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Levitated crystals and quasicrystals of metamaterials

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Summary

New scientific and technological opportunities exist by marrying dusty plasma research with metamaterials. Specifically, by balancing control and self-assembly, certain laboratory plasmas can become a generic levitation platform for novel structure formation and nanomaterial synthesis. We propose to experimentally investigate two dimensional (2D) and three dimensional (3D) levitated structures of metamaterials and their properties. Such structures can self assemble in laboratory plasmas, similar to levitated dust crystals which were discovered in the mid 1990's. Laboratory plasma platform for metamaterial formation eliminates substrates upon which most metamaterials have to be supported. Three types of experiments, with similar setups, are discussed here. Levitated crystal structures of metamaterials using anisotropic microparticles are the most basic of the three. The second experiment examines whether quasicrystals of metamaterials are possible. Quasicrystals, discovered in the 1980's, possess so-called forbidden symmetries according to the conventional crystallography. The proposed experiment could answer many fundamental questions about structural, thermal and dynamical properties of quasicrystals. And finally, how to use nanoparticle coated microparticles to synthesize very long carbon nanotubes is also described. All of the experiments can fit inside a standard International Space Station locker with dimensions of 8" x 17" X 18". Microgravity environment is deemed essential in particular for large 3D structures and very long carbon nanotube synthesis.

Motivations

New scientific and technological opportunities exist by marrying dusty plasma research with metamaterials. Specifically, by balancing control and self-assembly, certain laboratory plasmas can become a generic levitation platform for structure formation and nanomaterial synthesis.

Metamaterials are periodical structures with unit cells smaller than the wavelength of an electromagnetic wave (including visible light) used to interrogate them[1]. The seemingly exotic properties of metamaterials, such as negative index of refraction, arise from their structures, rather than from their atomic compositions. These unconventional phase properties of the materials can lead to fascinating applications such as quantum computers using light, superlenses, and cloaking (or electromagnetic

[1] N. Engheta and R. W. Ziolkowski (eds.), *Metamaterials: Physics and Engineering Explorations* (Wiley, 2006).

invisibility)[2]. Metamaterials were first developed for radio frequency waves since their wavelengths only require structures on the mm length scale.[3] Terahertz, infrared, visible and shorter waves would require corresponding reduction in feature sizes ranging from micrometers, sub-microns to nanometers. Because of the technological challenges, self-assembly is in the main stream of metamaterial development. Even so, most metamaterial structures are limited to two dimensions (2D) because of the need for a substrate. Dusty plasma environment, where both 2D and 3D levitated crystals of micrometer size particulates have been demonstrated also through self-assembly,[4] is largely unknown to the metamaterials community.

Dusty plasma research originated in the discovery of dust as a nuisance, to put it lightly, in plasma processing of computer chips and other microelectronics.[5] One of the major milestones of the research was the discovery of self-assembled dusty plasma crystals.[6] Although dusty plasma research remains one of most vibrant branches of plasma physics today and is critical to such diverse topics as the origin of the solar and other planetary systems, first-generation magnetic fusion power reactor, and further miniaturization of microelectronics, the research has been largely based on somewhat 'featureless' and thus 'functionless' materials such as latex microspheres and glass beads, or in less controlled environments, materials of unknown origin, composition and arbitrary geometry in the earliest low-temperature dusty plasmas and the present high-temperature magnetic fusion devices.

Introducing anisotropic microparticles and nanoparticles as unit cells into laboratory plasmas to form new types of metamaterial crystals is a natural step forward that brings two previously unrelated fields together. Metamaterials and their properties can be explored from a new angle. The time is ripe for this interdisciplinary approach since an extensive and rapidly expanding library of anisotropic microparticles and nanoparticles now exists,[7] allowing different sizes and shapes to be readily selected for structure studies. A levitation environment, including the microgravity environment in the international space station, can eliminate the need for a substrate and reduce the wall interferences significantly. Microgravity may be most important for large 3D structures. The proposed concept, along with the state-of-the-art in laboratory dusty plasma research, is illustrated in Figure 1.

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[2] J. B. Pendry, D. Schurig and D. R. Smith, *Controlling electromagnetic fields*, Science **312** (2006) 1780; V. M. Shalaev, *PHYSICS: transforming light*, Science **322** (2008) 384.

