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Electrical Properties Measurement of Carbon Nanotubes Using Atomic Force Microscope for Nano Sensor Applications

Zhuxin Dong, *Student Member, IEEE* and Uchechukwu C. Wejinya, *Member, IEEE*

Abstract— **In recent years, there has been an increasing interest in monitoring and controlling of pH. It has become an important aspect of many industrial wastewater treatment processes. At the same time, the demand for smaller electronic devices used for various industrial and commercial applications has greatly increased. Micro and nano materials, such as Carbon Nanotubes (CNTs) are known for their excellent electrical and mechanical properties, as well as for their small size, therefore they are good candidates to manufacture micro or nano electronic devices. These devices can be used for pH control. However, this cannot be achieved unless CNTs with metallic or semiconducting band structures can be successfully deposited, separated and aligned. In these processes, microchip fabrication, dispersion of CNTs and their electrical property measurement are involved. In this paper, an Atomic Force Microscope is employed to test the conductivity of both Single-Walled and Multi-Walled Carbon Nanotubes with a conductive cantilever-tip. The I-V characteristics of the carbon nanotubes is obtained to describe their electrical properties. Ultimately, this technological development will lead towards the efficient and effective manufacturing of CNT-based ISFET for pH sensor application.**

***Index Terms*— pH, CNT, AFM, ISFET**

I. INTRODUCTION

CARBON Nanotubes (CNTs) closely resemble hollow graphite fibers that exist in entangled bundles of tens to hundreds. They come in two different forms: Multi-Walled Carbon Nanotubes (MWCNT) and Single-Walled carbon nanotubes (SWCNT). SWCNTs and MWCNTs range in diameter from 1-10 nm and 10-50 nm respectively. About 70-80% of SWCNT tend to contain semiconducting properties, whereas 70-80% of MWCNT tend to contain metallic properties [1-3]. CNTs have also been known to possess remarkable electrical, mechanical, and thermal properties [4]. Metallic CNTs can be used as connecting wires for Micro-Electro-Mechanical Systems (MEMS) and Nano-Electro-Mechanical Systems (NEMS) because of their size and low resistance, while semiconducting CNTs can be used for nano transistors [5]. In order to determine the band structure, an advanced Atomic Force Microscope (AFM) with Current Sensing AFM (CSAFM) function is employed.

Utilizing Agilent 5500-ILM AFM, a general approach has been developed to determine the conductivity of individual nanostructures while simultaneously recording their structures. Conventional lithography has been used to contact electrically single ends of nanomaterials, and a force microscope equipped with a conducting probe tip has been used to map simultaneously the structure and resistance of the portion of the material protruding from the macroscopic contact [6]. Today, with rapid development of modern technology, AFM has been playing an important role in many areas, especially for applications in micro and nano scale. With this CSAFM function, many experiments related to particle electrical properties can be realized efficiently, including impedance measurement and testing of I-V characteristic. Hence, exploiting this advantage, an approach to measure the electrical properties of CNTs based on AFM has been developed and the results are presented in this paper.

Consequently, biomedical engineers have exploited primarily the possibilities of the chip technology to develop silicon-based sensors, which has been incorporated in the tip of a catheter since 1970. This technology should provide the clinicians with cheap sensors on electronic micro chips, which would become continuously cheaper, even with improved characteristics. Moreover the reproducibility of sensor characteristics should be highly improved compared to the usually piecewise-assembled sensors, due to the replication procedure on which the silicon technology relies. Therefore, many of the first papers on silicon sensors appeared in biomedical engineering literature, for example with respect to the development of ion sensors. Ion-Selective Field-Effect Transistor (ISFET) pH sensor [7] is one of the most well-known examples. Furthermore, with more study on CNTs, CNTs with metallic and semiconducting properties may have a huge potential to produce more compact devices for pH measurement applications based on ISEFT. However, CNT-based ISFET for pH control application has not yet been explored. If this is made possible, it will be a significant contribution for applications in

Zhuxin Dong is Ph.D. Candidate in the Department of Mechanical Engineering, University of Arkansas, Fayetteville, AR 72701 USA (corresponding author to provide phone: 479-575-6821; fax: 479-575-6982; e-mail: dzhuxin@uark.edu).

