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## Bubbfil Nanotechnology 百博丝纳米科技

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### Song of bubble electrospinning

### Ji-Huan He<sup>\*</sup>

Your geometry makes me sing, my bubble! How beautiful the bubbles are!

The mighty voice in heaven crying, "Hallelujah! Bubble electrospinning."

Could people feel the bubble?
Could Confucius understand the bubble?
Could Newton and Einstein catch the bubble?
Eureka! I got it!

A thin wall,
Geometrically small surface tension,
And a gradual extension under an electrostatic field.

The mighty voice in heaven crying, "Hallelujah! Bubble electrospinning."

Why did the bubble deliver its most important information to me? Why did I happen to receive the most important application for spinning?

Learning is not of master of problems, mastering restricts development.

In my academic career, I seemed to immerse in a no one involved area of interdisciplinary knowledge of textile mathematics, at my last gasp, I caught a bubble firmly!

The mighty voice in heaven crying, "Hallelujah! Bubble electrospinning."

It is God's masterpiece,

And China's hope for nano-industrialization.

<sup>\*</sup> Ji-Huan He, National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, 199 Ren-Ai Road, Suzhou 215123, China; and Nantong Textile Institute, Soochow University, 58 Chong Chuan Road, Nantong, China

### 百博丝赋

### 何吉欢

我惊叹几何的伟大, 感受气泡的优美。

我说:美哉,百博丝。

人们感觉到了吗? 孔夫子感觉到了吗? 牛顿爱因斯坦感觉到了吗? 我感觉到了!

薄的壁,

小的表面张力,

慢慢地被静电拉伸。

我说:美哉,百博丝。

气泡为什么将最有用的信息最先传给我呢? 我为什么最先感觉到了气泡可以用来纺丝呢?

学问在于不懂,学懂就不能发展。

在我的科研道路上,或许掉进了无人的知识海洋吧,奄奄一息的我把气泡紧紧抓住。

我说:美哉,百博丝。

上帝的杰作,

民族纳米产业的希望。

# From nonlocal elasticity to nonlocal spacetime and nanoscience

Wei Tang<sup>1,2</sup>, Ya Li<sup>1,2</sup>, Hai-Yan Kong<sup>1,2</sup>, M.S. El Naschie<sup>3</sup>

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#### **Abstract**

Eringen nonlocal elasticity is extended to an elastic Cosserat-like model of spacetime and a nano/micro scale charged jet in Bubbfil spinning process, respectively, to explain El Naschie's dark energy equation  $E = mc^2$  (21/22) and the hierarchy motion in the electrospinning process.

**Keywords:** Nonlocal elasticity, discrete element method, effective quantum gravity, modified relativity, dark energy, semi-classical field theory, instability, electrospinning, size-effect (nano-effect)

#### To cite this article:

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#### 1. Introduction

Unlike in Einstein's relativity assuming true mathematical continuity, applying Newton's differential calculus in its modern formulation is objectionable not only in condense matter physics and material engineering but also in philosophy [1-3]. In fact we could think in terms of zero and infinity and perform accurate computation without assuming the validity of the "naïve" continuum of classical spacetime geometry [4-9]. It seems that electrical, mechanical and fluid dynamics engineers with an inclination towards fundamental thinking were among the first to realize that there are profound practical consequences for seemingly marginal theoretical concepts such as the rotation of a "point" which is meaningless in the "naïve" conception of the continuum of Einstein's relativity [4,7]. To a reasonable extent, the work of the brothers Cosserat as well as C. Eringen on various physically discrete "granular" elastic and plastic "continua" is well known in engineering science, applied mechanics and mathematics [10-12]. However except for certain extensions of relativity, the deep concept of infinite but "granular" spacetime is relatively far less established in theoretical quantum physics as well as quantum cosmology [13].

The present work is an attempt to show how we can use many fine results obtained within the framework of nonlocal elasticity to resolve fundamental issues connected to

nano science apart of elucidating the density of the "missing" dark energy of the cosmos and its surprising accelerated expansion and even extend these results to become exact by introducing certain "fractal" refinements [14-16].

#### 2. The discrete element model of nonlocal elasticity

In what follows we will assume the reader to be reasonably familiar with the basic facts of Eringen nonlocal elasticity and will not explain it here due to space limitations [10,12]. Luckily however there is a simple finite element like discrete method resembling a Hencky chain-like model developed by the author [10,11] which preserves the main features of nonlocal elasticity and has the considerable advantage of analytical and computational simplicity [10,11]. It is this model which was used by Elishakoff and his school in the USA with considerable skillfulness to reproduce some extremely important results for the purpose of the present work which we will consider next [10]. Following the methodology explained by Challamel, Wang and Elishakoff in [10], the following nonlocal buckling instability Eigenvalue was found (see equations 79 to 84 of Ref. 10):

$$P(nonlocal) = \frac{P(Euler)}{1 + \frac{P(Euler)}{EL/L_c^2}}$$
(1)

where P(Euler) is the buckling load familiar from strength of material of classical elasticity, EI is the bending stiffness and  $L_c$  is the critical buckling length [11]. Interpreting EI/ $L_c^2$  as a second Eigenvalue critical load due to nonlocal effects we could write P(nonlocal) using Dunkerely's well known theorem [11] as

$$\frac{1}{P(nonlocal)} = \frac{1}{P(Euler)} + \frac{1}{EL/L_c^2}$$
(2)

which is nothing but the previous equation for P(nonlocal) written in a different form.

#### 3. Nonlocal spacetime and El Naschie equation

Let us first recall that the Schrödinger equation was inspired by diffusion and wave equations [4] and that it is basically extending the classical quantization of vibration frequencies and buckling loads to quantum energy states [4,11]. Seen that way we could regard  $E = mc^2$  of Einstein's maximal energy as an Eigenvalue while the Planck maximal energy, beyond which measurement is meaningless [4,6,9], is a second Eigenvalue related more to quantum mechanics rather than relativity although Witten's T-duality could be interpreted as setting the Hubble length and the Planck length on similar footing [17,18]. Thus we could start surmising if it would not be possible to combine the two Eigenvalues to find out information about a nonlocal Eigenvalue corresponding to quantum relativity which is effectively a quantum gravity theory [16]. This line of thinking is far from being outlandish in engineering and was in fact used in a similar context to develop the well known Rankin-Merchant formula for elasto-plastic buckling [11]. In this formula the elastic buckling load which could be compared to Einstein's  $E = mc^2$  and the ultimate plastic load which could be compared to Planck energy are combined to obtain a

reasonable estimation of the critical behaviour of columns in the complex elasto-plastic range [11]. That way we could write the following quantum relativity energy equation

$$E(nonlocal) = \frac{mc^2}{1 + \frac{mc^2}{E_p}}$$
(3)

or equivalently

$$\frac{1}{E(nonlocal)} = \frac{1}{mc^2} + \frac{1}{E_p} \tag{4}$$

where m is the mass, c is the speed of light and  $E_p$  is the esoterically large Planck energy thought to be in the region of  $10^{19}$  Gev [3,4,6] [15-24], which can be expressed as

$$E_p = \sqrt{\frac{\hbar c^5}{G}} \tag{5}$$

where  $\hbar$  is the reduced Planck's constant, and G is the gravitational constant.