[3] D. R. Smith, W. J. Padilla, D. C. Vier, S. C. Nemat-Nasser, S. Schultz, *Composite Medium with simultaneously negative permeability and permittivity,* Physical Review Letters **84**, (2000) 4184.

[4] Arp, O., Block, D., Piel, A., and Melzer, A., "Dust Coulomb Balls: Three-Dimensional Plasma Crystals," Physical Review Letters **93**, 165004 (2004).

[5] R. L. Merlino and J. A. Goree, Phys. Today **57**(7), (2004) 32.

[6] J. H. Chu and I. Lin, Phys. Rev. Lett. **72** (1994) 4009; H. Thomas, G. E. Morfill, V. Demmel, J. Goree, B. Feuerbacher, and D. Mohlmann, Phys. Rev. Lett. **73** (1994) 652; Hayashi Y, Tachibana K Jpn. J. Appl. Phys. **33** L804 (1994);

[7] S. C. Glotzer, M. J. Solomon, *Anisotropy of building blocks and their assembly into complex structures,* Nat. Mater. **6**, (2007) 557.

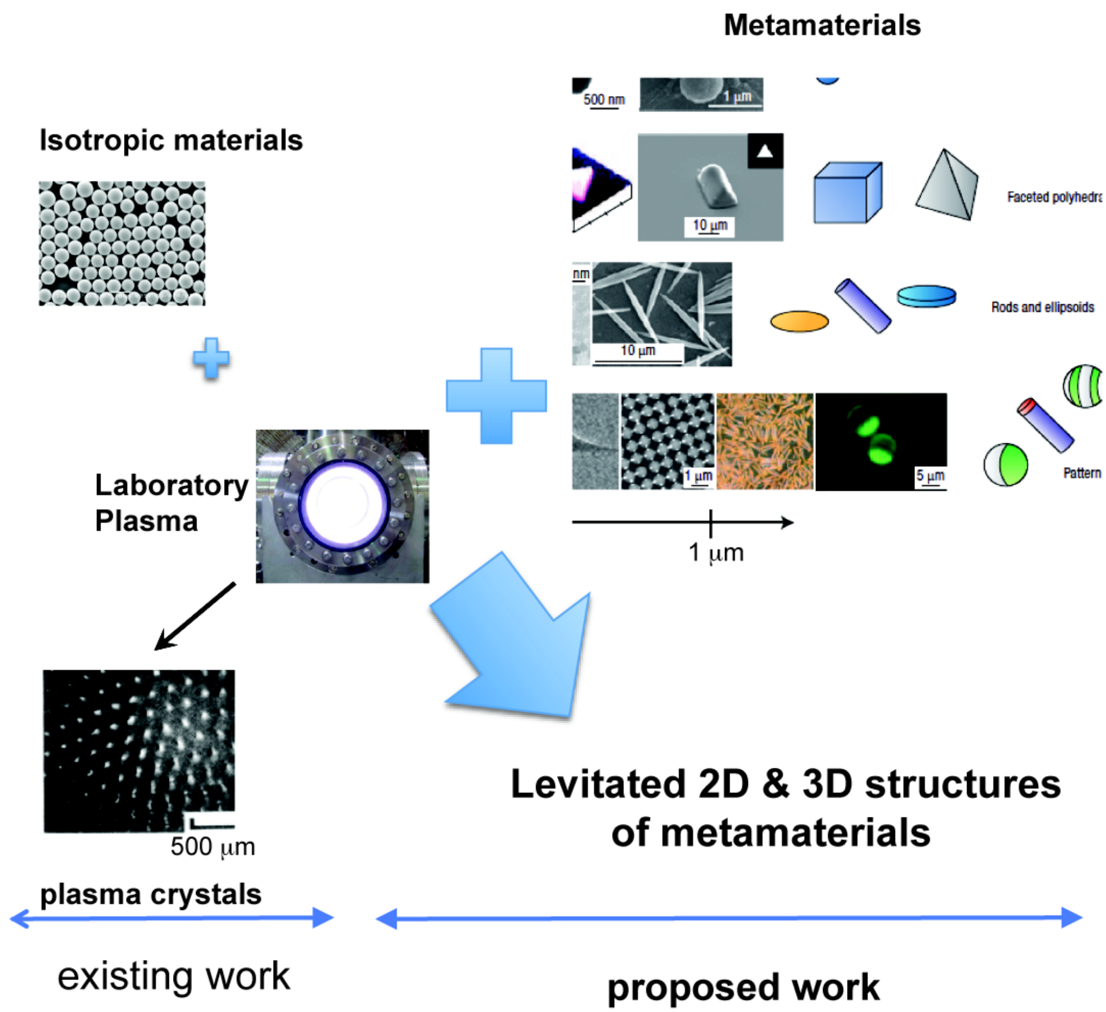

Figure 1. Using the existing and rapidly expanding library of anisotropic microparticles and nanoparticles, new ways to form 2D and 3D metamaterials are possible by using certain laboratory plasmas as self-assembly platforms. Picture credits: J. H. Chu and Lin I, Phys. Rev. Lett. 72 (1994) 4009; S. C. Glotzer, M. J. Solomon, Nat. Mater. 6 (2007) 557; and http://www.nanomi.com.

Below we discuss three types of experiments that are very similar in setup but each targets quite different aspects of metamaterials or synthesis. The first experiment titled *levitated crystals of metamaterials* examines structural formation and negative index of refraction of metamaterials. The second experiment titled *levitated quasicrystals of metamaterials* examines formation and properties of quasicrystals, which possess long-range order like a regular crystal, but these structures are forbidden from conventional crystallography perspective. The third experiment titled *carbon nanotube growth using levitated metamaterials*, explores the feasibility of growing very long carbon nanotubes without using a substrate.

Levitated crystals of metamaterials.