Uchechukwu C. Wejinya is an Assistant Professor in the Department of Mechanical Engineering, University of Arkansas, Fayetteville, AR 72701 USA (e-mail: uwejinya@uark.edu).

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various areas, including medicine, biology and industry.

II. CNT BASED ISFET

A. ISFET

An ISFET is generally used to measure ion concentrations in solutions. When the ion concentration, such as pH, changes, the current through the transistor will change accordingly. Here, the solution is used as the gate electrode instead of the traditional metal gate. The voltage between substrate and oxide surfaces arises due to an ions sheath. Actually, an ISFET's source and drain are constructed similarly as a Metal-oxide Semiconductor Field-Effect Transistor (MOSFET) [8]. Although an ISFET is very similar to a MOSFET, there are still some differences. As shown in Fig.1, the metal gate is replaced by the metal of a reference electrode, whilst the target liquid in which this electrode is present makes contact with the bare gate insulator. Both of them have the same equivalent circuit. Then, devices with this structure can be applied to pH measurement [7]. However, the final objective of our work on Nano pH sensor is to enhance the inversion layer with CNTs as nano wire to conduct electrons between the drain and source, the drain current might be much greater under the same gate voltage. Furthermore, the semiconducting CNTs are able to be fabricated as transistors. If all of these are verified, then these devices could be fabricated, manufactured and cheap earning to CNT’s unique mechanical and electrical properties, such as high current carrying capabilities.

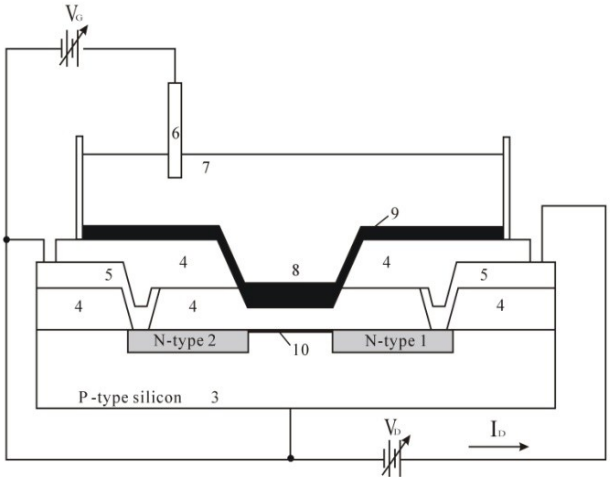

Fig.1. Schematic diagram of a composite gate, dual dielectric ISFET: 1 drain; 2 source; 3 substrate; 4 insulator; 5 metal contacts; 6 reference electrode; 7 solution; 8 electroactive membrane; 9 encapsulant; 10 inversion.

B. FET Fabrication

The basic FET structure is originally made up of four layers from bottom up: silicon wafer, 300Å of silicon dioxide, 200Å of chromium and 5000Å of gold, where the gold layer is thick enough to solder for wire bonding, and fabricated using surface micromachining techniques. The fabrication flowchart is illustrated in Fig. 2. For the electrode fabrication, a mask as shown in Fig.3 is first designed for the desired chips. Triangular electrodes with angle of 30, 60 and 90 degrees, with electrode gaps of 1, 2, 5 and 10 microns are designed. 24 micro-chips are fitted on a circular diameter of 125 mm.

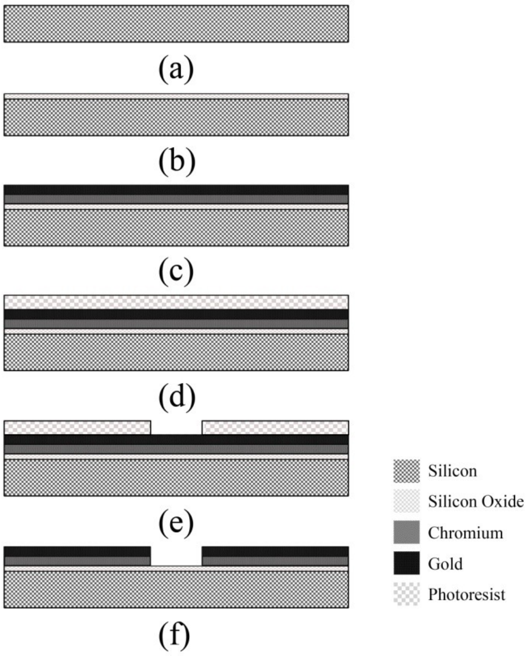

Fig.2. Fabrication process of micro electrode: (a) silicon substrate; (b) 300Å silicon-dioxide by thermal oxidation at 900°C for 1 hour; (c) both chromium and gold are deposited on the silicon dioxide surface by evaporation and electro plating; (d) cover the surface by photoresist layer; (e) photoresist is patterned and exposed; (f) the metals are etched as patterned and the rest of photoresist is stripped off completely.

