutes
2) Draw SACNT into drawing direction
3) Lay onto PDMS, spread alcohol over in order to prevent sticky of neighboring layers or sticky to ambient environment
4) Wait for evaporation, take off the frame and then cut to get the size of the strain sensor you want to have

The unique features of super-aligned CNT arrays are that the CNTs have very clean surfaces, and consequently there are strong van der Waals interactions between them. When pulling the CNTs from a super-aligned array, it is the van der Waals force that makes the CNTs join end to end, thus, forming thin sheets which can be cut into a strain sensor with any desirable size. The stretch direction is perpendicular to the drawing direction, in which it is ideally the most flexible.

5. RESULTS OF THE SACNT STRAIN SENSOR

Several experiments were conducted to test the linear relationship between strain and resistance, durability, creep, and the relative change in resistance for the initial loading and unloading cycle for both non-packaged and packaged sensor.

1) Relative change in resistance versus strain for the SACNT strain sensor
   Fig.7a. demonstrates a monotonic increase up to 380% strain (strain speed at 10%/sec) at which point the PDMS substrate ruptured. This monotonic increase in resistivity with strain demonstrates the potential use of the SACNT sensor as a gauge to measure strains much higher than the 5% limit of conventional metal strain gauges.
   The result indicates that the sensor can be stretchable in a very large range.

2) Relative change in resistance for the initial loading (red) and unloading (blue) cycle
   Fig. 7b. Both loading phase and unloading phase showed the linearity between relative change in resistance and the strain. This indicates that the linear relationship holds in both conditions.

3) Relative change in resistance during cycles between 0 and 100% strain
   Fig.7c shows relative change in resistance with an up-and-down shape (linear increase and linear decrease) of strain change. The response (blue) to the strain shape (red) is very consistent.

4) Relative change in resistance in response to a 0-100% step function of mechanical strain.
   Fig. 7d showed the sensor was cycled between 5% and 100% strain at a speed of 10%/sec and with a recovery time of 5s. The response of the carbon-nanotube strain sensor to the strain was fast, with a lower overshoot of 2% and recovery time of 5s. This is markedly different from the 8.8% overshoot and more than 100s recovery time observed for polymer composites with conductive fillers, even with a three times lower strain speed [2]. The delay time was in the range of milliseconds.

5) Durability test
   Fig. 7e. Relative change in resistance versus strain for multiple-cycle tests – 3000 cycles at 100% strain at 10%/sec.

6) Inset of durability test
   Fig. 7f shows an inset of the durability test presented in Fig. 7e of the 2501th to 2510th cycle.

There have been several reports of the individual strengths and advantages of other stretchable materials, but no material has achieved this level of stretchability and durability. The SACNT material has low cost and can be made in a large scale, which is favorable for the requirement of industrial applications. The traditional and rigid metal strain gauge can only hold up to 5% strain before it breaks.