In [20] Magueijo and Smolin combined quantum field theory, relativity and the idea of varying speed of light in a thoroughly ingenious way to produce a quantum gravity formula corresponding to Einstein's "non-quantum" formula [17-20]

$$E = mc^2 (6)$$

This formula is derived based on continuous spacetime, however, on the Planck scale, any "macroscopic" phenomena are almost disappeared, and the Planck energy can be explained as the energy of "zero" point in Cantonian spacetime.

The Magueijo-Smolin formula is nothing else but our equation No. 4 E(nonlocal) which we just derived using extremely simple analysis. This agreement speaks volumes about the unity of physics, engineering and mathematics. This formula was further extended by El Naschie using unit interval Cantorian physics to reproduce both the ordinary measurable energy of the cosmos E(O) in macroscopic scales and the dark cosmic energy density E(D) in Planck scale [17,18,21]. Readers interested in the subject are referred to the concerned literature [22,23]. In the classical domain  $E_p > \infty$  mc<sup>2</sup>, we have

$$\frac{1}{E(nonlocal)} \approx \frac{1}{mc^2} \tag{7}$$

That means in macroscopic scales, we have Einstein's famous equation

$$E(\text{nonlocal}) \approx E(\text{local}) = E(\text{Einstein}) = \text{mc}^2$$
 (8)

In addition it was found that [6-9]

$$E(O) \approx mc^2 / 22 \tag{9}$$

and

$$E(D) \approx mc^2 (21/22) \tag{10}$$

Eq.(9) is the El Naschie dark energy equation. In other words, quantum mechanics was well hidden inside Einstein's "classical" formula all this time [17-28].

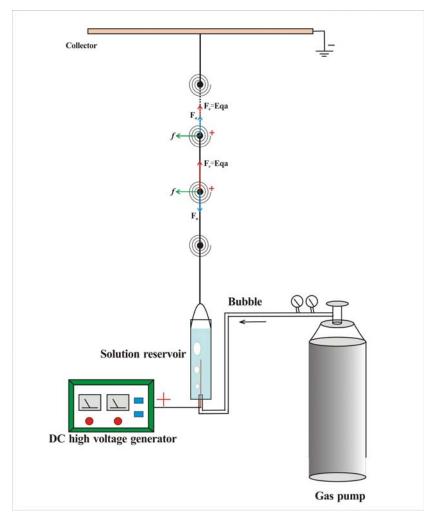


Fig. 1. Nonlocal model for Bubbfil spinning (bubble electrospinning) process

#### 4. Nonclocal Nanoscience

In the view of El-Naschie's E-infinite theory[3], systems in nano-scale may possess entirely new physical and chemical characteristics that result in properties that are neither well described by those of a single molecule of the substance, nor by those of the bulk material[29]. In nano scale, size–effect or nano-effect occurs [30-32] in for example, nano/micro scale charged jets in electrospinning and its modifications including bubble electrospinning[33].

A size-effect[34] is predicted in the stability of the charged jet which changes rapidly from several millimeters to hundreds of nanometers and can be described using a Cosserat-like model[34]. The Cosserat model[34] can best explain the basic property of a spider silk which is an assembly of nanofibers with diameters of about 20 nm[32,35]. The Cosserat model predicts that each slender nanofiber in the assembly will appear more stiff than expected classically[34].

The instability of the micro/nano scale structural problems can apparently be handled efficiently via Eringen's nonlocal elasticity with a nonlocal length scale[10]

$$L_c = \frac{a}{\sqrt{6}} \,. \tag{11}$$

To explain that, let us consider a Bubbfil spinning which is used for polymer bubbles or polymer membranes for fabrication of nano or micro materials including nanofibers, superfine film, crimped nanofibers, and nanoparticles. The nano/micro scale charged jet as illustrated in Fig.1 is discretized into n-cells, the segments connected by elastic rotational springs. The jet is loaded by an axial electronic force denoted by  $F_E = Eqa$ , and by some distributed vertical forces denoted by f and Coulomb forces between two cells.

Generally the distance between two cells scales with the jet diameter is

$$a \propto d$$
 (12)

That means the nonlocal length for instability of the charged jet scales is

$$L_c \propto d$$
 (13)

During the spinning process the diameter of jet changes enormously from several millimeters to hundreds of nanometers and the critical nonlocal length of the jet changes also from a larger value, which corresponds to a larger circular motion, to a much smaller value which results in much smaller circular motion and as a result hierarchy motion of the charged jet is predicted[36] as shown in Fig.2. This is also the reason for the instability of the electrospinning[37].

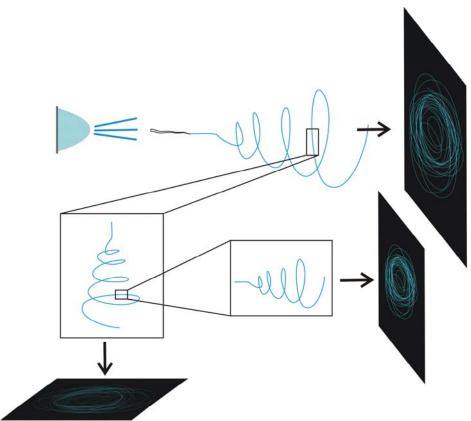
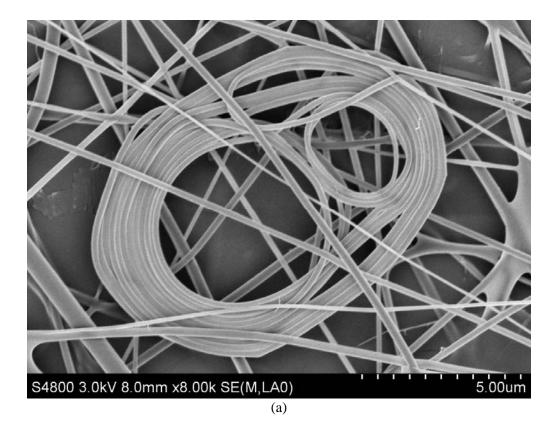
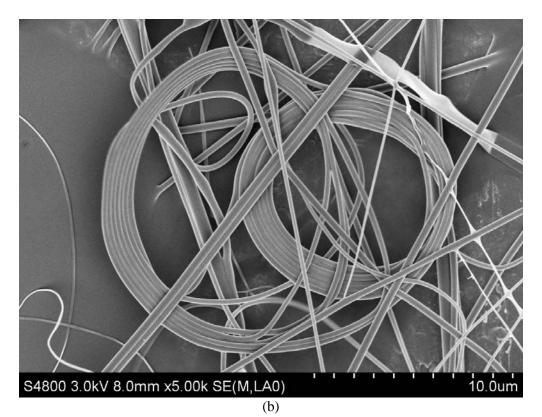