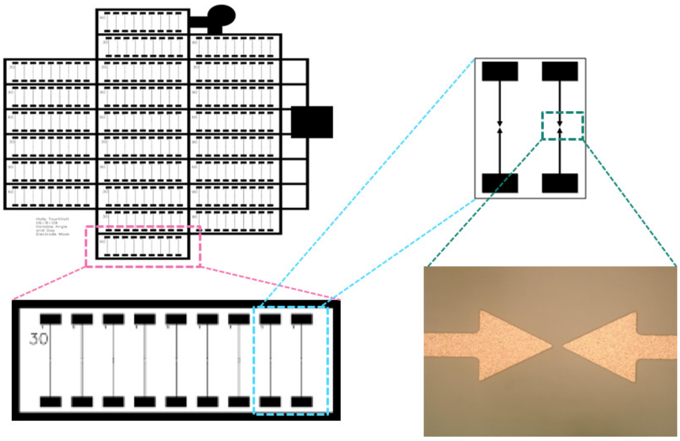

Fig.3. Mask design and Au microelectrodes on Si substrate as FET.

III. ELECTRICAL PROPERTY MEASUREMENT OF CNT USING AFM

A. Theory

To measure the electric properties of CNTs, we need a conductive surface to sustain the tubes. In our experiment, a glass slide is coated by an indium tin oxide (ITO) layer on the top, which guarantees the surface conductivity. A droplet of

CNT solution on the surface is carried out, and the glass wafer is dried by heating. Then the CNT sample is ready for scanning. Agilent 5500-ILM supplies a Current Sensing AFM (CSAFM) capability, where an ultra-sharp AFM cantilever, coated with conductive film, probes the conductivity and topography of the sample surface simultaneously. CSAFM requires a special 10° nose cone containing a pre-amp. A bias voltage is applied to the sample while the cantilever is kept as virtual ground. During scanning, the tip force is held constant and the current is used to construct the conductivity image of the surface. It has proven useful in joint I-V spectroscopy and contact force experiments as well as contact potential studies. Fig.4 shows the schematics how the measurement is done.

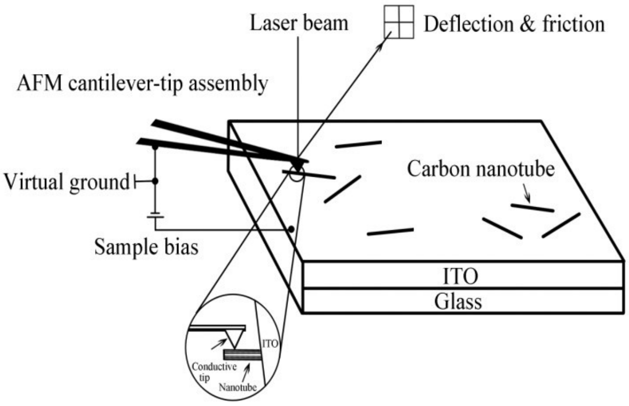

Fig.4. Schematics of electrical properties measurement of SWCNTs through AFM.

B. CNT Solutions

Two CNT stocks, consisting of 0.5mg SWCNTs powder, 998µl DI water, and 2µl Triton; and 0.8mg MWCNTs powder, 1500µl DI water, and 5µl surfactant (Nanosperse) respectively, are used to provide samples. The solution is also sonicated for about 1 hour to achieve uniformly suspended CNTs. Finally, droplets of 20µl from the stocks are deposited on the ITO surfaces to scan.

C. AFM Probe

The resonant frequency and spring constant of the silicon AFM probes are 13kHz and 0.2N/m respectively. These probes are coated by Cr/Pt conductively on both sides. The special nose cone assembled has a sensitivity of 10nA/V.