The experiment can be broken down into three phases. The first is to form 2D periodical structures of anisotropic microparticles. The second is to form 3D metamaterials. The third is to examine their properties, in particular to experimentally verify the negative index of refraction for THz or shorter wavelengths. Further experimental details are given below for the 2D structure formation, which are essentially the same for the 3D experiment with the following two possible modifications: (1) The RF electrode used to couple RF energy to plasma is heated up to 80°C, creating a temperature gradient that helps to lift microparticles. This may not be necessary in a microgravity environment. (2) A glass box may be placed on the top of the electrode to modify the boundary for microparticle trapping.

For 2-D periodical structures using anisotropic microparticles, a possible experimental setup is shown in Figure 2. Crystal formation is expected to take place above an electrode surface that can be biased using an RF power supply. The crystal will be illuminated with a visible laser that can be scanned across different areas of the experiment. Two CCD video cameras will look at the crystal region from different angles. The crystal formation can be controlled by adjusting the ambient gas pressure, RF power and by using different gases. Besides a flat electrode surface, it is also possible to explore other electrode configurations to control the formation process. For example, a segmented electrode may be used and different segments can be biased at different electrical potential.

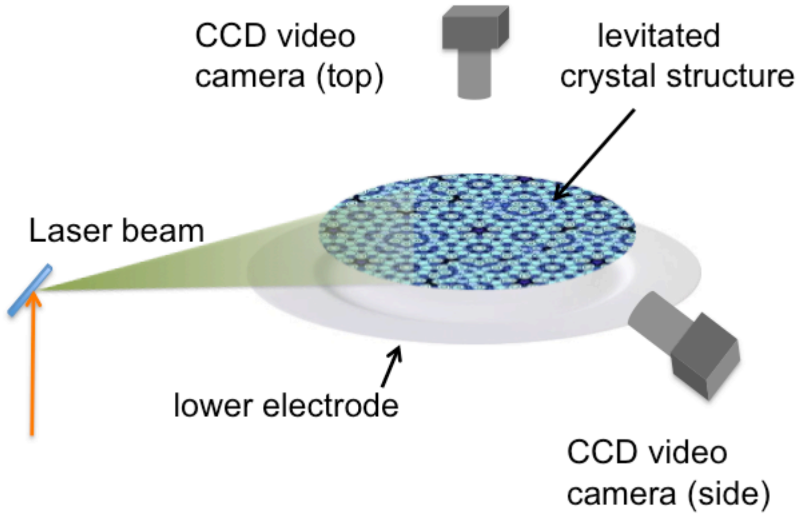

Figure 2. A possible experimental setup to study crystals formation using anistropic microparticles. The three key components of the experiment are a.) A proper electrode configuration (the details will be investigated experimentally) to control the formation process in a plasma environment; b.) A scanning laser system to illuminate the microparticles; and c.) A CCD video imaging system to record the formation process in real time.