Fig.2 Hierarchy motion in Bubbfil spinning process





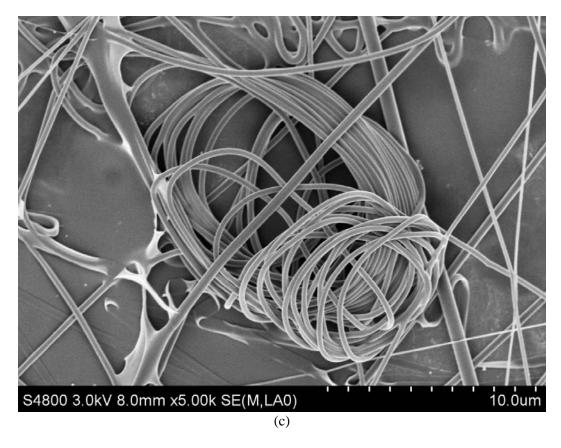


Fig.3 Experimental observation for hierarchy motion

An experiment was conducted to verify the hierarchy motion. Polyvinyl alcohol (PVA) with a degree of 1750±50 was dissolved into distilled water with the temperature 14.9°C and the humidity 32%. Then the mixture was stirred with the aid of electromagnetic stirrer at 90°C for 3 hours to get a homogeneous and transparent solution and cooled to room temperature. The PVA concentration was 8 wt. %. PCM (phase-change material) and was added gradually into the PVA solution until its concentration was 0.5 wt. %. The mixed solution was then put into the ultrasonic cell disruption system for 60 minutes to make it homogeneously mixed. During the Bubbfil spinning (bubble electrospinning), the voltage and collector distance were set as 25KV and 10cm respectively. Fabricated fibers were collected on an aluminum foil. The morphology of electrospun fibers were observed with scanning electron microscopy (SEM, S-4800, Hitachi, Tokyo, Japan) as illustrated in Fig.2, where we can see hierarchy circular motion in different scales.

#### 5. Conclusion

Quantum physics and relativity and nanoscience may seem sometimes to be remote and very far away in concepts and mathematical formulation from classical mechanics [3,4]. The present analysis contests this view and asserts the unity of not only science but also science and engineering and in particular nano technology. Following ideas related in particular to C. Eringen's nonlocal elasticity [10,12], we were able to derive basic equations related to fundamental questions not only in quantum physics and

cosmology but also in nano technology. Thus a formula on multi-Eigenvalues due to Dunkerley was found to combine Einstein's maximal energy  $E = mc^2$  with Planck energy  $E_p \approx (10)^{19}$  Gev [24] to give information on the ordinary energy density

$$E(O) = \frac{1}{22} mc^2$$

and dark energy density

$$E(D) = \frac{21}{22} mc^2$$

of the cosmos respectively. It is a little surprising if not surreal that a quasi-classical field theory like that of Eringen can be used as successfully as a gauge theory for gravity [23,24] and can also be applied in nano technology. Application of the above to more elaborate and various problems in nano technology [25,26] is currently a focus of a small group working with the authors and we hope to report upon that in the near future.

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### Burst of a fast axially moving micro/nano jet

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#### Abstract

In bubble experiments with high electrostatic force, a micro/nano jet is observed, which can be caused to rupture when the jet velocity reaches its threshold value. The collapse of the moving jet is normally violent enough to be observed with the unaided eye, and often generates unsmooth nanofibers due to the high evaporation of solvent associated with the collapse. The process can be used for mass-production of nanofibers.

**Keywords:** Bubble electrospinning, bubbfil spinning, mass production, porous surface, nanofibers

#### To cite this article:

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#### 1. Introduction

Nano/micro scale flows have appeared widely in nanotechnology[1-3], such as MEMS, capillary blood, flows in carbon nanotubes but little was known about the fact that a nano/micro scale flow will burst into smaller daughter jets and that the phenomenon can be used for mass-production of nanofibers. When an axially moving jet, which is formed from a ruptured polymer bubble or film, is accelerated by an electrostatic force, it becomes thinner and thinner until it reaches a threshold value when the jet will burst into hundreds of daughter jets, the process of which is called as the bubbfil spinning process[4]. Attempts to understand the process have mostly focused on fabrication of smooth nanofibres. However, the precise mechanism of the burst jet is rare and preliminary. Here we show the mass conservation plays an important role. We demonstrate that the diameter and the velocity of the jet are the crucial parameters that are necessary to understand the various observations referred to above. We identify the conditions required for a ruptured jet to form smaller daughter jets. We also find that there is a critical velocity to induce daughter jets, below which only a smooth fiber is predicted. We anticipate our assay to be a starting point for a more sophisticated study of the bubbfil spinning and for mass-production of nanofibres.

Nanotechnology is of indispensable importance for the scientific and economical revival of each country. Similar to the nuclear age, as explained by El Naschie[4], the nanoage will be something of a Hemingway line of demarcation between the have and the have nots, and mass-production of nanomaterials becomes an urgent problem needing to be solved as quickly as possible.

Some effective approaches to mass production of nanofibers appeared in literature[5-9]. However, none of the techniques can be used for industrial applications with a high output of, for example, tens of tons of nanofibers per day. Among all the possible techniques electrospinning has caught much attention due to its simplicity. This technology uses a high electrostatic force to overcome the surface tension of a Taylor cone for fabrication of micro/nano fibers, the diameter of the jet during the spinning process changes 4~6 orders of magnitude from, for example, 10mm of the initial detachment diameter after the Taylor cone or a macro liquid in needless electrospinning process to 100nm of the final fibers, and the spinning process is totally uncontrollable. Furthermore the low throughput hinders its industrial applications.