IV. EXPERIMENTAL RESULTS

A. Preamp

Before measuring the I-V curve of CNTs, the electrical environment in the microscope should be examined by preamp process. A test resistor is employed to construct a connection by placing one end directly on the CSAFM nose cone, held by the spring clip, and the other to the 3-wire EC cable that normally connects to the sample plate. The test assembly then takes the places of the sample and cantilever and then we can run a current versus bias sweep to see if the preamp is operational. The plot should of course be a straight line running from -10nA to +10nA as the voltage sweeps from -10V and +10V. As shown in Fig.5, we can say the electrical circuit is reliable to carry on electrical property measurement.

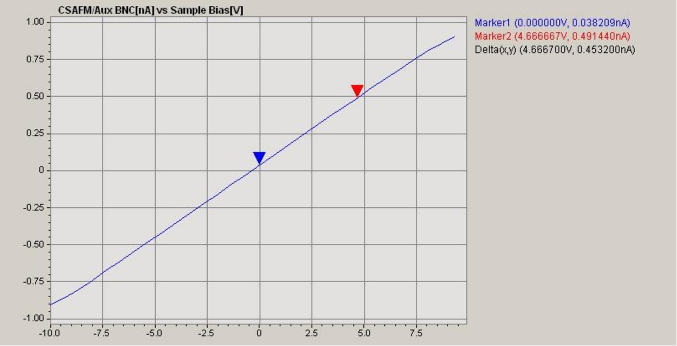

Fig.5. Preamp plot for electrical circuit calibration.

B. SWCNT Measurement

Fig.6 illustrates the topography image of the surface in 10µm square from scanning. In this image, it is clear to find a single-walled nanotube in the middle separating from the others. While scanning the surface, the conductivity map of the same area is also generated with a bias of 200mV as shown in Fig.7. This potential bias is applied from the microscope sample plate, which is connected to the ITO surface through a Cu wire. Afterwards, the scanning is stopped and the tip is moved to contact with the nanotube at one point of its body (see Fig.6) and the set-point, which controls the force of the probe acting on its target, is increased to confirm the electric connection. Next, the sample bias is modified and input in terms of range from -3V to 3V to draw the I-V curve. In Fig.8, we can see the SWCNT has a non-linear curve of CSAFM/Aux BNC vs. Sample Bias. Eventually, a conclusion that these SWCNTs are semiconducting is established.

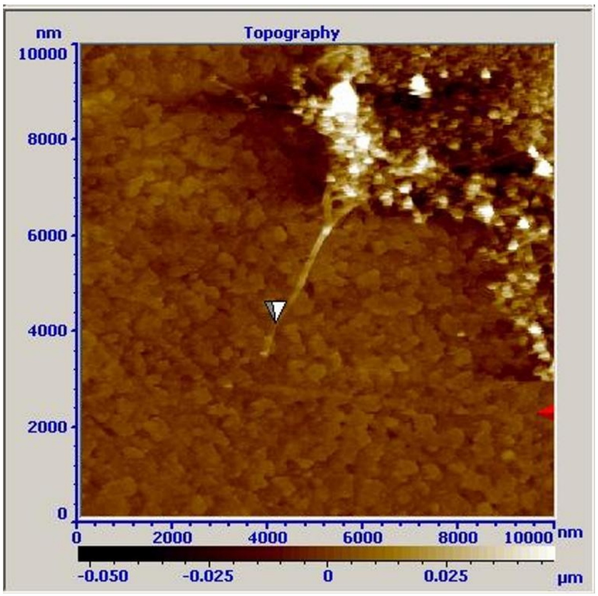

Fig.6. Topography scan of ITO surface with SWCNTs sitting on: the position of white cursor is where the probe tip is located to measure.