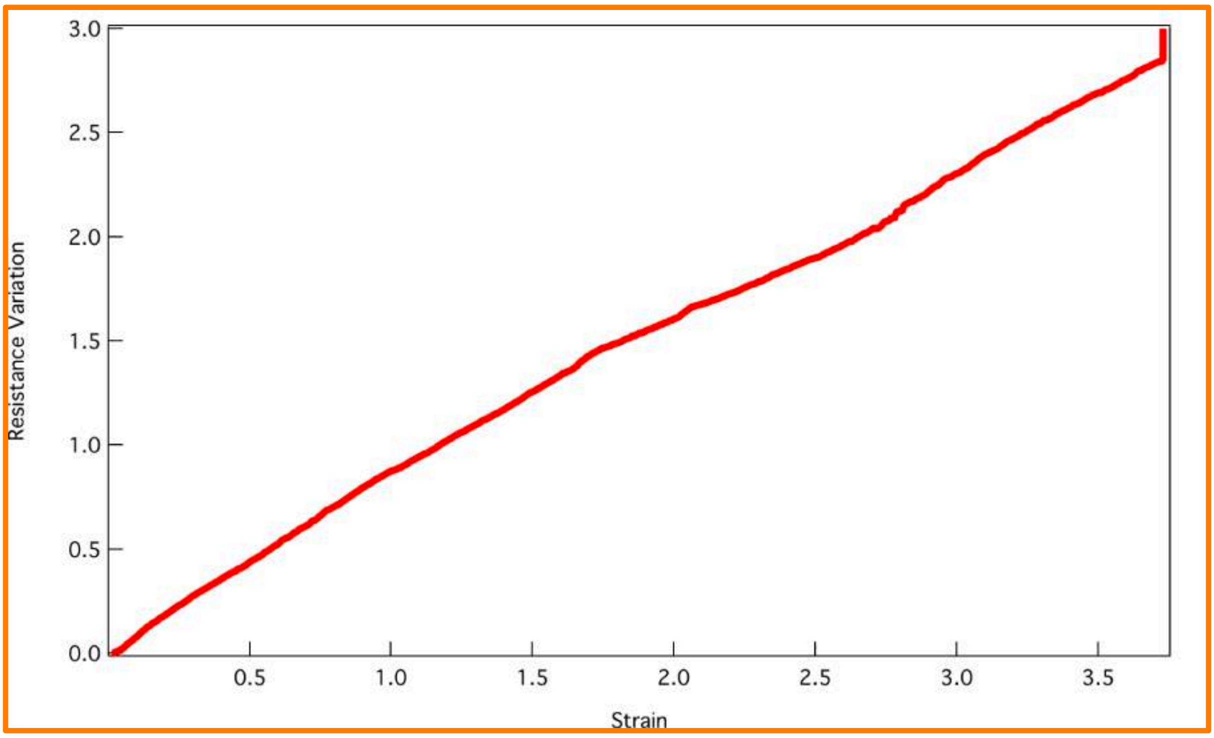


Fig.7(a) Full strain

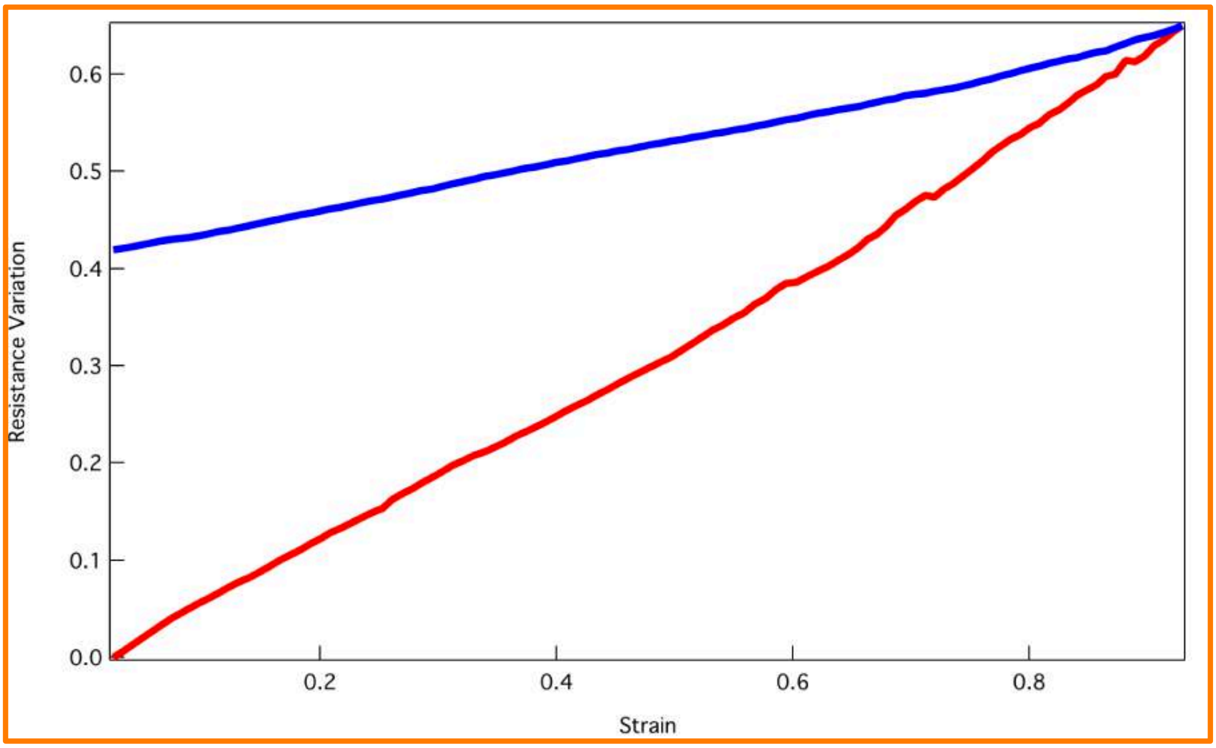


Fig.7(b) Initial loading and unloading.