#### 2. Bubbfil spinning

To solve the problem we develop a bubbfil spinning process[4], see Fig.1, which uses electrostatic force (bubble electrospinning[10]) or blowing air (Blown bubble electrospinning[11]) to overcome the surface tension of polymer membranes[12,13] or polymer bubbles[10,11] for mass-production of nanomaterials. The most interesting property of a bubble is that its surface tension depends geometrically upon its size. According to the Young-Laplace equation[14,15,16], the surface tension of a spherical bubble can be expressed as

$$\sigma = \frac{1}{4} r \Delta P \,, \tag{1}$$

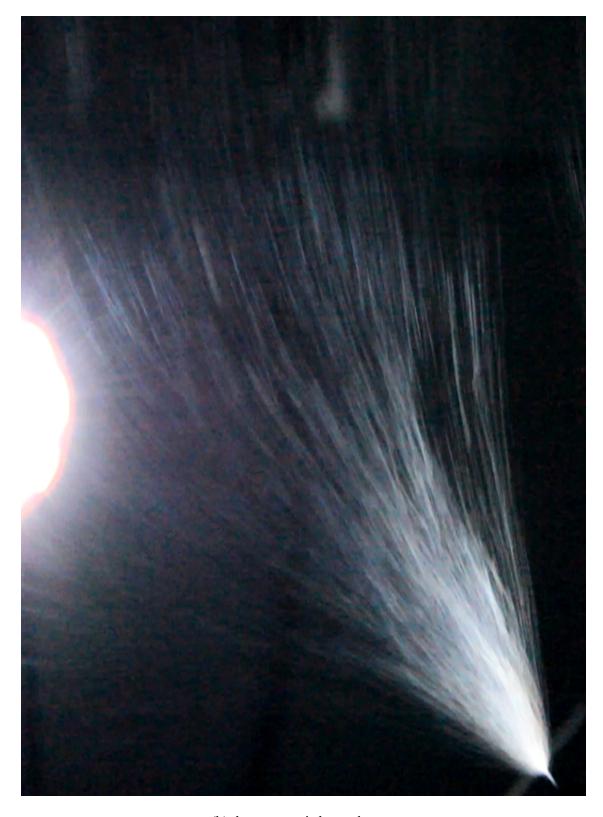
where  $\sigma$  is the surface tension, r the radius of the bubble,  $\Delta P$  the pressure difference. This formulation is still valid for nano-bubble surface tension [17,18].

Polyether sulfones (PES) particles were bought from Sinopharm Chemical Reagent Co. Ltd. (injection-moulding grade). N, N- Dimethylacetamide (DMAc, molecular weights: 87.12, density: 0.938~0.942g/ml at  $20^{\circ}C$ ) was purchased from Sinopharm Chemical Reagent Co. Ltd. All stuffs were used as received without further purification. A 27wt% PES solution was prepared by dissolving PES particles into DMAc solvent. The applied voltage was varied from 30kV to 37 kV and the distance between the solution surface and the metal receiver was varied from 18cm to 30cm. All the experiments were carried on at temperature  $20^{\circ}C$  with the relative humidity of 43%.

The morphology of the bubble-electrospun nanofibers given in Figs. 2 and 3 was observed by Field Emission-Scanning Electronic Microscopy(S-4800, Hitachi Ltd., Japan), and the process of bubble-electrospinning was filmed by Motion Analyzing Microscope(VW-5000E, Keyence Ltd., Japan). We used Image J software to measure the diameter of nanofibres.



(a) The receptor is located above the bubbles



(b) the receptor is located

Fig.1 Bubbfil spinning process with different receptors

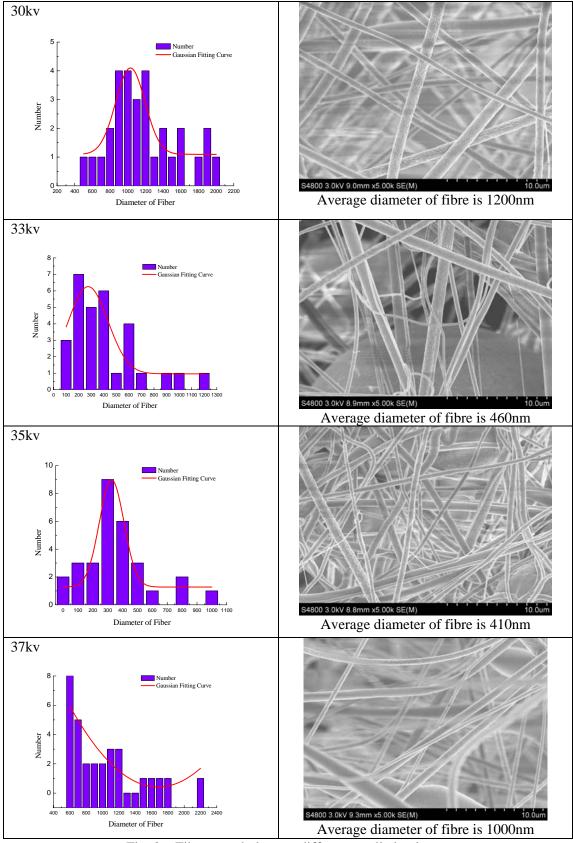
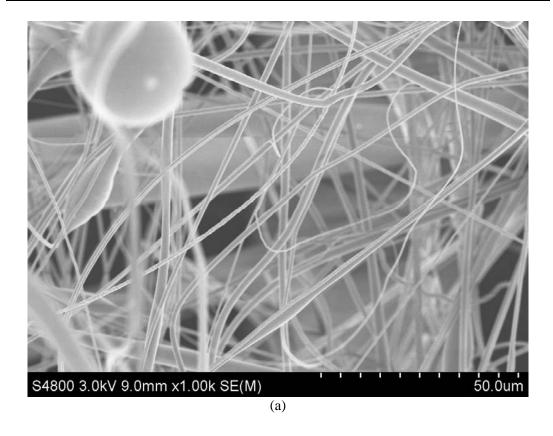
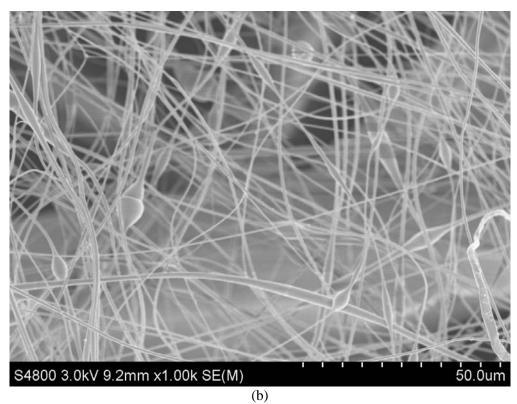
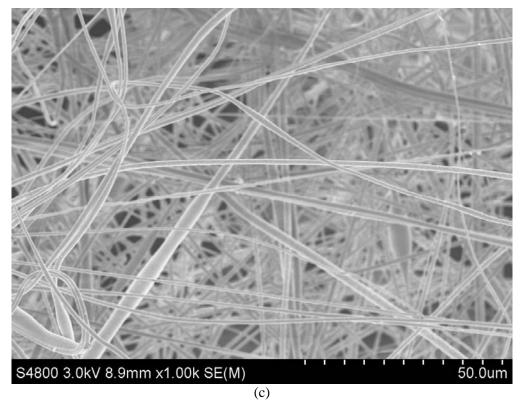