The lattice spacing of the crystal is given by $b = (3N_d / 4\pi)^{1/3}$ with N_d being the microparticle density. b is intrinsically related to the ratio of average electrical potential energy to thermal energy of microparticles, also known as the coupling constant, $\Gamma = (Q_d^2/4\pi\varepsilon_0 b)/kT_d$, where Q_d is the average charge on each microparticle and T_d is its temperature. When $\Gamma \geq \Gamma_0 \sim 170$, the crystal forms out of a collection of charged microparticles.[8] Close to each negatively charged microparticle, the space charge is positive (ion shielding). The thickness of the ion shielding layer is described by the Debye length $\lambda_D \sim \lambda_{Di} = (T_i/4\pi ne^2)^{1/2}$, since $T_e >> T_i \sim T_d \sim$ *ambient gas temperature > the room temperature* which is adjustable (such as through RF power, through external heating method using an oven, or through UV lamps that can change the number of charges on microparticles). In the limit of $b \leq \lambda_D$, the ion shielding can be neglected. The number of microspheres in the lattice also depends on the dimension of the electrode and the drag forces due to ion flow. We will experimentally map how the shape and inter-particle spacing b of the crystal varies as a function of (1) the nature of the microparticles (metallic, dielectric, shape, amount and sign of the electrical charge, coatings, *etc.*); (2) the medium in which the particles are levitated (gas type, gas pressure, ambient temperature, gas flow rate, and plasma parameters through visible light spectroscopy); and (3) the presence of UV radiation that will control the charge on individual microparticles.

Portable terahertz time-domain spectroscopy (THz-TDS) may be used to verify the existence of negative index of refraction.[9] THz-TDS coherently measures the broadband impulsive THz radiation in time domain. After performing Fourier transformation, the transmission spectra simultaneously give the amplitude and phase information, thereby the effective material properties can be easily obtained such as the frequency-dependent effective dielectric function and permeability. Femto-second fiber lasers with micrometer wavelengths allow one to build very compact THz-TDS systems.

Levitated quasicrystals of metamaterials.

A quasicrystal is a perfectly ordered structure that can be extended infinitely, and it yet never repeats itself. Quasicrystal structures are not tied to any length scale. In other words, a quasicrystal can, in principle, be constructed on any scale using properly shaped tiles. On the centimeter and larger scale, one can form quasicrystal patterns using Penrose tiling. Another macroscopic example is Islamic mosaics, which have been constructed by Islamic artisan as early as the 15th century. Since their discovery in 1984 on the atomic scale,[10] quasicrystals have been found in many highly synthesized materials and in natural minerals.[11] They are often binary or ternary metallic alloys.

[8] H. Ikezi, *Coulomb solid of small particles in plasma*, Phys. Fluids **29** (1986) 1764.

[9] Chen, H.-T., Padilla, W.J., Zide, J.M.O., Gossard, A.C., Taylor, A.J., Averitt, R.D., *Active terahertz metamaterial devices*, Nature **444** (2006) 597.

[10] D. Shechtman and I. Blech, *Metallic phase with long-range orientational order and no translational symmetry,* PRL **53** (1984) 1951; D. Levine and P. J. Steinhardt, *Quasicrystals: a new class of ordered structures,* PRL **53** (1984) 2477;

[11] L. Bindi, P. J. Steinhardt, N. Yao, and P. J. Lu, *Natural quasicrystals,* Science **324** (2009) 1306.

Organic materials can also exhibit quasi-periodic order. Many features of quasicrystals can be explained, but their atomic structures remain a mystery.[12] Although applications of quasicrystals are limited to mostly coating applications, growing interests towards these materials are derived from their unusual mechanical, thermal, electrical, magnetic, and optical properties.[13]

We propose to experimentally investigate whether macroscopic (millimeter and larger) quasicrystals can be formed using microparticles of a few micrometers in size. This is a new approach to examine the structural, thermal and dynamical properties of quasicrystals. Regarding the structures of quasicrystals, some of the fundamental questions are: How does a quasicrystal come into existence? Are there new laws governing the structures of quasicrystals?[14] The symmetries of synthesized and natural quasicrystals found so far are only pentagonal, decagonal, dodecagonal, or icosahedral. Thermal stability of quasicystals has attracted much attention since the beginning. As a matter of fact, the first quasicystals produced by Shechtman and collaborators were very small (micron size) grains that, when heated, transformed irreversibly into common crystalline phases. More recent work[15] showed that nearly perfect quasicrystals may be grown to centimeter sizes, a dynamic range in size that extends almost eight orders of magnitude. It should be mentioned that since the quasi-periodicity allows an infinite non-repetitive choices in microscopic structures, it is possible that none of the two macroscopic quasicrystals would have exactly the same structure. Formation of macroscopic quasicrystals that are easy to image and characterize (see below) would allow us to examine *if and how microscopic structural differences in quasicrystals would affect their macroscopic properties*.