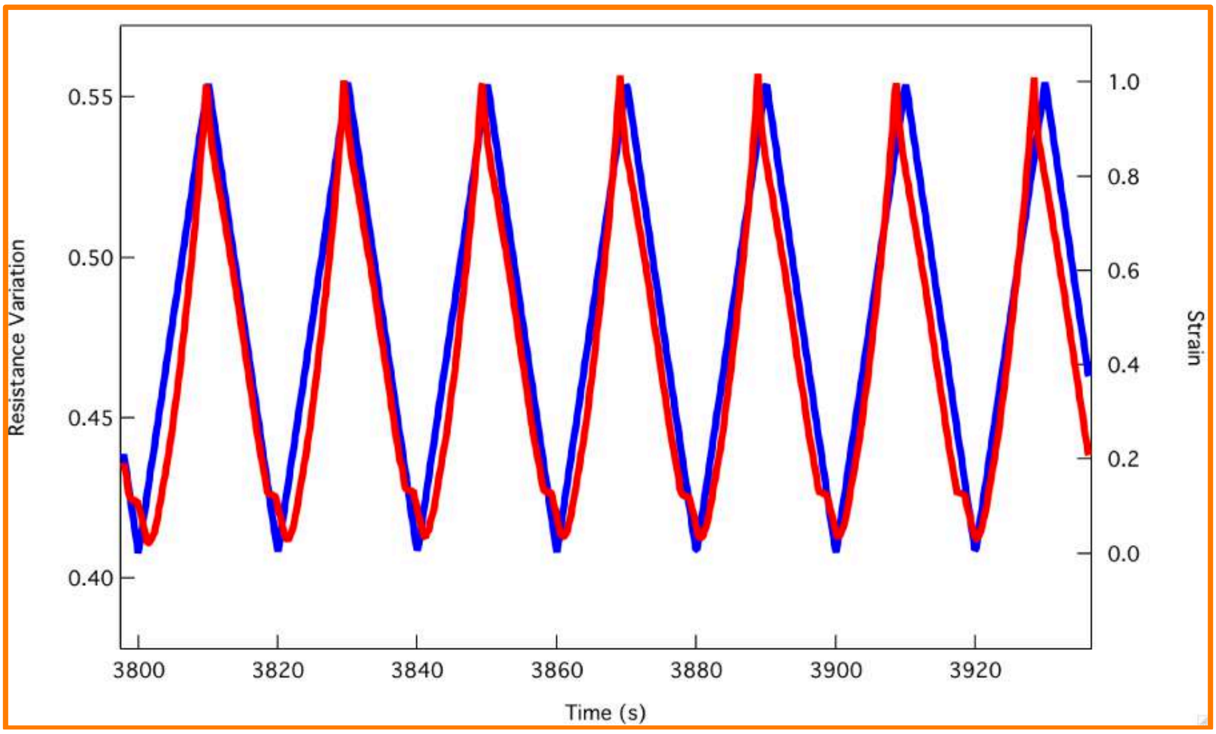


Fig. 7(c)

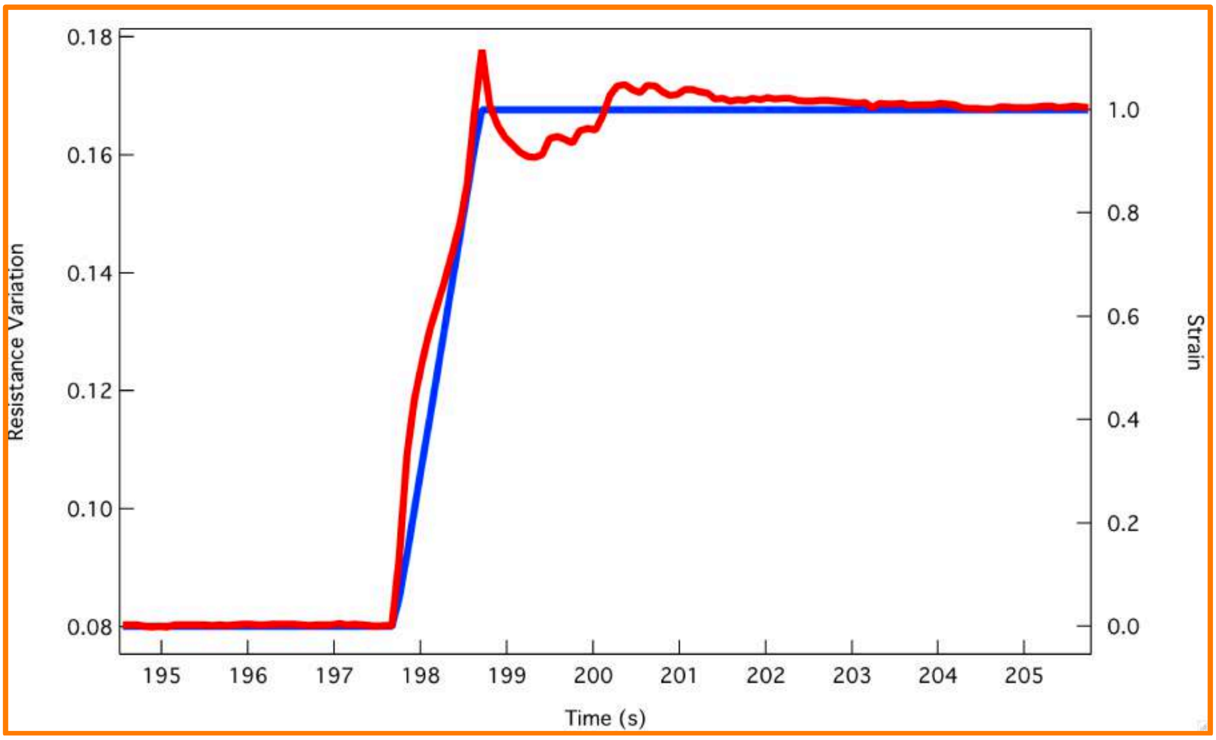


Fig.7(d) Response to a step function.