Fig. 2 Fiber morphology at different applied voltages







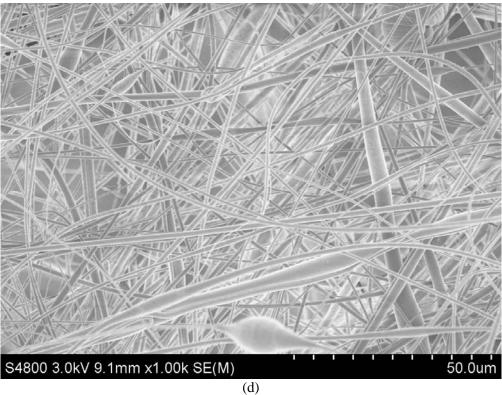


Fig. 3 Fiber morphology at different receipt distance (a) 18cm; (b) 22cm; (c)26cm; (d)30cm (30kV, 27%PES)

#### 3. Porous nanofibers

In this Letter, we investigate a polymer membrane in the presence of an electric field and blowing air as illustrated in Figure 1. A polymer liquid membrane is produced by a metal ring rotating through the polymer solution and the membrane is pulled forward by blowing air to form a bubble under the presence of a high electronic field. When the bubble is ruptured, multiple jets are ejected and accelerated by the electronic field to produce nano fibers. Our results can be extended to the case of multiple bubbles and bubble interaction. We neglect gravitational effects because the bubble thickness is generally in nano or micro scales and the film weight is small compared with the electronic force or surface tension. Tarkan et al. found that the initial thickness of a solvent-coated air bubble is about 3  $\mu m$ , and the rupture thickness is less than 500 nm[19] and the initial bubble radius R0 typically increases to Rm by a factor of only 10[19]. The collapse of the bubble leads to ultrahigh compression and temperature which are so high as to generate light flashes attributed to sonoluminescence in some special cases[20,21]. Similarly for a charged polymer bubble under the electrostatic field, the thinning wall cannot afford the electronic force. Once the electric field exceeds the critical value needed to overcome the surface tension, a hole is created somewhere in the film and the bubble suddenly explodes (see Figures. 1 and 2, Supplementary Movie 1 and Movie 2). The minimization of surface energy and action of the electronic field results in three distinct morphologies: spheres, fibres and strips, depending on the size and thickness of the ruptured film[10]. For a cylindrical fiber it requires d = 4h, where d is the initial diameter of the jet and h is the thickness of the film of the ruptured bubble. According to Tarkan et al.[19], the initial diameter of the jet is about 2000nm and the jet is still accelerated by the electrostatic force.

According to the conservation of mass of a steady and incompressible jet, we have

$$\pi r^2 \rho u = Q \,, \tag{2}$$

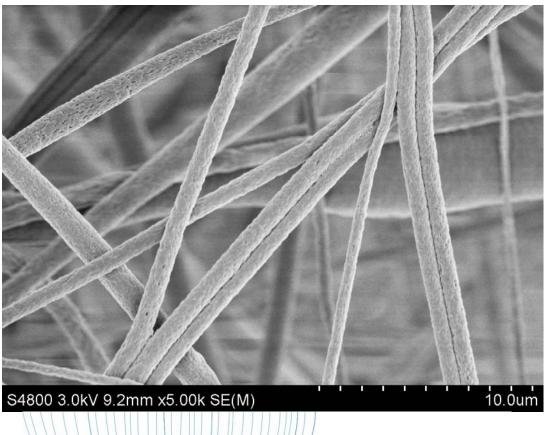
where Q is the volume flow rate,  $\rho$  is the liquid density, u is the velocity, r is radius of the jet, the radius of the jet decreases with the increase of the velocity of the incompressible charged jet.

When the electrospinning velocity reached its maximum in a very short time before inducing instability, macromolecules of the polymers and the solvent (water) are compacted together tighter and tighter during the spinning process as illustrated in Figure 1. There must exist a critical minimal radius  $r_{cr}$  for all electrospun jet  $r \le r_{cr}$  for continuous ultrafine fibers and the critical maximal velocity is

$$u_{cr} = Q/\pi\rho r_{cr}^2,\tag{3}$$

see Fig.4.

However, the velocity can exceed this critical value  $u_{cr}$  if a higher voltage is applied. In the case when the radius of the jet reaches the value of the critical value  $r = r_{cr}$ , and the jet speed exceeds its critical value  $u > u_{cr}$ , in order to keep conservation of mass equation, the jet bursts into smaller daughter jets.



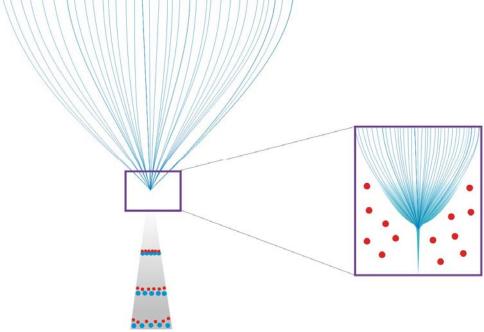


Fig.4 Macromolecular chains and the solvent are compacted during the bubbfil spinning. When the jet bursts, the solvent will evaporate immediately from the mother jet and its daughter jets as well (The red points in the illustration present solvent molecules), and the obtained nanofibers are always observed with a porous surface.

#### 4. Discussion and Conclusion

In 2002, it was reported that there was an evidence for nuclear emissions during acoustic cavitation[20] though with dispute[21], but it is a known fact that acoustic cavitation can be generated by microsecond pulses of ultrasound[23], and daughter bubble cascades are observed when a bubble is uptured[24], lightning-like cascade is also found in bubble electrospinning[25]. All those phenomena are open for further discussion and insight into.

Our results are necessary for understanding nanoscience, which bridges the gap between deterministic classical mechanics and indeterministic quantum mechanics. Generally nanomaterials can remarkably enhance the mechanical properties, remarkably improve surface energy and surface reactivity, and have excellent thermal and electric conductivity, independent upon their bulk materials. Because of ultra improvement of the high specific surface, the new discontinuous backbone-like materials are potentially of great technological interest for the development of electronic, catalytic and hydrogen-storage systems, invisibility device (e.g. stealth plane), photonic structures, sensors, medicine, pharmacy and drug deliver and others, The periodic wrinkled structure also enables applications in adsorption, separation, filtering, catalysis, fluid storage and transport, electrode materials or as reactors. Far-reaching implications are emerging for applications including radiation protection, medical implants, cell supports, materials that can be used as instructive three-dimensional environments for tissue regeneration and others.

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## **Blown bubble-spinning and micro yarns**\*

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#### Abstract

This paper uses polymer bubbles to produce macro-yarns by the blown bubble spinning. A swirling air is used to overcome the surface tension of bubbles and twisting the multiple jets into a micro-yarn during the spinning process. The experiment process is illustrated in details, and the structure of the resultant yarn is discussed.

**Keywords:** micro yarn, nanofibers, bubble electrospinning, blown bubble spinning

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#### 1. Introduction

It is interestingly noted that the surface tension of a polymer bubble depends geometrically upon its size and the pressure difference[1], based on the following Young-Laplace equation

$$\sigma = \frac{1}{4}r\Delta p\tag{1}$$

where  $\sigma$  is the surface tension, r is the radius of the bubble, and  $\Delta p$  is the pressure difference between inner and outer walls.