Compared with a quasicrystal of atomic scale tilings, one of the major advantages of micrometer tiling is the ease to image structure formation at all length scales using off-the-shelf CCD cameras. A levitation environment, including a microgravity environment, will be essential to minimize heterogenous phase transition due to the container wall.[16] Micrometer size dust particles are routinely used in dusty plasma experiments that led to the discovery of levitated dust crystals in the mid 1990's.[17] Similar experiments have also been carried out in the International Space Station (ISS). The proposed experiment can be made to fit inside a standard ISS locker with dimensions of 8" x 17" X 18". Microgravity environment is expected to be essential for formation of 3D structures.

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[12] P. W. Stephens and A. I. Goldman, *The structure of Quasicrystals,* Scientific American *April* (1991) 44; http://www.icq9.ameslab.gov/index.html/; M. Senechal, *What is a quasicrystal?* Not. AMS **53** (2006) 886.

[13] D. V. Louzguine and A. Inoue, *Formation and properties of quasicrystals, Annu. Rev. Mater. Res.* **38** (2008) 403.

[14] M. Senechal, Quasicrystals and Geometry, Cambridge Univ. Press (1995).

[15] de Boissieu M., et al., Phil. Mag Let. **65** (1992) 147; Yokoyama Y., et al., Mater. Trans., Japan Inst. Metals **33** (1992) 97; S. W. Kycia and A. I. Goldman et al., *Dynamical x-ray diffraction from an icosahedral qnasicrystal*, Phys. Rev. B **48** (1993) 3544; Boudard M., et al., Phil. Mag Lett. **71** (1995) 11.

[16] K. F. Kelton, G. W. Lee et al., *First X-ray scattering studies on electrostatically levitated metallic liquids: Demonstrated Influence of Local Icosahedral Order on the Nucleation Barrier*, PRL **90** (2003) 195504.

[17] V. Nosenko and J. Goree, *Shear Flows and Shear Viscosity in a Two-Dimensional Yukawa System (Dusty Plasma)*, Phys. Rev. Lett. **93** (2004) 155004.

There are two challenges to the experiment. First and foremost is to identify proper microparticles for the experiment. Fortunately, an extensive library of anisotropic microparticles and nanoparticles now exists,[18] allowing different sizes and shapes to be readily selected. We plan to experiment with different combinations of microparticles and search for the 'good pairings' of microparticles based on evidences of quasicrystals. Second, if more than one type of microparticle are used, the uniform mixing of different microparticles also needs to be demonstrated. In a typical dusty plasma experiment, usually there's a problem mixing microparticles of different sizes -- the two sizes tend to separate, and never mix. That's the case with the parallel-plate rf plasmas when the position of microparticles has a balance of two forces, the electrostatic force due to electric field qE and ion drag due to Coulomb interactions, since the ion drag force is proportional to q^2 and the amount of charge (q) is proportional to the surface area of the microparticles. For microparticles of comparable sizes but different shapes, whether mixing will become an issue is not obvious and will be investigated experimentally. If necessary, one can also modify the microparticle surfaces by coating with nanoparticles.

Carbon nanotube growth using levitated microparticles

In addition to their uses as *self-assembly platforms* for microparticles, the same apparatus can also be developed into *synthesis platforms* for nanomaterials, including zero-dimensional (0D) materials such as quantum dots, one-dimensional materials such as single- and multi- wall carbon nanotubes (CNT), nanowires, and two-dimensional materials such as single- and multi- layer graphene sheets. There is much excitement on various forms of nanomaterials because of their technological and commercial interests. It should be pointed out that plasma technology has been used for nanomaterial production since the very beginning. The key difference here is a more controlled ('gentle') way to produce nanomaterials. A lot of plasma environments, such as an arc, do not meet this requirement, resulting in nanomaterials with large dispersion in size and structures; subsequently, their properties and functions differ by equal measure. Another motivation to examine nanomaterial synthesis is the possibility to 'freeze' a levitated structure after they have been produced. Crystals described in the previous sections will collapse, agglomerate, and be lost after the plasma is turned off. If these structures can somehow be bonded together using nanoparticles and nanowires, then the crystalline structures may be preserved, transported and used afterwards.