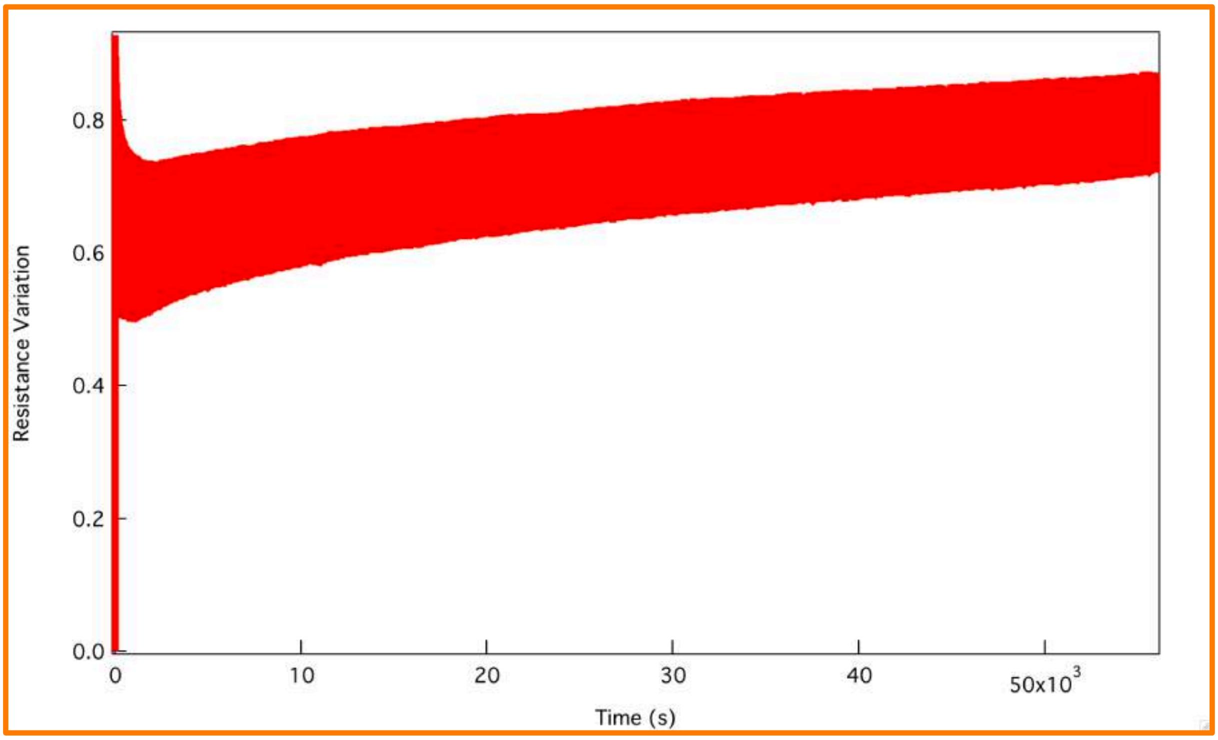


Fig.7(e) Durability test

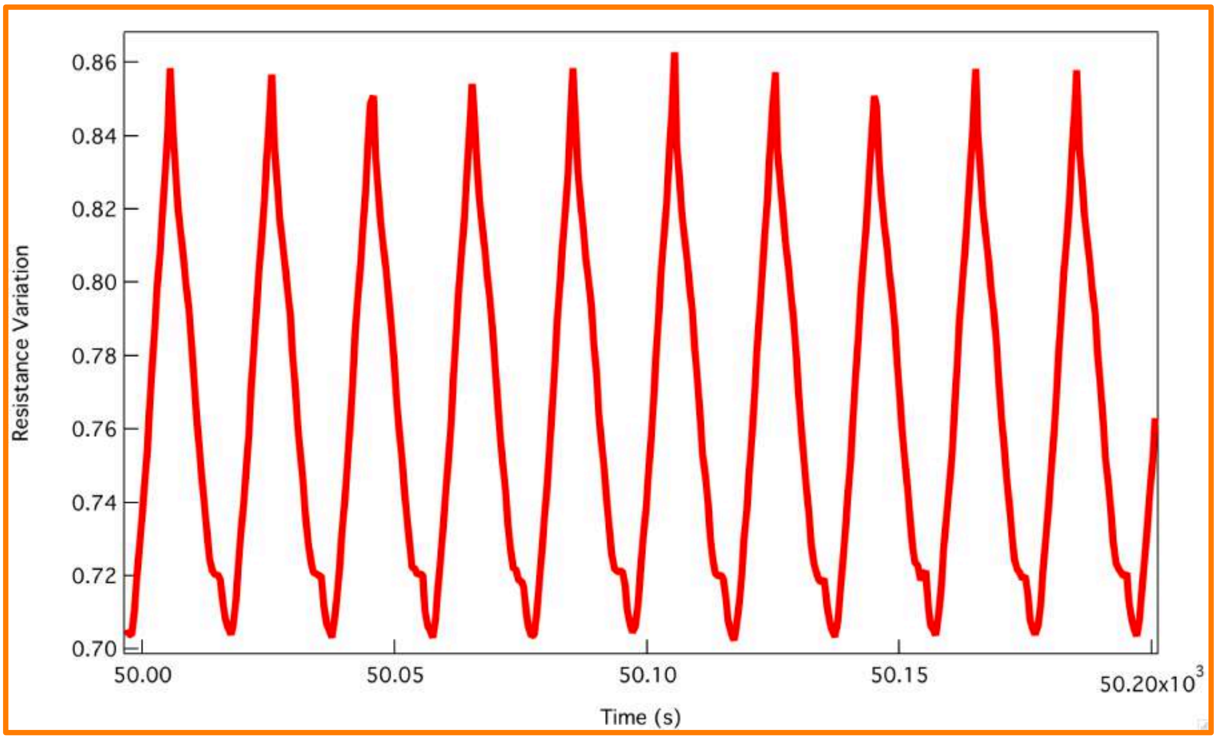


Fig.7(f) Inset of durability test

6. APPLICATIONS

6.1 Step Counter

To demonstrate the potential of the SACNT sheets in stretchable and wearable devices, I made a simulated step counter (pedometer) that counts steps taken by using SACNT as strain sensor. The stretching device (stretching a SACNT strain sensor), which stretches and releases the sensor at a linear rate, is connected to an Arduino micro control unit, to create a counter. This device verifies that the SACNT strain sensor is capable of making stretches and measuring strain accurately, which then converts to a number of steps. Fig.8 illustrates the device.