The polymer bubbles can be used effectively for fiber fabrication by overcoming the surface tension with all kinds of forces in the bubble-spinning method. Bubble-electrospinning[2-3] is developed as a candidate for mass production of superfine fibers. Different from the bubble-electrospinning, a novel method called the blown bubble-spinning is introduced here with hot airflow as motive power instead of high electronic field force. In this paper, a special micro yarn composed of nanofibers was obtained successfully, which resembles the fibril structure of natural materials.

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<sup>\*</sup> Part of the work was presented in IC4N 2013, Greece.

#### 2. Experimental

#### 2.1 The process of blown bubble-spinning.

The experimental set-up of the blown bubble-spinning was shown in Fig.1. Briefly speaking, a single bubble is rising along the tube and formed on the top of the orifice; at the same time, the blowing hot air in the form of two streams that shape a v-slot pulls the bubbles upwards rapidly and continuously, then superfine fibers are obtained on the above collector.

### 2.2 Materials and experimental.

Nylon6/66( $C_{18}H_{37}N_3O_5$ , Mw375,5000 Da)was purchased from Sigma, USA. The spinning solution was prepared by dissolving nylon6/66 at the concentration of 13% w/v in formic acid (88% v/v, Sinopharm Chemical Reagent Co., Ltd, China) under slight stirring for 4hours. The diameter of orifice is 5.5mm. Temperature and airflow volume used in this experiment are 150°C and 500L/min, respectively.

#### 2.3 Characterization.

The morphology of fibers were observed with scanning electron microscopy (SEM, S-4800, Hitachi, Tokyo, Japan) at 20 °C and 60% relative humidity, and illustrated in Fig. 2 and Fig.3. The diameters of the fibers were measured from randomly collected SEM images with the Image.J software.

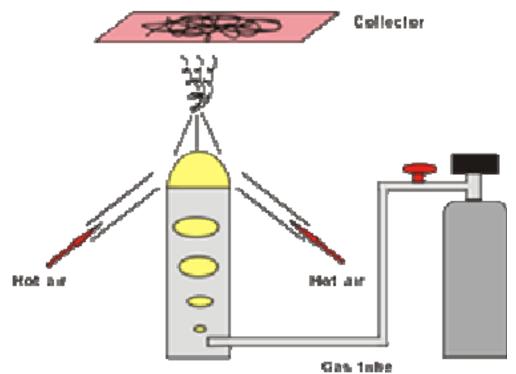


Fig.1The experimental set-up of the blown bubble-spinning

#### 2.4 Results

From Fig.2, we can see that the average diameter of obtained yarn in the experiment is  $22.88\pm5.43\mu m$  and variations in yarn diameter are due to the complex inner nanofibers whipping phenomenon that originates from the turbulent nature of the air jets, but this has no serious influence on the uniformity of a single yarn. On the other hand, SEM images from Fig.3 taken at high magnification indicate that the diameter of nanofibers is  $376.67\pm127.85nm$  without defects such as droplets. The finest nanofiber is more or less 100nm.

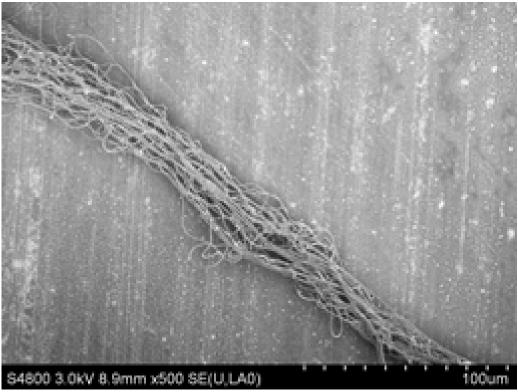
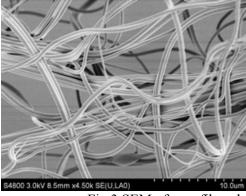


Fig.2 SEM of a micro yarn by the blown bubble-spinning



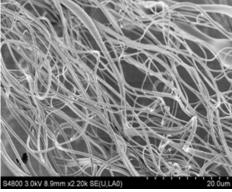


Fig.3 SEM of nanofibers by the blown bubble-spinning (left: magnification=×4500; right: magnification=×2200)

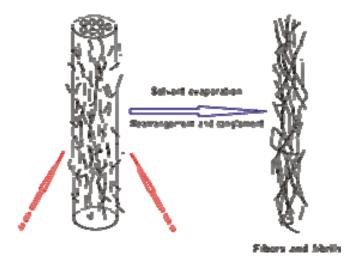


Fig.4 Mechanically controlled air flow forcing on fibers

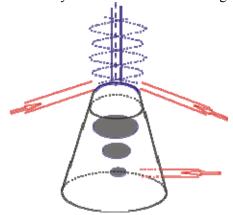


Fig.5 Schematic of the air vortex in blown bubble-spinning process

#### 3. Discussion

Many reports [4-7]have shown that polymers apparently can be melt blown as long as its melt viscosity is low enough to facilitate significant attenuation of the extrudate. Blown bubble-spinning is carried out in a simple way by acting hot airflow on the polymer bubble by overcoming its tiny surface tension. The joint hot airflow driven from two sides has strong draw force to pull the polymer bubble, which causes deformation, extension, and reorientation of the polymer chains to form yarns in a line direction (shown in Fig.4). Meantime, aerodynamic interactions generate amounts of nanofibers and lead to rapid evaporation of the solvent, which further cause finer fibrils (shown in Fig.5).

The results presented in this report have demonstrated the potential of blown bubble-spinning to produce nanofibers. Compare with melt blowing[7-9], it is used at a low temperature much less than polymer's Tm; Moreover, the diameter of orifice is far greater than that in traditional melt blowing(generally less than 0.2mm).

Future work prompted us to undertake research with the objective of obtaining higher-quality outcome by investigating parameters based on complete theoretical analysis.

#### Acknowledgement

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### A mathematical model for bubble electrospinning

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#### **Abstract**

This paper suggests a practical one-dimensional model under the assumption of the steady and incompressible flow during the bubble electrospinning process.

**Keywords**: electrospinning, nanofiber, mathematical model, bubble electrospinning

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#### 1. Introduction

Some useful mathematical models for electrospinning were summarized in Ref.[1], including Spivak-Dzenis model[2], Wan-Guo-Pan model[3]. Additional mathematical models include a mathematical model for AC-electrospinng [4], a mathematical model for electrospun nanoporous microspheres [5], a thermo-hydrodynamical model for the bubble electrospinning[6], and a mathematical model considering coupled fields[7,8,9]. A brief review on various models for electrospinning were summarized in Refs.[10,11]. In this paper, we will suggest a practical model for 1-D charged jet for bubble electrospinning.