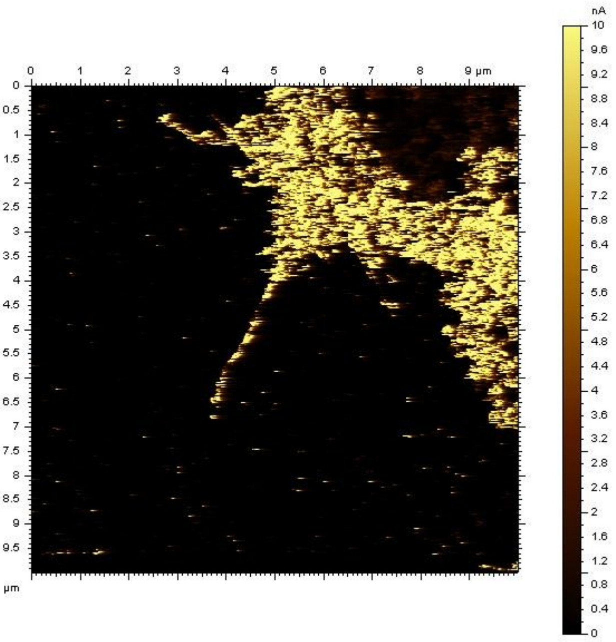

Fig.7. Conductivity map obtained simultaneously with topography at bias of 200mV.

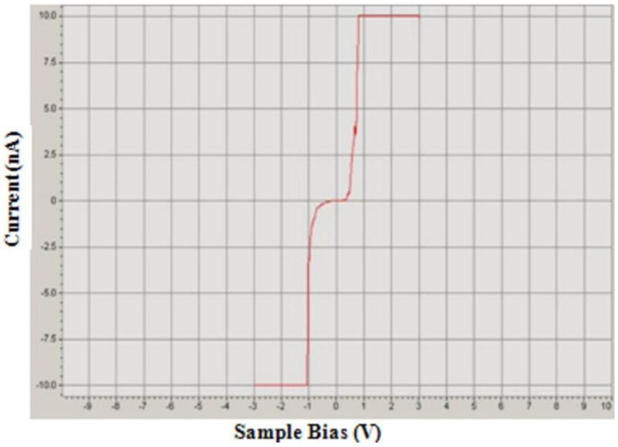

Fig.8. I-V curve measurement on SWCNT body with bias from -3 to +3V.

C. *MWCNT Measurement*

These MWCNTs are 0.5~2μm long and 30~50nm in diameter. Fig.9 illustrates the topography scanning image of the sample surface in a 1μm square in the middle of which a nanotube is forming an “island”. The conductivity map of that area is also obtained simultaneously with a bias of 200mV as shown in Fig.10. After that, scanning is stopped and the tip is moved to contact with the nanotube body (see Fig.11). The set-point, which controls the force of the probe acting on its target, is increased to confirm the electric connection. Then the cross-section information is measured at the location as shown in Fig.11. Fig.12 shows the diameter of this nanotube is about 45nm, which further convinces us it is a MWCNT. Finally, a potential range from -10V to 10V is applied to draw the I-V curve. In Fig.13, we can see this MWCNT has an approximately linear curve of CSAFM/Aux BNC vs. Sample Bias. Eventually, a conclusion that these MWCNTs are metallic is established.

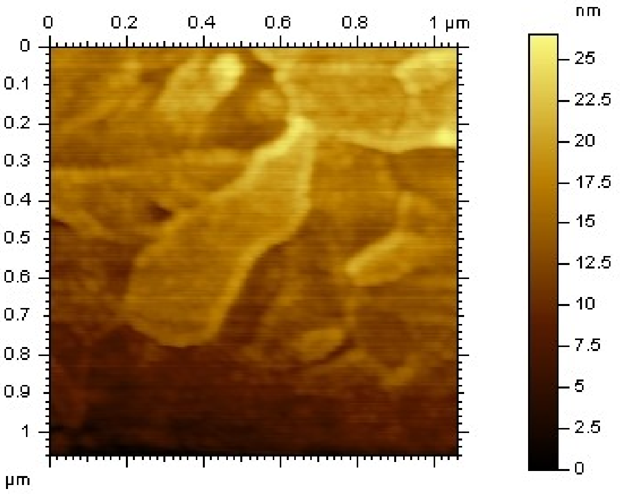

Fig.9. Topography scan of ITO surface with MWCNTs sitting on.