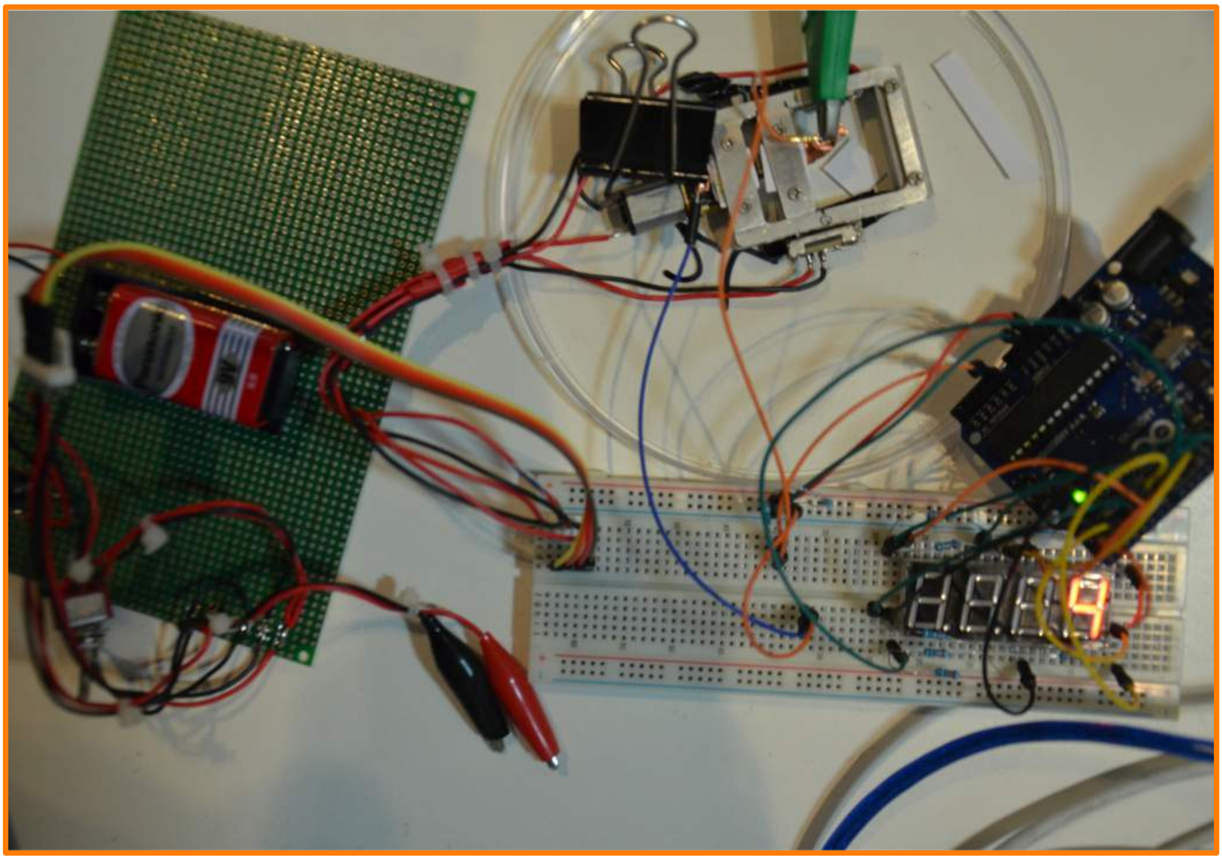


Fig.8. Setup of the step counter using SACNT strain sensor

When the sensor is stretched by the motor continuously, the screen shows the number increases. It indicates that the SACNT strain sensor stretches appropriately.

6.2 Data Glove

In order to demonstrate that the SACNT strain sensor can reflect the linear relationship between strain and resistance when it is bent in any range of motion, i.e. mimicking the motion of the human body, I made a data glove. The data glove was made from five independent SACNT strain sensors that covered the main knuckle on each finger and assembled on a single glove. The data glove is an interactive device, resembling a glove normally worn on the hand, which can facilitate fine-motion control in robotics and virtual reality. Fig. 9 shows the date glove with five independent SACNT strain sensors assembled on a tight cloth-made glove.