#### **2.** Governing equations[1,10,11,12]

Assume that the charged jet during the electrospinning process is steady and incompressible, the one-dimensional governing equations can be expressed in the form 1) The force balance of the charged jet

$$\frac{d}{dz}(\frac{1}{2}u^2) = \frac{2\sigma E}{\rho r} + \frac{1}{\rho}\frac{d\tau}{dz} \tag{1}$$

where u is velocity,  $\rho$  is the liquid density,  $\sigma$  is the surface charge r is radius of the

jet, E is the applied electric field,  $\tau$  the is viscous force. For Newtonian flow, the viscous force can be written in the form

$$\tau = \mu \frac{\partial u}{\partial z} \tag{2}$$

2) Conservation of mass gives

$$\pi r^2 \rho u = Q \tag{3}$$

where Q is the flow rate, r is radius of the jet.

3) Conservation of charges

$$2\pi r\sigma u + k\pi r^2 E = I \tag{4}$$

where k is the dimensionless conductivity of the fluid.

The current in the charged jet is mainly composed of two parts: the bulk conduction current and surface convection current.

#### 3. A nonlinear model

From the above equations, Eqs.(1)-(4), we can obtain a single differential equation for u, which is

$$\frac{d}{dz}(\frac{1}{2}u^{2}) = \frac{2E(I - k\pi r^{2}E)}{2\pi u\rho r^{2}} + \frac{\mu}{\rho}\frac{d^{2}u}{dz^{2}} = \frac{E(I - k\pi r^{2}E)}{Q} + \frac{\mu}{\rho}\frac{d^{2}u}{dz^{2}} = \frac{E(I\rho u - kQE)}{Q\rho u} + \frac{\mu}{\rho}\frac{d^{2}u}{dz^{2}}$$
(5)

Using Eq.(3), and assuming that the flow rate keeps unchanged during electrospinning process, Eq.(5) becomes

$$\frac{1}{2} \left(\frac{Q}{\pi \rho}\right)^4 \frac{d}{dz} (r^{-4}) = \frac{E(IQr^{-2} - k\pi QE)}{Q^2 r^{-2}} + \frac{\mu Q}{\pi \rho^2} \frac{d^2}{dz^2} (r^{-2})$$
 (6)

The relationship between I and E can be obtained experimentally, in Ref.[13] a power relationship was suggested.

Eq.(6) can be solved by some an analytical method, e.g., the homotopy perturbation method[14] or the variational iteration method[15], a complete review on various useful analytical methods is available in Refs.[16-18].

#### 4. Discussion and conclusion

For non-Newtonian flow, the viscous force can be expressed in the form[12]

$$\tau = \mu \frac{\partial u}{\partial z} + \varepsilon \left(\frac{\partial u}{\partial z}\right)^n \tag{7}$$

where  $\mu$  is viscosity coefficient,  $\varepsilon$  and n are constants, and similar nonlinear differential equation for r can be obtained.

Eq.(6) is very useful for explanation of various phenomena, especially the morphology of the obtained fibers. For example, Ref.[19] obtained a critical length of straight jet in electrospinning after some simplification; and Ref.[12] gave a mathematical explanation and experimental verification of the beaded fibers.

Due to high spinning velocity, the air drag should be considered, Eq.(1) should be modified as

$$\frac{d}{dz}(\frac{1}{2}u^2) = \frac{2\sigma E}{\rho r} + \frac{1}{\rho}\frac{d\tau}{dz} + \frac{2c(V-u)^2}{\rho r}$$
(8)

where V is air velocity, c is a constant. The last term must be included for the blown bubble-spinning[12,20].

#### Acknowledgments

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### China Patents for Nanotechnology 中国纳米技术专利

### **Bubble Electrospinning for Fabrication of Yarns with Hierarchical Structure**

层次结构超细纤维制备方法及装置

Patent Number: CN 102851752 A

Inventors: Ji-Huan He, Hai-Yan Kong, Li-Xia Zhou

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摘要: 一种制备层次结构超细纤维的装置,包括多个旋转贮液池、高压静电发生器、 气源装置、多个喷头、接收装置、导气管、金属电极和接地电极,旋转贮液池上方 开口,底面设有垂直向上的喷头,旋转贮液池和喷头的数量一致,喷头通过导气管 与气源装置相连,导气管与气源装置相连处高于旋转贮液池的液面,旋转贮液池通 过金属电极与高压静电发生器相连,上方设有接收装置,接收装置与接地电极相连。 采用该装置可实现层次结构的超细纤维的高效率、低耗能、连续化生产,通过多个 旋转贮液池同时纺丝, 通过旋转, 纳米纤维缠绕, 可实现层次超细纤维的大量生产, 生产效率高,生产成本低,设备简单,易操作,适应性强。

**Abstract:** This invention is used for mass-production of yarns with hierarchical structure using bubble electrospinning. It includes multiple rotating solution reservoirs for different spun solutions, each solution is used to produce a strand for the resultant yarn. Each solution can also produce multiple jets when an electrostatic force is added, which can be combined together due to the rotation of the solution reservoir. The jets can also be combined with a filament to enhance the strength of the strand, and the multiple strands, with or without an additional filament, are combined together to form various yarns.

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#### 1. Introduction

A wool (see Fig.1) possesses an optimal configuration with tree-like hierarchical structure which endows the fiber a special thermal property[1], and a tendon(see Fig.2) has a similar structure with extraordinary mechanical property[2]. Blossman-Myer and Burggren[3] found that the cocoon of the silkworm, *Bombyx mori*, while creating a tough barrier offering mechanical protection to the pupa, imposes no barrier to the diffusion of oxygen or water vapor. In view of its mechanical properties, silk cocoon is an "emperor's new clothes" for pupa. The secret of the cocoon is also its hierarchical structure as discussed in Refs.[4,5]. A better understanding of the mechanism of the hierarchy could help the further design of bio-mimetic artificial fibers or clothes for special applications. This invention uses the bubble electrospinning[6] for mass-production of yarns with hierarchical structure.

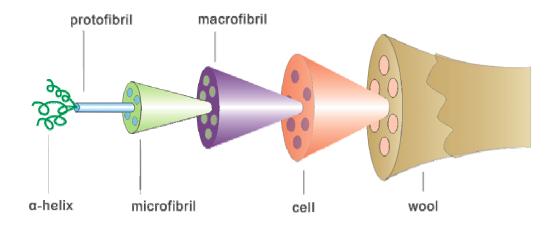


Fig. 1 Hierarchical structure of a wool

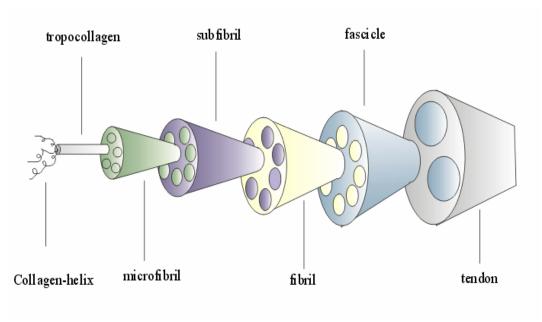


Fig.2 Hierarchical structure of a tendon

### 2. Invitation description

The principle of the invitation is illustrated in Fig.3, it includes multiple rotating solution reservoirs. It reduces to the classic bubble electrospinning if only one solution reservoir without rotation is used. If the solution reservoir keeps rotation during the spinning process, a micro or nano scale strand can be produced, and multiple strands can be combined together to form a yarn with hierarchical structure, see Fig.4 and Fig.5.