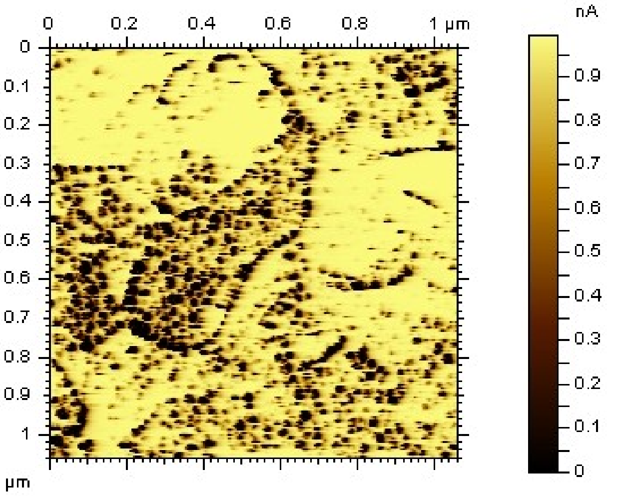

Fig.10. Conductivity map obtained at bias of 200mV.

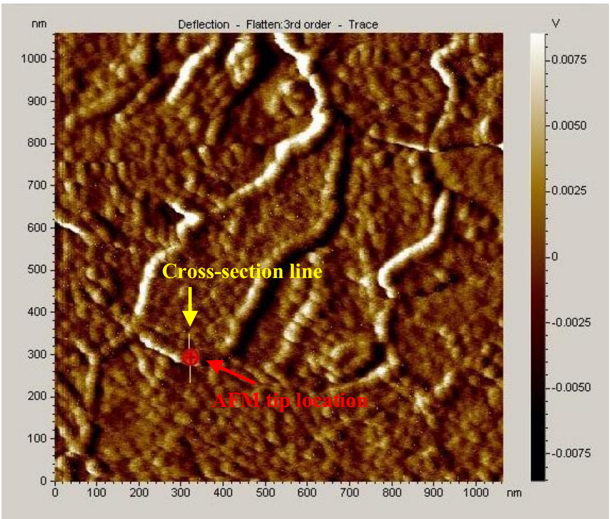

Fig.11. Deflection scam image shows the contact position on the CNT body.

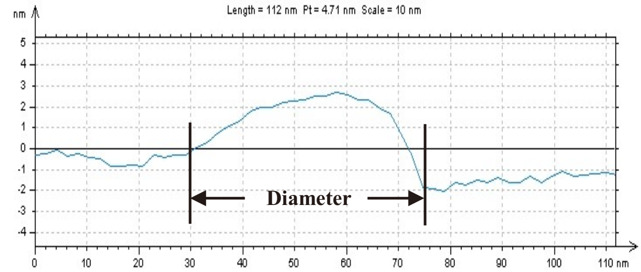

Fig.12. 112nm long cross-section line for CNT size measurement.

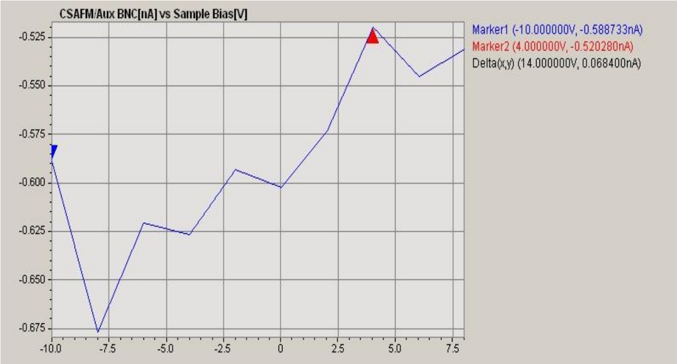

Fig.13. I-V curve measurement on MWCNT body with bias from -10 to +10V.

V. CONCLUSION

In this paper, we have proposed a novel idea for developing CNT based NANO pH sensor based on existing ISFET. The basic FET structure has been fabricated by means of surface micromachining. Furthermore, testing of CNT I-V characteristic was conducted using Atomic Force Microscopy in order to verify their band structure--metallic or semiconducting. CNTs with metallic properties have significant potential to take the place of the inversion layer in ISFET working as the conductive media owing to its unique advantages, such as high current carrying capacity, compact and cheap, while CNTs with semiconducting properties are able to be applied to the manufacture of the transistor in FET. According to the experimental results, we can tell whether the CNTs have metallic or semiconducting properties using CSAFM function. Generally, this novel idea on development of nano pH sensor based on CNTs has great value for research and commercialization.

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