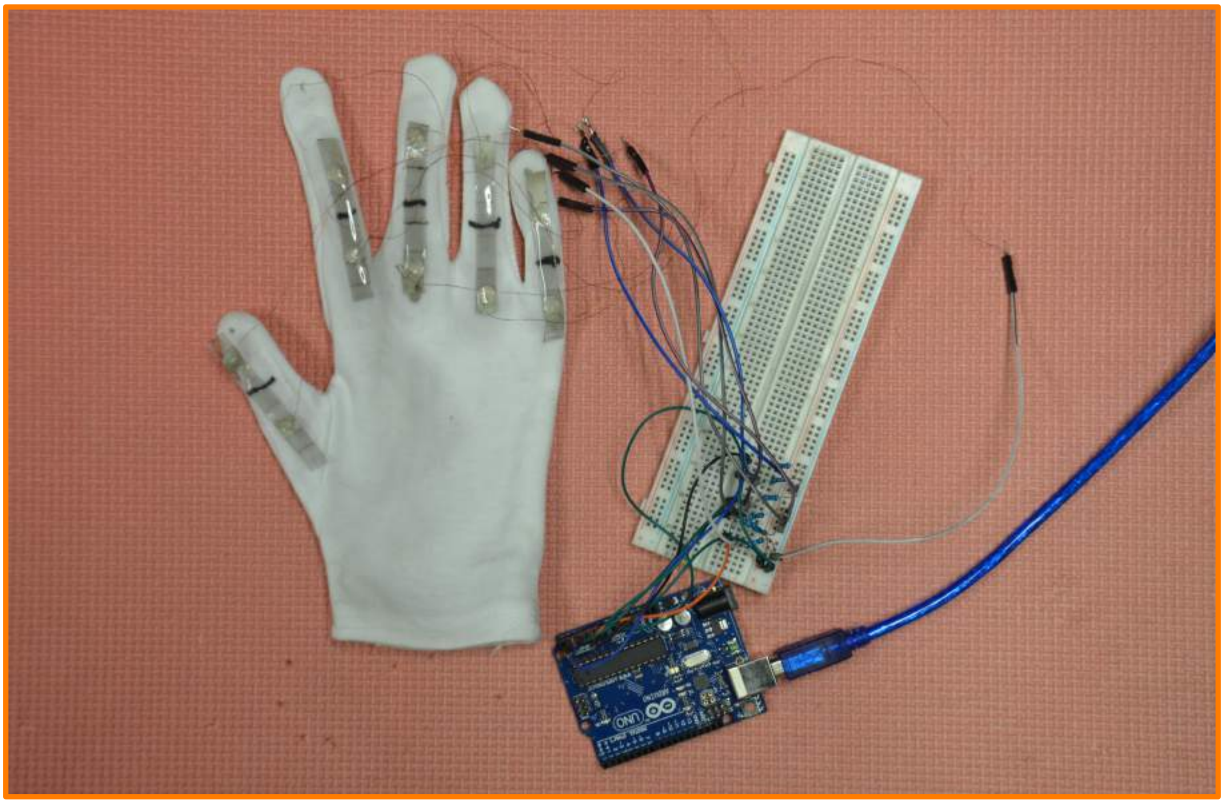


Fig. 9 Data glove connected to circuit board and Arduino (micro control unit)

It is very important to handle the junction between the stretchable SACNT sensor and rigid electrodes. It needs not only to conduct electricity well, but also to be glued tightly to avoid mechanical failure.

1) I tried a couple of ways to handle the connecting points. The first method was to use a conductive paste to glue the electrodes and strain sensors together. The second method was to mix the PDMS with graphite to make a conductive paste. In both ways, the conductive paste was painted on the ends of the SACNT sensor and dried to form an elastic conductor. Finally, the PDMS glue was used to cover the electrodes, both for reinforcement and to fix the device onto the glove.
2) I also tried two methods to handle the sensors – a packaged sensor with a covering layer of PDMS, and non-packaged sensor. The results showed that the packaged sensors perform more stable since the packaging helps to reduce the environmental effects on the sensors.
3) I also tried two different types of textile gloves – a cloth glove and a rubber glove. I found that the tight cloth glove performed better and was more stable.

4) I also tried the data glove with different length of the sensors and found that the longer sensors produce more stable results. The resistance changes for the long length of the sensor will not be easily affected by the unavoidable detected noise as will ones with shorter sensors.

The data glove was connected to the Arduino (micro control unit), and then connected to the computer. Then, a program is created in Processing to plot the live data of resistance in each of the sensors, showing the individual finger movements.

Fig. 11 shows the plot when the index finger bends. The resistance starts to increase and the curves to start to climb up correspondingly. Fig.12 shows the plot when the index finger gets back to unbent position. When the finger completely released, the resistance goes back to baseline. The resistance change reflects the movement of the finger.

Fig.13 shows the plots for movements of five fingers. When all fingers are bent, the resistance increases. When all fingers are released, the resistance goes down to the baseline. The results indicate that the SACNT strain sensor works appropriately when the fingers move in any form. The data glove could detect the motion of the finger precisely. The data glove is light, simple, and does not limit any range of motion of the hand. The device demonstrates the potential future applications of SACNT strain sensors. For example, the device might be used as a master hand to control a remote slave robot to remotely perform surgical procedures (telesurgery) or perform tasks that human beings cannot perform directly.

Fig. 11 The bending movement of index finger.