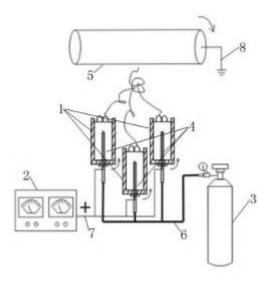


Fig.3 Experimental illustration

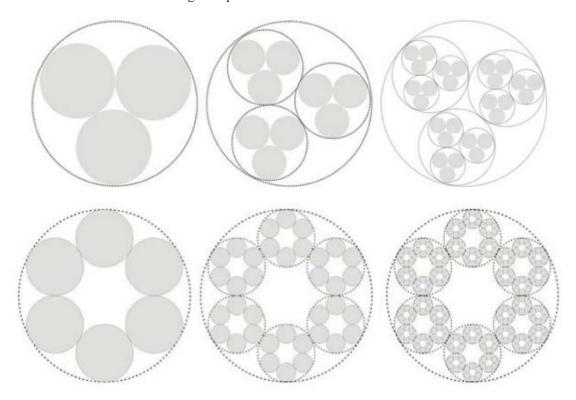


Fig.4 Yarns with hierarchical structure

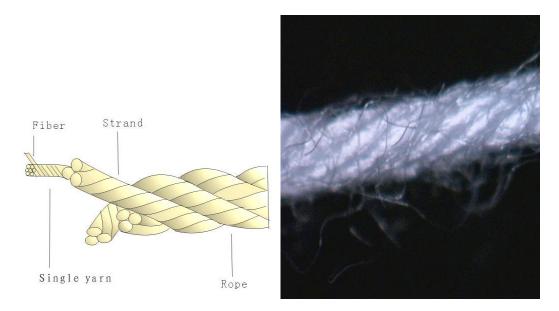


Fig.5 Hierarchical yarn

Each solution reservoir can rotate either clockwise or anticlockwise, the number and place of solution reservoirs will affect the hierarchical structure. The solutions in solution reservoirs can be different, and it can used a filament to enhance the strand or yarn.

#### Acknowledgement

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### **China Patents for Nanotechnology**

### 中国纳米技术专利

### **Bubble Electrospinning Device**

气泡静电纺丝装置

Patent Number: CN 103614789 A

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**摘要:**一种气泡静电纺丝装置,其包括储液池、置于储液池中的喷气管、延伸入喷气管的导气管、连接导气管的气流泵、金属电极、与金属电极连接的高压静电发生器、接收板及与接收板连接的接地线,所述接收板为两个平行放置且带负电荷的导电板,纤维排列在两个导电板之间。本发明通过用两个带负电荷的平行导电板作为接收装置,受电场力作用,纤维集中排列在两个导电板之间,电场的拉伸力大大提高了纳米纤维的有序度。本发明结构简单、操作方便、控制简单、工艺流程短。

**Abstract:** This invention is used for fabricating high alignment nanofibers by bubble electrospinning. It includes two conductive plates separated by a variable insulating gap which are served as a collection device, and each conductive plate is provided with the same amount of negative charge. Directed by electrostatic interactions the charged jets are stretched to span across the gap and become uniaxially aligned arrays. It can greatly enhance the degree of alignment of bubble-electrospun nanofibers.

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#### 1. Introduction

Bubble electrospinning is a straight forward method to produce mass nanofibers from

polymer solutions or melts [1]. However, most bubble electrospun nanofibers are collected in the form of randomly aligned and isotropic nonwoven mats [2-3]. Parallel electrodes method has been used to fabricate aligned nanofibers by electrospinning [4]. And the inclined gap method has been successfully applied to improve the alignment quality of the electrospinning nanofibers [5]. This invention uses the bubble electrospinning [6] for mass-production of nanofibers with uniaxially aligned morphology.

#### 2. Invitation description

The principle of the invitation is illustrated in Fig.1. It includes two conductive plates separated by a variable insulating gap which are as a collection device. It enhances the degree of alignment of bubble-electrospun nanofibers due to electrostatic interactions. And it can easily fabricate a large amount of uniaxially aligned arrays, see Fig.2.

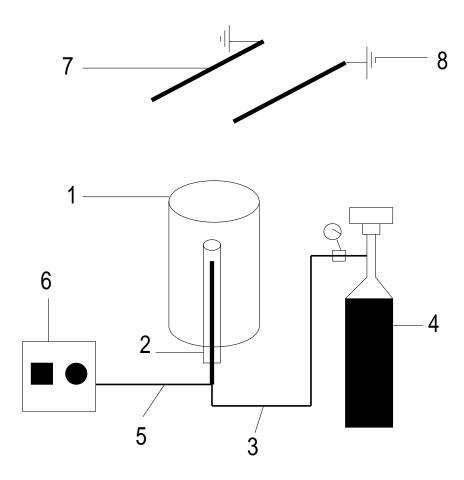
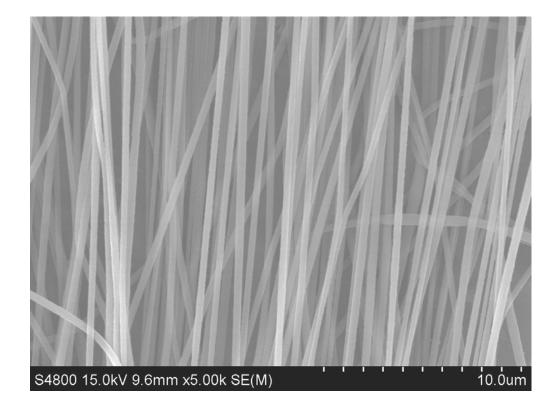


Fig.1 Experimental illustration



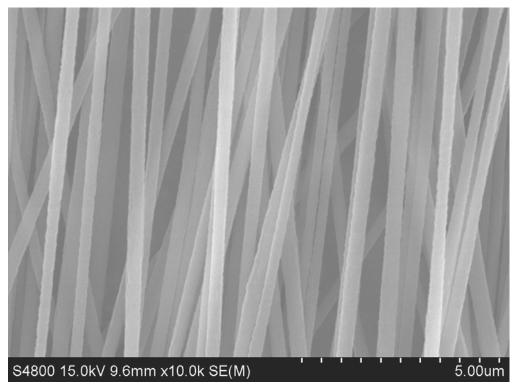


Fig.2 Aligned nanofibers

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