Attachment of nanoparticles to macroscopic, mesoscopic, or microscopic substrates is an overarching theme of virtually all nanoparticle applications for a number of reasons. Unique optical, electronic, or catalytic properties of nanoparticle are size- and shape- dependent, which requires the NP's to avoid agglomeration or coalescence and thus "maintain their individual identities". However, a large number of nanoparticles are required to achieve measurable optical, electronic, or chemical functions at macroscopic scale. If a large number of "stand-alone" nanoparticles are allowed to

[18] S. C. Glotzer, M. J. Solomon, *Anisotropy of building blocks and their assembly into complex structures,* Nat. Mater. **6**, (2007) 557.

aggregate and form “clumps”, they most likely will lose their unique properties. Therefore, massive nanoparticle production and self-assembly of nanoparticle onto substrates (sometime in the form of a nanoparticle core with stabilizing organic surfactant) are necessary. In addition, substrates need to have large surface-to-volume ratio to accommodate as many number of nanoparticless as possible. Since the surface-to-volume ratio of a spherical object is proportional to 1/*r*, with *r* being the characteristic radii/size of the substrate, microparticles in the range of 100 nm to 10 μm are good candidates for the substrate on which to hold the nanoparticles. These constraints combined lead to a generic “crystalline” structure with nanoparticles-modified miniature substrates as building-blocks.

We propose here to study the use of levitated microparticles for very long carbon nanotube (CNT) growth, such a method is available previously. Although some of the longest CNT (a recent record is nearly 20 cm long) has been produced using chemical vapor deposition (CVD),[19] large dispersion in length is common, see Figure 3. We would like to experimentally investigate whether by removing the supporting substrates, one can produce more uniform and longer CNT’s.

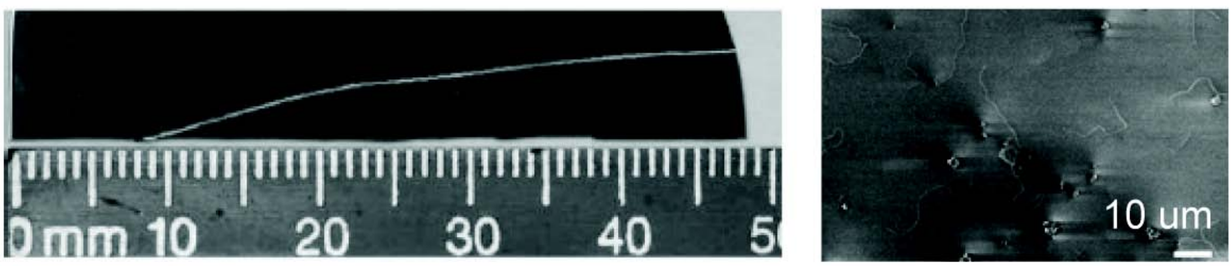

Figure 3. Large dispersion in sizes and properties exists for substrate-based synthesis strategies. The method of levitated synthesis is unavailable in the past. (Left) One of the longest carbon nanotubes produced using chemical vapor deposition. Picture Credit: L. X. Zheng et al., Nat. Mat. 3 (2004) 673. (Right) Carbon nanotubes produced under the same condition. Picture Credit: Dr. L. X. Zheng.

Without repeating the details, the experimental approach will be very similar to the previous two above. One key difference is here different gases that will used. Some of the scientific questions will be addressed include, a.) How the nanoparticles coverage/density on microparticles determined the CNT growth; b.) how the levitated microparticle environment, plasma background, ambient gas type, density, temperature, and flow rate, affects the growth rate of CNT’s; c.) how the size and composition of microparticles and the crystalline structures affect the growth of CNT; d.) if and how the CNT grown by the method are different from conventional surface-substrate-based CVD methods.

[19] L. X. Zheng et al., *Ultralong single-wall carbon nanotubes*, Nat. Mat. **3** (2004) 673; X. Wang et al., *Fabrication of ultralong and electrically uniform single-walled carbon nanotubes on clean substrates, Nano Lett.* **9** (2009) 3137.