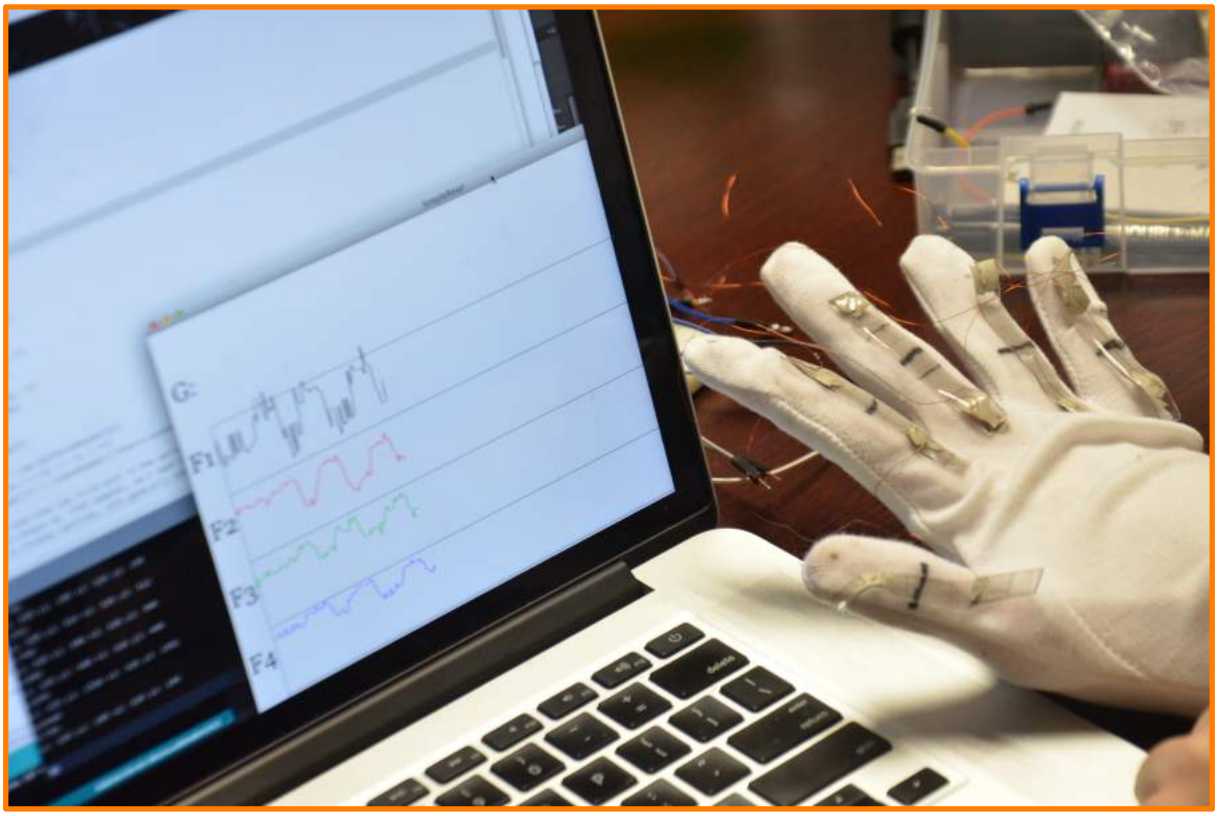


Fig.12 The unbending movement of the index finger.

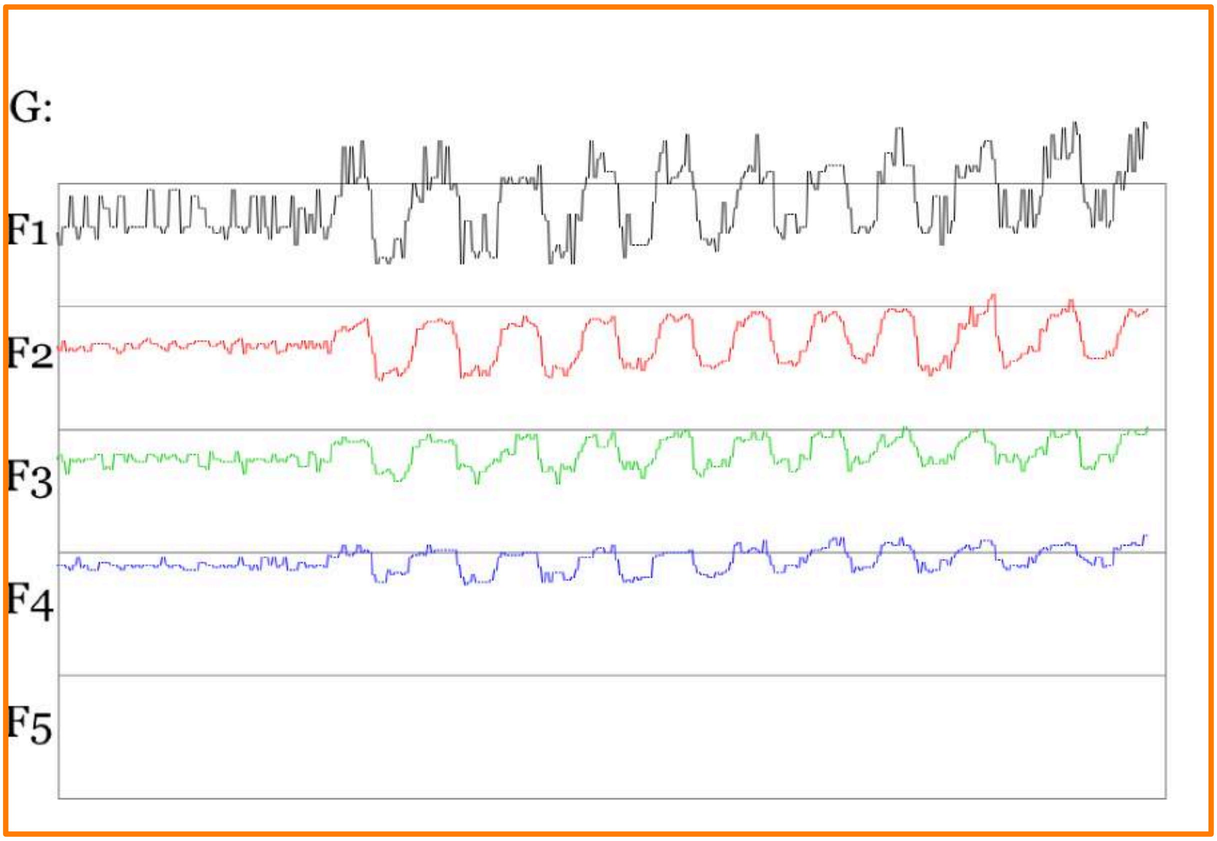


Fig.13. The bending and unbending movements of all five fingers. The plots reflect the movement of each finger.

7. DISCUSSION AND CONCLUSION

SACNT films posses super anisotropic properties, e.g., along the axial axis the electrical and thermal conductivity is much higher than that in the radial direction. Almost all research groups have paid attention to the unique properties along axial direction and demonstrated some applications using high electrical and thermal conductivities, e.g., making transparent conducting films. However, I have found that SACNT film can be a favorable candidate for making a stretchable and flexible strain sensor because of the fact that along the direction perpendicular to the axial direction, the flexibility is much higher than that along the axial direction. Owning to the super aligned nature of SACNT and that no carbon nanotubes are twisted along the axial direction, it is thus much more flexible along the radial direction.

In order to test my findings, I have conducted several tests on SACNT strain sensors to show that the relationship between resistance and strain sensor is linear, the strains can go up to 400% (80 times higher than the traditional rigid metal sensors) with high durability, fast response time, and low creep. To my knowledge, none of the research groups have reported this super performance of SACNT strain sensors. In addition, the SACNT films can be made at a low cost and produced at a large scale. This allows the industrial applications to be possible.

In order to demonstrate potential applications of the SACNT strain sensors, I have made two devices – a step counter and a data glove. The step counter demonstrates the stretchability of the SACNT sensors. The data glove with SACNT sensors glued on each finger demonstrates the wearability of the SACNT strains sensors. The data glove is simple and light, and allows detection of any range of motion of the finger.

In this project, I have demonstrated that the stretchable and wearable strain sensors using a new type of material – SACNT -- can be used to develop human-friendly devices with realistic functions and abilities that would not be feasible by conventional technology. I believe that such devices could eventually find a wide range of applications in industries such as recreation, virtual reality, robotics, and health care.

8. REFERENCES

1. Rogers, J.A., Someya, T. Huang, Y.G., Materials and mechanics for stretchable electronics. Science, Vol.26, March, 2010.

2. Khang, D.Y., Jiang, H., Huang, Y., Rogers, J.A. A stretchable form of single-crystal silicon for high-performance electronics on rubber substrates. Science, 311, 208-212 (2006).

3. Mattmann, C., Clemens, F. & Troster, G. Sensor for measuring strain in textile. Sensors 8, 3719-3732 (2008).

4. Cochrane, C., Koncar, V., Lewandowski, M., Dufour, C. Design and development of a flexible strain sensor for textile structures based on a conductive polymer composite. Sensors 7, 473-492 (2007).

5. Lacour, S.P., Jones, J., Wagner, S., Li, T., Suo, Z.G. Stretchable interconnects for elastic electronic surfaces. Proc. IEEE 93, 1459-1467 (2005).

6. Ren, Z.F., Lan, Y.C., Wang, Y. Aligned carbon nanotubes: physics, concepts, fabrication and devices. Springer Publisher, 2013.

6. Jiang, K.L., Li, Q.Q., Fan, S.S. Spinning continuous carbon nanotube yarns. Nature. Vol.419 (2002)

7. Zhang, X.B., Jiang, K.L., Feng, C., Liu, P., Zhang, L., Kong, J., Zhang, T.Y., Li, Q. Q., Fan, S.S. Spinning and processing continuous yarns from 4-inch wafer scale super-aligned carbon nanotube arrays. Adv. Material, 18, 1505-1510 (2006)

8. Liu, K., Sun, Y.H., Chen, L., Feng, C., Feng, X.F., Jiang, K.L, Zhao Y.G., Fan, S.S. Controlled growth of super-aligned carbon nanotube arrays for spinning continuous unidirectional sheets with tunable physical properties. Nano Letters, Vol.8, 700-705 (2008).

10. Feng, C., Liu, K., Wu, Jeah-Sheng, Liu, L., Cheng, J.S., Zhang, Y.Y., Sun, Y.H., Li, Q.Q., Fan, S.S., Jiang, K.L. Flexible, stretchable, transparent conducting films made from superaligned carbon nanotubes. Adv. Funct. Mater. Vol. 20, 885-891 (2011).